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LONGMANS, GREEN, & CO. 39 Paternoster Row, London
New York and Bombay.

METALS

THEIR PROPERTIES AND TREATMENT

NEW EDITION

BY

A. K. HUNTINGTON

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NEW IMPRESSION

LONGMANS, GREEN, AND CO.
39 PATERNOSTER ROW, LONDON
NEW YORK AND BOMBAY
1904

PREFACE TO THE NEW EDITION

This work is based on that originally compiled by the late Charles Loudon Bloxam, Professor of Chemistry in King's College, London, published in 1872, and in great part re-written and augmented by myself in 1882.

In bringing up to date the present enlarged edition, I have had the much-valued co-operation of Mr. W. G. McMillan, who, when assistant in this Laboratory, piloted the 1882 edition through the press.

The original edition contained 312 pages, that of 1882 452; the present edition consists of 562 pages.

The object of 'Metals' is to make clear the principles which have guided the evolution of the metallurgical arts and industries, avoiding multiplicity of detail, which tends to obscure main issues.

The very great development which has taken place in the practice of Metallurgy in recent years, and the considerable accumulation of literature on the subject, make it extremely difficult to treat adequately, in a small volume, each branch of the subject in proportion to its relative importance. The task would have been easier if the subject-matter had been entirely re-written.

Whilst conscious of deficiencies, we have done our best to ensure that the good reception which this book has had in the past should be extended to it in the future.

Acknowledgment is specially due to:—Mr. Darby, of Brymbo, for the drawing of the most recent form of Semet-Solvay coke oven; 'Mineral Industry' (Novak, Czermak, Gascue-Rodriguez mercury furnaces, and Mr. Titus Ulke's scheme of Boston-Colorado Co.'s complex ore working); Mr. Frederick Siemens (modern forms of closed hearth gas-producer, open hearth steel-melting furnace and regenerative furnace); Messrs. Fraser and Chalmers (battery of stamps, Frue vanner, Brown horse-shoe, Brückner and Stetefeldt calciners, amalgam retort, and water-jacketed copper blast furnace); Mr. Bernard Dawson (producer); Messrs. Thwaites Bros. (Stewart Cupola); 'The Engineer' (micro-metallographs); Hofmann's 'Metallurgy of Lead' (Rachette furnace); Howe's 'Metallurgy of Steel' (Blair's sponge-making furnace and Bessemer plant, Trasenter); and Thorpe's 'Dictionary of Applied Chemistry,' for several diagrams.

A. K. HUNTINGTON.

METALLURGICAL LABORATORY,
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January, 1897.

CONTENTS

METALS:

THEIR PROPERTIES AND TREATMENT

FUEL

THE word FUEL comes, through the low Latin *focale* and Norman-French *fuayl*, from the Latin *focus*, a hearth or fire-place, and means, therefore, anything which can be burnt on the *hearth* with generation of heat.

Heat is due to molecular motion, and as in the production of heat from fuel molecular motion is not induced by mechanical action, such as friction, it follows that some other agency must be at work. The motive force in this case is termed *chemical affinity* : the force which, under suitable conditions, unites certain dissimilar bodies into a single homogeneous substance. Thus, if the elementary substance carbon, the largely predominating constituent of our principal fuel, be heated to a certain point in contact with atmospheric air, union takes place between the carbon and the oxygen, with evolution of heat and the production of a homogeneous gaseous compound. The maximum combining power of carbon with oxygen is one atom[1] of carbon with two atoms of oxygen, represented symbolically by the formula CO_2. Combination to this extent having taken

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[1] Greek *atomos* = indivisible.

place, the maximum amount of heat obtainable from the combustion of carbon has been produced.

All that is essential in order that a substance may with reason be termed a fuel is that it can be practically employed for the generation of heat.

From this point of view, many substances which the advance of science has caused to be utilised for the production of heat in various metallurgical processes should be classed as fuel ; and, in order to obtain a proper appreciation of the subject, it is essential that it should be so. Thus, *sulphur* in the minerals iron and copper pyrites is in certain cases just as much a fuel as the carbon in coal, since it is capable of uniting with oxygen, evolving at the same time very considerable heat, which can be utilised. Similarly, *silicon* and *phosphorus* play an important part in the production of heat in certain processes, which we shall have to consider later on in treating of the manufacture of iron and steel.

In the ordinary acceptation of the word, fuel is composed of, or derived from, vegetable matter, which has, at some time or other, grown on the surface of the earth ; and vegetable matter is composed of carbon, hydrogen, and oxygen, with smaller proportions of nitrogen and earthy matter.

Calorific Power.—Although there is no means of estimating the *absolute* quantity of heat evolved by the combustion of a body, yet the *relative* quantities of heat given out during the combustion of different bodies may without difficulty be determined. This is done by finding the number of parts by weight of water which one part by weight of the substance will, on perfect combustion, raise one degree in temperature. In this way it has been substantiated that one part by weight of carbon, in the form of purified wood-charcoal, in uniting with $2\frac{2}{3}$ parts by weight of oxygen to form carbonic acid (CO_2), in which state carbon is oxidised to the maximum, evolves heat sufficient to raise 8,080 parts of water one degree.[1] In the same way it may be shown that the unit of hydrogen, in uniting with 8 parts by weight of oxygen to form water (H_2O), would raise 34,462 parts by weight of water one degree. In considering the *useful effect* which can be obtained from the combustion of hydrogen, allowance must be made for the heat required to maintain the product of combustion in the state of vapour. This being done, the number 29,161 is obtained instead of 34,462.

The heat-evolving power of a substance during its combustion will be spoken of as its *calorific power*. The absolute amount of heat given out by a substance in burning is the same whether the combustion takes place rapidly or slowly, but the *intensity* will be greater in the one case than in the other. This is a very important point in considering the value of a fuel for any given purpose. The calorific intensity of a fuel will depend partly on the state of its aggregation and freedom from moisture, partly on its composition, and partly on the nature both of the atmosphere in which it is burned, and of the ultimate products of combustion. The products of combustion are usually either gases or vapours, and as their specific heats vary with their composition, the temperature obtainable must depend upon the composition of the fuel and the way in which it is burnt.

Calorific Intensity.—We have seen that the calorific power of hydrogen is 34,462, but the product of combustion of hydrogen is vapour of water, and it therefore becomes necessary, in considering the intensity of the heat produced, to deduct the heat required to maintain the water in the vaporous condition. For one part of water this amounts to 537 heat units. Therefore, in the combustion of one part of hydrogen, which produces nine parts of water, $9 \times 537 = 4,833$ heat units are occupied in keeping the product in the state of vapour.

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[1] The centigrade thermometer scale has been adopted throughout the book. For comparison with the Fahrenheit scale, reference may be made to Table VIII. in the Appendix.

In the estimation of the calorific power it will be understood that this vapour is condensed, and the so-called latent heat becomes sensible, and does work in the calorimeter by melting ice or raising the temperature of water as the case may be. In calculating the intensity of combustion we have further to take into account the specific heat of steam (=0·4805), and also the difference between the specific heat of water and of steam. For the sake of simplicity the initial temperature is assumed to be 0° C., and the barometric pressure 760 millimetres of mercury. The pressure is also assumed to be constant.

Then, T being the temperature[1] to be ascertained, we have

$$T = \frac{34{,}462 - \{[(1 - 0{\cdot}4805) \times 100] + 537\} \times 9}{9 \times 0{\cdot}4805} = 6{,}743^\circ \text{ C.}$$

The calorific power of carbon we have seen to be 8,080. The specific heat of carbonic acid, as determined by Regnault is 0·2164. There is an important distinction between this case and that which we have just considered: the product of combustion is not condensable at ordinary pressures, and we have, therefore, in making our calculation, nothing to do with its latent heat; and further, the products of combustion in the case of hydrogen are relatively heavier than those of carbon. $3{\cdot}\dot{6}$ parts by weight of carbonic acid are produced by the combustion of 1 part of carbon, therefore

$$T = \frac{8{,}080}{3{\cdot}\dot{6} \times 0{\cdot}2164} = 10{,}183^\circ \text{ C.}$$

The essential difference between calorific power and calorific intensity should be sufficiently clear from the foregoing calculations. Roughly speaking, the calorific power of carbon is to that of hydrogen as 3 : 13, whereas their

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[1] It will be shown, later, that these temperatures cannot actually be attained in practice (see p. 7).

calorific intensities are in the ratio of 3 : 2. The advantage of a high percentage of carbon in fuel to be employed for the generation of high temperatures must also be apparent, as well as the importance of using dry fuel.

Although the foregoing considerations sufficiently express the *difference* in value of various substances in respect to their heat-evolving power, and the *relative* intensity of that heat, yet, for reasons to be explained, the numbers we have so far obtained for the intensity do not accurately represent the state of things which exists in practice. In the first place, we have supposed the combustion to have been effected by pure oxygen. When atmospheric air is employed, which would ordinarily be the case, the quantity of nitrogen, carbonic acid, and moisture present, and their specific heats, have to be taken into account. For the sake of simplicity we will assume that nitrogen and oxygen are alone present in the air to be used; then, as in air for every part of oxygen there are 3·35 parts by weight of nitrogen, and as $2{\cdot}\dot{6}$ is the quantity of oxygen required to burn one part of carbon, the nitrogen to be heated during the conversion of one part of wood-charcoal into carbonic acid will amount to $3{\cdot}35 \times 2{\cdot}\dot{6} = 8{\cdot}9\dot{3}$. The specific heat of nitrogen is 0·244. Introducing these figures into the equation, we have

$$\frac{8{,}080}{(3{\cdot}\dot{6} \times 0{\cdot}2164) + (8{\cdot}9\dot{3} \times 0{\cdot}244)} = 2{,}718^\circ \text{ C.},$$

instead of 10,183° C. The presence of carbonic acid and moisture would still further reduce the temperature, and certain other conditions, such as the incomplete oxidation of the carbon, would have the same effect. In the same way it may be shown that, instead of 6,743° C. in the case of hydrogen we should only get 2,684° C. when atmospheric air (free from carbonic acid and moisture) is used.

Incomplete Combustion of Carbon.—So far we have only considered the oxidation of carbon to carbonic acid, which takes place when a suitable quantity of air is supplied to the fuel, and other conditions are favourable; but when this is not the case, a lower oxide of carbon, known as carbonic oxide (CO), may be formed. The formation of this oxide takes place when carbonic acid is passed through red-hot carbon: thus, $CO_2 + C = 2CO$. Suppose, for the sake of example, that a tall upright cylinder be filled with red-hot fuel, and that air be admitted at the bottom beneath the fuel, then carbonic acid will be produced where the atmospheric oxygen comes in contact with the fuel; as, however, the carbonic acid traverses the next layer of hot fuel it will be reduced to carbonic oxide, as shown in the equation, and in this state it will remain until it reaches the top of the cylinder; if it there come in contact with a supply of air, it will combine with oxygen and re-form carbonic acid. Now, it is clear that the temperature at the bottom part of the cylinder will be that which would result from the direct formation of the lower oxide from carbon, since whatever excess heat is given out during the first formation of carbonic acid is re-absorbed during the subsequent reduction of the carbonic acid to carbonic oxide. It remains, then, to ascertain the quantity and intensity of the heat produced when carbon is burnt to carbonic oxide. This cannot be arrived at by direct experiment; but by ascertaining the amount of heat evolved during the conversion of carbonic oxide into carbonic acid and deducting that amount from the heat evolved by carbon when burnt direct to carbonic acid, the required information is obtained. By experiment, the heat given out by carbonic oxide whilst burning to carbonic acid has been found to be 2,403 heat units. The amount of carbon in carbonic oxide is $\frac{12}{28} = \frac{3}{7}$ of its weight. Therefore, to compare with the figures obtained in calculating the calorific power of carbon, it is necessary to multiply by $\frac{7}{3}$; thus, $\frac{7}{3} \times 2{,}403 = 5{,}607$ are the number of heat units obtained by the combustion of carbonic oxide to carbonic acid. But carbon in burning to carbonic acid evolves 8,080 units, therefore, in the production of carbonic oxide, 8,080 − 5,607 = 2,473 heat units only become sensible, *i.e.* less than one-third of that which results from complete oxidation. The calorific intensity of carbon burning to carbonic oxide in pure oxygen is 4,323° C., the specific heat of carbonic oxide being taken as 0·245; but if, instead of in oxygen, carbon were burnt to carbonic oxide in air (free from CO_2 and H_2O), the calorific intensity would be only 1,494° C. The fact, that so much less heat is generated by the union of carbon with oxygen to form carbonic oxide than during the oxidation of the latter to carbonic acid, is to be explained by the circumstance that in the first case a solid body passes into the gaseous condition, and in the accomplishment of this transition energy is absorbed which otherwise would have taken the form of heat.

Use of Calculations of Calorific Intensity.—These calculations of calorific intensity must not be regarded as giving the actual temperatures obtainable, because the data upon which they are based are not strictly accurate, owing to the variations in the specific heats of gases at different temperatures, and because chemical combination would be checked by dissociation long before such temperatures were reached, as will be explained hereafter. Yet the numbers are useful for purposes of comparison, and therefore possess great interest from an economic point of view. The few figures just considered show better than any words could do the enormous loss which results, when fuel is burnt without suitable arrangements for a supply of air in proper proportion and in such a way that the heat generated can be utilised to the greatest advantage. The introduction of an excess of air is nearly as objectionable as an insufficient supply, for the excess has to be heated at the expense of the heat of combustion, and the intensity is proportionately reduced.

The calorific intensity or thermal effect of carbonic oxide burnt in oxygen is 7,073° C., and in air 2,982° C. It will be observed that in the latter case the thermal effect is greater than in the case of carbon, though in the former it is less. This result is traceable to the differences in calorific power, and in the weight of the products of combustion in the two cases.

Influence of Varying Conditions on Calorific Intensity. For the sake of comparison, the initial temperature of combustion has been assumed to be 0° in all cases. It is manifest that whatever heat is possessed by the fuel and air before combustion must assist in the ultimate intensity obtained. The figures which represent this initial temperature should, therefore, be incorporated in the numerator of the equation when the actual temperature in any particular case is required to be known. Within the last sixty years great progress has taken place in blast-furnace practice, in consequence of advantage having been taken of this means of increasing the available heat of combustion; and within the last thirty years a new industry, the manufacture of so-called soft steel in the Siemens furnace, has sprung into existence from a similar cause.

There remains one more means of increasing the intensity of combustion. It will be remembered that, besides assuming the initial temperature to be 0°, the pressure was taken as constant at 760 mm., *i.e.* the gases as they were heated were free to expand. If the pressure be increased, the maximum temperature at any given moment will also increase; and the *specific heat at constant volume* is less than the *specific heat at constant pressure.* The ratio between them, based on the theory of gases, is[1]

Air	1 : 1·409	Hydrogen	1 : 1·413
Oxygen	1 : 1·402	Carbonic acid	1 : 1·257
Nitrogen	1 : 1·420	Carbonic oxide	1 : 1·411

In practice, the difficulty of working under pressure is

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[1] Jamin, *Cours de Physique*, 1878, vol. ii. p. 74.

very great. In all cases, however, where a blast is employed the pressure in the immediate vicinity of the point at which the blast is introduced, which is also the point of maximum temperature, must be greater than that of the atmosphere.

Effect of Dissociation.—Where, then, is the limit to the temperature to be obtained by heating the fuel and the oxygen or air required for its combustion, and by working under pressure? The limit is closer at hand than at first might have been anticipated. In the single word *dissociation* we have the keynote to the answer. If a gas consisting of two or more different atoms, chemically combined, be maintained at a constant pressure, and its temperature be raised, at a certain point the force which retains the atoms in union will be overcome, and a portion of the gas will be split up into its constituents in order to restore the tension at which the particular gas is stable. By reducing the pressure the temperature at which dissociation commences is lowered. H. Sainte-Claire Deville compares the dissociation of a gas below the temperature of its formation to the evaporation of volatile substances below their boiling points, and he defines the tension of dissociation and vapour tension in exactly the same way. Thus, he found that the vapour of water commences to undergo dissociation between 1,100° and 1,300° C. Yet it has been shown that the ignition of a mixture of hydrogen and oxygen in equivalent proportions, and at the ordinary atmospheric temperature, gives a temperature of about 2,500° C. Similarly, carbonic acid partially decomposes into $CO + O$ between 1,100° and 1,200°.

At a pressure of nine to ten atmospheres, Bunsen found that carbonic oxide in uniting with oxygen was capable of producing a temperature of 3,000° C., as against 2,600° to 2,700° obtainable at the ordinary pressure of the atmosphere. Similar experiments with hydrogen gave a temperature of about 2,850°, as compared with 2,500° C. at the ordinary pressure. When air instead of oxygen is employed, according to Bunsen, carbonic oxide, burnt under a pressure of seven or eight atmospheres, produces a temperature of about 2,000° C., and hydrogen about the same. These figures correspond to about 1,700° to 1,800° C. at the ordinary pressure.

At about the ordinary atmospheric pressure, Deville found that carbonic oxide began to dissociate into carbon and oxygen at a bright-red heat. From considerations based on the temperature of the sun, Bessemer some years ago proposed to construct a furnace to work under pressure. Up to the present, no important advance has been made in this direction. Improvements of this nature can result only from the application of mechanical contrivances by skilled engineers.

Calorific Power of Complex Fuels.—From the foregoing considerations it is not difficult to determine the relative useful effect obtainable from hydrogen, carbon, and carbonic oxide respectively, when these substances are burnt separately. When, however, a complex body, containing carbon, hydrogen, and oxygen, has to be dealt with, the difficulty is very greatly increased. In the case of a solid, such as wood or coal, the hydrogen and oxygen, which we have hitherto been considering as gases, may be regarded as being in the solid condition, and their state of union with the carbon and with one another is to a great extent unknown; so that the heat absorbed or evolved during combustion by the decomposition of the original compounds cannot be estimated. Coal is an extremely complex body, and neither the carbon nor the hydrogen that it contains is in the free state; but the fuel value of elementary substances, or of compounds which have the same elementary composition, has been found to vary inversely as the state of condensation of the molecules. It thus often happens that calculations based on the assumption that the constituents of any given fuel are arranged in some preconceived way, and that during combustion they will be given off in some particular state of combination, give results different from those obtained in practice, a discrepancy of as much as 20 per cent. having been observed in isolated cases. Two fuels may perfectly well have the same elementary composition, yet the molecules may be differently constituted, and the proportion of volatilisable matter in the two cases will not be the same. In consequence of this, it has been necessary to fall back upon generalisations derived from a number of experiments on fuels of different composition. In this way it has been substantiated that the calorific power in the case of coal and lignite increases and decreases with the proportion of solid residue or coke produced. This is, however, only true within certain limits, which do not include anthracite coal and bituminous lignites; the former being excluded on account of the excess of carbon they contain, the latter on account of their excess of hydrogen. In order, then, to judge fairly of the nature and value of a coal it should be submitted to experiment, to determine the relative proportion of volatile and solid matter it will yield when heated with exclusion of air, and also what kind of coke is produced, *i.e.*, whether it is compact and hard, or light and friable. In this way more reliable information will be obtained than by making an analysis to determine the relative proportion of the ultimate constituents. Cornut has given the following formula for calculating the calorific power of a coal, which, although it is not accurate, gives less erroneous results than that formerly used :—

$$\text{Cal. Power} = 8{,}080\ C' + 11{,}214\ C'' + 34{,}462\ H.$$

This formula is based on the assumptions, first, that the percentage of carbon (C') which is left in the coke was present in the solid condition from the first, and therefore has the calorific value of ordinary carbon, whilst the carbon (C'') in the volatile portion was initially present in the gaseous form; and secondly, that since an atom of gaseous carbon (in the form of CO) evolves 5,607 heat units in combining with one atom of oxygen, it would give out twice that amount, or 11,214 heat units, in uniting with two atoms to form carbonic acid, both carbon and oxygen being supposed to be gaseous.

Determination of Calorific Power.—The total heat of combustion of any fuel is usually determined by burning a weighed sample in a current of oxygen in a vessel sunk beneath the surface of a known weight of water; the products of combustion pass through a coil of narrow tubing also immersed in the water, so that all the excess heat is given up to the latter. The rise in the temperature of the water being ascertained by means of thermometers, the number of parts by weight of water heated 1° by the combustion of one part of the fuel can be found by a simple calculation. Such an instrument is termed a *calorimeter*. For accurate measurements, many precautions must be observed, which call for experience and skill, and render the process tedious. Hence a special calorimeter has been devised by Thompson for use with coal; it gives rapid results, requires but little manipulative skill, and yet is sufficiently accurate for most practical purposes. It consists of a copper bell, containing a definite weight of the fuel mixed intimately with potassium chlorate and nitre. A slow-burning fuse is half-buried in the mixture, and ignited, the whole apparatus is then plunged into a measured volume of water, and in a few moments combustion sets in vigorously, owing to the presence of the nitre and potassium chlorate, which provide the whole of the oxygen required; all the products of combustion pass out of the bell, through perforations at the bottom, and bubble up through the water, to which they impart most of their heat. There are many sources of error, but under constant conditions they may, for practical purposes, be compensated by an addition of 15 per cent. to the result obtained.[1] The weight of water usually employed is equal to that of the coal taken multiplied by the number representing the latent heat of steam ; so that the increase in the temperature of the water gives a direct reading of the *evaporative power* of the fuel, expressed as pounds of water converted into steam from and at 100° C.

An equally rapid, but far more accurate, result can be obtained with the Mahler-Berthelot bomb-calorimeter. Here, the coal is contained in a strong gold-lined steel vessel, into which oxygen is forced under great pressure ; the vessel is then tightly closed, and completely immersed in water. Ignition is started by the momentary application of an electric current, and the operation rapidly comes to a conclusion, no gas being allowed to escape until the whole apparatus is at the temperature of the water.

Estimation of High Temperatures.—In the determination of high temperatures *pyrometers* are employed ; and nearly every possible variation in the physical properties of substances (proportional to changes in temperature) has been utilised in the construction of instruments for this purpose. For moderately high temperatures, hard glass thermometer bulbs containing a fluid alloy of sodium and potassium, air thermometers, or gauges for the indication of the pressure of mercury vapour developed in an enclosed space at the temperature to be ascertained, have been successfully employed. Siemens introduced a pyrometer, from which the temperature was found by determining the increase that it produced in the electrical resistance of a platinum wire ; and Callendar's modification of this instrument is one of the most accurate pyrometers available. Its chief rivals are those which depend upon the generation of the thermo-electric currents that always result from joining two different kinds of wire at both ends, and so placing

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[1] Scheurer-Kestner has shown that an allowance of 15 per cent. is usually more correct than the 10 per cent. originally recommended by Thompson.

them that one joint is hotter than the other. The readiness with which a photographic record can be obtained with an instrument of this kind has brought it prominently into favour ; and a recording apparatus, used in connection with a junction of platinum, and platinum-rhodium or platinum-iridium wire, has been adopted in many works, both for research and as a check upon the temperatures of furnaces. Two long wires are used twisted together at one end, and this junction is introduced into the space the temperature of which is to be ascertained. The free ends of the wires are kept cool by surrounding them with melting ice, and they are coupled up with the two connections of a very sensitive (D'Arsonval) galvanometer. The strength of the electric current produced is nearly proportioned to the rise of temperature in the hot junction ; but the instrument is calibrated by making observations with the aid of substances of known melting point. The current generated passes through the galvanometer, and the deflection of the spot of light reflected from the mirror of this instrument indicates the strength of the current (and hence the temperature). The spot of light falls upon a photographic plate, which is slowly moved by clockwork at a known rate ; so that readings of both time and temperature are obtained automatically. The intensity of the light emitted by glowing substances may also be measured, and is thus turned to account in estimating their temperature in one form of optical pyrometer. But this is really only a refinement of the original method of judging temperature by the colour of the light emitted. The minimum temperature of substances just visible in the dark averages 470° C., while in daylight it is about 520° ; at 700° the luminous object is dull red, at 850° it is 'cherry red,' at 1,000° bright cherry red, and at 1,300° white, whilst at 1,500° it is dazzling white, and above this blue-white.

FUELS

Wood.—Wood consists almost entirely of cellulose, a body to which the formula $C_{12}H_{20}O_{10}$ has been assigned. The percentage composition of this substance, and those of different kinds of wood after thorough drying, are summarised in the following table :—

	Cellulose	*Dry Wood*	
Carbon	44·44	50·9 – 48·2	Mean = 49·3
Hydrogen	6·17	6·9 – 5·4	,, = 6·3
Oxygen	49·39	44·5 – 41·7	,, = 43·3
Nitrogen	—	—	,, = 1·1

The other organic constituents vary with the species of tree ; for example, the ease with which pine inflames is due to the resin it contains, and the sap of oak contains much tannin. The relative combustibility of the different woods is, however, mainly dependent on their density and dryness.

Unless in exceptional cases, the ash ranges between 1 per cent. and 2 per cent. The ash consists mainly of lime and potash and smaller proportions of soda and magnesia, oxides of iron and manganese, in combination with carbonic acid mainly, but to a small extent also with chlorine and with sulphuric acid, phosphoric acid, and silicic acid. The soluble portion of the ash amounts to about 15 to 20 per cent.

It will readily be seen from the composition of wood that it is unsuitable for use where it is required to produce a high temperature. The calorific power of cellulose has been experimentally determined to be about 3,600. An additional reason for not employing wood in metallurgical operations is to be found in the fact that it retains, even after prolonged air-drying, 18 to 20 per cent. of moisture. The desiccation of wood is greatly prolonged by the removal of the bark. The younger branches of trees contain, as a rule, about twice as much water as the older and the trunk ; the quantity of moisture in either case being least at the fall and the beginning of the year, and greatest in the spring when the leaves and shoots commence to form. By air-drying, wood may shrink to the extent of $\frac{1}{10}$, or more. By drying at 100° C., the whole of the moisture may be expelled, but on subsequent exposure to the air at the normal temperature, the wood will reabsorb from 18 to 20 per cent. of water. The specific gravity of freshly cut wood ranges, usually, from 0·78 to 1·07, according to the species, and after air-drying it may be as low as 0·37 to 0·68. But these differences are mainly due to the varying porosity of the different kinds of wood ; for if the air be expelled from the pores, as by long soaking in water, the specific gravities of all specimens are practically the same, viz. 1·5, which represents therefore the true specific gravity of the woody fibre. 'Water-logged' wood is thus found to sink in water. Wood inflames at a temperature of about 300° C. in the presence of oxygen or air.

Charcoal.—It will be observed that in wood there is a large proportion of oxygen present, and as it is in chemical combination with the hydrogen and carbon, it follows that a given weight of wood cannot produce the same amount of heat as would an equal weight of a substance composed of carbon and hydrogen alone. For all practical purposes it is as if the carbon and hydrogen had already been partially burnt, and the products of combustion remained mixed with the unburnt wood. When wood is converted into charcoal by being strongly heated, with, as far as possible, the exclusion of air, these compounds are given off as gases and vapours, and the residue consists almost entirely of carbon, a little hydrogen and oxygen being retained even under the most favourable conditions. The volatile products of the distillation consist mainly of water, wood spirit, pyroligneous acid, oils and tar, and, towards the end, principally of carburetted hydrogen gas, carbonic oxide, and carbonic acid. The process of distillation commences at about 150° C., and is practically complete at about 360°

to 400° C. The nature and relative quantity of the volatile products will be dependent mainly on whether the heat is slowly or rapidly increased, and on its initial intensity. A glance at the result of submitting wood to distillation is sufficient to make it clear that, except considerable local heat is required, it would be more economical to dry the wood only before use, unless the products of the distillation can be collected and utilised.

Good charcoal preserves the form of the wood from which it is made. Its density will depend to some extent on that of the wood employed, but also to a considerable extent on the way in which the carbonisation has been conducted. If very rapidly, the charcoal may be light, fissured, and friable ; if slowly, compact and dense. A high temperature also conduces to this latter result as well as to the more complete expulsion of the gaseous elements, which, however, at the highest temperature we can command, are never entirely got rid of by the action of heat alone. When properly made, charcoal should be perfectly black, hard, and sonorous, and it should not soil the fingers when touched. If the charcoal does not answer to this description, either the temperature has been too low, or it has been partially burnt by undue admission of air. In the latter case it will be of a dull appearance, tender and friable, and more or less cracked, and will mark the fingers.

Charcoal, like artificially dried wood, absorbs moisture from the air, the extent to which this takes place depending on the temperature at which the charcoal has been produced, and on its density. These latter conditions also determine the temperature at which combustion will commence. When the charcoal has been prepared below about 400° C., the temperature required to ensure its ignition is greater than that at which it was prepared ; above 400° C. it is less. Thus, if prepared at 400° C. it would inflame at about 370°, but if prepared at the fusing-point of steel the temperature required to start combustion would be about

600° to 800° C. For most purposes it is not desirable to prepare charcoal at a higher temperature than 360° C.

Preparation of Charcoal.—The operation known as charcoal-burning is carried on sometimes by building the wood into a stack or pile in the open air, in a way hereafter to be described; sometimes by placing the wood in closed chambers of brick, stone, or iron, and subjecting it to the action of heat, which is applied externally, and is occasionally obtained by the combustion of the volatile products of the distillation. When the charring is effected in piles in the open air, a dry and level piece of ground, sheltered from the wind, and, if possible, near a water supply, should be chosen. In a circular pile the bed on which the pile is to rest should be made to slope upwards slightly towards the centre. Three stakes are driven into the bed at its centre; round these are piled pieces of wood, which in some districts are placed vertically and concentrically in two or more layers, in others horizontally, a few pieces round the chimney only being in a vertical position. In either case the top is covered over with smaller pieces, laid horizontally and concentrically, so as to bind the whole together. All interstices are also filled up, as far as possible, with small wood. Next a row of forked sticks is driven into the ground at the base of the pile, and a layer of branches placed on the top of them to support the cover, which is then constructed of turf, the grassy side placed inwards. Instead of these sticks and branches, stones are

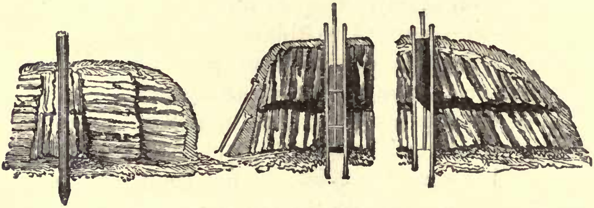

FIG. 1.—Circular Pile for Burning Charcoal.

sometimes used. The cover is completed by plastering over the turf with a mixture of *breeze*, *i.e.* small refuse charcoal, and earth, or earth alone. The pile is lighted by igniting some easily inflammable wood, placed in the chimney formed by the three stakes. When the centre of the pile is well kindled, any sinking-in which has occurred is made good, and the cover is extended over the top. Much water now condenses on the inner surface of the cover and round the base, and yellowish-grey smoke escapes from the opening at the base. This is termed the *sweating stage*. When the colour of the smoke is observed to turn to light grey this stage is complete, and the covering is at once extended down to the ground, so as to completely envelop the pile ; at the same time the dried and partially charred wood is consolidated by the aid of a pole, the cover being in places rapidly removed for the purpose, and replaced with the greatest expedition possible. The stack is now left to itself for several days, a few small holes, however, being made near the bottom to allow the escape of vapours, and to admit a little air to assist in keeping up the temperature, which would otherwise soon become too low to carry on the operation. In order to complete the charring in the cooler portions of the pile near the surface, it becomes necessary towards the close of this part of the process to make vents at the level of the top of the lowest layer of wood. The thick yellowish smoke which at first issues from these holes gradually becomes blue and thin. They are then stopped, and others opened a little lower down. In large piles several rows of vents may have to be opened one after the other. When it is judged, from the appearance of the smoke issuing from the lowest vents, that the whole pile is completely and properly charred, the cover is made as impervious to air as practicable, after which the stack is again left to itself for several days. Certain precautions have to be observed in withdrawing the charcoal. It is not found expedient to allow the pile to cool down below the point of ignition ; the time required would be considerable, and there would be inevitably a certain amount of loss, besides which it is stated that the charcoal is of better quality when it has been rapidly cooled. The usual method is to uncover a portion of the heap near the bottom, and withdraw the charcoal, rapidly covering up all but the region actually being worked upon. The drawn charcoal is at once quenched with water or covered with damp breeze. The details of this method of charcoal-burning necessarily vary slightly in different localities. The object of the burner, in all cases, is to conduct the process in such a way as to ensure the combustion proceeding with regularity from the centre towards the circumference, and at the same time from the summit gradually to the bottom. This he does by carefully regulating the direction and the amount of the air admitted to the pile, and by making good as they occur any hollow spaces.

FIG. 2.—Rectangular Pile for Burning Charcoal.

In some localities, instead of three central stakes one only is used, in which case ignition of the pile is effected by means of a channel left in the base of the pile from the centre to the circumference.

Rectangular piles are in favour in some parts of the Continent, more especially in parts of Sweden. The ground should preferably slope about 18 in. in 24 ft. The wood is cut into lengths of about 8 ft., and arranged horizontally so as to form a pile which, when complete, is about 24 ft. long, and gradually increases in height from 2 ft. to 7 or 9 ft. Air is prevented from having access to the sides of the pile by boards arranged all round, and supported by stakes driven into the ground about 6 in. from the pile and 2 ft. apart, the space between the boards and the stack being filled with breeze rammed tightly in. The larger pieces of wood should be placed at the thick end, and, as in the case of the circular pile, all interstices should be filled with small wood.

The top of the pile is covered over with small branches and leaves, and then with a layer of breeze. Ignition is effected from the lower end, where a hole is left for the purpose. This hole is kept open until only light-blue smoke escapes from the cover in the vicinity, when it is closed, and several others are opened in the small end, but somewhat higher up. Following the same indications as before, after a time these holes may be closed also, and the carbonisation should then be complete at the lower end of the pile. In order to carry on the process holes are now made some feet nearer the thick end, and about 2 ft. from the ground. In this way the process is conducted until carbonisation has taken place throughout the mass. Each set of holes should be made a little higher from the ground than those preceding. Charcoal can be withdrawn from the thin end when the openings have reached within about 8 ft. of the thickest part.

A modification of the foregoing method consists in arranging the wood lengthwise, and slanting upwards towards the thick end. In this way carbonisation takes place more rapidly, and the products of the distillation may be collected by means of a pipe inserted at the top of the high end.

All these methods have the advantage that they can be employed close to the spot where the wood is obtained, no special construction being required. In localities in which transport is difficult and expensive—and this is commonly the case where wood in quantity suitable for charcoal-burning is obtainable—the economy of burning on the spot is very considerable, the wood weighing at least five times as much as the charcoal which can be produced from it.

The tar and pyroligneous acid produced during charcoal-burning are collected, in some districts, by means of a specially constructed bed of brickwork or stone, on which the pile rests. Instead of sloping up, the bed is made to slope down to the centre, at which point there is a cavity, loosely covered, and connected by a channel with a closed reservoir.

Charring is sometimes conducted in retorts or furnaces of various shapes. This, however, can only be done economically when the wood can be very cheaply transported, or when the chief object in view is to obtain pyroligneous acid. The charring may be effected either by the heat produced by the combustion of a small proportion of the charcoal and products of the distillation, air being admitted in suitable quantity for the purpose, or by heat externally applied, and obtained in many cases by burning the volatile products. When charcoal-making is carried on in retorts, the tar is collected by pipes opening into the floor. Care is required to regulate the temperature in retorts, otherwise a too dense charcoal, unsuited for most purposes, is produced.

The yield of charcoal by weight varies considerably according to the way in which the charring has been effected, and also with the age and circumstances attending the growth of the wood. The weight of charcoal produced varies between 15 and 28 per cent. of the weight of the wood employed, but the mean from piles is about 21 per cent. The more slowly the charring is carried on the greater will be the yield. The yield by volume is from 50 to 75 per cent. The weight of ash ranges usually from 2·5 to 3 per cent.

For commercial purposes charcoal is always estimated by volume, as the varying amount of moisture it contains renders it impossible on a large scale to determine the true weight. The measure employed is a sack.

Charcoal takes up on an average about 12 per cent. of moisture when left exposed to the air. It has also the property of absorbing other gases and vapours, in some cases in great quantity; *e.g.* one volume of charcoal will absorb about 100 volumes of ammonia vapour, 80 of hydrochloric acid, and 60 of sulphurous acid gas.

Peat.—The formation of peat is due to the gradual alteration of the substance of plants, especially mosses, under conditions favourable to the presence of much moisture, and consequent partial exclusion of air. There are very great accumulations of peat in different parts of the world, in what are known as peat-bogs. Being a product of recent origin, it is always found on or near the surface. As would be expected, the greater the depth from which the peat is obtained the more the original organic structure will have become obliterated. The structure of peat is favourable to its retaining moisture in considerable quantity, even after it has been removed from the conditions which attended its formation. After what has been said concerning vegetable tissue, it will be readily understood that the organic part of the most recently formed peat has approximately the same ultimate composition as wood. The inorganic or earthy portion of peat is considerably in excess of that of wood. This is traceable to the action of wind and water, carrying matter in suspension, which in greater or less quantity becomes mixed with the decaying plants. The darker the peat is the more will the composition differ from that of the original plants, *i.e.* the more carbon will it contain. It is easy to see that, according to its age, and the circumstances attending its formation, peat will vary considerably in its composition and structure. Owing to the way in which peat forms, its ash always contains, in more or less quantity, phosphates and sulphates, if not sulphides.

The specific gravity of peat in the air-dried condition is stated to vary between 0·1 and 1·0, but is usually between 0·3 and 0·6. In order to determine the true specific gravity it would be necessary to expel all the air from the pores. Sir Robert Kane, in writing of the industrial resources of Ireland, says that a cubic yard of light peat, so much used there for domestic fuel, weighs about 500 lb., of good peat, packed close in the form of sods, about 900 lb., and of the densest peat as much as 1,100 lb.

Frost deteriorates fresh peat very much; when it is subsequently dried it does not consolidate properly, remaining light and friable. Irish peat, as it is obtained ordinarily in commerce, contains about one-fourth its weight of water; before drying it contains from 70 to 90 per cent. of moisture. When heated to about 120° C. the organic matter commences to undergo permanent change, and volatile products distil off. The calorific power of air-dried peat is 3,000, or about one-third that of coal.

In order to obtain peat in a suitable condition for subsequent treatment it is generally only necessary to drain the ground by means of trenches, and, having removed the surface material which has not undergone sufficient change, to cut the peat into rectangular pieces by means of a tool consisting of two pieces of iron at right angles to one another. In Hanover it has been found that five men can easily cut and carry to the drying ground 3,000 cb. ft., or 12,000 peats, in a day. After the peat has remained some time on the drying ground, where it has been thrown down in barrowfuls, it is taken away to a suitable position and built up into walls a peat and a half thick. In about a month's time the peats, which should then be about half dry, are removed, and either stored in magazines or built into large stacks. 1,000 cb. ft. of good black peat, freshly cut, yield about 270 cb. ft. of thoroughly air-dried peat; the same amount of freshly cut light-grey peat yields about 700 cb. ft. when similarly dried.

In Dublin it has been found that well-dried black peat, which costs 8*s*. a ton, was less economical than coal for use in locomotives (Percy). On the Continent, notably in the north of France, along the banks of the Somme, the Oise, and the Aisne, and in Prussia, peat-cutting machines are employed. They have the advantage that the peat can be cut without its being necessary to drain the ground, which in itself is often a considerable expense when the peat extends to some depth. The cutter is like an iron box with the bottom removed ; it is forced down into the peat, and by means of a lever a flat piece of iron is driven horizontally under it ; the cutting of a peat is thus completed, and it can be lifted by the machinery above to any required height, irrespective of the presence of water. The large peats brought up by the cutter are subsequently divided, so as to be more conveniently handled.

Sometimes peat occurs in a more or less muddy condition. This is the case in Holland. Under these circumstances it has to be dredged out by means of canvas bags, usually about 18 in. deep, fixed to an iron ring. As much moisture as possible having drained off from the bags, the peat is turned out on to a flat piece of ground fenced round with planks, where it is allowed to dry to a certain extent, after which it is consolidated by men treading over it with boards attached to their feet, or it is beaten down with a suitable flat-headed tool. In this way it is reduced to about half its original thickness, *i.e.* to about 6 in. ; it is then cut up and air-dried.

In its ordinary air-dried state peat is very tender and crumbles to pieces under pressure ; it cannot, therefore, be employed with advantage in blast-furnaces, neither can it be transported to a distance without much loss. Its great relative bulk as compared with other fuels is also a drawback to its use, not only in respect to cost of carriage, but also on account of the space occupied by it in the furnace. A further objection is the large amount of hygroscopic moisture present.

Preparation of Peat.—Amongst the methods which have been employed to render peat more suitable for metallurgical purposes may be enumerated the following :—

I. Compression of raw peat, with subsequent air-drying.
II. Compression of air-dried peat, cold.

III. Compression of air-dried peat, hot.

IV. Raw peat, ground, $\left\{\begin{array}{c}\text{consolidated}\\\text{or}\\\text{compressed,}\end{array}\right\}$ and $\left\{\begin{array}{c}\text{air-dried or}\\\text{artificially}\\\text{dried,}\end{array}\right\}$ &c.

I. Drying is considerably hastened by subjecting the fresh peat to pressure, so as to squeeze out a portion of the moisture ; in practice much benefit is not, however, found to result when this plan is adopted. Undoubtedly the removal of 20 to 30 per cent. of the moisture enables desiccation to be effected more rapidly, but it is questionable whether there is any real economy in this plan. As the removal of moisture by compression proceeds it becomes more and more difficult and costly, the power required being considerable. The peat obtained is said not to be so satisfactory as that produced by some other methods ; it has a tendency to fracture in the direction of the original bedding. This method, in any case, cannot be applied to muddy peat, as the filtering medium of the compressing apparatus soon becomes choked by the fine particles.

Various machines have been invented for compressing peat before air-drying it. In some, a frame fitted with a flat piston is employed ; in others, various forms of rolls are used. The best filtering material is said to be cloth made of goat's hair.

II. The second method has been successfully applied where good earthy peat could be obtained. The peat having been drained and freed from its superficial covering, is ploughed up into furrows, and then harrowed from time to time until quite air-dried ; it is then forced into moulds by means of stamps weighing about 2 cwt. each. The blocks made in this way have sufficient tenacity to admit of their being cut with a saw. The compression reduces the peat to about two-fifths of its original bulk. A cubic foot of the compressed peat weighs about 80 lb.

III. In the neighbourhood of Munich and Augsburg the third plan referred to has been adopted. The peat is first air-dried in much the same way as that just described, after which, as it contains many roots, it is passed through a bolting-machine made of wire gauze. The coarse pieces thus separated are used to obtain the necessary heat to raise to 100° C. the temperature of the finer material which has passed through the bolting-machine, and to work the compressing-machine used to mould the heated peat into blocks. The drying is effected in a series of compartments, heated externally, the peat being gradually transferred from one end of the series to the other by a kind of archimedean screw made of sheet iron. The dimensions of these peat blocks are about 8 × 3 × 1 in. A single press is stated to yield about 8,000 blocks per hour. Contraction to the extent of from one-fifth to one-fourth takes place during the compression; 10 to 20 per cent. of moisture still remains, and there is generally present about 8 per cent. of ash. The cost of production is stated to be about twelve shillings per ton, exclusive of interest on outlay and wear and tear of plant.

This method certainly possesses advantages, but the expense is considerable, and it is essential that good peat should be used.

It only remains to consider the fourth method.

IV. The peat, if of a muddy nature, is passed through a rotating sieve, having on the inside four radial arms carrying brushes, which traverse the surface of the sieve, and assist the passage of the fine material through the mesh. The material which passes the sieve is next ground in a pug-mill, somewhat similar to that used by brickmakers, and then pumped into reservoirs formed on flat ground, the sides being built up with clay and boards. In the course of a week, more or less, according to the weather, the peat-mud, which at first is about 20 in. thick, begins to crack; it is then consolidated by men walking over it with boards on their feet, and left to itself for about another week, at the expiration of which it is cut in one direction at intervals of about 3½ in., and, after a further lapse of the same time, in the direction at right angles. The blocks are then ready to receive their final drying.

Fibrous peat is either reduced to a pulp by rotating cutters, or is first cut to a certain degree of fineness, and then ground in an apparatus somewhat resembling a coffee-mill.

The peat-mud thus obtained, in some cases, is dried in the way already described, the separation into blocks being effected by means of a frame divided by thin partitions into compartments of the size the blocks are intended to be. The peat is allowed to dry for about a week, by which time it will have acquired a felt-like consistency ; the frame is then pressed down on it so as to indent it. On further desiccation the peat breaks along these lines into brick-shaped pieces, which are then ready for air-drying.

In Weber's method the peat is worked into a pulp, and is then moulded, without compression, into bricks, which are first air-dried under cover, and then by artificial heat. It is claimed for this peat by some that it is not inferior to compressed peat either in tenacity or compactness. There is a decided advantage in air-drying the peat blocks before subjecting them to artificial heat. Treated in this way they are less likely to crack and get out of shape, and in the end they are denser in structure, there being considerable difficulty in completely drying the centre of the brick without the aid of artificially applied heat. The temperature of the currents of air in the drying sheds ranges between 56° and 63° C. ; the heating is effected by flues extending from one end of the shed to the other, and arrangement is made for the admission of fresh air, and for the escape of that charged with moisture. The drying is complete in from eight to twelve days. The air-dried peat, when first introduced into the drying house, softens and swells until it has attained the temperature of the surrounding atmosphere, when it rapidly shrinks, and becomes firm and dense. The weight of a cubic foot of peat prepared in this manner is said to be about 34 lb. It still contains about twelve per cent. of moisture.

In some other systems the general details are much the same as in those already described; but the blocks are moulded by pressure, by means generally not differing greatly from those employed in making ordinary bricks.

Various other methods, in principle the same as Weber's, but differing in detail, have been employed. In some of these, kilns are so arranged that the hot waste gases from furnaces can be passed through them, either from the top downwards, or in the reverse direction. The temperature of the gases as they enter is regulated, by the suitable admission of air, so as not to exceed 150° C. in contact with moist peat, and 120° with dry peat, and not to fall below 100°. Instead of waste gases, air specially heated is substituted in cases where the former are not available for the purpose. The maximum rate of flow of the gases or air on entering is about 400 cb. ft. per minute, for a kiln which has about 4,000 cb. ft. of drying space. In different arrangements this will necessarily vary somewhat. In the best forms of apparatus the working is continuous, peat being charged in at the top as fast as it is drawn at the bottom.

One of the most important points to keep in view in constructing a kiln is, that the hot air should be made to enter in such a way as to come first in contact with the peat that is wettest. In this way there is a greater economy of heat, and less danger of the peat igniting. It is also important that the walls of the kiln should be as air-tight as possible, otherwise local cooling of the peat would take place, and the desiccation would proceed unequally.

Machines have been invented for removing the moisture from peat by centrifugal action; they have not as yet had much success. The chief difficulty in this method is to prevent the sieves from becoming choked up, and it is not easy to see how this can be overcome.

There is an important objection to peat made into bricks in the ordinary way, namely, that when charged into a furnace they are very apt to fall with their flat faces together, leaving insufficient space for the passage of air. The best remedy would be to make the peat into ball-shaped pieces; but this is not practicable owing to the expense involved. In the pulping process the peat can be forced out of the machine in a continuous cylindrical piece, and then cut up into lengths. These cylindrical pieces are better suited for burning than the square bricks.

In consequence of the large amount of ash in peat from low lands, and the nature of that ash, it is not well suited for use in the metallurgy of iron, in operations in which the fuel and the metal are contained in the same compartment. Peat can, however, be satisfactorily employed when the combustion is carried on in a separate chamber, as in a reverberatory furnace. Prepared peat can also be employed in the blast-furnace, when a high-grade iron is not required. The useful calorific value of peat is slightly lower than that of wood, in the condition in which both are usually obtained in commerce.

Peat can be made into charcoal, but the product is not by far so satisfactory as in the case of wood. In parts of Germany it is used to a certain extent, in admixture with wood charcoal, in high-blast furnaces, and in common forge-fires. Attempts to create an industry for the preparation of peat charcoal and the recovery of ammonia and other valuable products of distillation, have lately been renewed.

Lignite and Coal.—It has been stated that peat is of recent origin. But if these things are going on under our eyes at the present day, it is reasonable to expect that something similar has occurred in past geological ages. During those remote times, the extent of which, as evidenced by geological science, is so vast as to be almost beyond the grasp of the average human mind, there flourished a luxuriant growth of plants and trees, extending over large areas. It is to those plants and trees that we owe the wealth of coal which has given such an enormous impetus to civilisation during the last hundred years. Vegetation is the natural store-house of the heat of the sun which reaches the earth. Under its influence vegetable life assimilates carbon, hydrogen, and oxygen from the moisture and carbonic acid which form part of our normal atmosphere. The compounds thus formed, when raised to a sufficiently high temperature in the presence of air, yield up the heat absorbed during their formation. If complete combustion be effected, not a fraction of the heat which originally contributed to the growth of the plant is lost. The vegetable substances were built up from carbonic acid and moisture, and these bodies are the sole products of the *complete* combustion of organic matter of every kind.

It is perfectly well established that lignite and coal, equally with peat, are not formed from vegetable matter which has undergone *decay* from exposure to the atmosphere. It follows that the vegetation from which coal has originated must have been protected from direct atmospheric influences, and there is no reason to doubt that this took place in a similar manner to that which accompanies the formation of peat, *i.e.* that the coal-plants grew in swampy ground, probably forming the estuary of some large river. Owing to subsidence (until the earth's crust in that region was below water) the coal-plants ceased for a time to grow, and the deposit of lifeless vegetable matter became covered with a layer of earthy material, borne down by running water and gradually deposited. After this sedimentary deposit had increased to a certain thickness, vegetable life again became possible. In this way a series of strata has been built up, in which seams of coal alternate with layers of clay, limestone, sandstone, and ironstone. These deposits, which are found over areas hundreds of miles in extent, are called the *coal-measures*. The nature of the coal, as we now find it, will depend on the time which has elapsed since its formation, and the amount of pressure to which the strata have been subjected. The longer the time and the greater the pressure, the more hydrogen and oxygen will have been eliminated, and the more closely will the residual substance approximate to

Grüner's Classification.

Names of the five types or classes	Composition per cent. of the organic constituents			Number of parts by weight of oxygen,[1] taking the weight of hydrogen as unity	Percentage of coke	Nature and appearance of the coke
	Carbon	Hydrogen	Oxygen[1]			
Dry coals, burning with a long flame . .	75–80	4·5–5·5	15–19·5	3–4	50–60	Pulverulent, or, at the most, fritted
Fat coals, burning with a long flame, or gas coals . .	80–85	5–5·8	10–14·2	2–3	60–68	Caked, but very friable
Fat coals, properly so-called, or furnace coals .	84–89	5–5·5	5·5–11	1–2	68–74	Caked, moderately compact
Fat coals, burning with a short flame, or coking coals . .	88–91	4·5–5·5	5·5–6·5	1	74–82	Caked, very compact, but little friable
Lean (maigres) coals, or anthracite . .	90–93	4–4·5	3–5·5	1	82–90	Fritted or pulverulent

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[1] Including nitrogen, the proportion of which is stated rarely to exceed one per cent. of the organic constituents.

pure carbon. Although these changes are so gradual that no alteration in any seam of coal would be apparent to a careful observer during a human lifetime, yet that they go on is conclusively shown by the accumulation of the resultant gases in mines where there is not sufficient ventilation to carry them off.

Classification of Coal.—The following classification of coal is due to Dr. Percy. It will be observed that it is based on variation in the chemical composition of the substance:—

Lignite.	
Bituminous Coal	Non-caking, rich in oxygen. Caking. Non-caking, rich in carbon.
Anthracite.	

Grüner's classification of coals given above (p. 32) has in view the industrial application of each particular kind. It differs from Dr. Percy's only in being more detailed.

The reader must carefully bear in mind that whatever classification is adopted it is only for convenience of description. As has been shown by Dr. Percy in the following table, there are coals the analyses of which form a series unbroken in continuity from wood to anthracite. Peat appears to be inserted in the table not because it properly forms a link in the chain, but rather because it is a product

Table showing the gradual Change in Composition from Wood to Anthracite.

Substance	Carbon	Hydrogen	Oxygen
1. Wood (the mean of several analyses)	100	12·18	83·07
2. Peat (the mean of several analyses)	100	9·85	55·67
3. Lignite (mean of 15 varieties) .	100	8·37	42·42
4. Ten-yard coal of the South Staffordshire basin	100	6·12	21·23
5. Steam coal from the Tyne . .	100	5·91	18·32
6. Pentrefelin coal of South Wales .	100	4·75	5·28
7. Anthracite from Pennsylvania, U.S.	100	2·84	1·74

of more recent origin than lignite, and therefore approaches more in composition to ligneous tissue, thus filling the gap which time has made between wood and lignite. For the sake of comparison carbon has been taken in all cases as 100.

Lignite.—This term is synonymous with the *braunkohle* (brown coal) of the Germans. It is employed to designate substances which form the link between peat on the one hand and true coal on the other. In those kinds which approximate most closely in their composition to peat, the only essential difference is that they have been derived from woody matter, whereas peat owes its origin to mosses, for the most part, and to plants of small growth. Lignites of this description still retain the structure of the original wood more or less, according to the stage of alteration which they have reached. As the original structure becomes obliterated by pressure and chemical action, the fracture tends to become conchoidal. The change which goes on during the formation of peat and lignite, and the less bituminous coals and anthracites from the more highly bituminous coals and lignites, is due to the gradual elimination of oxygen and hydrogen in combination with one another (and mainly with carbon), as carbonic acid and carburetted hydrogen or marsh-gas. It thus happens that certain mineral fuels might equally well be classed with coals as with lignites, it being difficult to define where the one ends and the other begins. Fibrous lignites (fossil wood) contain sometimes as much as 50 per cent. of moisture, and even after being artificially dried they take up 12 to 15 per cent. The remarks which have been made with respect to the ash in peat will apply equally to lignite. Fossil wood yields on distillation about 35 to 40 per cent. of solid residue ; earthy brown coal, which is a convenient term by which to distinguish lignite in a somewhat more altered condition, 40 to 50 per cent. Lignites (sometimes called pitch coal), to which the term conchoidal brown coal may with advantage be applied, in point of quantity of residue left after distillation do not differ sensibly from bituminous wood. Lignites of this last description do not contain, generally, more than 5 to 10 per cent. of moisture. They burn with a long smoky flame. In appearance they are dark-brown or black, hard, tenacious, sonorous, and they break with a conchoidal fracture; they do not alter much in structure on exposure to the air. The average composition of brown coals is as follows:—

Lignite or brown coal	Carbon	Hydrogen	Oxygen and nitrogen	Approximate calorific power
Fibrous	57–67	5–6	28–37	5,000
Earthy	45–70	5–6	25–30	5,700
Conchoidal . . .	65–75	4–6	21–29	6,500
Bituminous . . .	70–80	6–8	12–24	7,000

Lignites containing much water may be air- or kiln-dried with better results than in the case of peat. Lignites, with few exceptions, are *non-caking*; *i.e.* when powdered and strongly heated, with exclusion of air, the particles will not cohere together to form what is known as *coke*.

Bituminous Coal.—The kind of coal into which lignite merges in its most altered stage is bituminous coal. Although these two substances in some cases may be difficult to distinguish one from the other, yet that is far from being the case when average specimens of each are considered. The density of bituminous coal is, as a rule, greater than that of lignite or brown coal; it contains less water in its natural state than lignite, and after drying at 100° C. is also less hygroscopic. It has previously been stated that bituminous coals may broadly be divided into two classes, viz. caking and non-caking.

A caking coal is one, the fragments of which tend to become united on heating, so that even the small coal or dust forms a coherent cake. Some coals appear almost to fuse, swelling up and yielding a porous vesicular mass; and this effect is always attended with the evolution of tarry matter and gas, for it is an unvarying characteristic of coal that it cannot fuse without decomposition. The character of these liquid and gaseous products of distillation appears to determine the caking power of the coal. Those coals which contain a large excess either of hydrogen and oxygen, or of carbon, are non-caking coals, and the fragments retain their original shape on heating, showing little or no tendency to cohere. The two classes merge into each other imperceptibly, and it may happen that a coal having practically the same ultimate composition as another will not have the same properties, by reason of the different chemical grouping of the elements, and must be placed in a different class. Every degree of coking may thus occur; and the density and strength of the *coke* produced when different specimens of coal are heated in the absence of air is, consequently, very variable.

Before leaving this part of the subject it will be profitable to glance briefly, but systematically, at the different varieties of bituminous coal, commencing with those most nearly allied to lignites. For this purpose the French classification framed by Grüner can be advantageously followed, substituting, however, for the terms *dry*, *fat*, and *lean* the more familiar expressions caking and non-caking.

It should here be remarked that true coals contain no actual bitumen; and the term 'bituminous coal' is a misnomer that appears to have resulted from the observation of the similar behaviour of the two materials during combustion. *Flaming coal* has been suggested as an alternative name.

1. **Non-caking Coal, with a long flame.**—These coals when treated for coke crack, but preserve their original form; and if originally in powder the particles do not become consolidated. Coals of this kind are hard, compact, and but little friable. A cubic foot of them may, for purpose of storage, be estimated to weigh about 44 lb. The fracture is often conchoidal, and of such a nature as to have given rise to the

name *splint-coal.* It is not common in France or Germany, but in Derbyshire, Staffordshire, and Scotland it exists in considerable quantity ; in colour it is rarely perfectly black ; the powder is brown. The calorific power ranges between 8,000 and 8,500, taking the two extremes of the class and assuming the absence of moisture and extraneous matter. One part of the dried coal has been found to convert 6 to 6·5 parts of water at 0° into vapour at 112° C., when burned under boilers with only just sufficient air for combustion. In the lower part of the basins the coal passes into that comprehended in the next class, viz. :—

2. **Caking Coals, with long flame.**—As the title indicates, these coals coke ; those nearest in nature to class 1, however, when powdered, barely become cemented together on being heated. They go by the name of cherry-coal in the North of England. In hardness they do not equal class 1, and the fracture tends less to be conchoidal ; they are also blacker and brighter. A cubic foot weighs from 44 to 47 lb. when stored. Like the last described, they burn with abundance of flame and smoke ; they take fire readily, and burn rapidly. The coke is light, friable, and porous, and therefore unsuited for metallurgical purposes ; but for the manufacture of lighting-gas these coals are very valuable, the gas, though in quantity not so great as that from the non-caking coal of class 1, being of higher illuminating power. The coke is, besides, good enough for use where it will not be subjected to much pressure or a strong blast. The calorific value ranges between 8,500 and 8,800. According to practical trials made at Portsmouth and Woolwich, 1 part of this coal in its ordinary condition (say containing 5 to 8 per cent. of water and ash) will convert 7 to 7·75 parts of water into vapour. Coal of this description occurs notably in the neighbourhood of Newcastle and in South Wales.

3. **Caking Coal, properly so-called.**—Coals of this type have a less lamellated structure than the last ; they are also blacker, brighter, and much softer on the average, and the

flame is shorter and more brilliant, giving less smoke. When heated they soften, even to fusion in some cases. Although they contain less volatile matter than those last considered, they swell up more in coking. The properties of this coal render it well suited for use in blacksmiths' forges, and for making coke; though for the latter purpose the coals of the next class are even better suited. The weight of a cubic foot is 47 to 50 lb. as stored, and the calorific power 8,800 to 9,300. In the condition in which they are obtained in commerce, containing from 5 to 15 per cent. of extraneous matter, including moisture, 1 part of these coals was found to vaporise 7·5 to 8·5 of water. This description of coal is found largely on the Continent: in France, particularly in the St. Etienne basin and the north; in Belgium, in abundance in the neighbourhood of Liège and in the Mons basin; also in Westphalia. In England they occur more especially in Durham and Yorkshire.

4. **Caking Coals, with short flame.**—These coals have often the appearance of being made up of alternate bright and dull layers. The character of their fracture resembles that of class 3; they are less rich in volatile matter, and are generally very friable, *i.e.* crumble under moderate pressure. They inflame with difficulty, burning with a short, bluish-white, and generally smokeless flame. This coal is the best suited of all for coking, the product being compact and hard, and relatively large in quantity, and it possesses the highest calorific power of all, viz. 9,300 to 9,600. A cubic foot weighs about 50 lb. in store.

In England this coal is located more especially in the neighbourhood of Cardiff, in South Wales; in France, near Creusot, and in the St. Etienne and other basins to some extent. The trials made of the Welsh coal of this type show that it is capable of vaporising 9 to 9·5 parts of water per unit of coal. As compared with the caking coal from the North of England basin, they have a greater actual calorific value, but the northern coal burns more rapidly, and in consequence produces a greater amount of heat in a given time.

5. **Non-caking or Anthracitic Coals, and Anthracite.**—The first of these are characterised by dull streaks; they are harder than class 4, and become more and more so as they approach anthracite in nature. The weight of a cubic foot is about 53 lb. (stored). They give but little flame, and often decrepitate in the fire, an extremely inconvenient property, for if they split up into small pieces it becomes difficult to maintain a sufficient draught through the fire. Some kinds are, however, successfully employed in the blast-furnaces of South Wales; they are found in the neighbourhood of Swansea and Merthyr Tydvil. They also abound in Pennsylvania, U.S., but are not of frequent occurrence on the Continent. Their calorific power ranges between 9,200 and 9,500, and their steam-raising power is about 8·5 to 9·5 when, say, 6 per cent. of ash &c. is present. It is difficult to ensure anything like complete combustion.

With *anthracite* we have reached the end of the series. In the most highly altered kinds it is brilliantly black, and even when in powder has no brown tint. It is hard, brittle, and generally conchoidal in fracture. It does not soil the fingers. The weight of a cubic foot is usually 53 to 56 lb. in bulk, but it may be even higher if much ash is present. When heated it often decrepitates—even when gradually heated. American anthracite is said not to have this property. Anthracite burns with difficulty, requiring a strong draught. The calorific value is much the same as that of the anthracitic coals, but to obtain the same effect greater care is required. South Wales, Pennsylvania, and the French Alpine districts are the localities in which anthracite is most abundant.

General Considerations concerning Coal.—It has already been pointed out that coals having the same elementary composition may have a different calorific power, owing to the different way in which the elements are combined in the two cases. It is for a similar reason that overlapping takes place in the classification just considered. An analysis will tell us approximately in which class a certain coal should be placed; it is, however, only on submitting the fuel to distillation that the point can be conclusively settled. One coal may contain a greater percentage of carbon than another and yet produce less coke. It is important to note that these considerations apply generally only to coals from different basins. Coals from the same basins have, with few exceptions, been subjected to like conditions, and although they may be in various stages of alteration, yet the series is perfectly continuous and free from overlapping.

It will be observed, on referring to the table, that at the same time that the percentage of carbon gradually increases, the oxygen is eliminated in a greater degree than the hydrogen, until the fourth class is reached, when the hydrogen begins to decrease down to the most altered form of anthracite. This explains the fall at the same point in the calorific power, already referred to.

In selecting a coal it is important to ascertain the extent to which it cakes. If it cakes very much the grate may become blocked. In order to obviate this, in some cases it is necessary to mix a certain proportion of non-caking or *free-burning* coal, as it is called, with the *binding* coal.

Impurities in Coal.—*Ash of Coal.* For practical purposes it is very important to note the nature of the ash, as well as the quantity, which may range from 1 to 10 per cent., and in many foreign coals often exceeds 20 per cent. This is done by burning off the combustible matter in a platinum crucible. In examining the ash the first thing to consider is the amount of oxide of iron present; this is indicated by the reddish colour. The oxide of iron in the ash is mainly derived from iron pyrites—it will therefore roughly indicate the amount of sulphur in the coal. At the temperature of most furnace operations oxide of iron forms with the remainder of the ash a fusible compound, termed *clinker*. Clinker tends to block the grate and prevents proper access of air; its consistency is determined by the proportion of oxide of iron. As a rule, the less clinker a coal makes the better. In one particular case, however, it has been made to serve a useful purpose, viz. in South Wales, where a bed of clinker, supported by a few bars, is commonly allowed to form to a depth of from 12 to 20 in. at the bottom of the furnace. This clinker bed is used as a substitute for a grate, being broken up from time to time by means of a bar, so as to let sufficient air through. By this contrivance inferior small coal can be burnt, which would be useless in an ordinary grate.

Sulphur occurs in coal, probably, in three conditions, viz. as iron pyrites, in organic combination, and in the form of sulphates. It is, however, mainly present as iron pyrites. Coal containing much sulphur is not suited for the manufacture of coke, nor for use in those processes in the manufacture of iron in which the metal comes in direct contact with the fuel. Even in reverberatory furnaces some metals under certain conditions are liable to absorb sulphur from the furnace gases.

Phosphorus, in more or less quantity, nearly always occurs in the ash of coal. This should not be lost sight of in the selection of coal for certain processes in the manufacture of iron and steel.

Arsenic sometimes exists in coal, being doubtless present as arsenical iron pyrites. *Antimony*, *lead*, and *copper* have been occasionally noticed.

Weathering of Coal.—Coal when exposed to the action of the atmosphere undergoes certain changes, due to the action of oxygen in the presence of moisture. A certain amount of carbon and hydrogen is eliminated in combination with oxygen, and at the same time some oxygen becomes fixed; as shown by the fact that, if a coal is dried at a temperature not exceeding 100° C., it will lose weight up to a certain point, owing to the removal of moisture and gases, and will then begin to gain in weight, the oxygen taken up more than compensating for the carbon and hydrogen lost.

The caking property of coal appears in some cases to be materially affected by weathering. It is said that a coal obtained at Penclawdd, near Swansea, even in so short a space of time as two days loses its power to cake. Many coals on exposure for a few months become much deteriorated in quality. It has not yet been determined whether the change is due to the escape of volatile matter or to oxidation; it is probable that both conduce towards the result, oxidation, however, being the initial cause of the mischief. Moist air, acting upon the pyrites in coal, gradually converts it into a compound (ferrous sulphate) which has more than seven times the bulk of the pyrites; the effect of weathering upon highly pyritous coal is, therefore, to cause disintegration due to the wedging action of the expanding mineral.

Coke.—Coke bears the same relation to coal that charcoal does to wood. The first production of coke appears to have been due to an endeavour to find a substitute for wood charcoal, coal having been found not to answer the purpose. Indeed, the only method for the making of coke practised for a long time was that of burning coal in piles, much in the same way as was done with wood for the production of charcoal. The loss, which by this method is very considerable, has led to the use of coke ovens. Coal is only treated in retorts as distinguished from ovens when the principal object in view is to obtain the volatile products, as in the manufacture of illuminating gas. The coke produced in this way is never so good as that obtained from ovens; it is much more tender and friable, and not well suited for use where considerable pressure will be put upon it, as in the blast-furnace or cupola.

Coke produced in ovens is much harder and denser than that made in open heaps, and called *yard-coke*. The latter kind of coke, and that produced in retorts when coal is distilled for the sake of its volatile products, may be used in default of better with cold blast, when the pressure of superincumbent material is not too great.

Coking in Piles.—In coking in piles, owing to the greater density of coal, the same precautions are not required as in charcoal-burning. The process, however, when conducted to the best advantage, is essentially the same. The central chimney is made in brickwork, air spaces being left all the way up, and a cast-iron damper is fitted to the top. The cover of the pile consists of powdered coke or rubbish, there not being the same occasion for a yielding cover as in charcoal-burning. When highly bituminous coal is being coked, it is often desirable to allow the heap to become thoroughly ignited throughout before applying the cover; in such cases, also, owing to the tendency of the coal to fuse, great care has to be taken to keep the air-channels properly open. Some prefer to build the pile on moist ground, with the intention to promote the removal of sulphur; this point will be discussed later on. The presence of moisture is also considered advantageous in checking too rapid combustion. It must, however, not be lost sight of that steam is decomposed at a red heat by carbonaceous matter, with the production of carburetted hydrogen, hydrogen, carbonic oxide, and carbonic acid. The loss incurred in this way must, therefore, be set against the advantages which may accrue.

Coking in Kilns.—In some localities rectangular kilns are in vogue, and very excellent coke is said to be produced in them, with less loss than occurs in the ordinary piles. These kilns consist of two parallel walls of brickwork, about 5 ft. high, 8 ft. apart, and 40 to 60 ft. long; the floor and the inner portion of the walls are of fire-brick. In each wall is a series of openings (E F), about 2 ft. apart, and leading from them are vertical channels (G H). In order to charge the kiln, one end is first bricked up; coal slack is spread over the bottom, damped, and stamped down until it reaches up to the openings (E F), *i.e.* about 2 ft. from the bottom. Slightly tapering pieces of wood, about 6 in. in diameter at the thick end, and long enough to reach across the kiln, are placed with their ends in the openings (E F). The remainder of the kiln is then completely filled with slack, which is damped and stamped down as it is charged in; the top is then covered with coal dust or loam, the end through which the charging has been effected having first been bricked up. The pieces of wood are now carefully drawn out; thus channels are formed through which ignition can be effected, and these also serve as means by which to carry on and regulate the process, by the admission of a suitable quantity of air. Before lighting the kiln, by means of easily inflammable sticks, all the vertical flues or chimneys on one side are closed, and also the horizontal openings on the opposite side. When the ignition has travelled through to the opposite side, the channels in the brickwork which were

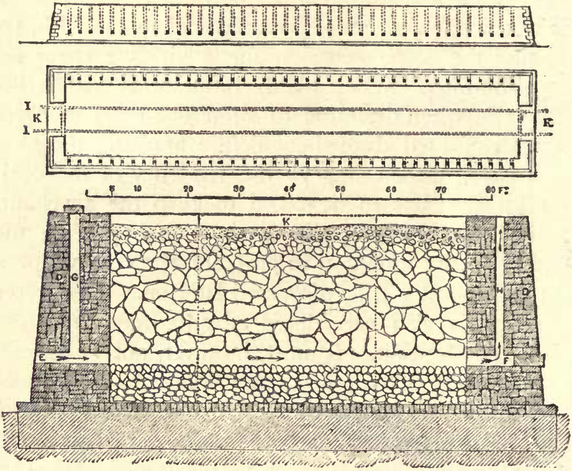

FIG. 3.—Coke Kiln.

open are closed, and the others opened. This reversal of direction takes place, at the discretion of the workmen, every two or three hours until the process is complete; the direction of the wind at the time will have an important influence on the working, if not carefully counteracted. This method requires about eight days for completion. Where wider kilns, *e.g.* 14 to 15 ft., are used, the channels are constructed by means of lumps of coal instead of the wooden poles. Unless great care be exercised very considerable loss may occur through the burning away of the coal. There is no doubt that both this plan and that previously described are very wasteful as compared with the methods of coking in ovens, which are now almost universally adopted.

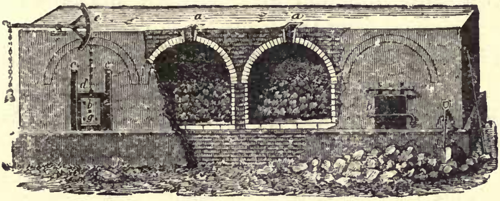

FIG. 4.—Welsh Coke Oven.

Beehive Coke Oven.—The simplest form of oven is that known as the beehive oven. They are sometimes circular, but often square or oblong, as in the Welsh modification. The height and diameter vary up to about 10 ft. These ovens are usually built in blocks, to economise heat; the dividing walls are about 2 ft. thick, the inner facing being of fire-brick. At the top is an opening for the escape of the volatile products; through it the ovens are usually charged, from coal-trucks brought immediately over the ovens by means of a branch line of rails. In front is a door through which the coke is removed; charging is also sometimes effected through this opening. The door often consists of a perforated plate of iron; more generally it is formed of fire-brick loosely piled up or enclosed in an iron frame, attached to a lever. Through the door air is admitted in suitable quantity, some of the spaces being blocked with clay when it is necessary to check too rapid action, which usually first takes place after the expiration of about two or three hours from the commencement. After the lapse of about twenty-four hours the door is entirely plastered up, and in another twelve hours, when flame no longer issues from the top opening, that also is closed. The oven remains undisturbed for another twelve hours; the door is then opened, and the coke raked out into iron barrows or trucks, the ovens being built at a convenient height from the ground for the purpose. The tool employed to withdraw the coke is termed a *drag*. It consists of a piece of flat iron, having attached to it at right angles a rod long enough to project from the front of the oven when the flat piece is in position at the back. By means of a windlass the drag is pulled out, and with it the whole of the coke. In some places the coke is pushed out from the back. It is important, in any case, that the oven should be rapidly cleared, so as to avoid its being unduly cooled down. It is preferable to quench the coke before drawing it, failing which it should be done immediately afterwards.

The heat necessary to carry on the dry distillation of the coal should be as far as possible obtained from the combustion of the volatile matter by means of air admitted *above* the fuel, but in practice it is not possible to prevent the combustion of some of the coke. The heat thus produced is radiated from the top mainly, but also from the hot sides and bottom, and maintains the required temperature. The coking gradually extends from above downwards, and from the bottom and sides towards the middle. If the process is properly conducted only a slight consumption of the coke takes place, since the air should only come in contact with the gaseous compounds above the coke. Much economy is effected by leading the excess gases under boilers, and there burning them. More than enough steam for all the purposes of a colliery can be raised in this way.

The beehive ovens are certainly not so economical as some which have since been invented, yet, owing to their relatively small cost, both initially and in repairs, the ease with which they may be put up, and the good quality of coke producible in them, they have up to the present very successfully held their own. It is observable, however, that gradually some more modern and economical inventions are superseding the old beehive oven. It is natural that progress in these matters should be slow : a manufacturer rightly hesitates before giving up an old tried servant for another who claims to have greater accomplishments, but whose trustworthiness has yet to stand the test of time.

Object in Coking.—In order to put ourselves in a position to fully appreciate the claims of modern inventions of this kind, let us consider, seriatim, what are the main objects which it is desirable to attain.

I. The introduction of air in such a way as to completely burn the gaseous products of distillation, but not the coke.

II. The prevention of loss of heat by radiation and conduction, and during the drawing of the coke.

III. The promotion of uniform coking, from the exterior in all directions towards the centre.

IV. Rapid coking. The quality is improved and the yield increased by rapid coking.

For purposes of illustration, the Appolt, Coppée, Pernolet, Aitken, Simon-Carvès, and Semet-Solvay ovens have been selected.

Appolt Coke Oven.—This consists essentially of a large brick chamber, containing, in the most recent erections, eighteen compartments or retorts (A), tied together at a sufficient number of points to ensure solidity, but having a continuous free space round all of them. Charging is effected through an opening at the top of each retort ; the bottom is provided with a cast-iron door, over which a layer of coke dust is spread before charging. The retorts are about 4 ft. long and 1 ft. 6 in. wide at the base; they taper slightly, so that at the top they are about 3 ft. 8 in. by 13 in.; in height they are about 13 ft. At about 18 in. to 2 ft. above the bottom of each retort are two rows of small horizontal openings (C), say 5 in. by 2 in.; it is through these openings that the volatile products of distillation pass into the external spaces, and are there burnt, by means of a suitable quantity of air admitted through openings in the long sides of the oven. In treating highly-caking coal, other vents further up are required. The products of the combustion of the gases are taken off by means of sixteen flues, four at the bottom and four at the top of each long side of the chamber. Each set of four is led into a longi-

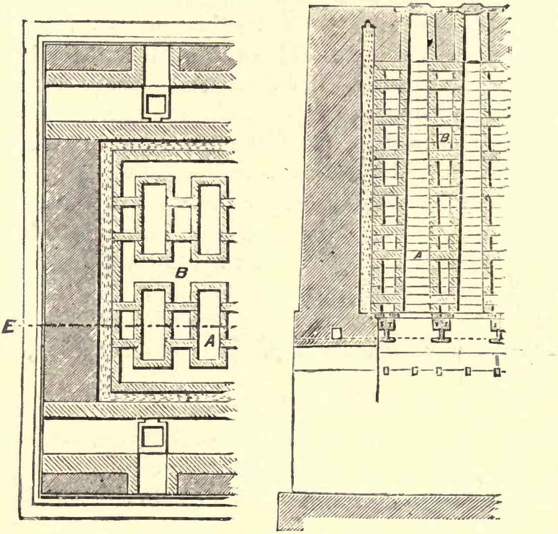

FIG. 5.—Plan and Longitudinal Section of Appolt Oven.

tudinal flue, divided into two by a partition, and connected with a chimney similarly partitioned. Dampers are placed in the vertical flues, where they are connected with the horizontal flues. In this way the heat throughout the oven can be regulated as required. The distance between two compartments is about 8 in. to 10 in. Between the walls forming the chamber and the outer mass of brickwork, which is necessary to avoid, as far as practicable, loss of heat by radiation and conduction, there is a layer of loose non-conducting material, such as sand or brick-earth, which allows the brickwork to expand and contract, and thus prevents the oven pulling itself to pieces, and at the same time assists in keeping the heat in. In removing the coke, it is allowed to fall on sloping iron plates, to avoid its being unduly broken.

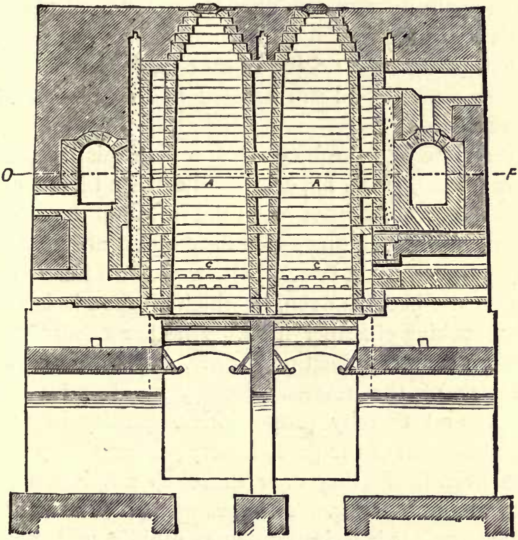

FIG. 6.—Transverse Section of Appolt Oven.

It is desirable that the coals should contain at least 20 per cent. of volatile matter, but, on the other hand, they should not be too strongly caking, for then the coke is very troublesome to remove from the oven. Any difficulty of this kind is easily met by mixing coals of different natures. The ovens are charged in succession ; the eighteen compartments will take about 24 tons of coal ; the coking is complete in about twenty-four hours. Each retort is charged again immediately after the withdrawal of the coke, so that the process once in working, there is always heat sufficient to start the coking of each fresh charge.

Moist washed coal can be used in these ovens without inconvenience.

The waste of coke by oxidation is in this oven reduced to a minimum, as the air, even should there be cracks in the sides of the oven, cannot reach the inside of the retorts, the gases in the surrounding space forming an absolute barrier. In this respect, then, the Appolt oven has a marked advantage over the beehive oven, in which all the air is admitted into the coking-chamber itself. Another advantage is the very large extent of heating surface, and the comparatively small size of the retorts, whereby rapid carbonisation is ensured, and thereby proportionate density in the coke. The combustion of the gases is very perfect, the arrangement of the oven facilitating their thorough admixture with the proper amount of air. The arrangement for withdrawing the coke enables it to be done very rapidly, and the cooling of the ovens is proportionately less. The height of the retorts acts beneficially, as it tends to increase the density of the coke. The construction of these ovens is also favourable to the production of coke uniformly from the sides of the retort to its centre. Owing to the low conductivity of coke for heat, the process goes on more and more slowly as the thickness of the layer inside the retort increases.

The addition of water to caking coal is said to act beneficially in preventing it from swelling up too much and becoming fixed tightly in the retort. The yield of these ovens is said to be as great as that which can be obtained in a crucible on the small scale, *i.e.* 10 or 12 per cent. more than that obtained in the older ovens.

Ovens based on the Appolt type are largely used abroad, and coals differing very considerably in their character are treated successfully in them.

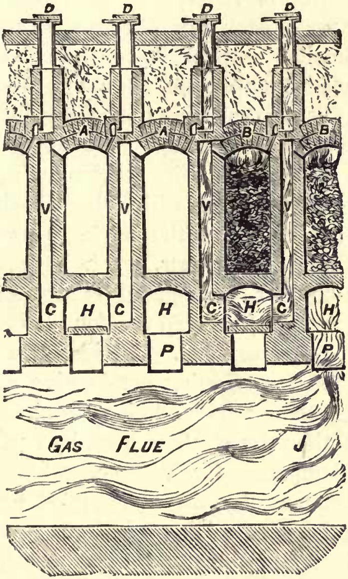

FIG. 7.—Coppée Coke Ovens.

Coppée Coke Oven.—The principle of these ovens is essentially that of the Appolt system; the method of carrying it out is, however, somewhat different. In the Coppée system the retorts are long horizontal chambers, very much the same thing, in fact, as if the retorts of the Appolt oven were placed horizontally instead of vertically. The retorts are about 29 ft. long by about 17 in. wide, and 4 ft. high at the crown of the arch. They taper from the back to the front to facilitate the removal of the coke, which is effected from the back by means of a ram. At each end of a retort there are two doors, the lower one being about 3 ft. in height, the upper about 1 ft. In the partition wall between each two coking-chambers there is a series of twenty-eight vertical flues (V), which lead the volatile products from the top of the retorts to a horizontal flue (H), passing under *one* of each pair of retorts in the direction of its length. Smaller vertical flues, through which air is admitted to effect combustion, communicate with the top of each of the flues leading from the coking-chambers. The products of combustion having passed under one retort, as just described, are led into a similar channel under the other retort, from the front end of which they are drawn off into the main flue (J), leading to the stack. Beneath the horizontal flues, under the retorts, are a series of channels, through which cool air is circulated by means of a separate stack, the object being to keep the foundations from being damaged by excessive heat. Besides the air-channels already described for effecting combustion in the vertical flues, there are others which admit a certain amount of air into the top of the retorts. The quantity of air admitted is regulated by dampers. Having to pass for some distance through the hot masonry, the air supplied for combustion becomes heated before mixing with the volatile products from the coal. The products of combustion, before being taken up the stack, are often first led under boilers, and their heat thus utilised to the utmost. The top of the ovens is covered with a thick layer of rubbish, to keep in the heat as much as possible.

It will be observed that the way in which the air is admitted to the ovens partly resembles the method in the beehive oven, and partly that of the Appolt. The amount of air, however, which is admitted directly into the coking-chamber of the Coppée oven is very small, and cannot burn the coke if properly regulated.

These ovens are particularly suitable for the treatment of coals which are not very bituminous, and which are therefore difficult to coke in ordinary ovens. The coal must be crushed to about the consistency of very coarse meal ; it is therefore easy to wash it before coking, if desired. It is

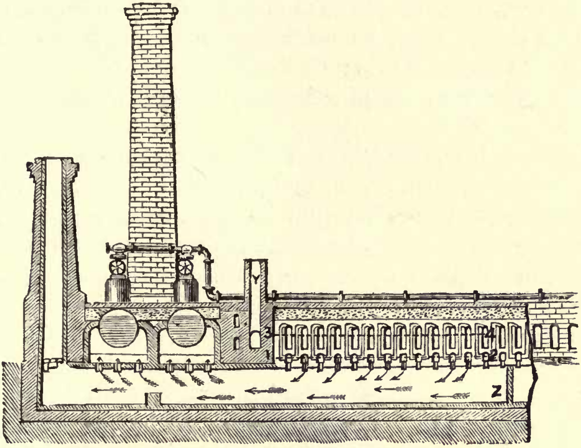

FIG. 8.—Battery of Coppée Ovens (Sectional Elevation).

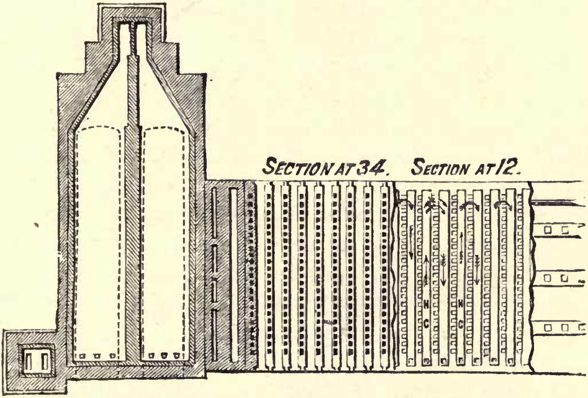

FIG. 9.—Battery of Coppée Ovens (Plan).

found most convenient to build the ovens in batches of about thirty, and to work them in pairs or sometimes in groups of four; the charging is so arranged that each oven receives a fresh charge when its neighbours have reached a more advanced stage. Owing to the arrangement of flues, the temperature is thus kept sufficiently uniform in each group of ovens.

It has been pointed out that a coal which is highly caking may give trouble in an Appolt or a Coppée oven by rendering it difficult to withdraw the coke, and that this difficulty can be overcome by mixing with the binding coal a certain amount of free-burning coal. The principle herein involved may be further extended. The slack, or small of non-caking coal, may be utilised for the production of coke by mixing it with bituminous coal. The two kinds of coal should be ground separately, the caking coal being reduced to a fine state of division, whilst the non-caking may be in pieces about the size of a pea. In this way even anthracite may be used, the particles becoming firmly cemented together by the caking coal. In this case it is necessary to add a small amount of pitch as well.

Collection of the Products of Distillation of Coal.—This is done, as has already been stated, in the manufacture of ordinary lighting gas; but the coke produced, when the chief object is to obtain as great a quantity of volatile products as possible, is lighter and more porous than that made in ovens such as have just been considered. Numerous ovens have been devised with the object of producing good coke, and at the same time to enable the tar, oils, ammonia, and gases to be collected and utilised.

The manufacture of good hard dense coke is incompatible with the production in *large quantity* of valuable condensable gaseous compounds. This follows from the established fact that the higher the temperature, and, within certain limits, the longer the coke is submitted to that temperature, the greater will be the yield, and the more dense the coke. At low temperatures volatile bodies, rich in carbon, are formed, and may be collected; at higher temperatures these compounds are decomposed and deposit their carbon. Thus, the substances which distil off from the central cooler region of a retort will, on coming in contact with the outer layer, be decomposed if not rapidly removed, provided the temperature be sufficiently high. A temperature which is not sufficiently high to effect the decomposition of the richer hydrocarbons is below that necessary to produce a good dense and hard coke. In the manufacture of good *oven-coke*, so called to distinguish it from *gas-coke*, the gas produced cannot be highly luminous, for at the temperature required to produce such coke, the principal light-yielding constituents of gas used for illuminating purposes would be decomposed.

From what has been said it will be gathered that, provided the proper conditions for obtaining a hard dense coke be attended to, there is no real objection to the collection of such tar and ammonia as may then be formed, which in the aggregate may amount to a considerable quantity; but these substances must always be of secondary importance, attention being mainly directed to the regulation of the process so as to produce sound coke, the conduct of the process having to be varied somewhat for each kind of coal.

Pernolet Coke Oven.—The *Pernolet* oven was one of the first of this class to assume practical importance. It was patented in 1862; an almost exactly similar patent was taken out in 1850 by Pauwels and Dubochet. Pernolet claims, firstly, to make coke suitable for metallurgical, railway, and other purposes, in greater proportion than when manufactured in the ordinary manner; secondly, gas suitable for burning and heating; thirdly, tar, and different oils obtainable therefrom; and, fourthly, ammonia and ammoniacal salts.

The coking is to be conducted 'very slowly'; air is excluded as far as possible after thorough ignition has been effected; the products of distillation, which are either drawn off by the draught of a high chimney or by exhausting machines, are condensed and collected by suitable machinery, much as in gas works.

In this country it has been tried by several large companies. The yield of coke is greater than that of a beehive oven, but not more than that of a Coppée or Appolt oven. Considerable quantities of tar, &c., have been collected, but the quality of the coke is not so good, and the expense in labour and repairs is greater. As the quality of the coke is a matter of great importance in iron smelting, it is not surprising that this method of making it has been practically abandoned in this country; an additional reason is to be found in the fact that little or no real saving could, at any rate, until recently, be effected, as the tar, ammonia, &c., realised very low prices, owing to the large quantities produced in gas works. The prices of these bye-products have, however, within the last few years risen considerably, owing to increased demand.

On the Continent the Pernolet system has met with more favour, but there is no reason to believe that the coke there produced is better in quality than that obtained here. Ovens of all sorts of shapes have been tried. As the result of two years' experience by Bell Bros. in the north of England, preference was given to the beehive shape; but the process was finally abandoned, mainly, it is said, owing to the flues and floors being constantly destroyed by the excessive heat of the gases. The gas was drawn off from the top of the oven by means of a pipe, and conveyed to the condensers and scrubbers for the extraction of its tar and ammonia, whence it was wholly, or in part, returned to the oven, and burnt in a flue beneath the floor, the ignition of the gas being ensured by a small fire. It will be observed that in these ovens the coking proceeded from the bottom upwards. In England it was found that about 5 per cent.

more coke was produced than in the beehive oven, using the same coal, and, in addition, about one quarter of a ton of ammonium sulphate and an equal quantity of tar were obtained from every hundred tons of coal treated.

Aitken and Jameson Ovens.—The beehive oven has more recently been modified by Jameson, as well as by Aitken and others. In the Aitken oven, a blast of air is introduced by means of tubes connected with openings near the base of the roof. The liquid and gaseous products of distillation are drawn off through channels in the floor, and after passing through the condensers, are in part returned to the top of the oven at the points where the air enters.

By this simple plan, an oven which is cheap to build, and which has been proved to produce the best coke, can be made to yield also valuable bye-products, and in the opinion of Aitken without injuring the quality of the coke. In this oven the gases are burned above the coke, as in the ordinary beehive oven, but with the advantage that the air is so introduced that it is less likely to burn the coke, and, being forced in, it is more under control, whilst the temperature at which the coking is effected could be regulated by heating the air, and if necessary the gas, to any desired degree, on the regenerative principle. A really important difference which may affect the character of the coke is that the hydrocarbons which ordinarily distil from the cooler interior of the fuel, and become dissociated in the hotter layers above, depositing carbon in the pores of the already coked coal, are in the Aitken oven drawn off from below undecomposed. Also the progress and character of the coking must be modified to some extent by drawing the hot products of combustion and distillation downwards through the charge, but whether injuriously, and if so, to what extent, there is not at present sufficient evidence to show.

The ovens which have been designed to combine the manufacture of good coke with the recovery of bye-products are for the most part adaptations either of the beehive or of the Coppée type. In the former class, of which the Jameson oven is a type, air is usually admitted into the oven as above described; but it is found that the resulting tar, in this case, contains little or none of the constituents from which coal-tar colours are derived, and which therefore render the material specially valuable. Hence, in spite of the more elaborate construction, the modifications of the Coppée oven are in greater favour with those manufacturers who recover the bye-products. Of this class the Simon-Carvès and Semet-Solvay ovens may be regarded as representative.

Simon-Carvès Oven.—In the Simon-Carvès oven the shape is similar to that of the Coppée, but the gases are drawn off through a single pipe in the roof, which leads through a water-sealed joint into the hydraulic main that runs along the top of the battery of ovens, and serves to conduct the gases from all of them to the condensing apparatus, in which the tar and ammonia are deposited. The purified gases are returned through pipes communicating with flues beneath the ovens, and are there burned by the admission of heated air, the flame and the products of combustion being led through zigzag flues built in the side walls of the ovens to a pair of long horizontal flues which run parallel underground to the stack. Other similar horizontal flues are built alternately with these, and the air to be used in burning the gases under the ovens is passed through them, becoming warmed by the heat conducted through the brickwork from the waste gases traversing the adjoining flues.

Semet-Solvay Oven.—Fig. 10 illustrates the most modern (1896) construction of the Semet-Solvay oven, from which it will be seen that the oven (*d*) is long and narrow, with a door at each end; and that the roof is supported by substantial masonry, whilst on either side of each oven is a zigzag horizontal flue of four turns, through which the gases

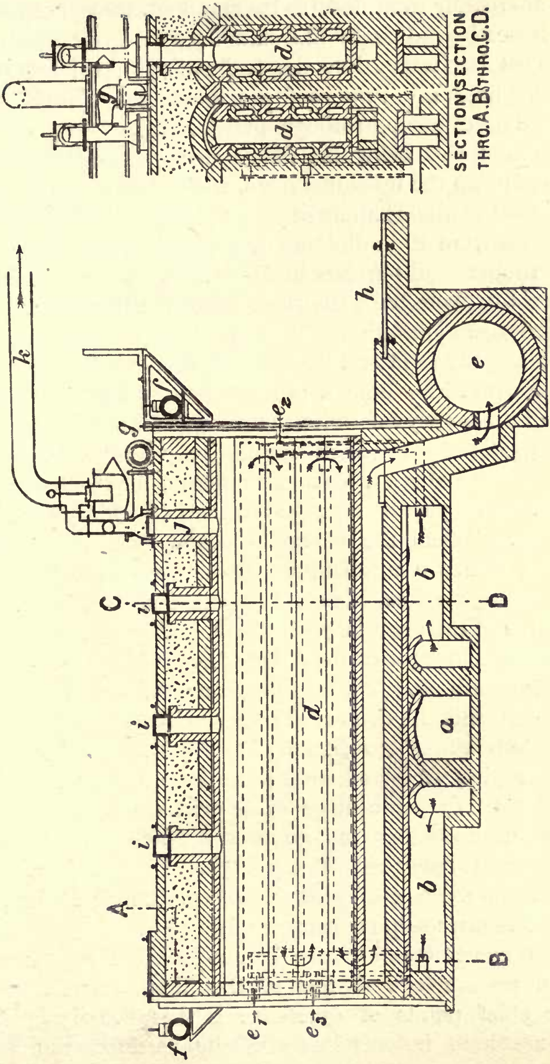

Fig. 10.—Diagram of Semet-Solvay oven.

pass alternately from front to back and *vice versa*, to a return flue beneath leading to the chimney-flue (*e*) at the back. The coal is charged into the hot oven through the three charging-holes (*i*) in the roof, which are then closed. The distilled gases escape through the gas-outlet (*j*) at one end of the roof, this being the only aperture left open; thence they pass into the hydraulic main, which is a wide pipe running over the whole battery of ovens, and there, mingling with the gases from the adjoining ovens, they are conducted to the scrubbers and purifiers in which all tar and condensable matter are deposited. By the action of a blowing-fan the purified gases are returned through smaller mains (*f*) running along the front and back of the line of ovens, and are thus conveyed by branch pipes (e_1, e_2, e_3) into the zigzag flues, in which they meet with sufficient air for combustion and are burned, the products of combustion passing beneath the ovens to the chimney. The air required for combustion is pre-heated by passing through channels (*a*, *b*) in the heated masonry. When the charge is coked, or in a little less than 24 hours, a mechanical ram is brought behind the oven, along the line of rails (*h*), both doors are opened to the full, and the coke is pushed out bodily by the ram on to the space in front of the oven, where it is quenched with water from a hose. The ram is then withdrawn, the doors are closed, and the oven is at once re-charged. The ovens are usually about 30 ft. long and 5 ft. 6 in. high, the width varying from 13 or 14 in. for coals yielding but little (15 to 17 per-cent.) volatile matter, up to 16 or 17 in. for those yielding, say, 30 per cent.; they are built in batteries of twenty-five. The purifying of the gas is effected much as in the case of coal gas, except that no attempt is made to remove sulphur compounds.

The construction of the Semet-Solvay oven bears a general resemblance to that of the Simon-Carvès. One of the chief points of difference is that the zigzag side flues are built independently of the partition wall that has to support the weight of the roof, thus presenting the double advantage that the main fabric of the oven requires less frequent reconstruction, whilst the repairs to the flues themselves are less costly. In each of these ovens provision may be made for burning solid fuel in addition to, or in substitution for, gas to heat them, so that the purified gases may be utilised, if desired, for other work. It will be observed that these ovens are practically gas retorts of very narrow construction, so that the heating is very rapid ; and the temperature is higher than that usually employed in making lighting gas. The average temperature of coking lies between 700° and 800° C. The yield of bye-products depends upon the nature of the coal, and the method of treatment. With a fairly good coal, treated in a good retort-like oven, from 3 to 5 per cent. of tar, and from 1 to 1·5 per cent. of ammonium sulphate may be obtained.

Good coke has been referred to as hard and *dense.* It must be understood that there is a practical limit to the value of density ; it would not do, for instance, to compress the coke by artificial pressure.

The most economical and generally satisfactory coke-ovens yet produced are unquestionably those based on the principles embodied in the Coppée, Appolt, Simon-Carvès, and Semet-Solvay systems, where all spare heat is utilised for raising steam. There are yet many improvements to be made in applying these principles in practice.

Removal of Sulphur from Coke.—The iron pyrites (FeS_2), which exists in more or less quantity in every coal, undergoes decomposition during the coking process ; one half of the sulphur is distilled off, and unites with oxygen to form sulphurous acid (SO_2), during the combustion of the volatile products. The remainder of the sulphur is found in the coke, in combination with the iron, as FeS. It is an important problem how to remove this residual sulphur from the coke, supposing it to be present in such quantity as to detract from the value of the coke for furnace purposes.

It is a matter of common observation, that if water be thrown on red-hot coke or coal a strong odour of an objectionable kind is at once perceptible. This arises from the decomposition of the protosulphide of iron, oxide of iron and the offensively smelling gas, sulphuretted hydrogen (SH_2) being formed. From this it might be argued, that in order to desulphurise coke it would only be necessary to pass steam into the oven. It must, however, be borne in mind that the amount of sulphur in coke, as compared with the carbon, is very small, and that it is practically impossible to ensure the steam permeating the coke throughout. The impossibility of removing anything like the whole of the sulphur in this way is still more apparent when it is remembered that red-hot carbon decomposes steam, with formation of carbonic oxide, carbonic acid, marsh gas, and some free hydrogen. It is easy to overrate the amount of sulphur removed by steam if it be judged only by the sense of smell, the odour of a little sulphuretted hydrogen being very powerful. Desulphurisation by means of air, either at the ordinary pressure of the atmosphere or at higher pressures, has been tried. It is obvious that the objections to the use of steam apply equally to air.

The addition of such substances as carbonate of soda, lime, carbonate of lime, oxide of manganese, chloride of sodium, &c., has been tried, but only with indifferent success, not warranting the extra expense entailed. This method has for its object the transference of the sulphur from the iron to the substance added, which having entered into combination with the sulphur will, for instance, tend to prevent its passing into iron melted with the coke in a cupola.

It follows, from the foregoing considerations, that at present there is no satisfactory method known by which sulphur can be completely removed from coke. The best way of meeting the difficulty is to disintegrate the coal before coking it, and subject it to a washing process by means of which the shale and pyrites which it contains can be to a considerable extent removed, by reason of their greater specific gravity. This treatment cannot be applied to non-caking coals unless they are subsequently mixed with a sufficient quantity of caking coal to make them coke.

Patent Fuels.—Means have been resorted to for the utilisation of non-caking small coal, by mixing various carbonaceous substances with it as a cement. Thus, anthracite or coke breeze mixed with tar will produce a solid coke on being subjected to heat. *Patent fuels* consist of mixtures of this kind, moulded into the form of bricks with or without the application of heat. Resin is said not to give satisfactory results as a cementing material unless mixed with tar. Mucilaginous substances prepared from farinaceous bodies are also used. The use of patent fuels is almost entirely confined to raising steam for navigation and on railways, for which purposes they answer very well, as the space occupied is small compared with that required for ordinary fuel. *Briquettes* made with starchy substances should be rendered impervious to moisture by dipping them into coal-tar oil immediately after their withdrawal from the drying oven.

The tendency of brick-shaped fuel to interfere with the furnace draught has been already alluded to. To meet this difficulty small egg-shaped blocks are sometimes made by passing the fuel, with its agglomerant, between rollers, on the surfaces of which are corresponding oval cavities that give the required shape to the mixture passing between them.

GASEOUS FUEL.

Theory and Use of Gas-Producers.—The theoretical calorific values of carbonic oxide and of hydrogen have already been fully discussed ; it remains to show in what way these gases can best be turned to practical account.

It will be recollected that the intensity of combustion of hydrogen and of carbon, when burnt in air, is practically the same, whilst the heat of combustion of carbonic oxide in burning to carbonic acid is somewhat greater than that of carbon likewise oxidised to the maximum. So far, then, as the actual intensity obtained on combustion is concerned, it would appear that it matters little whether we employ solid or gaseous fuel ; in practice this is very far from being the case. When the fuel is gaseous it is much easier, for instance, to apply heat uniformly to a given surface, or locally, as may be required in some cases, and further, the regulation of the temperature is much more within control, and complete combustion can be ensured. This is well illustrated by the system of heating coke-ovens constructed on the principle of the Coppée and the Appolt. Another point, which is sometimes advantageous, is that the gases can be generated in any convenient place, and led by pipes, or other suitable means, to the spot where their combustion is required to be effected. In this way valuable space may be economised, and working room obtained where it is most required.

These are very far from being the only advantages which may be derived from the use of gaseous fuel. When great intensity of heat is required it is possible to produce it by heating the gases and the air required for their combustion ; and, if desired, the gas and air can be burnt under pressure, thus still further increasing the temperature obtainable, the only limit being that fixed by dissociation. In practice these high temperatures could not be obtained by simply heating solid fuel and the air supplied for its combustion, though there is, up to a certain point, a very decided gain in heating the air.

Strictly speaking, all heating operations are conducted, to some extent at least, by means of gaseous fuel, for all fuels yield on distillation gases, with the exception, practically, of coke and anthracite; and, apart from the products of distillation, it is essential to the manner in which combustion is effected that carbonic oxide should be formed, which subsequently burns on being brought into contact with air on the exterior of the heated fuel. Thus, in reverberatory furnaces, in which the fuel is burnt in a chamber, separated by a low wall from that in which the smelting or other operation is to be effected, the two chambers being in communication above the walls, the heating of the bed of the furnace is really accomplished by gaseous fuel.

The products due to the distillation of the upper and cooler fuel, and the carbonic oxide derived from the decomposition of the carbonic acid, first formed by the admission of air under the grate, are drawn over the partition-wall or *firebridge* by a chimney at the opposite end of the furnace, and, becoming mixed with a suitable quantity of air, undergo combustion over the hearth. The relative amount of combustion which takes place on the hearth and above the fuel in the grate will depend on the quantity of air allowed to enter the opening through which the fuel is charged in. The principle of the modern gas-producer is essentially the same as that just described; in fact, as now commonly constructed, the gas-producer is simply a modification of the fireplace as originally constructed in a reverberatory furnace. The gas-producer first assumed importance on the introduction of the Siemens 'regenerative' system in 1856.

Siemens Gas-Producer.—The arrangement then adopted (fig. 11) consisted of a chamber lined with fire-brick; one side sloped at an angle of from 45° to 60°; at the bottom was a grate (c). The fuel was introduced through a hopper, and allowed to fall on to the sloping side, down which it gradually moved to supply the place of that which had been converted into gas in the region of the grate. Air was admitted only through the grate, and combustion proceeded from below upwards, the volatile portion of the fuel being distilled off without coming in contact with air, whilst the coked coal was converted into carbonic oxide gas. A small quantity of water was admitted by a pipe to the ash-pit, where it evaporated, and, becoming decomposed by the incandescent fuel, enriched the producer-gas by the formation of carbonic oxide and free hydrogen. By means of a plug-hole the interior of the producer could be inspected, and, if necessary, the fuel stoked with an iron rod.

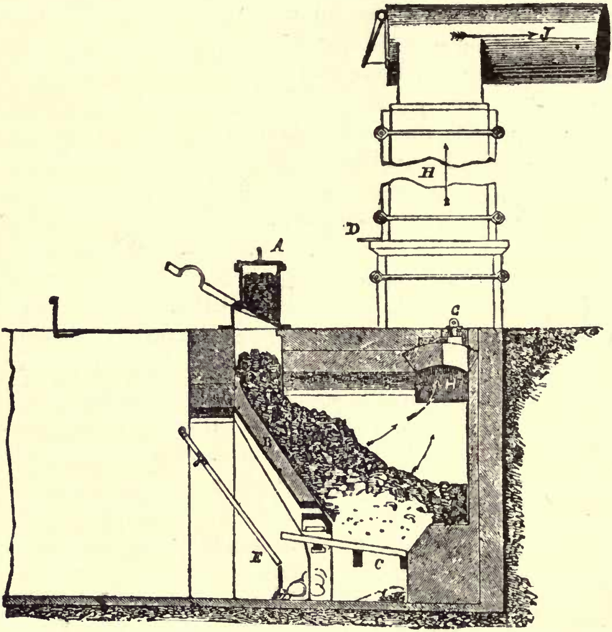

FIG. 11.—Early form of Siemens Gas-Producer.

It is important that a slight outward pressure should be maintained in the flue, to prevent the gas being partially consumed by an indraught of air through crevices in the brickwork. If the furnace can be placed about 10 ft. higher than the producer the required pressure is at once obtained; in practice this arrangement was not always convenient, and the following plan was adopted. The gases, which on leaving the producer have a temperature of about 400° C., passed to an uptake-tube, rising 10 to 20 ft. vertically; thence they traversed a horizontal iron *cooling-tube*; at the end of the cooling-tube the gases, having then a temperature below 100° C., descended a tube called a *down-comer* into a main, communicating with the furnaces. The effect of cooling the gases was to increase the relative weight of a given volume by 50 to 60 per cent. Thus a sort of siphon action was set up, the heavier gas in the down-comer representing the longer leg of a siphon; at the same time, by this arrangement an outward pressure was maintained in the flues of about $\frac{1}{10}$ to $\frac{2}{10}$ in. of water above that of the external atmosphere. By cooling the gases aqueous vapour is condensed and deposited.

Although the desired results were obtained in this way, yet it will be observed that it was only arrived at by the dissipation of a great deal of heat. Had this not been so, however, a chimney or an exhaust-engine would have been required to draw the gases from the producer; so this heat must be looked upon as doing important work.

Use of Steam in Producers.—It has been stated that steam may with advantage be admitted with the air supplied for combustion. The advantage which steam possesses over air is due to the large quantity of inert nitrogen in the latter. For, when air alone is used in the producer, the volume of incombustible nitrogen in the resulting gas usually exceeds 60 per cent., whilst with steam alone practically the whole of the gas may be combustible. Nevertheless, it must not be forgotten that in the decomposition of steam by carbon heat is *absorbed*; if, therefore, much steam were admitted, the temperature would eventually be so much lowered that combustion would only proceed with the greatest difficulty, if at all.

Up to a certain amount steam may with advantage be admitted; beyond that it does harm. It is very important that this should be properly understood, since a great deal of misconception exists as to the use of steam. It should only be introduced when there is an excess of heat in the gas-producer beyond that required to carry on with sufficient rapidity the conversion of the solid fuel into gases.

That heat is absorbed during the reduction of aqueous vapour by carbon is easily shown. One part by weight of hydrogen, in combining with eight parts of oxygen to form gaseous steam, evolves about 29,000 units of heat (see p. 3), and exactly the same number of units will be absorbed again on the water being broken up into its constituents. The eight parts of oxygen liberated will combine with six parts of carbon, evolving 14,838 units, since carbonic oxide is the final product so far as the gas-producer is concerned; most of the hydrogen will remain in the free state, but a little may unite with carbon to form, mainly, carburetted hydrogen gas (CH_4), evolving about 16,000 heat units for each unit weight of hydrogen. Supposing that the whole of the hydrogen of the decomposed steam remains uncombined, then the total heat units absorbed and evolved would stand as follows :—

Absorbed by decomposition of 9 pts. $H_2O = 29{,}161$ heat units.
Evolved by combination of 8 pts. $O + 6$ pts. $C = 14{,}838$,, ,,

Balance in favour of absorption $= 14{,}323$,, ,,

It will be seen from these numbers that there is an absorption of $14{,}323 \div 6$, or nearly 2,400 units of heat for each unit weight of carbon that reacts with steam in the manner described. But we know, that if one unit weight of carbon were converted into carbonic oxide by the action of air alone, 2,473 units of heat would be evolved; hence it might seem that, starting with incandescent carbon, so much steam could be introduced continually with the air, that one half of the carbonic oxide produced in any given time should be due to the steam, and one half to the oxygen of the air, for in this case the heat absorbed in the one reaction would be almost exactly balanced by that evolved in the other. But it must be remembered that there is considerable loss of heat due to radiation from the apparatus, and the gas, leaving the producer at a high temperature, carries with it much sensible heat. In consequence of this constant removal of heat, the temperature of the carbon in the producer would in a few minutes be reduced below that at which it is capable of attacking steam, or even of combining with oxygen. In practice it is found that only sufficient steam must be admitted to react with, at most, one fourth (not one half) of the carbon ; or, in round numbers, the weight of steam used in any given time must not exceed one-twelfth of the weight of air introduced with it.

Water-Gas.—Obviously the equivalent of the heat absorbed in the decomposition of the water-vapour may be supplied in other ways than by mingling air with the steam ; and it is possible to obtain pure *water-gas*, as the product of the reaction of carbon with steam is termed, by using a retort in which the requisite temperature is maintained by the combustion of other fuel outside. But this has not been found generally practicable on a large scale. When water-gas is required, it is prepared by grouping several producers together, and using each alternately for the production of water-gas and producer-gas. One of the producers being at a very bright red heat, steam alone is turned into it and the resulting water-gas is drawn off through a special flue to a gas-holder, until the temperature of the carbon has fallen so low that no further reaction can take place ; the steam is then diverted into another producer, and the gas thus made is collected in the same holder. Meanwhile air is blown into the first producer until it has re-attained its initial temperature, the producer-gas being drawn off through a different pipe and stored in a second holder. Since the cooling action of the steam on the oxygen is greater than the heating power of the oxygen, the period during which air must be passed over the carbon is in excess of that permissible for the steam, which cannot exceed a few minutes' duration. Three or four producers must therefore be employed simultaneously, of which only one will be generating water-gas at any given moment, unless the air be delivered at an increased rate, in which case the period of re-heating is correspondingly reduced. The proportion depends upon the construction of the producer, the relative pressure of air and steam, and other variables. In some types of producer, the regenerative system has been applied with success to prolong the period during which the water-gas is prepared.

Modern Gas-Producers.—The majority of modern gas-producers aim at a combination of the air and steam systems, the highest possible proportion of steam, generally more or less superheated, being introduced with the air. This is usually accomplished by injecting high-pressure steam into an air-pipe which communicates with the bottom of the producer, so that the steam aspirates the air through the tube, and the two together are thus forced into the midst of the incandescent fuel. Coke or anthracite may be employed as in the Dowson producer, which is largely used for making gas for gas-engines and also for heating ; but generally coal is now used in 'blown' gas-producers constructed for furnace work (see figs. 12 and 13). The coal is introduced through a hopper which is provided with a valve below and a cover above ; a charge of coal having been placed in the hopper, the lid is closed and the valve is then opened, so that the falling of the coal into the producer may be attended with the minimum loss of gas. The solid fuel gradually sinks as the portion below it is consumed, and only at long intervals is it necessary to introduce a bar through the holes provided for the purpose to alter the distribution of the material in the chamber. A jet of steam under high pressure, placed at the open end of a pipe communicating with the bottom of the producer, serves as an air-injector, and forces a mixture of air and steam through the heated fuel at the bottom of the producer, and the mixture of combustible gases formed rises through the six-foot thickness of material above, converting the newly admitted coal into coke by its heat, and carrying along with it through a *down-comer* the gaseous and volatile tarry products of distillation. The resulting gas is therefore a mixture of coal-gas and producer-gas, and should leave the producer at a temperature of about 300° to 350° C. Owing to the pressure under which the air is forced into the chamber, no cooling tube is necessary in order to create a draught, and the gas may be led direct to the furnaces in which it is to be used. The coal which has become coked passes down the producer, and its carbon is converted into gas by the action of the steam and air at the moment of their introduction, whilst the ash accumulates in the lower portion of the chamber, often fusing and causing a clinker which seriously interferes with the passage of the in-coming gases, and reduces the output of the plant, besides necessitating heavy labour to effect its removal. In the older forms of Wilson and Dawson producer, many of which are still in use, the clinker is removed once every day by stopping the supply of steam and air, driving heavy iron bars through the lower part of the charge, the ends of the bars being supported by the casing of the producer, and then breaking up the clinker beneath them, and extracting it through doors which can be opened for the purpose. But in the more recent patterns, or *water-bottom* producers, the bottom of the chamber is filled with water to the depth of a few inches, so that the fuel stands in water below the level at which the air is admitted. The effect of this is to maintain a somewhat lower temperature at the twyer level, and to reduce the proportion of clinker; whilst any clinker formed becomes quenched and is afterwards more readily disintegrated by the water. The ash of the coal is thus left in a pulverulent condition, and is removed as it accumulates, with the aid of a shovel introduced into a side well communicating with the floor of the producer.

Fig. 12 represents the modern form of Siemens producer, in which D is the hopper and C is a rectangular chamber to contain the coal and the fire-bars F. The ash-pit is closed by a hinged door in front; but on each side there is an air-port B, through which air is injected by means of the steam jet A. The bottom of the ash-pit is provided with an iron tray, which is kept filled with water. The producer-gas formed ultimately passes through the flue E to the furnaces.

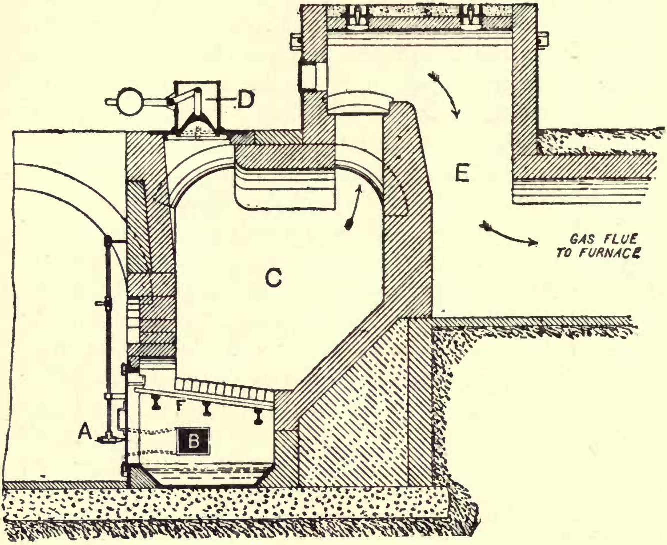

FIG. 12.—The Modern Siemens Gas Producer.

The cylindrical type is illustrated by the Dawson water-bottom producer shown in fig. 13. Here, A is the steam injector, and B the air-port, C is the water-bottom, the use of which has been described above, and E E are apertures which may be temporarily opened for the introduction of iron rods to break down any clinker or obstruction that may be formed. The entrance to the down-comer flue is at one side close to the top of the chamber, but being on the nearer side it is not indicated in the drawing.

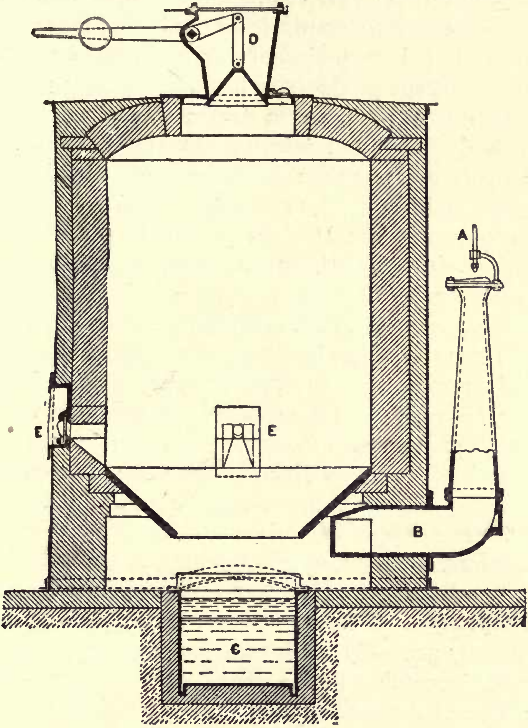

FIG. 13.—The Dawson Water-bottom Producer.

Tar in Producer-Gas.—The tar which results from the use of bituminous coal in the producer is a source of trouble if the furnaces are at any distance from the producers, the thick deposit of tar and soot which forms in the flues having to be removed—generally by firing—at intervals of about a week. Taking advantage of the fact that tar is, for the most part, broken up into permanent gases on being heated to bright redness, some modern producers are so constructed that the gas is drawn off, not from above the cold fuel just charged, but from a part in which the coke is incandescent. This may be accomplished, either by altering the position of the off-take as above indicated: or by building a fire-brick curtain across the producer, as has been done in a modified type of Siemens producer, in such a way that the distilled gases are deflected under the curtain, and thus through the hottest part of the coke: or by reversing the direction of the gases, and placing the steam jet above, and the exhaust flue below, as in the Howson producer. These methods cannot be said to have been very successful. In some instances, the gases have been deprived of tar and ammonia by condensation, as in the manufacture of coal gas.

The removal of tar, however, is not always so desirable as might appear. In the present type of Siemens steel-furnace, the melting of the charge is effected to a very large extent by radiation from the flame; and the presence of tar in the gases leads to the production of a more luminous flame, which being a better radiator, may give a decided economy of fuel. The deposit of carbon which is apt to form in the regenerators, when a tarry gas is employed, may be kept in check by adjusting the periods of reversal for the gas and air.

Composition of Gases.—Modern producer-gas may be said to vary generally within the limits given in the following table, according to the character of the coal, and the proportion of steam to air:—

Carbonic oxide	20 to 30	per cent. by volume.
Hydrogen	6 ,, 18	,, ,,
Marsh gas and other hydrocarbons	0 ,, 6	,, ,,
Carbonic acid	3 ,, 10	,, ,,
Nitrogen	50 ,, 65	,, ,,

Of these the first three constituents only are combustible, so that at the best more than one half is valueless for heating purposes. The gas produced by passing steam alone over red-hot coke varies in composition with the temperature, an average result being :—carbonic oxide, 34 ; hydrogen, 54·5 ; marsh gas, 1·5 ; and carbonic acid, 10 per cent. by volume.

Regenerative Gas-Furnaces.—The idea of heating, by what is now known as the regenerative system, the air supplied for the combustion of solid fuel occurred to Robert Stirling in 1816. The method by which he proposed to carry it out, as set forth in his patent, is very crude, and would have been in that form impracticable. Still it embodies the notion which, forty years afterwards, was again conceived by Frederick and C. W. Siemens, in whose hands it has brought about results of incalculable value. They, like Stirling, began with the idea of heating air for the combustion of solid fuel, the general arrangement in both cases being very similar. There was to be a heating chamber with two fire-places, one on each side of the chamber, and beyond each fire-place a regenerator. The regenerator in the Siemens arrangement consisted of chequer-work of brick, *i.e.* a chamber packed with bricks so placed as to leave spaces, through which the spent gases had to pass on their way to the chimney. Stirling proposed to use thin partitions of metal or glass. In either case the object was to cause the gases to give up their heat to the cooler fire-brick or other material.

When the regenerator through which the products of combustion had been made to pass had become sufficiently heated up, the direction of the current was reversed, and the air as it entered then became heated by the hot masonry which it had to traverse, whilst the other regenerator in its turn had its temperature raised again by the products of combustion. Reversal of the direction of the currents was to be effected at such intervals as would prevent the regenerator through which the air was passing becoming cooled to too low a temperature. The conditions of this arrangement necessitated that the operation being carried on in each furnace should be completed in the time between the reversals —a state of things at the best extremely inconvenient, and for most purposes altogether impracticable.

It was at this point that the brothers Siemens conceived the idea of employing gaseous instead of solid fuel, and heating it *as well as* the air by means of regenerators. It would be difficult to overestimate the importance of the results which have followed the introduction of this system. By its means the highest attainable temperatures can with ease be produced, the only limit being that at which dissociation takes place.

Furnaces on this system have been applied with very great success to the manufacture of soft steel, and for reheating iron and steel; also to zinc smelting, and in gas, glass, pottery, and porcelain works. It is not too much to say that there is no purpose for which a high temperature is required for which it might not with great advantage be employed, in respect both to general convenience and economy.

Fig. 14 represents the furnace, the upper part of the figure showing a sectional plan through the doors B, and the lower part a longitudinal section; the gas coming from the gas-producer passes in through the gas flue and the reversing valve, by means of which it is directed into the bottom part of the regenerator chamber (E), on the left. The gas flowing up through the mass of brickwork that the chamber contains, and which is placed so as to form a large aggregate surface, with intricate zigzag passages, will become heated, provided any heat has been accumulated therein. In the first place there will be no heat, and the gas will pass unheated through this chamber and thence through the flue (G), to the combustion-chamber of the furnace (A). At the same time, a current of air is admitted through the air-reversing valve into the air regenerator chamber (D), which is larger than the gas-chamber. The

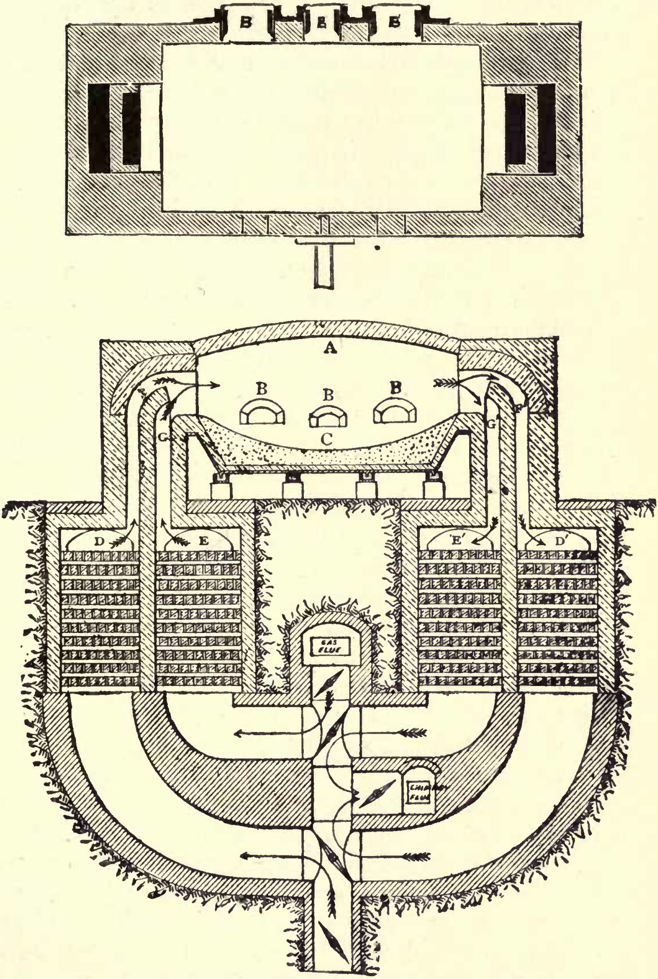

FIG. 14.—Siemens Regenerative Steel-melting Furnace ; Plan Longitudinal Section.

Note.—The flues and valves are here indicated diagrammatically, and the part of the drawing below the regenerators is shown in *plan*.

air passing up through the chequer-work to the flue (F) will reach the same point as the gas does at the entrance into the combustion-chamber of the furnace; and the mixture of the gases is ensured by having the ports, or orifices, for the admission of the heavier air above those for the admission of the gas. Now, since both the air and gas are cold, and as they meet for the first time at the entrance into the furnace, they will, if there ignited, produce a temperature certainly not superior to what would be produced if solid fuel had been burned there instead; on the contrary, gas of the description we are dealing with is a poorer fuel than solid fuel, and the temperature produced in the furnace will, therefore, be very moderate indeed. But the flame, after passing over the bed of the furnace, does not go to the chimney direct, but has to pass through the two regenerative chambers (D′, E′) on the right, similar to those already described; the larger proportion of the heated products of combustion will pass through the air regenerator chamber, simply because it is the largest channel; and another portion will pass through the gas regenerator. The products of combustion pass from these chambers through the reversing valves, and are by them directed into the flue leading to the chimney. The *butterfly valves* are now commonly applied only to the air flues, the direction of the producer-gas being controlled by valves, similar in their effect, but of a type less liable to leakage through the buckling of the metal at high temperatures.

The operation, therefore, is simply this: the air and combustible gas pass up into the furnace through the one pair of chambers, and pass away, after combustion, towards the chimney through the other pair; but in passing through the second pair the heat of the products of combustion is given up to the brickwork. The upper portions of this brickwork take up the first, and, therefore, the highest degree of heat, and, as the burnt gases are passed downward through the regenerators, they are, by degrees, very completely deprived of their heat, and reach the bottom of the chambers and the chimney comparatively cold. After this action has been going on, say, for half an hour, the reversing valves are turned over. These are simple flaps or the equivalent acting like a four-way cock, and, by throwing over the levers which work them, the direction of the currents is reversed. The gas and air will enter now through the second pair of chambers, and the air passing up one regenerator and the gas passing up the other will take up heat from the bricks previously heated by the descending current. The gases so heated, say, to 500° C., will enter into combustion, and if the temperature produced at the former operation was 500°, it ought this time to be 1,000°, because the initial temperature is 500° higher. The products of combustion will also escape at 1,000°, and passing through the chequer-work of the first pair of regenerators, its uppermost ranges will be heated to very nearly 1,000°. The temperature will diminish by degrees in descending till the gaseous currents have again reached the bottom nearly cold. Again reversing the process, after another half-hour (more or less) the gas will take up heat to the extent of nearly 1,000°, and since another 500° is again produced in combustion, the temperature of the furnace will this time attain 1,500°; and in this way it might be argued that, unless work is done in the furnace, the heat developed in combustion will, step by step, increase the temperature of the furnace 500°, or something less, each time a reversal of the valves takes place, till we arrive at the practical limit imposed by the melting-point of the most refractory substance we can find (pure silica, in the form of Dinas brick), of which the melting-chamber is usually formed. This high temperature is obtained by a gradual process of accumulation, and without any such current as would be likely to destroy, by oxidation, the metal in the bath, or cut away the sides and roof of the melting-chamber.

There is, however, a theoretical as well as a practical limit to the degree of heat obtainable in combustion, which was first pointed out by H. St. Claire Deville, namely, the point of dissociation at which carbonic acid would be converted back into its constituents, carbon and oxygen. If carbonic oxide, or any other combustible gas, and air enter the furnace at a temperature very nearly equal to the point of dissociation, it is evident that association or combustion cannot take place, and thus nature fortunately steps in to restrict the increase of heat by accumulation within comparatively safe limits. In a furnace fully heated up to the melting-point of iron, this action of dissociation can be very clearly observed. At first, when the gas and air are comparatively cold, combustion takes place sluggishly, the gases will flow through the furnace and produce only a dark-red flame ; the next time the valves are reversed a whitish flame is produced ; the next time, a short white flame ; and after having reached a full white heat, exceeding the welding-point of iron, the flame will again become a long one, but this time not red and of little apparent power, but bluish-white and flowing in clouds. This indicates a near attainment to the point of dissociation ; combustion can no longer take place, except to the extent that the heat is dispersed to surrounding objects, which is very considerable, or to the metal in the furnace. The temperature thus obtained is about that required for the process of making steel on the open hearth.

In the original form of regenerative furnace the roof was built with a depression in the centre, so that the flame might be deflected downward to the hearth of the furnace, and there impinge upon the objects that were to be heated. This was subsequently shown by Frederick Siemens to be undesirable, both on account of the action of the flame upon the substances with which it comes in contact, and because combustion is not perfect unless ample room is left for the full development of the flame. Modern steel furnaces are therefore built with a nearly flat roof, and the hearth being considerably below the level of the ports, the heat required for melting is derived mainly from the radiation of the flame, and scarcely at all by direct contact.

New Type of Siemens Furnace.—In a still later development of the Siemens furnace, the gas-producer is made a part of the furnace structure, the gases are sufficiently hot on leaving the producer to be led direct to the furnace, and only the air required for combustion is passed through regenerators. A point of novelty is that a portion of the intensely heated waste products of combustion leaving the furnace is diverted from the passage to the regenerative chamber, and is again forced through the gas-producer by means of a steam-jet injector. These gases contain much carbonic acid, besides water-vapour, the latter resulting alike from the use of the steam injector, and from the combustion of hydrogen in the furnace. The carbonic acid is attacked by the carbon in the producer and re-forms carbonic oxide, which is the principal constituent of producer-gas. The advantage of the system is explained by the fact that, whereas in the ordinary gas-producer two atoms, or 24 parts by weight, of coal-carbon, are required to form two molecules, or 56 parts by weight, of carbonic oxide, because oxygen and carbon are there uniting together immediately, in the new form of producer only one atom, or 12 parts by weight, of the coal-carbon is consumed to produce the two molecules of carbonic oxide, the second atom of carbon being derived from the otherwise useless carbonic acid contained in the waste gases injected. In other words, the carbonic acid, which is incombustible, takes up carbon from the coal to form combustible carbonic oxide, and in doing so produces an apparent economy of an equal weight of carbon. It must be remembered, however, that carbonic acid acted upon in this way, causes an absorption of heat, similar to, though less than, that produced by the use of steam; and also that the volume of steam accompanying the carbonic acid is necessarily considerable. The resulting loss of heat is compensated for, in part, by the large amount of sensible heat contained in the gases at the time of their introduction into the producer; and in part by the use of admixed air, introduced by a steam-jet in the ordinary way. The air employed is used pre-heated, by intercepting a portion of that which has passed through the regenerator on its way to the furnace. The new plant has been largely applied to re-heating furnaces, and in some places to puddling and other furnaces.

Figs. 15 and 16 represent respectively a transverse section and a plan of the new type of Siemens furnace. A is the long rectangular gas-producer, forming a part of the furnace structure; from it the gases are shown as passing direct by the flue B, to the port H, where they are mixed with air, admitted through the channel G, from the regenerator F. The flame traverses the furnace hearth C, and the products of combustion pass through the other port (H′) to a second regenerator, and thence through the valve D to the chimney-flue M. The portion of the hot burned gases that is to be re-utilised is aspirated (without passing through the regenerative chamber) by the steam jet X′, through the passage W′ and the fire-clay tube N′, into the closed ash-pit P beneath the gas-producer; at the same time pre-heated air from the other regenerator is forced by the corresponding steam-jet X, through W and N, beneath the opposite end of the producer; the quantity of air or burnt gases may be regulated by adjusting the pressure of steam in the corresponding injector. A subsidiary supply of cold air may be introduced if desired by the injectors R and R′. As the producer-gas enters the furnace direct from the producer at a sufficiently high temperature, the air alone is regenerated, and the direction of the current is reversed in the usual way, whilst the gas is admitted with the air to each port alternately, by means of the valve V in the passage B, and by a corresponding valve in the passage B′. The flame in the hearth of the furnace is thus passed alternately, after successive reversals, from H′ to H and from H to H′.

Recuperative Gas-Furnaces.—The regenerative system is only well suited for use when very high temperatures are required. For comparatively low temperatures the following arrangement, which has been patented several times during this century, is better suited, though up to recently there

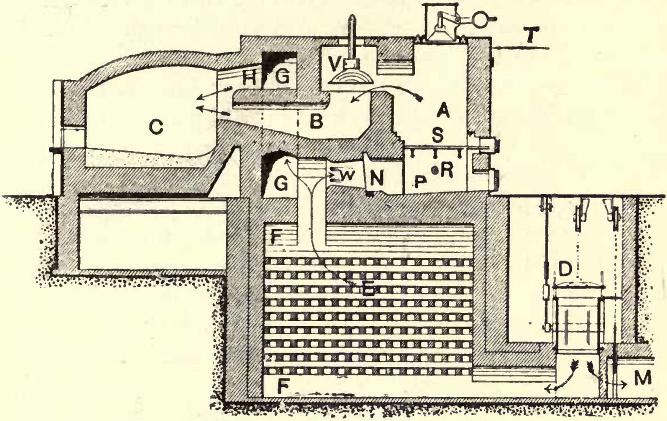

FIG. 15.—Transverse Section of the new form of Siemens Re heating Furnace.

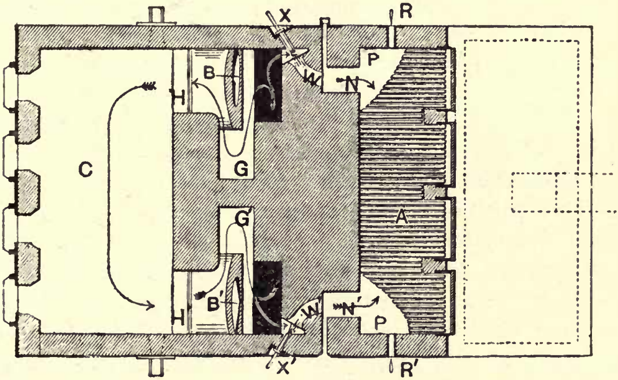

FIG. 16.—Sectional Plan of new form of Siemens Re-heating Furnace.

have been difficulties in the way of carrying it into effect. A parallel series of long narrow passages is arranged so that the hot products of combustion and the air to support combustion are passed in *opposite directions* through alternate passages. In this way the heat of the outgoing gases is communicated to the air and carried back into the furnace. It was at first proposed to make the partitions of sheet iron; this, however, did not prove satisfactory, owing to the leakage and the inability of the partitions to stand the wear and tear consequent on the high temperature. Fire-brick partitions were substituted for iron, but with no better success, as the air and gases mingled through the cracks and interstices. The objection to the use of fire-brick is said now to have been satisfactorily removed by the simple device of glazing the surface of the partitions. If this be the case, then regenerators on this system, or *recuperators* as they are sometimes called to distinguish them from the ordinary reversing regenerators, have a wide field open to them. They cannot be employed when a very high temperature is required, as the heat is not accumulated, and the temperature of the air can never be higher than half that of the outgoing gases. For heating gas-retorts specially moulded bricks containing the necessary channels with only ½-in. partitions between them are in successful operation.

Utilisation of Blast-Furnace Gases.—Although the use of iron partitions was not successful, yet in a modified form this system has since been largely employed in the manufacture of iron. The air to be heated is passed through a series of cast-iron pipes, arranged in a chamber, through which are made to circulate the waste gases, as they are termed, from the blast-furnace. There is, however, an important distinction between these gases and those obtained from reverberatory furnaces. In the latter case they have practically undergone complete combustion, whereas in the former, owing to the combustion being effected from the bottom of the furnace, and the products having to pass through incandescent fuel before escaping at the top, and for other reasons connected with dissociation, the gases contain a very considerable quantity of carbonic oxide, which, on combustion in the *stove* for heating the pipes, is capable of producing a temperature very much higher than that which could be obtained were only the sensible heat being carried off by the gases available.

The gases collected from the top of blast-furnaces contain on the average about 25 per cent. by volume of carbonic oxide, and hydrogen varying in quantity, according to circumstances, up to 7 or 8 per cent. From this it will be seen that, in point of heat-evolving power on complete combustion, blast-furnace gases are nearly equal to producer-gas. Until within the last few years these gases were allowed to burn uselessly at the top of the blast-furnaces; now they are generally collected, and employed for heating the blast and raising steam; in many works, no other fuel is required for such purposes.

The use of iron pipes has always been attended by a serious drawback, viz. that if by carelessness the temperature were allowed to rise above 550° C., the pipes would be ruined, so that practically about 500° C. is the maximum temperature with which it is safe to work; more commonly 300° to 450° has been employed, until quite recently. Another objection is that leakage is liable to occur, owing to the unequal expansion and contraction of the different parts of the stove-pipes.

The Cowper Stove.—Soon after the introduction of the regenerative system by the brothers Siemens, Cowper proposed to construct a stove on that principle, as a substitute for the iron-pipe stoves. Since their introduction these stoves have been modified in several ways, chiefly by increasing their height and arranging the channels so as to allow the gases a free passage, and at the same time to withdraw the main part of their heat.

Figs. 17 and 18 show the stove in its present form,

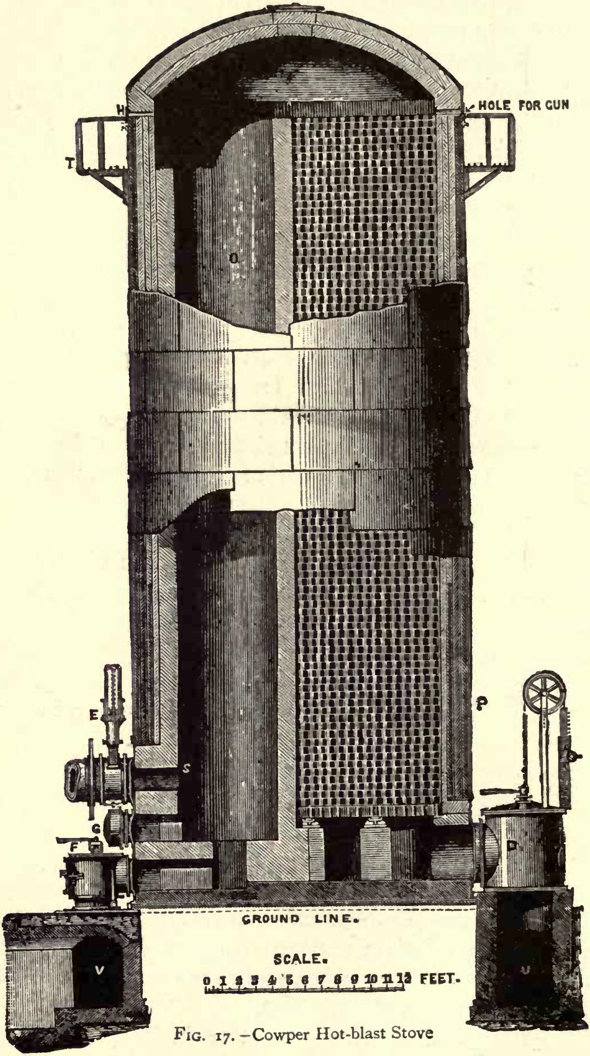

FIG. 17.—Cowper Hot-blast Stove

excepting that the chequer-work here drawn is now replaced by specially shaped bricks, which are so built that they form perpendicular, continuous, and uniform hexagonal channels, in place of the irregular passages formed by the older arrangement ; a cross section of the regenerator resembles that of a honeycomb. The gases are drawn off from the top of the blast-furnace by a tube called a down-comer, and passing into the gas flue V, enter the stove by the valve F ; by means of the valve G a suitable quantity of air is admitted, which, mingling with the gases, effects their complete combustion in the flame-flue O, from the top of which the highly heated products pass into the regenerator P, consisting of a long column of chequer-work ; from the bottom of the regenerator the gases are drawn off by the chimney through the flue U, the draught being regulated by the valve D. The flame flue is now often made ᗡ-shaped instead of circular, whereby the useless angles of the regenerator crescent are eliminated.

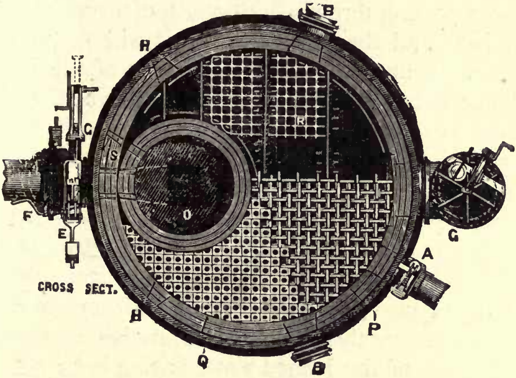

FIG. 18.—Cross section of Cowper Stove.

The whole of the stove, with the exception of the valves, is enclosed by several courses of fire-brick, encased in iron. As the gases pass through the regenerator they give up the greater part of the heat they contain to the top layer, there being a gradual shading off, as successive courses of bricks are passed through, until the bottom is reached, when they will be found to have a temperature of only about 150° to 200° C. It should be borne in mind that some heat must be left in, to create a sufficient draft in the chimney. The temperature of the gases issuing from an iron-pipe stove is, however, between 650° and 700° C., so that a considerable waste of heat takes place. So soon as the top layer of the regenerator has become heated up to the temperature of the gases passing through it, it must of necessity cease to absorb heat, and the gases traverse it without undergoing any alteration until they arrive at a part of the brickwork at a lower temperature than themselves, which they then gradually raise to their own temperature. If the gases were passed through the stove for some time, the whole of it would eventually attain the temperature of the gases, which would then issue at the same temperature as that at which they entered. In practice, to avoid loss of heat, it is desirable to stop the heating up of the stove whilst the maximum temperature is still some way from the bottom; the gas and air are then admitted to another stove, and the chimney-valve of the heated stove having been closed, the blast of cold air which it is desired to heat is passed through it, entering by the valve at the bottom of the regenerator. The air, as it traverses the regenerator, becomes heated to the temperature of the stove, and, passing down the red-hot flame-flue, is conducted to the blast-furnace through the valve E. A peep-hole through which to observe the temperature of the blast is provided at S. By means of this stove the blast can be heated to 800° C., the reduction in temperature after blowing cold air through it for about three hours amounting only to about 50°, and 75° in four hours, as the air on entering soon becomes heated to the maximum temperature of the stove, and then passes on without withdrawing any heat from the remainder of the regenerator above, so that the temperature continues constant as long as a certain area of the regenerator remains at its initial temperature. According to Cowper the saving of fuel due to the use of these stoves amounts to 20 per cent., and in some cases is as much as 7¾ cwt. of coke per ton of iron made. Dust is prevented from entering the regenerator, as far as possible, by a special arrangement of the pipe supplying the gases; that which finds its way in is removed by turning on the cold blast, and shutting all the other valves; a special door is then opened several times; the sudden rushing out of the compressed air dislodges and carries with it the dust. In some works the same result is arrived at by firing into the stove, through openings provided for the purpose, a gun loaded with blasting powder: the dust collects at the bottom, and is removed through doors. The friction is very much less in these stoves than when pipes are used; the power necessary to produce a blast of the required pressure is therefore also less. The height and diameter of these stoves vary, the former up to over 60 ft., the latter to 30 ft.

The Whitwell Stove.—Fig. 19 shows a modification of the Cowper stove, known as the Whitwell stove. The arrangement is intended to facilitate cleaning. It is only fair to say that the Cowper stove, as now made, presents no special difficulty in this respect. Either stove is capable of heating the blast to as high a temperature as is at present employed in blast-furnace practice; they are both largely used, and not uncommonly are seen side by side in the same works. The figure shows the attachment to the blast main of the furnace. A is the gas valve, G the air inlets for the combustion of the gas. The air is warmed by being passed through the basement of the stove, which it thus protects from damage by excessive heating. C is the chimney-valve. It will be observed that the chequer-work of the Cowper stove is replaced by fire-brick partitions. At the bottom of the first and third of the smaller partitions are

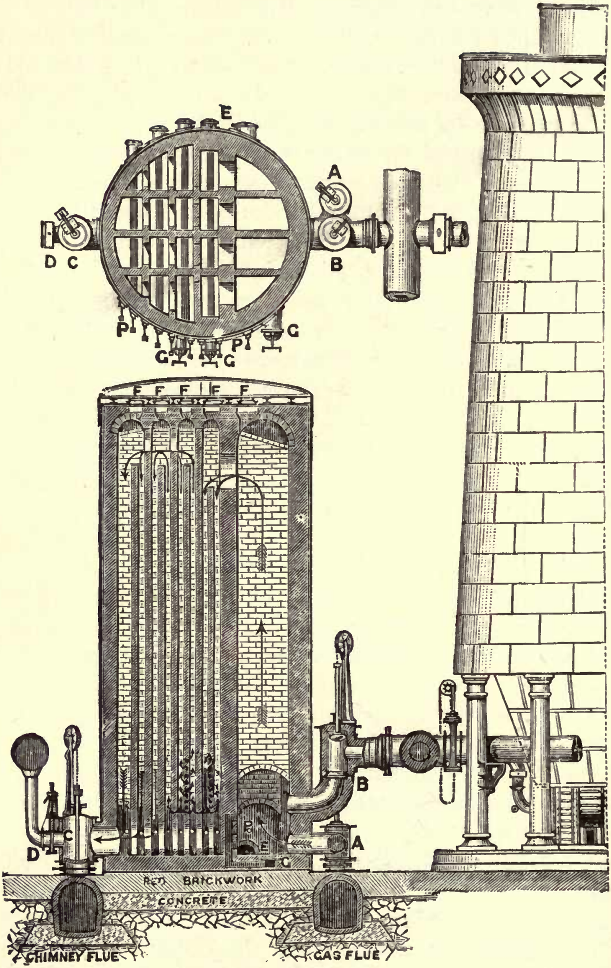

FIG. 19.—Whitwell Hot-blast Stove.

openings, through which a further quantity of air is admitted to complete the combustion of the gases.

The cold blast enters through D, and passes out heated at B; P P are the eye-pieces through which to observe the temperature. In order to clean the stove, the gas is shut off, and the chimney-valve (C) slightly opened in order to carry the heat downwards, the first top cleaning door (F) is taken off, and the movable plug in the crown of the arch lifted. Scrapers with $\frac{3}{4}$-inch tubular handles are introduced, and the walls scraped down, the dust falling to the bottom; the door is then replaced, and the next compartment treated in the same way, whilst the walls are still red-hot, and so on in rotation. The dust which has been detached from the walls is removed at the bottom through the doors (E).

These stoves, in America, have been made as much as 70 ft. high and 21 ft. in diameter, containing 30,000 sq. ft. heating surface.

Modified Stoves.—In America the above described stoves are now generally modified. The Massick and Crooke stove, for example, consists of a wide central tube for the combustion, surrounded by a concentric ring of small tubes, through which the burnt gases pass downwards, to be deflected upwards again through two sets of still smaller flues, forming a ring of flues outside the former. Finally they pass to a chimney which surmounts the whole.

The Gordon modification stove has also been erected in many places. In this stove, the gases pass upwards through the combustion chamber, which is at one side, then downwards through Whitwell passages, and finally upwards again; but in the last part of their path towards the chimney above, the channels which they traverse are narrower, and are constructed on the Cowper pattern, the object being to effect a more complete interception of heat before they escape into the air.

Petroleum.—The mineral oil, which is found in such abundance in the neighbourhood of the Caspian Sea, and in the United States, and in considerable quantities in Burmah and other parts of the world, is occasionally employed as a metallurgical fuel. Up to the present, however, its principal application as a fuel has been in the firing of steam boilers. Crude petroleum is a dark, viscous fluid obtained by sinking wells in the oil-bearing strata. It consists mainly of compounds of carbon and hydrogen, combined for the most part as paraffins, the approximate percentage composition averaging 85 of carbon, and 15 of hydrogen. Owing to the ease with which a large volume of flame is produced, and the absence of ash and other incombustible constituents, the oil is well adapted for use in raising steam, and for many purposes where a high calorific power is required. The evaporative power of petroleum is commonly fifty per cent. higher than that of a steam coal. The crude petroleum is usually distilled, in order to separate the numerous constituents with different specific gravities and boiling-points that it contains. In this way, petroleum ether, illuminating petroleums or paraffins, lubricating oils, petroleum jelly, and vaseline are successively obtained, each product having a higher specific gravity and a higher boiling-point than the preceding; and there is left in the retort a coke-like mass which may be used as a solid fuel.

For use as a liquid fuel the raw petroleum may be employed, but more generally some of the valuable products of low boiling-point are distilled off, and the residue is then burned with the aid of special apparatus. Commonly the petroleum is injected into a hot furnace-chamber in the form of spray by a jet of super-heated steam, and the spray being ignited burns with a large body of flame. A special arrangement of liquid-fuel furnace was for a short time employed in melting wrought-iron, the articles cast from the charge being sold under the name *Mitis* metal. The iron was fused in large crucibles placed in the path of a flame from burning petroleum. The petroleum was allowed to flow through a number of open iron troughs placed at the entrance to the furnace in such a way that all the air drawn in by the chimney draught had to pass over them; the heat radiated from the combustion chamber caused the oil in the troughs to evaporate, and the vapour, mingling with the air, produced on combustion a long flame, which filled the chamber and produced an enormously high temperature. The absence of sulphur from petroleum (with but few exceptions) renders it especially suitable for use as a metallurgical fuel. The convenience in handling this fuel, and the perfect control under which the supply—and therefore the rate of combustion and the resulting temperature—may be kept, are greatly in favour of its adoption wherever it may be conveniently applied.

In recent years exceedingly finely divided coal-dust has also been utilised as a fuel, after the manner of oil, by injecting it, suspended in the air required for its combustion, into a hot fire-brick chamber. In this way it burns as a mixture of oil or gas and air would burn. Crampton attempted to apply this system of firing to the puddling-furnace, but, after prolonged experiments, gave up the attempt. At the present time (1896), however, attention is being once more directed to the problem, and many steam boilers as well as a few crucible furnaces are being successfully fired by means of powdered fuel.

Accompanying petroleum there are frequently found large supplies of natural gas, analogous to coal gas in composition. The 'eternal fires' of the celebrated temples in Baku (Russia) are fed from such supplies. In Pittsburgh, a few years ago, the gas was evolved in such abundance, that metallurgical works sprang up and special furnaces and processes were devised to utilise it. The supply has now diminished to such an extent that these works have had, for the most part, either to be served by producer-gas or to be closed altogether.

REFRACTORY MATERIALS

THE term REFRACTORY is necessarily relative, the degree to which a substance is refractory depending on the circumstances under which it is employed, and notably on the nature of the substances with which it is brought in contact. For example, silica (SiO_2) heated alone, even to a very high temperature, is extremely refractory, *i.e.* it does not sensibly soften, but if it be brought into contact with some base, such as lime (CaO), oxide of lead, or oxide of copper, at an ordinary red heat, union takes place with the formation of a silicate, which in every case is much more fusible than silica, though differing in degree according to the base. It is obvious from the foregoing that in the selection of materials for the construction of furnaces the chemical affinities, which will be brought into action between the body of the furnace and the substances to be treated in it, must be carefully considered. This, however, is not the only point to be borne in mind in choosing a suitable material. Many substances are capable of resisting a very high temperature if gradually raised to it; but have not the power of resisting sudden changes of temperature, such as occur, for instance, when a crucible is heated suddenly by placing it in a hot furnace. For these purposes such materials would be unsuitable, and it would be necessary to select some substance or combination of substances capable of resisting sudden changes of temperature.

Fire-Clay.—The most important refractory material is that resulting from the so-called burning of clay. We will, therefore, first consider the composition of various kinds of clay, and the properties which give it so great a value in the arts.

The basis of clay is silicate of alumina, *i.e.* silica in chemical combination with alumina. All clays have been derived from the natural decomposition of felspars, which occur in nearly all igneous rocks and in some stratified crystalline schists. The character of each clay will be mainly determined by the nature of the rock from which it originated. The felspars consist essentially of anhydrous silicates of alumina, with variable proportions of silicates of potash, soda, lime, and magnesia, and a little oxide of iron. The relative proportions of these alkaline bases is found to vary with the state of occurrence of the felspar ; thus orthoclase and the other more silicious felspars containing potash are common in granite and all plutonic rocks, whilst the volcanic rocks are characterised by the presence of the less silicious felspars, containing soda and lime. By 'weathering,' *i.e.* exposure to the combined action of carbonic acid and water, the soda, potash, lime, and magnesia are dissolved away more or less completely, and at the same time the residual silicate of alumina becomes chemically combined with water, and is said to be hydrated.

In its purest state clay would consist of only silica, alumina ($Al\ O_3$) and water, combined in proportions probably in most cases represented by the following formula : $Al_2O_3.2SiO_2 + 2H_2O$, which corresponds to a percentage composition of 46·33 SiO_2, 39·77 Al_2O_3, and 13·90 H_2O. This state of purity is closely approached in china clay, used in the production of the best porcelain. The white, scaly, crystalline powder of which china clay consists, seen through the microscope, is found to be made up of flexible but inelastic hexagonal plates. These plates, with the aid of the microscope, can be discovered in greater or less quantity in every clay.

The degree of purity of a clay will depend not merely on the extent to which the felspar has been decomposed, but also on the greater or less completeness with which it has been separated from the containing rock by the action of running water. Thus, clay derived from orthoclase, which occurs in granite, will be found more or less admixed with quartz and mica. All clays contain more or less admixed silica, so that the usual composition of fire-clay ranges from 50 to 65 per cent. of silica, with from 22 to 32 of alumina, from 2 to 4 of lime, magnesia, alkalis and oxide of iron, and from 10 to 15 per cent. of water.

It will have been remarked that during the decomposition of felspar the silicate of alumina has passed from the anhydrous to the hydrated condition. It is to this, at first sight, unimportant change that clay owes its great value, for it is in consequence of the presence of this water of hydration that clay possesses its characteristic property of *plasticity*, or the capability of being moulded into any required form when moistened. If dry clay be moistened it can readily be made to take any required shape, and if it be then dried by the warmth of the sun, or by some similar moderate heat, it will preserve its shape, so long as it is not remoistened. If, on the other hand, the clay be subjected finally to a fairly high temperature, it will no longer possess the property of plasticity on being remoistened: it will be rigid, and practically a totally different substance to that from which it was derived. This change, so important in its consequences, is due simply to the fact that at the higher temperature the water in chemical combination has been removed, whereas at the lower temperature the mechanically admixed water alone was withdrawn. The chemically combined water once driven off at a sufficiently high temperature never again resumes its union: to this is due the stability of the innumerable structures made from burnt clay.

Since, then, clay has been derived from the gradual decomposition of certain portions of the earth's crust, and has, in most cases by the action of running water, been accumulated as a bed or stratum over large areas, it is easy to understand how it is that considerable variation in its composition and state of division may occur even within a comparatively limited space.

Clays are divisible, broadly speaking, into two classes, viz. ordinary clays, such as are used for building houses and the cooler portions of furnaces, and fire-clays, which, as the name denotes, are capable of withstanding a high temperature without rapidly deteriorating. The difference between the two kinds is due to the amount and nature of the impurities, *i.e.* foreign substances, which they respectively contain. The more potash or soda a clay contains the more easily fusible will it be. Oxide of iron, lime, and magnesia act in a similar manner, though to a much less extent. An account of the relative fusibility of the silicates will be given in the chapter devoted to fluxes.

The fire-clays, with which we are here more especially concerned, are obtained principally from the coal measures, in which they occur in great abundance. The neighbourhood of Stourbridge has long been celebrated for the quality of its fire-clay, which is largely used for the manufacture of bricks of various shapes, and for crucibles.

During the dehydration of clay by heat contraction takes place, the amount of contraction depending on the degree of heat applied. In bricks this shrinkage is not of so much consequence ; but in crucibles, owing to the variation in thickness and shape, the material would be liable to crack. In order to counteract this tendency a proportion of some substance which expands on heating, or at any rate does not contract, is added. For this purpose a certain proportion of burnt fire-clay is commonly mixed with the raw clay; sometimes coke dust, graphite, or silica is added, which last expands on heating. When burnt clay is used, a common proportion is one-third burnt clay to two-thirds raw clay. The amount of burnt clay necessary is, however, very variable, depending on the 'fatness' of the raw clay. It is important that the burnt clay should not be too finely powdered ; the size of the particles will depend on the use to which the material is to be put. The presence of particles of iron pyrites, of any appreciable size, in fire-clay used for crucibles should be carefully guarded against, as the oxide of iron, resulting from the oxidation of the pyrites under the influence of heat, combines with the clay, forming a fusible substance, and causing a hole to form at that point when the crucible is in use.

The power of any clay to resist a high temperature may be judged of by working up some of it with a suitable quantity of water, shaping it into a rectangular piece with *sharp* edges, and then, after drying it at a gentle heat, subjecting it to the temperature which it will be required to stand, care being taken to protect the clay from the action of the ashes, if solid fuel be employed for obtaining the requisite heat. If the edges have remained quite sharp, the clay may be considered refractory at the temperature of the experiment.

Fire-Clay Crucibles.—The manufacture of large crucibles is conducted in one of two ways. In the old method, and that still in general use, a mixture of various clays which experience has shown to be best for the purpose is ground under edge-stones, and, having been sifted, it is mixed with water and the proper proportion of burnt clay, for which the old pots are utilised. This mixture is then kneaded, by men treading barefooted, until it has acquired the requisite consistency.

The crucibles are fashioned by hand, with the assistance of a block of the form of the inside.

Crucibles are now also made successfully by machinery. A sufficient quantity of the substance to be made into a crucible is dropped into a mould, which is then made to rotate; a fixed wooden tool, which descends nearly to the bottom of the mould, presses the lump and causes it to take the required shape. The moulds are formed from plaster of Paris supported when necessary by a wooden casing on the outside, both the wood and the plaster of Paris being then made in segments. The mould containing the freshly made crucible is placed in a warm place; in a short time, owing to the plaster of Paris absorbing the moisture from the surface of the crucible, the latter readily detaches itself.

Clays vary considerably in their power to resist the corroding action of metallic oxides, such as oxide of lead or oxide of copper. This is often a matter of considerable importance, and is best ascertained by direct experiment on a sample. No clay can resist the action of these oxides in their uncombined state for very long ; some sulphides, *e.g.* galena (sulphide of lead), have the singular property of readily permeating clay crucibles without corroding them.

The finer and more regular the grain of a crucible the more readily will it, as a rule, resist corrosion and permeation ; but unfortunately these same conditions increase their liability to crack.

Small fire-clay crucibles are fired in kilns, and are allowed to cool down, as they can be heated up again without danger of their cracking. This cannot be done with large crucibles, such as are used for melting steel or large quantities of brass. They are first carefully air-dried, and then kept in a warm dry place until required for use, when they are gradually heated up to redness, *mouth downwards*, and are, after being inverted, ready for immediate use. This process is known as *annealing*. It has been found that if a large crucible receive its first heating mouth upwards it almost invariably cracks.

Silica Bricks.—In cases where an extremely high temperature has to be resisted, *e.g.* in a Siemens steel-melting furnace or a Bessemer converter, fire-bricks made of clay cannot be employed, and some material still more refractory under the conditions has to be substituted. For this purpose silicious bricks are employed ; bricks of this kind were not known before about the year 1882, when the method of making them was discovered. The rock of which they are composed occurs in considerable quantity in the Vale of Neath ; it consists of about 97 per cent. of silica, the remainder being made up of alumina, oxide of iron, lime, potash, soda, and combined water. It is locally known as 'clay.' The rock, having been sufficiently disintegrated, is mixed with about 1 to 3 per cent. of lime and some water; it is then pressed into moulds, dried, and fired hard for about a week. On one of these bricks being fractured, it will be seen to consist of angular fragments of quartz, embedded in a light yellowish-brown matrix. In setting these bricks a cement of the same material must be used. Bricks of this description are now also made by grinding up fine any pure silicious rock or stone, and mixing about 1 per cent. of milk of lime with it.

The addition of extraneous material to the silicious rock is in no way analogous in purpose to the case we have recently had under consideration, viz. the mixing of burnt clay, silica, or coke-dust with raw fire-clay. In the present instance we are dealing with a substance which is devoid of plasticity, and which, being in irregular pieces of variable shape and size, can only be made into a solid mass of a required form by the assistance of some cementing material. The small quantity of lime used answers this purpose very perfectly, as at a high temperature it unites with silica, forming a refractory silicate, which cements the mass together. If much lime were present the material would be insufficiently refractory at high temperatures. The presence of mica and oxide of iron in more than traces is also objectionable. Complex silicates, *i.e.* those containing more than one base in combination with the same silica, are more easily fusible than single silicates, the silicates of potash and soda excepted; it follows that the extent to which a brick is refractory will depend more on the number and relative proportion of the foreign substances present than on the actual quantity of any one of them. A clay containing a certain quantity of magnesia, and no lime, would be more refractory than if part of the magnesia were replaced by an equivalent quantity of lime.

Ganister.—Another silicious material, known as 'ganister,' is largely used for lining Bessemer converters. The finest quality of this material is obtained near Sheffield, where it forms the under-clay of a thin coal-seam ; it also occurs in Lancashire, in the Newcastle coal-fields, in those of Yorkshire, as well as in Shropshire. This substance appears to have been deposited in shallow seas, just after the mill-stone grit, and before the soil upon which the coal-measure plants grew. Geologically, it is probably the equivalent of the silicious rock of the Vale of Neath. It differs considerably from all other sandstones, except that from the Vale of Neath ; the particles of which it is composed are very fine, it has a waxy fracture, and is very hard and tough. Unlike other sandstones, it has the power of binding together, when ground fine and mixed with water. A fairly good substitute for this material can be made from powdered pure silicious stone, mixed with a small proportion of aluminous clay.

Natural silicious stones are occasionally used for the hearths of blast-furnaces and such purposes. They should be carefully dried before being strongly heated. The same remark applies equally to all bricks and crucibles, however produced.

Plumbago Crucibles.—In some cases in which sand, or a mixture of clay and sand, would not resist sufficiently well the corrosive action of certain slags, a greater or less amount of coke-dust or *débris* of charcoal is added. This mixture is termed 'brasque.' Crucibles for melting steel and brass are now commonly made of plumbago or graphite, mixed with about an equal weight of fire-clay to give strength. The presence of the graphite, which is an impure form of carbon, is especially useful in protecting the fire-clay of the crucible from being attacked by the oxides formed when metals are melted, as it reduces most oxides to the metallic state, and the metals are not able to combine with clay. Plumbago crucibles therefore have a longer life than clay pots, and in addition they resist sudden changes of temperature better, so that they can be cooled down and reheated many times, whereas ordinary fire-clay crucibles cannot. They are occasionally glazed after firing, so that, being impervious to, and therefore free from, moisture, they do not require the careful annealing that is necessary for ordinary clay pots.

Other Refractory Materials.—Talcose slate and soapstones have been used in some localities in the construction of furnaces. Serpentine resists corrosion well, but cannot with advantage be exposed to very high temperatures. Granite is also employed occasionally. Bauxite, a mineral which occurs in considerable quantity in several localities in France, in pockets in calcareous rock belonging to the cretaceous series, and which consists essentially of pisolitic oxide of iron in a matrix of alumina, the latter largely predominating, has a limited use for lining furnaces. It is also used as a source of the metal aluminium. Its composition is very variable, but on an average it contains in a hundred parts about 3 to 5 silica, 23 to 25 peroxide of iron, 50 to 60 alumina, and 10 to 15 water. It also mostly contains 2 or 3 per cent. titanic acid. This material is highly refractory, owing to the aluminate of iron, which forms at a high temperature, being very infusible.

In one important metallurgical operation oxide of iron is used as a furnace lining, viz. in the puddling process. Here, owing to the nature of the process, either silica or clay would be rapidly corroded and cause great waste of iron, whereas oxide of iron not only protects the masonry of the furnace, but takes an essential part in the process.

Iron itself is now largely employed in furnace-building, being kept sufficiently cool for the purpose by the circulation of cold water or air at the back of it; but in this case the slag which chills on the iron forms the real working surface.

Basic Linings.—We have seen how, in clay, alumina in combination with silica forms a very refractory substance. Alumina itself is even still more refractory, but owing to the difficulty of obtaining it in considerable quantity it is not available for use on a large scale. The same remark has hitherto applied to magnesia (MgO), which is also highly refractory.

Lime, which is infusible at any temperature we can command, is, on the other hand, extremely plentiful. In order to produce it, it is only necessary to drive off the carbonic acid from chalk or limestone by the application of heat. The use of lime, however, as a refractory material for furnace purposes is rendered impossible, owing to the property it possesses of combining readily with water, with the result that it swells up, and falls to pieces; so that, unless the lime be kept continuously at a high temperature, the structure composed of it crumbles to pieces by the mere action of the moisture in the air. For small operations, such as the fusion of platinum by the flame of an oxy-hydrogen blow-pipe, blocks of lime have found an application.

The want of some substance of the nature of lime which could be employed at high temperatures has long been felt. It is only recently that this want has been successfully supplied on a large scale. It has been found that magnesian limestone, which consists mainly of carbonates of lime and magnesia, unlike ordinary limestone or chalk, after it has been very strongly calcined can be reheated and cooled as often as required without crumbling. In consequence of this important discovery, iron ores, which previously were useless for the production of soft steel, are now being largely employed. This portion of the subject will be discussed when speaking of the manufacture of steel.

The most successful method of employing the magnesian limestone is, first to fire it strongly, then to grind it up fine and mix it with pitch. The bricks made from this mixture are then strongly fired. There is, however, considerable difficulty attending the construction of a lining with these bricks, because they have to be set with similar material, which it is almost impossible to fire satisfactorily, and which is very liable in any case to work out of the joints, owing to shrinkage. This difficulty is increased by the shrinkage of the bricks themselves during firing, which gives them a more or less curved form. These objections have been successfully overcome by making the material, which has been strongly calcined, into a 'slurry,' or liquid mass, and running it into a mould of the required shape and size, then by a gradually applied heat consolidating it by removing the pitch; or the mixture of magnesian limestone and pitch may be in such proportion that on the application of heat it will soften, the pitch finally being decomposed when the heat is increased. In this case the mixture may be shovelled into the mould in a solid condition.

All sorts of magnesian limestone (*dolomite*) are used at different works; but for material which is to be highly shrunk, and when it can be obtained, a limestone or mixture of the following composition is preferred: Magnesia, 36; lime, 52; silica, 8; and alumina and oxide of iron 4, per cent. For this analysis of what is now commonly known as 'basic' lining I am indebted to Mr. Percy Gilchrist, one of the patentees of the process.

It has been attempted to produce magnesia on a large scale by precipitating it from its chloride with milk of lime. It is simply a question of cost. If it could be done economically a very useful substance for the manufacture of basic bricks would be available. Magnesia exists in considerable quantity in several waste liquors.

If what has been said on the subject of materials capable of resisting the action of fire has been clearly understood, it will have become evident that, unless previously fired, they should only be used in such positions as will ensure their being subjected to a high temperature. It would, therefore, be objectionable to employ fire-clay mortar in a cool part of a furnace, as it would inevitably crumble out. On the other hand, ordinary mortar, which consists of sand and lime, is not suitable for use, except in the cool parts of a furnace.

In using silica bricks, the binding materials should be highly silicious, and may consist of a silica, similar to that employed in making the bricks, but mixed with a somewhat larger percentage of lime. This *silica cement* should become just sufficiently soft at the furnace temperature to consolidate the structure, without actually fusing as a fire-clay might.

Neutral, or Passive Materials.—It will now be understood that there are two broad classes of refractory materials, the *acid* and the *basic*, which may be utilised according to the character of the substances to be heated in contact with them ; of the former silica is a typical example, of the latter magnesian limestone. But there is a third class, sometimes termed *neutral*, or more correctly *passive*, of which the properties at the temperature employed are neither acid nor basic. Such a material is chrome iron ore, which commonly contains about 40 per cent. of chromium trioxide, 15 per cent. of protoxide of iron, 8 per cent. of silica, and a small proportion of lime, magnesia, alumina, and other bases. In the construction of basic lined furnaces for steel-making, it has been found impracticable to employ the usual basic materials in building the roof, as they contract too much on being heated. It is therefore necessary to erect a roof of acid bricks upon a basic hearth. In order to avoid the mutual fluxing action at the junction of these two materials, a *passive joint* is interposed, consisting of a layer of chrome ore a few inches in thickness. Carbon, which is a truly neutral material, owing to its combustibility and power of attacking metallic oxides, cannot be largely employed. It has, however, lately been used with success in lining the hearths and even the boshes of blast furnaces, where it does not come in contact with free oxygen or with reducible oxides.

FLUXES

Fluxes are substances added to ores, and to some metallurgical products in order to render them more fusible, and thus enable the metal, or the *matte* as the case may be, which it is desired to obtain, to separate by gravity from the useless portion, which when combined with the flux forms a fusible body, called *slag*. This they do by acting as solvents, or by forming chemical compounds. *Matte* is the term applied to describe the sulphides, antimonides, and arsenides of the metals; the last-named being sometimes called *speiss*.

The character of the flux must, obviously, depend upon the nature of the refractory material, upon the temperature to be applied, and upon the degree of fluidity that it is desired to produce. Usually an acid is employed as a flux for a refractory base, and a base for an acid; so that sand (silicic acid) and lime may play opposite parts at different times, each being a refractory substance at one time, and a flux at another. But the fusing point of the silicate of lime formed by their combination is too high for most purposes. It has already been stated that compound silicates are more easily melted than those which contain only one refractory base. Hence an addition of silicate of alumina (clay) in suitable proportions to the silicate of lime would produce a double silicate of lime and alumina, far more fusible than either of the ingredients alone; and the addition of a third silicate to these would still further lower the fusing point. In blast-furnace practice, for example, limestone is generally used as a flux; but if the ore to be smelted contain no clay or alumina in any form, some aluminous ore is added to the charge, in order to produce a cinder that shall be more fluid. Blast-furnace slag is essentially a double silicate of lime and alumina.

Among the single silicates, those which are formed from fusible bases, like soda or potash, melt most readily, and of all the possible mixtures of silica and such a base, that which contains least silica is most fusible. But of the different combinations of silica with a refractory base, such as lime or magnesia, those give the best results which contain a decided preponderance of silica, an excess of either refractory material naturally tending to diminish the fusibility. With the double silicate of lime and alumina, the best mixtures are those in which there are from three to six times as many molecules of lime as of alumina, and in which the oxygen contained in the silica is from one half to twice the amount present in the two bases together. Gredt has found that the most fusible of all has the formula $3CaO.\ Al_2O_3.\ 3SiO_2$, and melts at 1410° C. The substitution of 13 per cent. of magnesia for a like amount of lime produces a triple silicate melting at a temperature 50° lower.

Fluor spar and the sulphates of barium or calcium flux one another, and the former substance is frequently added to the charge in smelting copper ores.

Fluxes are also used to dissolve the oxide which forms upon metals when heated, in order that clean surfaces may be obtained for welding or soldering. In welding iron, sand is employed, because it forms with the scale a readily fusible silicate of iron that can be squeezed out under the action of the hammer, and so allow the contiguous metallic surfaces to be pressed into absolute contact at the temperature at which they are capable of uniting. In soldering with hard or brazing solder, borax is commonly used because it melts very readily by itself, and has the property of forming highly fusible double compounds with metallic oxides. It is too expensive to be largely employed as a flux in furnace operations with the common metals.

THE METALS

THE word METAL appears to be derived from the Greek μετ' ἄλλα, *in quest of other things*, whence come μεταλλάω, *to search after*, *to explore*, or, in gold-diggers' language, *to prospect*, and the corresponding substantive μέταλλον, *a mine.*

About fifty of the undecomposed or *elementary* substances are classed together under the head of METALS by the chemist, because they manifest certain properties when acted upon by chemical tests, without regard to those external characters which are commonly associated with the idea of a metal.

Many of these are unfit to be employed in the metallic state for any of the ordinary uses of metals, because they cannot be exposed, even for a short time, without being rusted or corroded, by combining with the oxygen of the air, to such an extent that they entirely lose their metallic character.

Among those which offer sufficient resistance to the action of air, many are excluded from useful application in their metallic state, on account of their rarity, or of the great difficulty which is experienced in extracting them from their ores.

The metals which are employed for useful purposes in their pure or metallic state are—

Aluminium
Antimony
Bismuth
Cadmium
Chromium
Cobalt
Copper
Gold
Iridium
Iron
Lead
Magnesium
Manganese
Mercury
Nickel
Palladium
Platinum
Rhodium
Silver
Sodium
Tin
Tungsten
Zinc

On considering this list, it will be seen that several of the metals named in it are employed to produce some effect dependent upon a peculiar property of the metal, and not upon qualities which belong to it in common with the rest. Thus, mercury or quicksilver is used for *amalgamating* or dissolving other metals, and also as a suitable liquid for constructing barometers and thermometers ; antimony owes its usefulness to its property of hardening lead and tin ; bismuth and cadmium are employed to render lead and tin capable of being melted at lower temperatures ; nickel is used to whiten copper in order to make German silver, to toughen steel, and to give a bright comparatively untarnishable surface to other metals ; and magnesium is valuable for its property of burning easily with production of a brilliant white light.

Moreover, gold, iridium, platinum, palladium, rhodium, and silver, being comparatively rare, and aluminium being obtainable by a relatively costly process, the useful applications of these metals are limited by their high price, so that there remain only TIN, LEAD, COPPER, IRON, and ZINC to be considered as metals largely employed for useful purposes.

The qualities possessed by these metals, rendering them fit for purposes which could not be fulfilled by non-metallic substances, are *lustre*, or the power of reflecting light ; *tenacity*, or resistance to any attempt to pull asunder their particles ; *malleability*, or the capability of being hammered or rolled into thin sheets ; *ductility*, or the property of being drawn out into wire ; high *specific gravity*, or relative weight ; high *conducting power* for heat and electricity ; and *fusibility*, or the property of becoming liquid when heated.

Metallic Lustre.—The power of reflecting the rays of light is possessed in a much higher degree by metals than by non-metallic substances. Although some of the latter class, such as iodine and plumbago, reflect much of the light which falls upon their smooth surfaces, they have a black appearance, caused by their absorbing a large proportion of the luminous rays, which is quite different from the true metallic lustre. The metals and alloys which exhibit the greatest lustre are those which are not quickly attacked by the oxygen and carbonic acid in the air, and are sufficiently hard to receive a high polish. Gold and platinum have considerable lustre because, though not very hard, they are unattacked by the constituents of the atmosphere ; silver is unattacked by oxygen, but is easily tarnished by sulphur which is present in small quantity in the air as sulphuretted hydrogen, especially in towns. When hardened by being alloyed with a little copper, silver takes a high polish. Metals, when highly polished, are less easily tarnished, because gases then have less tendency to condense on their surfaces. Iron, in the form of steel, is capable of exhibiting lustre in very great perfection, because the hardness of steel allows its surface to be ground perfectly smooth by the application of fine particles of very hard substances, such as emery, which rubs off minute projections from the surface without producing scratches or indentations. A surface so polished may send back directly to the eye of the observer almost all the light falling upon it, whilst a rough surface, being made up of a number of small surfaces, scatters the reflected rays in all directions. Tin, melted with twice its weight of copper, forms an *alloy* of great hardness and brilliancy, which is employed for the *specula* or mirrors of reflecting telescopes. Zinc and lead, on the other hand, exhibit metallic lustre in an inferior degree, because when exposed to air, the metal at the surface combines with oxygen, forming a thin film of oxide or carbonate which has no metallic lustre.

Colour.—Although most of the light which falls upon a polished metallic surface is reflected, a small proportion is absorbed ; but the rays that are blended in white light are not abstracted to an equal extent, so that the light after reflection, being robbed of a larger proportion of one constituent than of the others, is no longer pure white, but presents a combination of the residual rays. The surfaces of metals, therefore, are usually tinted ; and the more often the rays are reflected backwards and forwards from successive surfaces of the same metal, the more clearly the characteristic colour of the metal is seen. The colours of most metals—the red of copper, the yellow of gold, and the blue-white of zinc—are well known, and serve a useful purpose in enabling them to be readily recognised. For instance, it is a great convenience to be able to distinguish gold from silver at sight. The differences of colour are also of practical use in judging of the purity of such metals as copper and gold, or of their alloys. The blending of the colours of metals is studied in artistic metal work.

Mechanical Properties.—When a vertical bar of metal is held firmly at one end, and a gradually increasing weight is applied at the other, it increases in length. At first this increase is exceedingly small, being almost exactly proportional to the load applied, and a removal of the weights would cause the bar to return to precisely its original length. Under these conditions the metal is said to be perfectly *elastic* ; and it should be observed that *elasticity* does not necessarily imply great stretching power, but only the power of returning to its exact original shape when the load which produced distortion is removed. But if the load, or the *stress* as it is termed, be steadily increased, and the metal be more or less ductile, sooner or later a point will be reached when the extension, or *strain*, produced, increases with greater rapidity than the load, and then the bar will be found permanently stretched, even after the removal of the weights. This point, at which the ratio of stress to strain ceases to be constant, and beyond which *permanent set* (*i.e.* distortion) is observable, is regarded as the *limit of elasticity* of the metal. Beyond the elastic limit further loading produces deformation, both temporary and permanent, at a rate increasing more and more markedly until at last the extension becomes localised at the weakest point, where the metal will draw out more or less considerably in proportion to its ductility, and finally the bar gives way under the stress, and pulls asunder. From this maximum load the *tensile strength* of the bar is found ; it is usually expressed as the number of tons or of pounds required to produce the rupture of a one-inch square bar. The extension produced may be determined at the moment of fracture, or after the bar has given way, and is generally reported as a percentage of the original length of the bar. A careful plotting of the extensions produced by successive increments of load gives a 'stress-strain-curve' which yields valuable information, by mere inspection, as to the behaviour of the metal through the whole course of the test.

In the practical application of metals, these three characteristics—elastic limit, breaking stress, and extensibility—are of prime importance. In designing structures, it is not sufficient merely to know what weight a given bar of metal should sustain without rupture : it is of even greater importance to ascertain how much it will bear without permanent distortion, in order that the highest load that is likely to be applied to it may be well within the elastic limit of the material. A metal which is to be shaped under the hammer or in the press, may with advantage have a low elastic limit, combined with a fairly high tenacity, because the application of a relatively slight force will then enable it to assume the required shape, provided that its extensibility is sufficiently great ; although the finished work will be more readily distorted by accidental blows than if its elastic limit were high. Such a metal is usually tough because it will bear, without breaking, a considerable stress and much distortion, after the limit of elasticity has been passed. Hard steel is one of the strongest metals known, but its extensibility is relatively slight, and the hardest kinds are liable to be broken by sudden shocks. It is not easy, therefore, to shape this metal in the cold ; but on heating it to a dull red heat, the elastic limit is reduced to a much greater extent than the tenacity, and the steel may be worked readily into the desired form. Cast-iron, bismuth, and antimony are substances, the extensibility of which is almost *nil*, so that they cannot be sensibly altered in shape by mechanical means, but must be cast when fluid into moulds of the form required. Copper, on the other hand, has a fairly high tenacity and extensibility combined with a very low elastic limit, and it may be readily and safely hammered into the most elaborate shapes ; but the finished material is easily indented or bent by a comparatively light blow.

The working properties of metals, however, are more dependent on the power of resisting crushing than on tenacity. Although the determination of tensile strength is the most usual, as well as the most generally useful, of the tests that are made with the mechanical testing machines that are now indispensable in large iron or steel works, crushing or *compression* tests have often to be applied. Bending, or *transverse*, tests (made by bending a long bar around a central support) afford very valuable information, because the resistance of a bar to a transverse load depends partly upon its crushing strength and partly upon its tenacity, for the material is subjected to compression on the inner, and to extension on the outer side of the bend. Resistance to *torsion* or twisting is also occasionally determined by direct experiment.

In all these tests the load should be applied very gradually and steadily, any irregularity or intermittency altering the character of the test. But the power of resisting a dead load gives no certain clue to the behaviour of a material under shock, which depends upon brittleness. For railway rails or other materials that are liable to be subjected to heavy blows or to suddenly applied loads, the transverse resistance to a falling weight released from various heights above the centre of the bar, which is supported only at the ends, is found by means of a special form of testing machine. The resistance of a metal to impact is frequently termed its *resilience*.

The actual tenacity in tons per square inch of certain metals in the pure state is given in the following table. It will be seen that whilst a piece of sheet lead 1 sq. in. in section will break under a pull of 1½ ton, a similar rod of aluminium would require 11 tons, and one of iron 22 tons.

	Cast.	*Sheet.*	*Wire.*
Iron[1]	8	22	40
Copper	9	15	28
Aluminium	7	11	14
Zinc	3	7·5	10
Tin	2·5	—	3
Bismuth	1·5	—	—
Lead	0·8	1·5	1·2

The numbers given in tables of this kind must not be regarded as constants. The strength of metals is very greatly affected by variations in their structure, purity, and temperature. A cast metal is usually weaker than the same metal after it has been hammered or cold-rolled, all mechanical work in the cold tending to harden the metal, whilst it raises the tenacity and to an even greater extent the elastic limit, and at the same time diminishes the extensibility. It is often possible in this way to raise the elastic limit to the breaking load. As a metal is hammered, therefore, it becomes less and less easy to work, and at last it may be impossible to alter its shape still further without cracking it. Fortunately, the original softness may generally be almost entirely restored by heating the material to a temperature which must be suited to the metal under treatment, and allowing it to cool slowly. This process of *annealing* is resorted to at intervals during the cold rolling,

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[1] Cast-iron is not comparable with other cast metals, as it invariably contains carbon and other impurities.

drawing, or hammering of metals, as soon as the material gives indications of becoming dangerously hard. The internal strains in the metal are relieved at the higher temperature, and the structure is altered. The application of too high a temperature so far changes the character of the metal that it becomes weak and is said to be *burnt*; this effect of over-heating is especially noticeable in high carbon steel.

The effect of heat upon a metal is usually to lower its tenacity temporarily, but in a few instances a slight rise in temperature is accompanied by an increase in strength. Iron, for example, is strongest at a temperature of about 300° C. At temperatures below the freezing-point of water many metals are much stronger, but are frequently more susceptible to the influence of shock. The influence of the presence of foreign substances in metals upon their tenacity is very variable; the enormous increase in tenacity produced by combining a small percentage of carbon with iron is well known, and may be contrasted with the relatively greater reduction in strength caused by a trace of bismuth in gold. The presence of impurities or of alloyed metals usually tends to increase both the brittleness of metallic substances, and the *hardness*, or power of resisting the intrusive or abrasive action of other substances pressed into contact with them.

Metals which are brittle, so that they cannot be worked when cold, are said to be *cold-short*; whilst those which are unworkable at a red heat are described as *red-short*; the terms being corruptions of the older expressions *cold-* and *red-sear*.[1] Usually, malleable metals are most easily worked at some special temperature, and it does not necessarily follow that a metal non-forgeable in the cold is also red-short, nor on the contrary that one which is brittle when hot is also incapable of being treated mechanically when cold. Zinc, for example, which cannot be hammered or rolled without

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[1] *Sear* appears to be derived from the Anglo-Saxon *Searian* = dry.

breaking in the cold or near its melting-point, is quite easily worked at about 110° C.

Malleability.—The facility with which a mass of metal can be hammered or rolled into a thin sheet without being torn, must depend partly upon its softness, and partly upon its tenacity. If it depended upon softness alone, lead should be the most malleable of ordinary metals; but, although it is easy to hammer a mass of lead into a flat plate, or to squeeze it between rolls, any attempt to reduce it to an extremely thin sheet fails from its want of tenacity, which causes it to be worn into holes by percussion or friction. On the other hand, if malleability were entirely regulated by tenacity, iron would occupy the first place, whereas, on account of its hardness, it is the least malleable of metals in ordinary use; whilst gold, occupying an intermediate position with respect to tenacity, is one of the most malleable, which appears surprising to those who are only acquainted with gold in its ordinary forms of coin and jewellery, in which it is hardened and rendered much less malleable by the presence of copper and silver.

During the rolling or *lamination* of metals their particles flow over one another in a manner suggestive of the behaviour of liquids. In a homogeneous metal the flow should be uniform in all parts, so that the particles on the exterior should remain there during the operation of rolling or drawing.

In the following table the ordinary metals are arranged in the order of malleability :—

Table of Malleability.

1. Gold.
2. Silver.
3. Copper.
4. Tin.
5. Platinum.
6. Lead.
7. Zinc.
8. Iron.
9. Nickel.

Ductility.—The ease with which a metal can be elongated into a wire, by being drawn through the gradually diminishing holes of the wire-drawer's plate, will be greater in proportion to the softness of the metal; but the thinness of the wire to which it can be reduced is regulated by the tenacity of the metal, which enables it to resist, without breaking, the force required to draw it through the holes. And it is found that their tenacity has more influence upon the ductility of metals than upon their malleability, for the particles of a weak metal, like tin, may cohere under the hammer, although they would be easily torn apart by the direct pull necessary in wire-drawing. The increase in tenacity induced in passing the metal through the draw-plate enables the thicker undrawn portion to be passed through the draw-plate without fracture. Before repassing the wire through the draw-plate it may have to be annealed to remove the hardening effect of the previous drawing.

Gold, silver, and platinum, which occupy an intermediate position with respect to tenacity, are the most ductile of the metals, whilst tin and lead, which are lowest in tenacity, are the least ductile, though their softness gives them a higher place in the order of malleability.

Table of Ductility.

1. Gold.
2. Silver.
3. Platinum.
4. Iron.
5. Nickel.
6. Copper.
7. Palladium.
8. Aluminium.
9. Zinc.
10. Tin.
11. Lead.

Specific Gravity.—The relative weights of equal bulks of the metals exercise considerable influence upon their useful applications. The relative weight of gold being very high, it is well adapted for a circulating medium, a large value being compressed into a portable form. On the other hand, iron would be employed with far less advantage in building if its relative weight did not happen to be low, whilst aluminium, being the lightest of metals in ordinary use, is particularly well adapted for the production of small weights, such as fractions of a grain, enabling them to be large enough to handle; such weights being nearly nine times larger when made of aluminium than they were when platinum was employed. Aluminium, owing to its considerable strength combined with lightness, is, even at its present price, coming into use for many purposes.

The *specific gravities*, or comparative weights of equal bulks of the metals, are generally expressed by numbers which show that each metal is so many times as heavy as an equal bulk of pure distilled water ; thus, zinc is a little more than seven times as heavy as an equal bulk of water, so that its specific gravity is expressed by 7 and a fraction.

The first column of numbers in the following table gives the specific gravities of the metals in round numbers, which can be easily retained in the memory, and are sufficiently exact for ordinary purposes, the more accurate numbers usually employed in scientific works being given in the next column :—

Table of Specific Gravities of the Metals.

Platinum	$21\frac{1}{2}$	21·50	Copper	$8\frac{4}{5}$	8·82
Gold	$19\frac{1}{3}$	19·32	Cadmium	$8\frac{2}{3}$	8·60
Mercury	$13\frac{3}{5}$	13·59	Iron	$7\frac{4}{5}$	7·86
Palladium	$11\frac{1}{5}$	11·20	Tin	$7\frac{1}{3}$	7·29
Lead	$11\frac{1}{3}$	11·37	Zinc	$7\frac{1}{7}$	7·15
Silver	$10\frac{1}{2}$	10·53	Antimony	$6\frac{2}{3}$	6·71
Bismuth	$9\frac{4}{5}$	9·80	Aluminium	$2\frac{1}{2}$	2·56
Nickel	$8\frac{4}{5}$	8·90	Magnesium	$1\frac{3}{4}$	1·74

Conducting Power of Metals for Heat.—The sensation of cold when the hand is placed upon a piece of metal at the ordinary temperature of the air shows us that metals are better conductors of heat than non-metallic bodies, for the particles of metal rapidly transmit the heat away from the hand to adjacent portions. In consequence of the rapidity with which heat applied to one portion of a mass of metal is communicated to the whole of the particles composing it, metals may be suddenly heated or cooled with much less risk of causing them to crack or *fly* than is the case with non-metallic substances. When a glass bottle is placed upon the fire, the outside immediately becomes much hotter than the inside, and being expanded by the heat, tears apart the particles of the inside of the vessel and produces a crack, but in the case of a metallic vessel the heat is rapidly transmitted, and all parts of the vessel are expanded almost simultaneously. The much greater rapidity with which water can be heated in metallic vessels is another useful result of the superior conducting power of the metals.

In the following table the metals are arranged in the order of their conducting power, the first being the best conductor :—

Table of Conducting Power for Heat.

Silver	= 1000	Tin	= 152
Copper	= 736	Iron	= 119
Gold	= 532	Lead	= 85
Magnesium	= 343	Platinum	= 84
Aluminium	= 313	Antimony	= 40
Zinc	= 281	Bismuth	= 18
Cadmium	= 201	Mercury	= 13

Conducting Power of Metals for Electricity.—The conducting power for electricity, of metals, refers to the facility with which an electric disturbance excited in one portion of a mass of metal is transmitted to the other particles composing the mass. In electrical language the *resistance* of a metal to the flow of a current, is more often spoken of than the conductance, the latter property varying inversely as the resistance.

Only one non-metallic substance—carbon, in some of its varieties—at all approaches to the metals in the power of conducting electricity.

Those metals which are the best conductors of heat are also the best conductors of electricity, and in both cases the conducting power is seriously impaired by the presence in the metal even of small quantities of other metals, or of non-metallic bodies, as well as by an increase of temperature in the metal. When heated to the boiling-point of water, the metals have only about three-fourths of the conducting power which they exhibit at the freezing-point. But when cooled below zero, the conductance of the pure metals increases in such a ratio as to lead to the inference that, if they were cooled to the absolute zero of temperature (—273° C.), all alike would be perfect conductors, and would therefore present no resistance to the flow of the electric current. This, however, is not true for alloys.

The following table shows the relative conducting power of the most important metals, in a pure state, at 0° C., the conducting power of silver, which is higher than that of any other metal, being taken as 1000 :—

Table of Conducting Power for Electricity.

Silver	= 1000
Copper	= 999
Gold	= 806
Aluminium	= 551
Zinc	= 302
Platinum	= 167
Palladium	= 164
Iron	= 164
Tin	= 152
Lead	= 88
Nickel	= 79
Antimony	= 42
Mercury	= 25
Bismuth	= 12

Fusibility.—Although the property of becoming liquid at high temperatures is not confined to the metals, it must be mentioned among the properties which conduce to their utility, for it enables the founder to produce a large number of objects of a given pattern with little expenditure of time and labour, and offers to the worker in metals a ready method of soldering together, in a durable manner, the separate pieces of his work. Tin and lead, being the most fusible of ordinary metals, are the constituents of soft solder, whilst iron (malleable iron), as the least fusible of the common metals, is used for fire-bars, melting-pots, and similar purposes.

Table of Fusibility.

Tin	melts at	232° C.
Bismuth	,,	266
Cadmium	,,	321
Lead	,,	327
Zinc	,,	417
Antimony	,,	425
Aluminium	,,	625
Magnesium	,,	750
Silver	melts at	950° C.
Gold	,,	1045
Copper	,,	1050
Nickel	,,	1450
Palladium	,,	1500
Pure Iron	,,	1600
Platinum	,,	1775
Iridium	,,	2500

Structure.—The fractured surface of a bar of metal is usually an index of its character. It is best obtained by nicking the bar on one side with a chisel, gripping it in a vice, and breaking it by means of a hammer. In this way both the brittleness or the toughness, and the stiffness and general strength are shown by the angle through which it bends, and the force required to break it. When broken, any great want of homogeneity is at once shown by the irregular appearance of the fracture. The bar is said to be *crystalline* when it is made up of visible crystals, either coarse or fine. When the crystals are so fine as to be unrecognisable as such to the eye, the fracture is termed *granular* ; occasionally the grains are so minute that they present merely a silk-like sheen, such as may be seen in properly hardened tool steel, which is said to have a silky fracture. Wrought-iron, which has been rolled at a red heat from a spongy metal, saturated with plastic slag, consists of elongated masses of crystallised iron intermingled with long fibres of slag. Such a metal, when broken with a single very sharp blow of a hammer, shows a crystalline appearance, owing to the iron and cinder being broken off practically in the same plane ; but when it is fractured by a series of lighter blows, it breaks piecemeal owing to the imperfect adhesion between the numerous microscopic slag-fibres and the iron, and the immense difference in the toughness of the two materials. The fibre is thus commonly said to be developed (more correctly it is only made apparent), and the structure is termed *fibrous*. Usually, a coarsely crystalline or granular metal has less satisfactory working properties than one of the same class in which the fracture is finer ; and a fibrous material is likely to be tough, because the presence of the fibre is itself an indication that the metal was malleable enough to be rolled, at least at a red heat. It should be noted in passing that the size of the grain is often largely dependent upon the temperature at which a metal was cast, and upon the subsequent mechanical and thermal treatment that it has received. A metal which has been poured into a mould at a temperature far above its melting-point is generally coarser than one poured at a lower temperature, whilst the rapid cooling ensured by *casting in chill* (that is, in a metallic mould which conducts the heat away from the casting very rapidly) produces a particularly fine grain. Hammering tends to give a fine grain, and over-heating the metal renders it coarser. Very brittle hard metals often break with a glass-like lustrous or curved fracture that may be termed *vitreous* or *conchoidal*. The appearance of the larger facets of crystals in a fresh fracture often indicates the presence of impurities by the diminished lustre of the broken surface.

Metallography.—Formerly, practical men were content to examine the fractured portions of bars. In later years, however, metallurgists have applied the microscope to the examination of surfaces of metals, which have been highly polished and subsequently etched lightly with some suitable acid that will attack one constituent more readily than the others. This new branch of science, now known as *metallography*, has shown that materials, formerly believed to be homogeneous, are in reality most complex structures. The irregularities which are thus revealed in alloys, and in iron or steel, often account for the behaviour of the metals in practical use. This method has been most successfully applied as an adjunct to chemical analysis in the study of iron and steel. Analysis shows the ultimate chemical composition, but often fails to explain striking differences observable in the properties of two metals of identical composition. Here the microscope reveals the difference in structure, and very frequently detects the cause, which may usually be ascribed to special conditions in the mechanical or thermal treatment of the metals.

The series of figures shown on page 123 affords some idea of the varieties of structure shown by metals when polished surfaces are etched and magnified comparatively slightly to about thirty diameters. A magnification of over

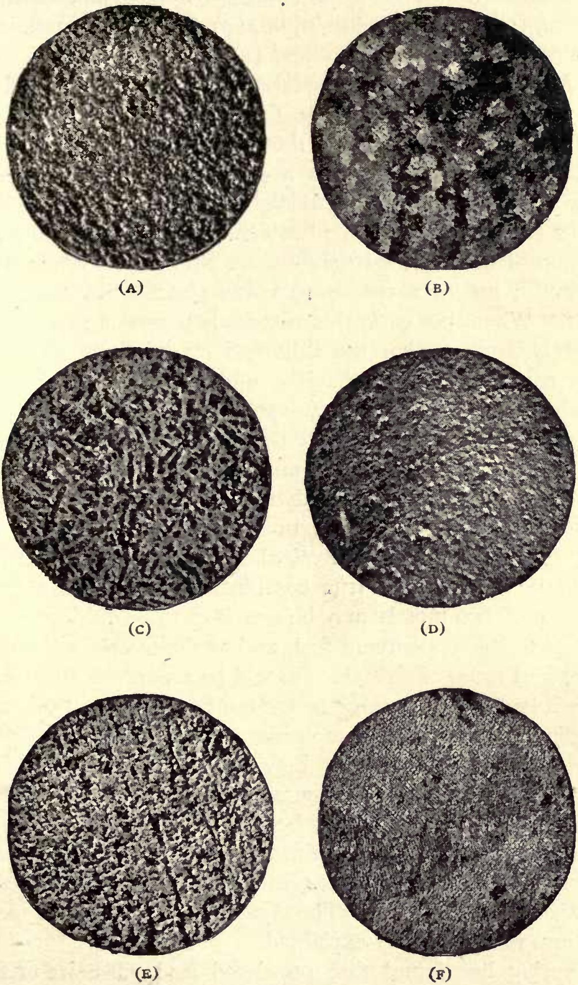

FIG. 20.

800 diameters is frequently employed in practice. Fig. 20 (A) is taken from a bar of mild steel, (B) from cast manganese bronze, (C) from cast aluminium, (D) from cast aluminium bronze, (E) from gun-metal, and (F) from cast brass.

Alloys.—Mixtures of metals are termed alloys. They are usually made by melting the metals together. A few metals refuse to unite under these circumstances, the heavier metal sinking to the bottom and carrying with it a small quantity of the other, whilst the lighter, floating above, retains also a small quantity of the heavier. Only a very small proportion of either zinc or aluminium will unite with lead or bismuth; but as a rule metals mix perfectly in the fluid state. When, however, the mixture is poured into a mould it rarely happens that the solidified mass is homogeneous. The reason of this is that the addition of one metal to another produces an alloy, the solidifying point of which is usually lower than it should be according to calculations based upon the proportions and fusing-points of the constituents. One particular mixture has a lower fusing-point than any other possible mixture of the metals employed, and this is termed the *eutectic* alloy of that series. Setting aside the possibility of true combinations of metals, a fluid mixture of two metals may be expected to begin depositing its less fusible constituent first, and as the temperature falls, more and more of this element will be separated, the other constituents concentrating in the fluid residue until this has acquired the eutectic composition, when it will solidify as a whole in the spaces left between the already solidified particles. Under these circumstances it will be seen that few mixtures of metals can be really homogeneous, or can solidify or fuse at an uniform temperature. The more slowly the material solidifies, the more marked will be the separation that occurs. The *liquation* that occurs in large castings is thus readily explained.

Spring has found that powdered lead will unite under a pressure of 13 tons per square inch, tin at 19 tons, and many other metals under 30 to 38 tons per square inch, the resulting materials having properties comparable with those of the corresponding fused substances. Alloys have also been made by uniting in this way the mixed powders of different metals, but no practical application of such a process has been devised.

The effect of alloying metals is to alter their physical properties very markedly; the fusing-point and electrical conductivity are generally reduced to below those of the means of the constituents, and the hardness and brittleness, and in some cases the strength also, are increased. In a few instances alloys have special characteristics which mark them out as true chemical compounds; but in the majority of cases the balance of evidence is in favour of their being mere mechanical mixtures.

When mercury is one of the components of an alloy, the mixture is termed an *amalgam*.

PRELIMINARY TREATMENT OF ORES.

With the progress of metallurgy ores, which either are more complex in character or contain a smaller proportion of metal than those previously treated, have to be dealt with. To accomplish this, some mechanical or chemical preparation of the ore is often necessary, such as crushing, dressing, and roasting. As these processes, in one form or other, are applied to a large number of different materials, it will be convenient to give here a general summary of the principles upon which they depend.

Crushing of Ores.—For many metallurgical processes it is necessary that the ore should be crushed to a fine and more or less uniform powder. Large lumps are therefore broken down either by hand or by a rock-crusher to about the size of a walnut, and are then passed on to a second machine, capable of reducing the material to the degree of fineness ultimately required. For the preliminary treatment, machines of the type of Blake's stone-breaker are largely employed ; in these the rock is fed into a wedge-shaped space between two very hard corrugated surfaces, one of which is fixed, whilst the other is suspended from a pin in such a way that, by means of a crank and levers, it may be alternately withdrawn a short distance from the fixed jaw and then caused to approach it more closely and with great force. During this approach the fragments of rock between the two surfaces are reduced in size, and as the space is gradually contracted, the larger lumps become broken up at the top into smaller pieces, which can then pass into a lower part of the machine and become still further crushed, until they are, at last, small enough to fall through the narrow opening that is left between the jaws at the bottom. The width of space thus left is regulated to the size of fragment required. In another machine the rotation of an eccentric cone within a fixed cup, both with hard faces, provides the necessary combination of crushing movement and alteration in space.

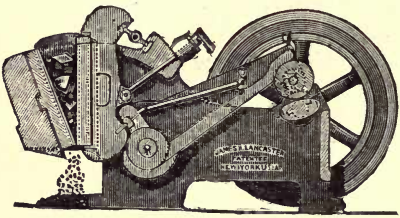

FIG. 21.—Blake's Rock-Breaker.

For the final reduction to powder, either wet- or dry-crushing machinery is employed. Among wet-crushers, *stamps* (fig. 22) are those most commonly used. They are practically a series of pestles and mortars actuated by machinery. Usually five stamps are placed in one box. The stamp itself is a wrought-iron rod, which may be 10 or 15 ft. long and 2 or 3 in. in diameter, set between guides, so that it is capable of vertical motion ; at the bottom of this stem is a tough cast-iron head 8 to 12 in. in diameter, and 15 to 20 in. long, with a movable steel or hard cast-iron shoe of the same diameter as the head, but about half the length. This shoe bears the brunt of the work, and, as it is worn out within a few weeks, must be made both very hard and readily replaceable. Near the top of the stem a cast-iron projecting block (*tappet*) is fastened; and engaging with this is a cam attached to a horizontal shaft driven by machinery. As the shaft revolves the cam is brought into action, and, lifting the stamp slowly to a height of from 6 to 12 in., releases it so that it falls suddenly by its own weight. All the stamps in the box are actuated by the same shaft, but the cams are so placed that the stamps fall consecutively, no two coming into action simultaneously. A hard replaceable block is placed beneath each stamp, to take the blow, and these five

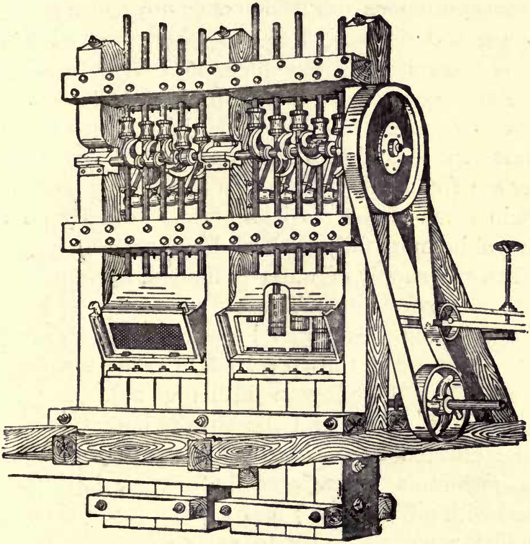

FIG. 22.—A Battery of Stamps.

blocks (or *dies*) form part of the mortar-box, which is made of cast-iron and has an opening on each long side. Into one of these openings the coarse-crushed ore is fed, together with a stream of water, whilst the other is closed with wire-mesh or a perforated plate. The stream of water constantly passing through the box carries the ore under the falling stamps, and then sweeps away with it all the particles of ore that are sufficiently fine to be passed through the perforations of the mesh or plate. The action of the stamps is therefore continuous, ore being constantly fed in at one side in lumps, and discharged at the other, crushed to a size which is controlled by the grade of the mesh employed. Each stamp commonly weighs from 4 to 8 cwt., and is raised and dropped from 40 to 60 times in a minute. In the treatment of gold ores one or two plates of amalgamated copper are frequently fixed within the mortar-box in order to retain some of the particles of free gold by an action which will be more fully explained hereafter.

When the supply of water is limited, dry-crushing may have to be resorted to. The ore may be passed between rotating crushing rolls placed horizontally, or into the track of heavy suspended rolls revolved in contact with a hard ring, as in the Huntington Mill (fig. 23). Coming between the hard rollers and the equally hard track, the ore may be crushed to an impalpable powder. Usually the whole apparatus is enclosed in a case, having outlets covered with a fine mesh; and an automatic arrangement is applied when necessary, to ensure that the material is re-crushed, until it is fine enough to escape through the perforations.

Concentration of Ores.—The process by which the heavy and valuable minerals are mechanically separated from the lighter gangue-stuff is known as concentration, and a detailed account of the various processes employed belongs rather to the sphere of mining than to that of metallurgy. Concentration is best effected by the agency of water, and when the particles of ore are as nearly as possible of equal size. Advantage is taken of the differences in specific gravity of the minerals to be separated. When a mixture of heavy and light particles of equal size is stirred up in water and allowed to settle, the former naturally tend to sink first and to concentrate at the bottom of the vessel. This principle was adopted in the *Tossing-tub*. Again, if such a mixture be conveyed by a stream of water, and the course of the stream be slightly checked, the heaviest particles will subside first. By passing the stream through a series of receptacles, the particles may be graduated according to their specific gravity, the heaviest settling nearest to the inflow, whilst the light gangue-stuff may even be carried away as *tailings* from the last tank, practically free from valuable metalliferous particles, though, unfortunately, this is not always the case owing to the ore having become in part too finely subdivided, forming *slimes* requiring a special treatment, that is not always so successful as would be desired. The *spitz-kasten* and *spitz-lute*, the *rack*, and various forms of *jigger* are adaptations of this system. By allowing a gentle stream of water to flow over fine ore,

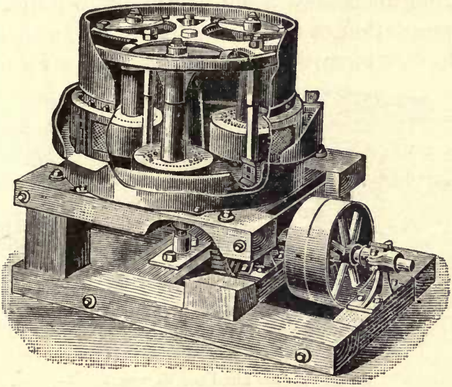

FIG. 23.—The Huntington Mill.

tailings or slimes, spread out upon a slightly sloping surface, and kept slightly revolving, the light particles may be swept away, leaving the heavier portion almost in its original position. This principle is employed in the construction of the *buddle*, which usually consists of a circular table sloping from the centre, at which point the ore and water are delivered on to it and gently stirred by means of radial revolving arms carrying brushes.

Of late, some of the best work has been done by a mechanical *vanner*. The mixture of fine ore and water flowing from the stamps is allowed partly to settle, so that a suitable proportion of water may be present, and it is then allowed to flow upon the upper portion of the vanner. The *Frue vanner* (fig. 24) consists of an endless rubber-belt, 3 or 4 ft. wide, strained over rollers placed at either end. The rollers are so placed that the top surface of the belt is slightly higher at one end than at the other, and they impart a slow *upward*-travelling motion to it. The pulp is fed on to this belt near to the top end, and the lighter particles carried by the water flow continuously down the slope. Meanwhile the heavier particles, which settle immediately, are carried upwards by the belt, and, after meeting with a gentle stream of water at the extreme top (sufficient to carry off any traces of gangue), pass over the end roller and are readily removed from the under side by passing the belt

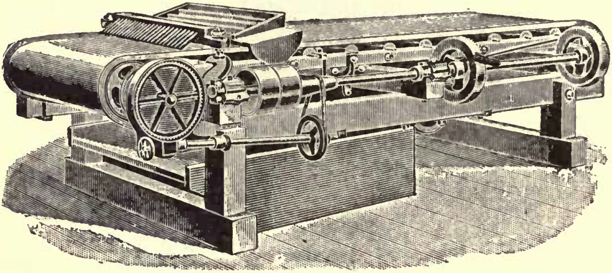

FIG. 24.—The Frue Vanner.

through a tank of water. The separation on the belt is greatly assisted by a sharp lateral oscillating movement mechanically imparted to it. The tailings flow away from the lower end of the apparatus, after having had time to deposit on the belt any heavy particles mechanically caught in them, and these are carried upward by the motion of the belt. In the Embrey concentrator the same principle of a belt and a stream of pulp travelling in opposite directions is used, but the oscillations are longitudinal instead of transverse.

Roasting of Ores.—In many metallurgical processes, the ores are either calcined to expel carbonic acid or water, or they are roasted in the presence of an excess of air to remove sulphur or arsenic as gaseous or volatile compounds by combination with oxygen. The former process will be sufficiently described in treating of the smelting of iron ; the latter, which is applicable to the sulphides of iron, lead, copper, zinc and silver, may be more conveniently dealt with at this point. The temperature must be regulated according to the metals present and to the compounds that are to be formed. In some instances a *dead-roast* is desired, in which all the sulphur is removed, in others it may be necessary to remove only a portion of the sulphur, whilst in others the conversion of one or more of the sulphides into sulphates, soluble in water, may be aimed at.

It has already been shown that iron pyrites is dissociated on heating, yielding part of its sulphur by distillation. In the presence of air, and at a very low red heat, a part of the remaining sulphur combines with oxygen, and forms sulphur dioxide, which passes off as a gas, the iron previously united with the sulphur combining at the same time with oxygen to form peroxide of iron. The remaining portion of the sulphide of iron is converted into sulphate. At the same temperature copper pyrites for the most part becomes copper sulphate by absorption of oxygen. The result, therefore, of roasting a sulphide ore at a low temperature is that a very large proportion of the metals present may be converted into sulphates which are soluble in water. At a slightly higher temperature sulphate of iron decomposes, the sulphur passing off as sulphurous acid, together with a portion of the oxygen, the iron being left as peroxide ; but the other sulphates may remain unaltered. By roasting a mixed ore, therefore, at this temperature practically the whole of the copper may be obtained in a soluble condition, and thus, by mere treatment with water, may be separated from the iron, which remains as insoluble peroxide. But if the ore become a little overheated, the copper sulphate itself will be more or less completely broken up, and will leave the copper in the form of insoluble oxide. At a slightly higher temperature zinc sulphate is also largely decomposed, while silver and lead sulphates remain unchanged. At a full red heat silver sulphate yields silver oxide, which at once splits up into metallic silver and free oxygen. Lead sulphate requires a white heat to convert it into oxide. Although at low temperatures silver sulphide undergoes dissociation, yet, when further heated in the presence of copper sulphate, it becomes converted into sulphate, which then behaves in the manner described above. By careful attention to detail, it is possible not only to obtain an 'oxidising' or a 'sulphating' roast at will, but to treat a complex ore in such a manner that a partial separation of the constituents with the aid of water may be possible. With some ores great attention is required in the earlier stages of the roasting operation to prevent clotting, due to the partial fusion of the particles. Occasionally lime or some other inert substance is mixed with the charge to prevent this. As the reactions become more advanced the temperature may be raised with less fear, inasmuch as the oxidised products are less fusible than the original sulphides. This clotting is especially marked in ores containing sulphide of antimony or of lead.

For the extraction of copper and silver, a 'chloridising' roast is frequently effected by mixing a small percentage of common salt (sodium chloride) with the ore before roasting. The sulphates formed in the usual way react with the salt, yielding sodium sulphate and the chlorides of copper and silver.

Arsenic usually becomes oxidised to arsenious oxide during the roasting, and as this oxide is very easily vaporised, it is carried off with the gases, and is recondensed into a white fume, when the temperature of the gases falls to about 200° C. If large quantities of arsenic be present, the gases on their way to the chimney are passed through a series of condensing chambers, in which the 'white arsenic' is deposited.

Calcining, or Roasting Furnaces.—In the case of poor ores, such as the nickel-copper ores of Sudbury in Canada and some of the Rio Tinto pyritous ores containing copper, the roasting is effected by stacking the lump ore in heaps, which may contain a thousand or more tons, with sufficient fuel to maintain the combustion. These heaps are commonly built over stone channels communicating with central chimneys, and are covered with fine ore to check the combustion, which is controlled by opening vents at suitable places, exactly as in the process of charcoal burning. For some purposes ores have been advantageously roasted in *stalls* instead of in heaps. The stalls consisted of spaces formed by building a series of dwarf brick partitions at right angles to a longer and (fig. 25) slightly higher wall; each stall had an opening at the back communicating with a flue in the rear wall. The ore and fuel were placed in the stall, and after ignition the front was usually temporarily built up

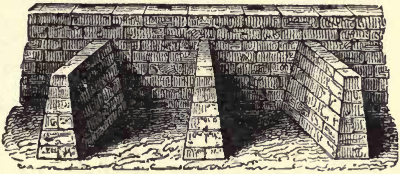

FIG. 25.—Roasting-stalls employed at Mansfeld.

with bricks. This arrangement was much less dependent upon the weather than was the heap; but except in a few isolated places both systems alike have had to be abandoned on account of the devastating action of the sulphurous products of combustion upon surrounding vegetation.

Furnaces or kilns are now substituted, which either discharge their gases at a great elevation, or deliver the sulphurous acid into a vitriol chamber, where it is converted into sulphuric acid. In the latter case the roasting is commonly conducted in such a way that when once started the action may be continued by the heat produced through the combustion of the sulphur itself, without necessitating the use of carbonaceous fuel, so that the gases are purer and more suitable for treatment. In this process, however, the temperature is less under control than when extra fuel is used, and for many metallurgical operations it is therefore preferable to allow the sulphur dioxide to escape. In all cases the ore is fine-crushed before treatment.

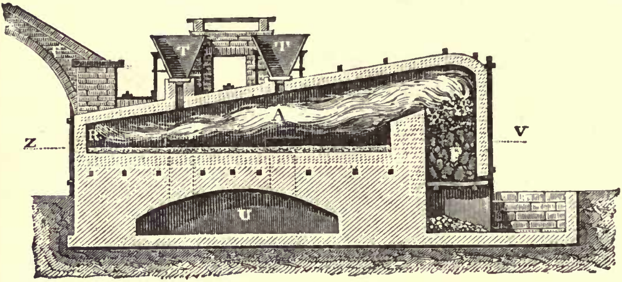

FIG. 26.—Furnace for roasting Copper Ores. Section through the line X Y of the plan (fig. 27).

Of the furnaces employed, the earliest was the simple reverberatory furnace, similar to that shown in figs. 26 and 27, which has long been used in the Welsh process of copper smelting. The ore is introduced through hoppers (T) and spread upon the hearth (A), where it is subjected to the action of the flame playing over it from the small fire grate

(F) on its way to the flues (R), which lead to the stack Coal is fed on to the grate, and the products of combustion and flame, passing over the 'fire-bridge' separating the grate from the hearth, mingle with an excess of air, which in the figure shown is admitted through the small opening *o*, and are deflected downward by the low arched roof. The charge is frequently turned over by means of tools introduced through the doors *p*; and when sufficiently roasted, it is raked through the openings (*r*) in the floor into a vault beneath. The hearth is then ready for another charge. The reverberatory furnace has been modified in many ways. For the dead-roasting of ores that tend to clot, it is sometimes built with from two to seven hearths, placed at different levels; the ore being charged upon the hearth nearest the chimney is partly roasted at a low temperature, and is then raked down to the next, and finally to that which is nearest to the hearth, and is therefore hottest. As soon as the ore has thus been drawn from one stage to the next the emptied hearth is replenished from the one above or, in the case of the uppermost stage, with fresh ore. In some instances these hearths

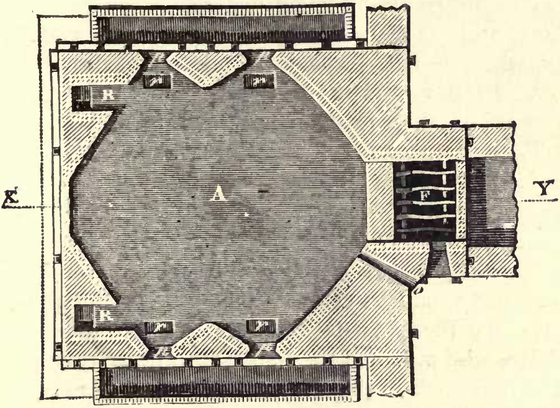

FIG. 27.—Furnace for roasting Copper Ores. Plan at the line z v of the section (fig. 26).

are built one above another, with the grate adjacent to the lowest stage; the air passing over each stage successively, beginning at the lowest. In this form, so little heat is lost by radiation that with ores containing much sulphur the action, when once started, is maintained by the heat of oxidation of the ore alone. No extra fuel being thus required, the sulphur dioxide produced by combustion is sufficiently pure to be utilised in vitriol chambers for the manufacture of sulphuric acid. The Spence kiln, which is of this type, has rakes automatically traversing each stage, turning over the ore, and gradually conveying it from one end to the other, where it falls through an opening on to the stage below. In the O'Hara furnace generally there are only two stages, but these may be nearly 90 ft. long, and the heat is supplied by fireplaces built at intervals along the sides; the ore is fed in through a hopper at one end, and is automatically moved by a series of ploughs over both stages, and is finally delivered completely roasted into a discharge chamber. The ploughs or rabbles are attached to triangular frames, which are fastened to endless chains actuated by machinery placed at one end of the furnace. This furnace was greatly improved by Allen, who mounted the frames on wheels running on a central iron track so that they were lifted off the bed of the furnace; the chains were similarly supported and thus kept above the ore. The ore is turned by the ploughs alternately towards the centre and the outside of the furnace. One of the latest developments of this furnace is that devised by Horace F. Brown (fig. 28) with the object of affording better protection to the mechanism. This is done by placing it in longitudinal chambers exterior to the hearth and separated from it by partition walls rising to about half-way to the roof. In furnaces working at a high temperature another partition constructed in fire-clay tiling inserted through the roof nearly meets the lower partition, leaving sufficient space for the arms carrying the stirrers to pass. The mechanism is similar to that used for cable tramways. The supports for

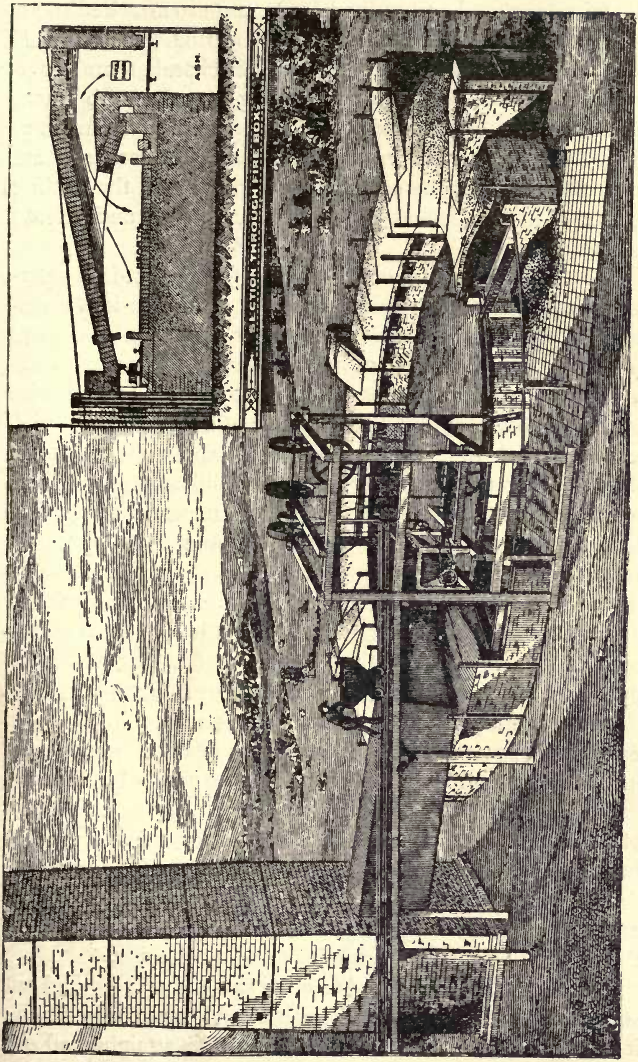

FIG. 28.—Brown Horseshoe Roasting Furnace.

the stirrers extend across the hearth, and are attached to an L-shaped frame with double-flanged bearing-wheels travelling on a T-rail in the inner annular chamber and to a broad flat-faced bearing-wheel rolling on a smooth track, usually made of vitrified bricks, in the outer chamber. When the furnace is in operation half the carriages are traversing it whilst the other half are resting in the cooling space. This is effected by an automatic grip and release arrangement.

The rabbles consist of steel arms having cast-iron wearing points. As they traverse the ore it is thrown into a succession of ridges and furrows. The wear of the cast-iron shoes is taken up by the arms covering them. The actual working bottom of the furnace is formed by placing about 2 in. of crushed oxide of iron, limestone, or other neutral material, on the brick bed. Should any accretions accidentally form they can be removed by lowering the rabbling points a little, so as to cut into the loose material, the necessity for barring being thus avoided. The ore is fed into the furnace by an automatic arrangement which delivers a weighed quantity at the passage of each stirrer. The ore is introduced in such a position that the dust settles before coming into contact with the draft of the furnace. After that the action of the stirrers is so steady and gentle that no dust is raised.

The heating is effected through openings in the roof communicating with the fire-boxes, the heat being gradually increased in the direction of the discharge end of the furnace.

Obviously this horseshoe shape for the furnace need not of necessity be adopted, though it has for many purposes been found to be very convenient. If desired, the furnace can be so arranged that the ore, for instance, after roasting and chloridising, may be passed over a cooling bed and thence into leaching vats by the same mechanism.

In the *Pearce Turret calciner* the same idea is worked out somewhat differently. The hearth is made annular in shape ; it is from 6 to 7 ft. wide, and if it could be straightened out would be nearly 90 ft. long; two fire-grates are provided on the outside of the circle, and the interior circular space, 20 ft. in diameter, is left open for the rotating mechanism, to which ploughs or rakes passing through a longitudinal slot in the inner annular wall are attached, and gradually convey the ore over the whole length of the furnace from the hopper, by which it is automatically charged upon the hearth, to the aperture by which the roasted material is discharged into a car placed ready to receive it. The rakes are attached to the ends of radial arms of stout gas barrel, and as the furnace is circular a continuous rotary motion suffices to give the required effect. These arms revolve at the rate of about three times to the minute, and being hollow, serve to convey an additional supply of air to the furnace, under slight pressure; and the air being discharged through small holes in the supports of the rake, serves to keep the latter from being overheated, whilst the air itself becomes warmed before admission. Valves are automatically closed and opened to prevent the passage of air when the rake is passing through the section of the furnace near the admission hopper. The air and burnt gases are caused to flow in a direction opposite to that in which the ore is travelling, and after traversing the hearth are led into an annular dust chamber beneath, before being discharged into the flue. The revolving arms pass through a continuous horizontal slot in the inner wall of the furnace, and the roof has therefore to be supported entirely from the outer wall. The slot is closed by an endless steel tape, which revolves with the rabble arms, whilst it is at the same time pressed throughout its length against the slot in order to prevent the access of cold air to the furnace, a possibility that is still further guarded against by the outward pressure produced by the air forced through the hollow arms of the rabble, and by a slight blast introduced under the grate. A double-decked turret-furnace has been tried with satisfactory results, especially in regard to economy of fuel. In the older *Brunton calciner*, which was largely used in roasting tin ore, the hearth was circular, instead of annular, and 8 or 10 ft. in diameter ; the ore was fed into the centre and was gradually spread over the hearth by rakes, and was at last discharged through an aperture at the circumference and under the chimney. But in this calciner the hearth itself slowly revolved, and the rakes were fixed in the roof. The hearth was of cast-iron, protected with fire-brick, and made three or four revolutions in the hour ; the heat was provided by two grates.

In another class of calciners, revolving cylinders are employed. These are worked either continuously or intermittently. The Oxland and Hocking calciner, which to a large extent replaced the Brunton calciner for use with tin ores, consisted of an iron cylinder about 40 ft. long, and 6 ft. in diameter, built so as to form a slightly sloping flue, connecting a fire-grate at the bottom with a condensing chamber for arsenic fumes at the top. The cylinder was lined with fire-brick built in longitudinal ridges from end to end, and was slowly rotated about its long axis. The ore was continuously introduced from a hopper at the upper end, and was caught in the ridges ; then, as the cylinder revolved, it was carried up the side by the ridges, until, being released, it fell back, and as the whole cylinder was inclined, the ore gradually gravitated to the lower end, being constantly raised and dropped through the ascending hot gases as it traversed the cylinder, until it was finally discharged dead-roasted into a vault placed quite close to the grate at the lower end. The *Brückner calciner* (fig. 29) is the best example of the intermittent type. It is a horizontally mounted iron drum, lined with brick, about 18 ft. long and 8 ft. in diameter. There is a grate at the end of the cylinder which is sometimes made movable by mounting it on a truck so that it can, if required, be used to start the calcination in a number of furnaces, being subsequently returned to complete the roasting when the greater part of the sulphur has burnt off. The drum is slowly rotated, and the gaseous products of combustion pass off by a flue at the end opposite to the grate.

Shaft furnaces are often employed, but are not usually

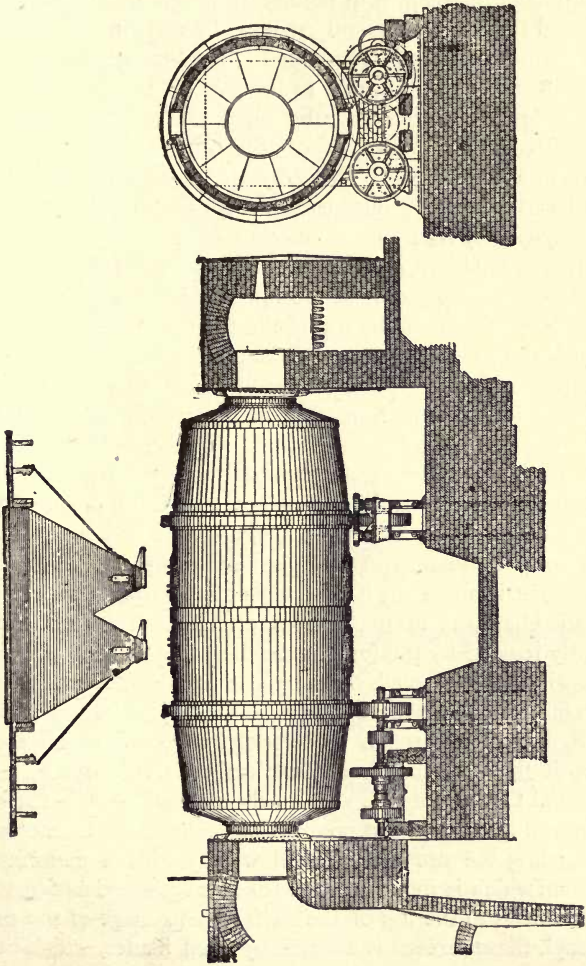

FIG. 29.—The Brückner Calciner.

to be recommended for dead-roasting. In the *Gerstenhöfer* type, the fine ore is introduced at the top of a vertical chamber, in which a number of narrow horizontal bricks continually intercept it in falling, its progress being so long delayed that it is sufficiently roasted by the time it reaches the bottom. A grate is provided at the bottom, but is only used in starting the furnace to bring it up to the temperature of ignition of the ore, after which the roasting proceeds unassisted. The products of combustion find an exit through a flue above. The *Hasenclever* kiln is somewhat similar in principle ; but instead of isolated bricks the ore falls by gravity from one to another of a series of sloping shelves stretching in a zigzag fashion across the shaft, leaving an aperture only at the lower side to allow the ore particles to fall upon the top of the shelf next below, and to permit the gases to pass upwards to the flue above. The ore may be finally discharged upon the hearth of a reverberatory furnace which may be made to complete the roasting at any required temperature. The *Stetefeldt furnace* (fig. 30) is especially suited to chloridising roasting, but has not been so successful in oxidising. In it the ore is auto matically sprinkled from the top of a shaft 25 to 50 ft. high, and 4 or 5 ft. square, and during its uninterrupted fall through this space, it meets the flame and hot gases from grates built in side chambers at the bottom of the shaft, and is sufficiently roasted by the time it reaches the bottom, whence it is withdrawn through a discharge door. The waste gases pass off through a down-comer connected with the top of the shaft, and then through settling chambers, in which they deposit the dust that is automatically carried over. It is essential that the ore be very finely crushed, and that it be delivered in the gentlest possible stream. This is effected by feeding the ore into a shallow tray with a perforated bottom, which is moved to and fro over a second perforated screen fixed to the top of the shaft ; the passage of the ore through these screens is assisted by fixed blades, which can be adjusted to any convenient height above the upper mesh so as to agitate the ore as the screen moves backwards and forwards. The top section of the shaft is commonly water-jacketed to prevent the overheating of the charging apparatus.

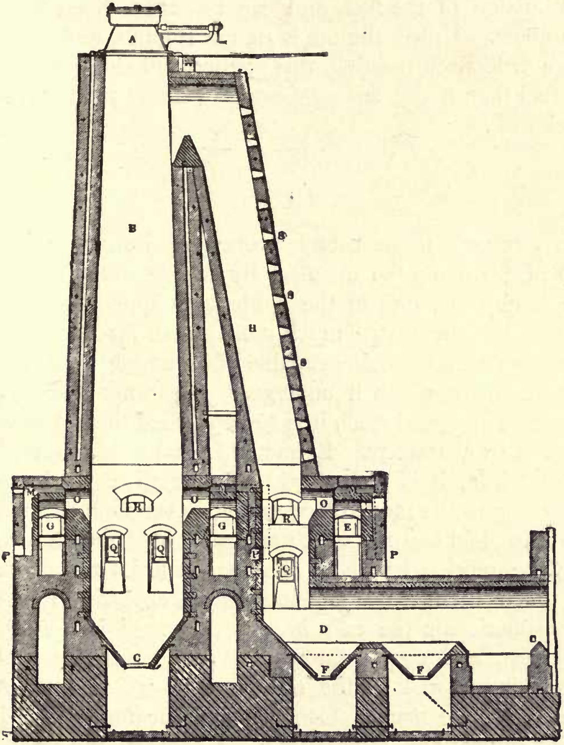

FIG. 30.—The Stetefeldt Furnace.

For some operations muffle furnaces are used. In general appearance they do not differ greatly from an ordinary reverberatory furnace, but there is no connection between the grate and the hearth, the products of combustion being made to pass between the walls of a double-arched roof, and then to circulate through a system of flues beneath the bed. In this way, for instance, the gases containing sulphurous acid resulting from the calcination of pyritous ores may be obtained free from the products of combustion of the fuel, and can be taken direct to vitriol chambers. Unless the ore is rich in sulphur, and therefore more or less self-roasting, this method will clearly cost more for fuel than if the ore were heated without the intervening brickwork.

IRON

With respect to its useful properties, iron occupies the first place among the metals. By far the strongest, and, at the same time, one of the lightest, its applications in the arts of construction are much more numerous than those of any other metal. Being capable of assuming, according to the treatment which it undergoes, the forms of malleable iron, cast iron, and steel, it is susceptible of the widest variations in its characters. Extracted from its ores in the form of cast iron, it is melted with comparative facility, and, according to the mode of operating in the foundry, may be made to yield castings which are easily filed and turned, or may be rendered so hard that only special tools are able to touch them. By judicious treatment with heat and atmospheric air the cast iron is converted into steel, the strongest, and one of the hardest and most elastic of all materials, as well as the only one of which a magnetic needle can be made. Continued a little further, the joint action of heat and atmospheric air converts the steel into malleable iron, possessing great strength and toughness, yet soft enough to be turned, bored, and punched with ease, and, especially when heated, to be easily wrought into the most varied forms without cracking. With less disposition to melt under the action of heat than any other common metal, wrought iron is sufficiently softened at a bright red heat to be *welded* or joined to another piece in the most perfect manner, without the use of solder of any kind. Being capable of acquiring and of losing the properties of a magnet with great rapidity, soft iron (malleable iron) is the only material which is adapted for the construction of certain parts of electro-magnetic and magneto-electric apparatus.

The main chemical difference between cast iron and malleable iron is that the former contains a considerable proportion of carbon and some silicon, the latter practically none. Steel occupies an intermediate position as regards carbon, but should be comparatively free from silicon.

Possessed of so many valuable qualities, iron is still the cheapest of all the metals, since the ores from which it is extracted are found in profusion through the crust of the earth, and can be made to yield the metal in abundance by a moderate expenditure of time, labour, and fuel.

Ores of Iron.—Iron in the metallic condition, or *native iron*, is only found in nature in small quantities disseminated in basalt and lavas, or in the form of *meteorites*. Occasionally metallic iron has resulted from a coal seam taking fire in contiguity with a seam of iron ore. When the native metal is of terrestrial origin, it is known as *telluric* iron ; but nearly all the specimens which have been examined have been *meteoric iron*, occurring in masses of irregular form, which have descended upon the surface of the earth ; but whence they are derived is at present only a matter for speculation. Such masses have been found containing 93 parts in the hundred of metallic iron, always associated with nickel, and sometimes with small quantities of other metals, and of phosphorus, sulphur, and carbon. They vary much in size ; a meteoric mass weighing 20 tons was found at Durango in Mexico. A small one, weighing about 190 lb., which was found at Lenarto in Hungary, was remarkably malleable, which is unusual for this material. It was found to consist of 90·88 of iron, 8·45 of nickel, 0·67 of cobalt, and 0·002 of copper per hundred. The presence of nickel is characteristic of meteoric iron.

An examination of the above specimen has led to the very interesting discovery that it contains about twice and a half its volume of hydrogen gas, apparently in an uncombined state.

Iron is most commonly found in a state of chemical combination with oxygen or sulphur, which disguise its metallic properties and convert it into earthy or stony masses. The compound of iron with oxygen, or *oxide of iron*, which is familiar to us in the form of *rust*, occurs in a very large number of mineral substances, and is often the cause of their colour. Sand, clay, and gravel, commonly owe their yellow, brown, or red colour to the presence of oxide of iron, a small proportion of which imparts a very distinct tint. No mineral substance, however, would be considered as an *ore* of iron which contained less than about twenty parts of iron in the hundred, for otherwise it would not repay the cost of its extraction.

The following table includes the mineral substances which are commonly regarded as ores of iron :—

	Composition		Iron in 100 parts of pure Ore
Magnetic Iron Ore	Iron, Oxygen	Fe_3O_4	72
Red Hæmatite	Iron, Oxygen	Fe_2O_3	70
Specular Ore	Iron, Oxygen		
Brown Hæmatite	Iron, Oxygen, Water	$2Fe_2O_3 . 3H_2O$	60
Spathic Iron Ore	Iron, Oxygen, Carbonic Acid	$FeCO_3$	48
Clay Iron Stone	Iron, Oxygen, Carbonic Acid, Clay		Variable, 17 to 50
Black-band Ore	Iron, Oxygen, Carbonic Acid, Clay, Bituminous matter		Variable, 21 to 43
Iron Pyrites[1]	Iron, Sulphur	FeS_2	46

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[1] Iron Pyrites is not worked as an ore of iron; but *Blue Billy* or *Purple Ore*, the oxide of iron produced by roasting pyrites in the extraction of copper from certain ores by the wet way, is utilised in various processes.

Magnetic Iron Ore, or *Magnetite*, derives its name from Magnesia in Asia Minor, where its power of attracting iron and steel was first observed. One variety of the ore constitutes the *loadstone*,[1] which is capable of rendering steel magnetic. This variety occurs chiefly in Siberia and the Hartz. Some of the common varieties of the ore do not attract iron, although they are capable, like steel, of becoming magnetic when brought into contact with powerful magnets.

This ore is generally met with in compact heavy masses of an iron-black or grey colour, and with considerable lustre. It frequently accompanies hæmatite ore. Its specific gravity varies from 4·9 to 5·2. It abounds chiefly in the northern parts of the globe, and is found in immense masses in Norway, Sweden, Russia, and North America. These ores are generally of excellent quality, but are occasionally deteriorated by sulphur and phosphorus, derived respectively from the iron pyrites and *apatite* (phosphate of lime), which are sometimes found associated with the magnetic ore. It has been found that by causing such ores in a state of fine powder to pass over magnets, with the aid of a suitable mechanical arrangement, the iron oxide may be separated almost completely from the apatite; and an ore that would otherwise be too impure to use may, after *magnetic concentration*, be smelted in any form of furnace that is capable of dealing with pulverulent material. The part that is not attracted by the magnet, and is therefore separated in the machine, may contain nearly the whole of the phosphoric acid. This process is largely used in America, where the ores are better adapted to its application than those in England. The bulk of the Swedish iron, so much valued for the manufacture of steel, is extracted

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[1] Probably corrupted from *lead-stone*, the stone which leads or guides, in allusion to its use for making the needle of the mariner's compass magnetic. In a similar way we have *load-star*, the star which leads towards the pole; *loadsman*, one who guides—a pilot; *load* or *lode*, the leading vein in a mine.

from the magnetic ore at Dannemora, where it is worked in an open quarry.

Magnetic iron ore often contains titanic acid, the oxide of the metal titanium, and this is especially the case with a variety of the ore, containing also non-magnetic titaniferous iron ore, which occurs as a heavy black shining sand in India, Nova Scotia, and New Zealand. This ore has been produced by the disintegration of crystalline rocks in which it had been disseminated in grains.

Red Hæmatite has been so called from the Greek word signifying *blood*, on account of its dark red colour.[1] In appearance it is the most striking of the ores of iron, sometimes appearing in rounded masses having externally a liver colour, with considerable lustre, and internally made up of layers having the appearance of the thick shell of some huge fruit, or of bundles of fibres, which look like petrified wood. The specific gravity of this variety is about 5·0. Such specimens are in general remarkably hard, and are useful for burnishing metals. But it is occasionally found in much softer earthy-looking masses of a brighter colour, and not uncommonly associated with clay.

Red hæmatite is much more generally diffused than magnetite, and is found in this country, at Whitehaven (Cumberland) and Ulverstone (Lancashire), as well as in Glamorganshire. The compact variety is exceedingly pure, and furnishes iron of the very best quality. For smelting purposes any ore consisting essentially of anhydrous peroxide of iron is termed red hæmatite. Large quantities of uncrystallised earthy hæmatite, very rich in iron, and practically free from sulphur and phosphorus, are now obtained from Spain and Algeria. Some of these ores are intermediate in composition between red and brown hæmatites, as they contain some water of hydration (chemically combined). Excellent red hæmatite is obtained in great

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[1] The termination *ite*, so generally found in the names of minerals, was originally derived from the Greek word for *stone*.

quantity in the neighbourhood of Lake Superior, whence it is taken a long distance, mainly by rail, to supply the furnaces at Pittsburgh and Chicago.

Specular Iron Ore is identical in composition with red hæmatite, though its appearance is so different, for it forms crystalline masses, and sometimes separate crystals of a steel grey colour and brilliant lustre, whence it derives its name (*speculum* [Latin], a mirror). It is also called *Iron-glance* (*Glanz* [German], lustre), and in one of its varieties, made up of shining scales, *Micaceous Iron Ore* (*micare* [Latin], to shine). When scratched with a knife, or reduced to powder, it exhibits the red colour of hæmatite. The specific gravity of specular iron ore is 5·2. The island of Elba has long been noted for specular iron ore, which is also found in considerable quantity in Russia and Spain. Very large deposits of magnetite and red hæmatite exist in the United States of America, Cuba, Brazil, Mexico, and elsewhere ; but they are either less pure than those just referred to, or are at present difficult of access. Enormous masses of exceptionally pure ore are found in Madras.

Brown Hæmatite contains the same oxide of iron as red hæmatite, but in a state of chemical combination with water, the latter varying from ten to fourteen parts in a hundred parts of the ore. Its appearance varies widely in different specimens. Sometimes it forms globular masses of considerable size, in other places it occurs in small round grains (*pea iron ore*) ; and occasionally it is found as stalactites ; the various soft earthy *ochres*[1] and *umbers*[2] consist, for the most part, of brown hæmatite, the dark brown shade, in the latter case, being caused by the presence of an oxide of manganese.

In this country brown hæmatite is found at Alston Moor (Cumberland) and in Durham, but it is a much more

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[1] Derived from the Greek for *sallow*, in allusion to their yellow colour.

[2] From *umbra* (Latin), shade, on account of their darker tint.

important iron ore in France and Spain. Some varieties of it contain a considerable proportion of phosphorus in the form of phosphoric acid combined with oxide of iron.

The *Black Brush Ore* of the Forest of Dean mines at one time used was a brown hæmatite containing 89 parts of peroxide of iron, and 10 parts of water.

Of the older brown hæmatites, those obtained from Spain are at present by far the most important. The principal Spanish ores are known as *Campanil*, a true red hæmatite, probably derived from spathic ore, *Vena Dulce*, containing some water of hydration, but less than *Rubio*, which is a true brown hæmatite (*limonite*). Brown hæmatites, sometimes more or less mixed with anhydrous peroxide, occur in the pisolitic and oolitic condition in considerable quantity in the tertiary and post-tertiary geological formations of France and Germany.

Aluminous Iron Ore is a brown iron ore of rare occurrence and considerable value, owing to its containing alumina largely in excess of the silica present, which enables it to be used as a flux for silicious ores. The most important localities in which it occurs are Antrim (Ireland), Beaux (France), and Wochein (Carniola).

The *Lake Ores* of Sweden consist of a variety of brown hæmatite ore which occurs at the bottom of lakes, and is collected by dredging with a kind of iron sieve attached to a long pole, and thrust down through a hole in the ice, the mud being washed away from the ore by shaking the sieve up and down under water. In this way a man will sometimes collect as much as a ton of ore in a day.

Spathic Iron Ore (*Spath* [German], spar), or *sparry iron ore*, is composed of carbonate of iron, or iron combined with oxygen and carbonic acid. Some specimens consist of a collection of nearly transparent shining crystals, which are almost colourless, and have the same crystalline form as calc spar (carbonate of lime). It is found in extensive beds in Styria and Carinthia. Spathic ore almost invariably contains manganese, which especially adapts it for the manufacture of certain kinds of steel, whence it has sometimes been termed *steel ore.* This ore is also found at Wearsdale in Durham, and on the Brendon Hills in Somersetshire ; but the deposits of the latter have been worked out.

Clay Iron Stone, *Argillaceous*[1] *Iron Ore* or *Clay-band.*—These ores are found mainly in the carboniferous series of rocks. They contain the iron in the same form of chemical combination (carbonate of iron) in which it exists in spathic iron ore, but in a state of intimate mixture with clay. This ore is by far the most important of British iron ores, being that which is most extensively mined in this country. It occurs in great abundance around Dudley, in Staffordshire, in Yorkshire, Derbyshire, and in South Wales. Both this ore and the black-band ore are found in layers which occur alternately with beds of coal, limestone, clay, and shale, whence they are often spoken of as the *Ironstones of the Coal Measures*, and the circumstance that the same pit, or neighbouring pits, will furnish the coal employed for smelting the ore, the limestone used as a *flux*, and even the clay for making fire-bricks for the furnace, allows English iron to be produced at a price with which, until lately, other countries found it impossible to compete. The coal formations of Belgium and Silesia also furnish large supplies of clay iron-stone.

This ore is found sometimes in continuous beds, and sometimes in irregular globular masses, imbedded in clay ; it is moderately hard and stony, and varies in colour, through different shades of grey, slaty-blue, and brown. It is lighter than the preceding ores, and a cursory observer might regard it as a stone rather than a metallic ore. The proportions of carbonate of iron and clay contained in the ore vary considerably, the former amounting to 80 or 90

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[1] *Argilla* (Latin), clay.

parts in the hundred in some specimens, and in others not exceeding half the weight of the ore.

Cleveland Ironstone.—This is an important ore, occurring in the Middle Lias, more particularly in the Cleveland district of the North Riding of Yorkshire. It is a carbonate, with a more or less bluish grey colour, due to a small quantity of ferrous silicate, and is oolitic in structure.

Black-band Ore differs from clay ironstone only by containing, in addition to its other constituents, a quantity of bituminous or coaly matter, sometimes amounting to one-fifth of the weight of the ore, and imparting the colour from which it derives its name. In Lanarkshire and Ayrshire, Scotland, the extensive deposits of black-band iron ore, first brought to light in 1801, have been to a great extent worked out. The presence of so much combustible matter enables the ore to be calcined without expenditure of fuel. Black-band ores are also mined in North Staffordshire.

The Northamptonshire iron ore, which is found in the *oolite* limestone in that county, appears to have been formed by the chemical alteration of clay ironstone, under the influence of air and water, for it contains carbonate of iron associated with clay, and with the red oxide of iron, which is formed by the action of air upon the carbonate. This ore contains much phosphoric acid.

Similar ores are worked in Lincolnshire, Leicestershire, and Rutland. On the continent, ores of like character occur largely, notably in Luxembourg and Lorraine, where the ore is known by the name of *Minette*, and in Bavaria and Wurtemburg.

Manganiferous Iron Ores.—These are of very great importance as accessories in the manufacture of all kinds of steel. They are either spathic ores containing carbonate of manganese, or brown iron ores (probably derived from spathic ores) containing pyrolusite (peroxide of manganese), or psilomelane. They are largely obtained from Carthagena (Portugal), Chili, the Caucasus, Nassau, and Carniola. A deposit of mixed carbonate and silicate of manganese with very little iron has also been worked in Carnarvonshire and Merionethshire.

Iron Pyrites[1] is composed of 46½ parts of iron in chemical combination with 53½ parts of sulphur, and is extensively used as a source of sulphur in the manufacture of sulphuric acid. Attempts have been made to extract iron from this mineral after the sulphur has been burnt off, and the iron is left in combination with oxygen from the air ; but its uses are limited owing to the fine state of division of the ore after calcination, and the expense of consolidating it by pressure. It is principally used in the puddling process.

EXTRACTION OF IRON FROM ITS ORES, IN THE FORM OF MALLEABLE IRON, STEEL, AND PIG OR CAST IRON

Although it is commonly conceded that bronze was in general use before iron, yet there is undisputed evidence to show that malleable iron was known and employed at least 2,000 years ago. Nothing can be simpler than the extraction of iron from rich ores. All that is necessary is to heat them to redness with carbonaceous matter, say charcoal, when the oxygen of the ore will combine with the carbonic oxide produced from the partial oxidation of the carbon, forming carbonic acid gas, which passes off into the atmosphere, and metallic iron, which is set free. However pure the ore may be, it will always contain some earthy matter, with which the iron, on being *reduced* from its ore, will be mixed. In order to separate the iron from the earthy matter the latter must be rendered fluid, so that the iron, by reason of its greater specific gravity, may sink through it and collect together. One of the principal constituents

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[1] The word *pyrites* is derived from the Greek for *fire*, probably in allusion to the circumstance that when this mineral is heated it gives off sulphur, which takes fire.

of the earthy matter is usually silica, and it so happens that protoxide of iron is the very substance which, more readily than any other available, forms a fluid compound with silica at a low temperature. The ores employed by all primitive workers were peroxides, or if a protoxide (carbonate) were used it was first calcined, which would have the effect of driving off the carbonic acid, and converting the protoxide into higher oxides by combination with a further quantity of oxygen. During the reduction of the ore by the carbonic oxide, the peroxide is first reduced to magnetic oxide, then to protoxide, and finally to metallic iron, thus:—

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2.$$
$$2Fe_3O_4 + 2CO = 6FeO + 2CO_2.$$
$$6FeO + 6CO = 3Fe_2 + 6CO_2.$$

Some of the protoxide produced in contact with the earthy matter combines with it, rendering it fluid, and forming slag. The result of heating an iron ore, consisting essentially of peroxide of iron, with carbon is, then, to produce a mass of malleable iron, semi-fluid, or pasty at the temperature of the furnace, and charged with more or less fluid slag or cinder. In order to remove the cinder and consolidate the iron, it only remains to subject the mass to sufficient pressure whilst still red-hot, when the slag will be squeezed out, and the metal, owing to the property of *welding*, which iron possesses in a high degree, will unite to form a solid mass, which can, subsequently, by reheating and hammering, be worked into any desired form.

Primitive Smelting Methods.—By such simple means as these iron has been made in India from time immemorial, and it continues to be so made both there and in Africa at the present day. The most primitive method of all is that practised by the Burmese. The furnace consists simply of a hole about 10 ft. deep, dug in a bank, at a distance of 2 or 3 ft. from its edge. The face of the bank is strengthened by pieces of wood placed crosswise ; the lower part of the bank is dug away, and a rectangular opening, about 1 ft. high and the whole breadth of the furnace, is made, through which the metal and slag are removed at the completion of the smelting operation. The opening at the base is closed with moist clay, through which are inserted about twenty small clay tubes, or *twyers.* These tubes are made by plastering moist clay over stems of wood, which are then cut into lengths of 4 in., and burnt. The twyers thus made are placed in the opening, in a single line, about half-way up. Lighted wood is then thrown into the furnace, and on it alternate layers of charcoal and ore, until the furnace is charged to the top. After the lapse of about eight hours the slag is removed, through an opening temporarily made for the purpose ; this operation is repeated every half-hour, until no more slag comes away. The smelting is complete in about twenty-four hours ; the weight of the iron produced averages about 90 lb.

In some parts of India an artificial blast is employed, produced by bellows made from goat-skins, or by means of some primitive form of blowing-cylinder ; the furnaces also show an advance in constructive power as compared with that just described, as they are built above ground. In Central India and the North-Western Provinces, *continuous working* is effected by removing the iron by means of tongs through the top of the furnace, the slag being run out, or *tapped*, through a small opening at the base. In this way, the furnace not being damaged by the withdrawal of the lump of iron, it can be re-charged again whilst still hot ; thus time, fuel, and labour are saved.

The Catalan Process.—In Spain a somewhat similar method of producing malleable iron direct from the ore has been in use, with but slight modification, since the earliest times of which we have any record.[1] This process is commonly known as the *Catalan*, owing to its having been

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[1] It was in use quite recently in one or two remote places.

principally practised in the provinces of Catalonia, where the magnetic ore and the hæmatite of the Pyrenees are smelted with the charcoal made in the neighbouring forests. The smelting works comprise a forge, a special form of blowing-machine, worked by the aspirating action of a stream of water and termed a *trompe*, and a hammer; but the first alone will be here described in order to illustrate this method of treating iron ores.

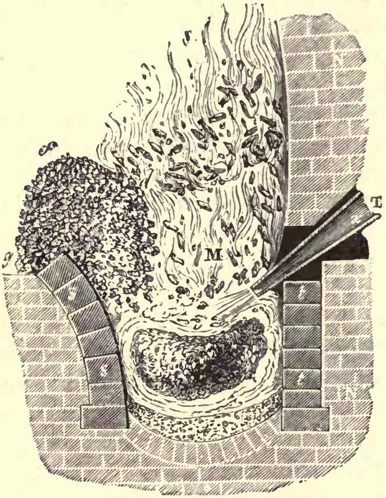

Fig. 31.—Catalan Forge.

The crucible or hearth is a nearly rectangular trough (M, fig. 31) well built around with masonry, about 17 in. deep, 21 in. long, and 18½ in. wide. The bottom of the crucible is composed of a block of granite, which is supported upon small arches to keep it dry.

That side of the hearth at which the blast from the twyer (T) enters is perpendicular, being built up of massive pieces of iron (*t*), the blast-pipe, or twyer, of copper, being supported upon the uppermost piece in such a manner that its inclination to the bottom of the crucible can be varied at pleasure, since this exercises much influence upon the success of the operation. The wall opposite to the blast is built up of wedge-shaped pieces of iron (*s*), and presents a curved surface. The working side of the hearth is composed of three thick pieces of iron placed end to end, the side opposite to it being lined with fire-clay, and having a moderate inclination.

Mode of Conducting the Process.—The ore is crushed by the hammer, and divided by sifting into lumps (*mine*) and very coarse powder (*greillade*). The furnace being still red-hot from the last operation, it is filled with charcoal nearly to the twyer; the hearth is then divided at about two-thirds of its length from the twyer into two parts by a broad shovel; on the blast side a further quantity of charcoal is added, whilst that on the other side having been rammed down firm, ore is added so as to fill that part of the furnace. On this is placed moistened charcoal dust, except at the highest point; a good blast is then turned on, and, if the whole is in good order, jets of blue flame at once issue from the uncovered portion of the ore. After a few minutes the pressure of the blast is lowered to 1·5 in. of mercury. At intervals during the process—which lasts about six hours—the blast is gradually raised until it reaches about 3 in. of mercury, the maximum usually employed.

During the whole of the process, at short intervals, *greillade* and charcoal are added, and well moistened with water to prevent too rapid combustion. After about two hours from the commencement the bottom portion of the wall of *mine* (*i.e.* ore in lumps) is pushed well forward under the twyer, and more *mine* from above is thrown into the space thus made. This part of the process is also subsequently repeated at intervals, until sufficient has been added to form a lump of iron, or *massé*, of the required size. From time to time slag is removed by opening the tap-hole. At the completion of the process a mass of metal is obtained weighing about 3 cwt., which invariably consists partly of soft iron and partly of *steely* iron and *steel*, *i.e.* iron containing more or less carbon, for the conditions in this furnace are very far from being uniform.

Reactions in the Furnace.—We have seen that in the one part of the furnace only charcoal and *greillade* are introduced, and in the other only lumps of ore. That the ore should be in lumps at that part is a very important point, for in this way the hot reducing gas, carbonic oxide (CO), generated by the action of the blast on the charcoal, is able to pass freely through the mass of the ore, the effect of which is that the water of hydration and the moisture are first driven out by the heat, and then, the ore having become easily permeable, the carbonic oxide reduces it to metallic iron by successive stages, as already described.

At the same time that these reactions are going on, the ore has become impregnated with carbon, derived from the decomposition of the gases, with which it is charged. That this would be the case, the experiments of Sir Lowthian Bell and others can leave no manner of doubt.

On the twyer side, where are placed the charcoal and *greillade*, the latter, as the charcoal is burnt away, descends rapidly, and to a considerable extent, doubtless, escapes reduction ; for the arrangement of the blast is such that most of the reducing gas is projected on to the lumps of ore, and does not pass up through that portion of the furnace occupied by the charcoal and *greillade*, which, besides, are constantly damped. The *greillade* is much richer in silica than the larger pieces, from which it results that the quantity of slag will vary with the *greillade* added, which is always very rich in oxide of iron.

What happens in this process appears to be this : carburised iron is produced by the reducing and carburising action of the carbonic oxide ; and this, coming in contact at the bottom of the furnace with slag, very rich in oxide of iron, the carbon of the one combines with the oxygen of the other, and the result is that iron containing more or less carbon is produced, according as little or much oxide is present.

The obvious conclusion would be, that the less there was of *greillade* present, the more steely would be the iron ; in practice this is found to be the case. This circumstance would naturally suggest the total suppression of the *greillade* when it was desired to produce steel. That would, however, be impracticable; for it is necessary that some of the oxide of iron should remain unreduced, in order to flux off the silica, which occurs in considerable quantity in the ore. In the modern blast-furnace this difficulty is got over by employing lime; but lime, at the temperature of the Catalan furnace, would not produce a sufficiently liquid slag.

Production of Steel by the Catalan Process.—All that can be done, then, when it is desired to produce steel, is to employ every available means to prevent decarburisation. In addition to using less *greillade*, the slag is tapped out more frequently, so that the lump of iron as it forms may remain as little time as possible in contact with it. The bank of ore is exposed for a longer time to the reducing and carburising gases, and is pushed more gently towards the twyer, so as not to become decarburised by the oxygen of the air, which has not had time to combine with the carbon of the charcoal. Lastly, manganese should be present. It is found that the presence of manganese has a very important influence, which is probably due to its power to replace iron in the slag. A slag in which some of the iron is replaced by an equivalent quantity of manganese is more liquid, and, according to François, has not the same tendency to cause decarburisation at the temperature of this process.

In order, then, that steel may be produced by this process, every precaution is taken to cause as much carburisation as possible, the unavoidable presence of oxide of iron in the slag effectually preventing the formation of cast iron, a more highly carburised metal than steel; the presence of oxide of iron, indeed, making it more difficult, as we have seen, to obtain steel; though the product of this furnace even when making malleable iron is certain to be steely in parts.

This process has been rather fully treated of, because the principle of it is not always well understood. Rightly looked at, it explains how steel was first obtained.

In the Indian furnaces steely iron and steel are also always produced in more or less quantity. In some districts the natives so well understand the necessary conditions that they can produce steel at will in their furnaces.

No matter whether it is the intention to produce malleable iron or steel, it is very difficult to obtain a homogeneous product from these furnaces. In practice the mass is broken up, and the pieces sorted according to their relative hardness and suitability for different purposes.

Wootz Steel.—The circumstance that when a high temperature existed in the furnace, because much charcoal was present, the iron obtained was more or less steely, we have seen, was taken advantage of in India to produce more or less steely iron, by regulating the conditions in the furnace. Once these facts had been grasped, it required no great powers of reasoning to suggest the production of steel by heating malleable iron in contact with carbonaceous matter. The steel produced in this way by the Hindoos is known as *wootz*; its manufacture dates from a very remote period, and is still carried on at the present day. They place in unbaked clay crucibles of the capacity of a pint, a piece of malleable iron, some chopped wood, and a few leaves of certain plants; the top of the crucible is then closed with clay, and the whole well dried near a fire. Several of these crucibles are then strongly heated for about four hours in a cavity in the ground, by means of charcoal, and a blast of air forced in by bellows. There is some reason to believe that an excess of carbon over that required to produce the hardest steel has to be added, in order to fuse the metal at the temperature which can be commanded in these furnaces. Before being drawn out into bars the cakes of metal obtained in this way are exposed in a charcoal fire, during *several hours*, to a temperature a little below the melting-point, the blast of air playing upon them during the time. The object of this is, doubtless, to remove the excess of carbon by a process the reverse of *cementation*, which will be explained presently.

In 1800 a patent was taken out by David Mushet for a process in every respect analogous to that just referred to. He appears, however, to have applied it to the manufacture of a metal low in carbon, and therefore intermediate between iron and steel, partaking to a certain degree of the properties of both ; corresponding, in fact, to what we have referred to as steely iron. Since this metal must have been in a state of fusion, Mushet must have brought to bear upon it a very high temperature. The manufacture was conducted in crucibles.

The Cementation Process.—Malleable iron left long in contact with strongly heated carbon, and protected from the direct action of the blast, becomes steely, and, if sufficient time be allowed, it is converted into steel without undergoing fusion or even becoming pasty. This circumstance could not long have escaped notice, and doubtless it was to the observation of this phenomenon that the method of producing steel known as the *cementation* process owes its origin. When or where the cementation process first came into use is not known. For many years past all the best steel for cutlery, &c., has been made in this way.

The cementation furnace (fig. 32) is dome-shaped, like the furnace of a glass-house, and is enclosed in a conical jacket of brickwork, which serves to carry off the smoke from the flues. The hearth of the furnace is divided into two parts by the grate (G), traversing the whole length (13 or 14 ft.) of the furnace, in which a coal fire is maintained, the flame being made to circulate above, below, and around the rectangular fire-stone,[1] or firebrick *pots* (C), placed one on each side of the grate, before escaping through the flues in the wall (H) and through the opening (M). These

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[1] A stone, resembling ganister, which resists changes of temperature, and which is obtained in the neighbourhood of Sheffield. The joints are made with fire-clay.

pots average 12 ft. long, and about 3 ft. in depth and width, so that each will contain seven or eight tons of bar-iron, together with the charcoal necessary for its conversion into steel. A small opening is left at about the middle of one end of each chest, through which *proof-bars* are withdrawn from time to time, through a small door in the wall of the furnace, for the purpose of watching the progress of the cementation. This is judged by breaking the bar after cooling, when the character of the fracture reveals the extent of the alteration which the bars have undergone; and the heat of the furnace and the further duration of the process are controlled accordingly. There is also a small door in the wall of the furnace, a little above the top of each trough, through which the bars of iron may be introduced and withdrawn, a larger door being made in the middle of the wall to allow the passage of the workmen.

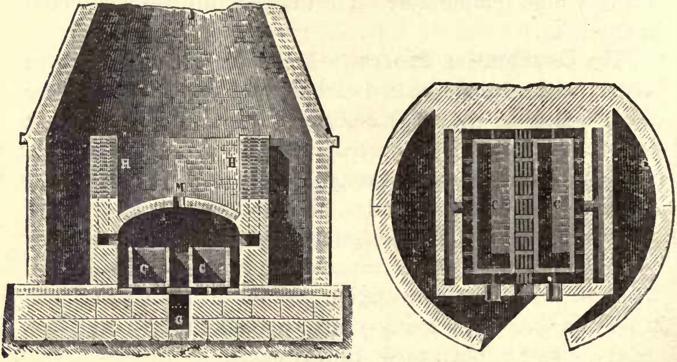

FIG. 32.—Cementation Furnace for converting Bar-Iron into Steel.

The cementing material is charcoal, in pieces from about a quarter to half an inch in diameter. Alkaline salts, and substances containing nitrogen are sometimes added, because they cause the formation of cyanogen, which is said to assist the acquisition of carbon by the steel. The bars of iron should be of the purest description, if the best steel is to be produced. They are about 3 in. broad, $\frac{1}{3}$ in. thick, and from 6 to 12 ft. long.

In order to fill the troughs, the workman stands upon an iron platform between the two, and sifts the cement powder into them, so as to form a layer of about half an inch in depth, upon which the bars are arranged at about an inch apart. More cement powder is now sifted over these, so as to fill up the intervals between them, and to cover them entirely to the depth of about an inch. Upon this a second layer of bars is placed, then more of the charcoal powder, and so on, until the trough is filled to within a few inches ; it is then covered with grinders' waste —'wheel swarf,' consisting mainly of silica and oxide of iron. The fire is gradually applied during the first two or three days, to avoid the risk of splitting the troughs. A temperature high enough to melt copper (estimated at about 1100° C.) is required to enable the bar-iron to acquire a proper proportion of carbon, and the troughs are maintained at this temperature for a period proportionate to the hardness which the steel is required to possess ; four days being sufficient for producing the steel of which saws and springs are made, while six or eight days are required for shear steel, and ten days or more are required for the very hard steel of which cold chisels are made. The fire is then gradually let down to avoid sudden change of temperature, so that some days elapse before the troughs are cool enough to be opened. About three weeks are commonly occupied in the conversion of the bar-iron into steel : one to get up the heat, one during which it is kept at the required heat, and one to cool it down ; so that only about sixteen cementations can be executed in a year by a single furnace.[1]

Blister Steel.—The bars are found to have upon their surface bubbles or blisters of considerable size, whence they are called *blister steel.* On breaking the bars the fracture

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[1] From 20 to 40 charges can be worked off before the pots require renewing.

exhibits a silvery lustre and a well-marked crystalline structure. The proportion of carbon which has entered into combination with the iron depends upon the duration of the cementing process, but it rarely exceeds fifteen parts in a thousand parts of the metal.

Theory of Cementation.—The chemical changes which are involved in the process of cementation are not yet thoroughly understood. The passage of infusible solid carbon into the interior of the solid iron bar obviously requires explanation. It may be imagined that the external particles of iron which are in contact with the charcoal, becoming charged with carbon, impart a portion of that element to the next layer, and so on, until the particles in the very centre of the bar acquire a share of carbon. Indeed, it has been clearly shown that carbon may thus be transferred to, and distributed through, iron at temperatures far below the fusing-point of the metal. It is even possible to carburise iron by heating it, in contact with a diamond, in a tube from which all air has been withdrawn, the diamond, which is the purest form of carbon, being gradually absorbed by combination with the iron.

In the light of the experiments with the diamond, it is most probable that carburisation is in a large measure due to direct combination of the iron with the carbon of the charcoal in which it is packed; the following explanation has, however, been commonly accepted. The small quantity of oxygen contained in the air remaining in the trough, and present in the pores of the charcoal, enters into combination with the carbon to form carbonic oxide gas; a small proportion of this gas, in contact with iron at a high temperature, gives up its carbon to the metal, and becomes converted into carbonic acid gas; but this carbonic acid, in contact with the strongly heated carbon surrounding the bars, is reconverted into carbonic oxide, which again transfers carbon to the metal, these changes recurring many times in the same order, until the whole of the iron is converted into steel. The observations of metallurgists during the last few years have shown that red-hot iron allows the passage of gas through its substance, and that this metal has the power of absorbing a considerable quantity of carbonic oxide, which renders it easy to account for the transference of carbon from the charcoal into the interior of the bar.

It is possible that the carbonic oxide occluded by the iron undergoes dissociation, depositing carbon and setting free oxygen, which immediately combines with a further quantity of carbonic oxide, forming carbonic acid. This point will be discussed more in detail further on.

Other gases containing carbon are capable of imparting that element to iron ; thus if coal-gas, which contains carbon in combination with hydrogen, be passed for an hour through an iron tube containing some soft iron wire heated to bright redness, the wires will absorb carbon from the gas, and become converted into steel.

The blisters, which are distributed sparsely and irregularly over the surface of the bars, are now known to be due to the action of particles of oxide of iron, or of slag, accidentally occurring in the iron bars, upon the carbon combined with the iron, giving rise to carbonic oxide gas, the expansion of which causes the blister. As might be anticipated, the blistered steel is only fitted for very rough articles ; its largely crystalline structure renders it deficient in tenacity, and the bars are further weakened by their want of uniformity and by the presence of the blisters. After tilting it is known as *bar-steel.*

Conversion of Blistered Steel into Tilted or Shear Steel. The quality of the blister steel is improved by a process similar in principle to the fagotting of bar-iron. For single shear steel, bars are chosen which have only been converted to a certain depth, so that the resulting bar is a mixture of iron and steel which, whilst possessing considerable tenacity, is capable of taking a fairly hard cutting edge. Such material is largely used for certain kinds of knives. Five bars of blister steel are bound together into a bundle, being secured by a stout steel wire; four of the bars are about 18 in. long, and the fifth is twice that length, so that it projects beyond the others, and forms a handle. This bundle is raised to a welding heat in a forge, sprinkled with sand to combine with the oxide of iron to form a fusible slag, and is placed under the *tilt-hammer.* This hammer weighs about 2 cwt., and it is so suspended that it may be raised by *cams* projecting from the circumference of a wheel, the revolution of which brings them down in succession upon the tail of the hammer, the head falling again upon the anvil as soon as the cam has passed. A few blows from this hammer soon weld the bars together, when the binding ring is knocked off, the bundle again heated in the forge, and hammered or *tilted* throughout its whole length, and on all sides, until it is reduced to a rectangular bar of the right dimensions. In order to avoid the necessity for reheating the bar during the process, the tilting must be effected with great celerity, and the hammer is made to deliver 300 or 400 blows per minute, the number being, of course, regulated by the rate at which the cam-wheel revolves. The workman, being seated upon a swinging bench which brings him upon a level with the anvil, is enabled to move to and fro with little effort, and to bring every part of the elongated bar under the strokes of the hammer. The fracture of a bar of shear steel shows it to possess a much more compact structure than the blister steel, and its tenacity and ductility have been much improved by the tilting. It is probable also, that, as in forging bar-iron, the proportion of carbon has undergone a slight diminution, the steel being found to become softer after repeated tilting. If *double shear steel* be required, the tilted bar is broken, and the two pieces welded into a single bar.

Although the want of homogeneity in steel made as just described, owing to unequal carburisation, and to the presence of slag, which always exists in more or less quantity in wrought iron, was well known, yet nothing was done to remedy it until about the year 1760, when Huntsman conceived and carried into effect the idea of fusing the blister steel. He had great difficulties to contend with at first, for there were no crucibles in existence then which would stand the requisite temperature. This was the first time steel was ever obtained in the molten state, unless we regard the Indian wootz as such; but the latter, when in the molten state, was probably too highly carburised to constitute steel. The fusion of blister steel was a great step forward.

The molten metal is cast into ingots, and, after being carefully reheated, is drawn down under a tilt or steam-hammer.

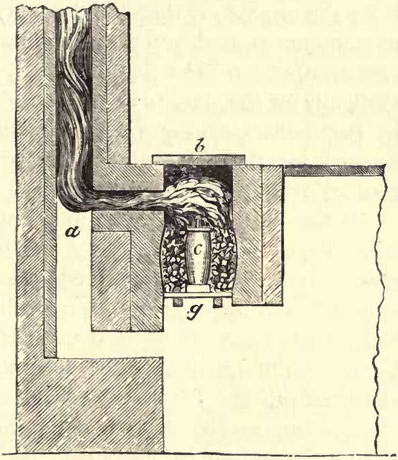

FIG. 33.—Furnace and Pot for Melting Steel. *g*, Grate. *c*, Crucible. *b*, Cover of Furnace. *a*, Chimney

Conversion of Blister Steel into Cast Steel.—The blister steel is broken up into pieces of a convenient size for packing close together, and about 50 lb. of it are introduced into a tall narrow crucible, about 2 ft. high, made of fire-clay mixed with blacklead, and provided with a closely fitting cover. Some steel makers add a little bottle-glass, to fuse over the surface and prevent oxidation of the steel.

The crucibles are placed in a small furnace (fig. 33) consisting of a number of oval melting holes, lined with ganister, usually large enough to hold two pots in each, about 1 ft. wide and 2 ft. deep, and their opening is usually on a level with the floor, to facilitate the lifting of the crucibles. These furnaces are provided with high chimneys, so that a powerful draught may be produced. Hard coke broken into small pieces is employed to raise the crucible to a bright red heat; the steel is then introduced, the crucible covered, and the furnace filled up with coke. When the steel is properly melted, the small quantity of slag on the surface is commonly removed by inserting a cold iron bar; the crucible is then lifted out with a pair of tongs, and its contents poured into a rectangular or octagonal mould of cast iron, which has been previously heated, and is placed vertically for the steel to be poured in. The mould is made in two halves, closely fitting together, so that it may be opened for the removal of the bar of cast steel, and is coated inside with coal-tar soot.

If the steel be not kept long enough in the furnace it will *teem*, or pour 'fiery,' *i.e.* it will boil up in the moulds, owing to the escape of gas, and the ingot will be 'honeycombed' and useless; on the other hand, if it be left in too long it will teem 'dead,' and the bar produced from it will be of inferior quality. It is generally considered that the change from the fiery to the dead condition is caused by the addition of silicon, reduced from the silica of the clay pot by the carbon in the steel. If kept unduly long, too much silicon enters the metal and lowers its quality.

Crucible Steel.—At the present time large quantities of cast crucible steel are made from iron which has not been *converted*, *i.e.* has not had carbon imparted to it by the cementation, or, as it is termed in the trade, converting process. Malleable iron, cut into small pieces, is charged into crucibles, and melted with a certain amount of carbon, the proportion of which will depend on the *temper* required in the steel. Towards the close of the melting operation some *spiegel-eisen* (iron rich in carbon and manganese) is added. In other respects the process is similar to the melting of converted iron. In the production of mild steel, *i.e.* steel low in carbon, if plumbago pots be used carbon need not form part of the charge ; a little spiegel-eisen is added towards the end.

Much scrap, consisting of crop ends, &c., of mild steel, produced by the Bessemer and Siemens processes, is largely used in the production of crucible cast steel, the scrap being simply melted down with the necessary quantity of charcoal and spiegel-eisen.

These methods, now largely used in the production of crucible steel, are to all intents and purposes the same as that employed by the Hindoos in the production of wootz, with the exception that they could not produce so high a temperature as is easily attainable in this country in an ordinary furnace. The addition of manganese is another point of difference in detail of some importance. This was first suggested and patented by Josiah Heath in 1839. He had been in the Civil Service in India, where he observed the influence which manganese had on the wootz steel. By the addition of manganese during the melting operation, in the form of an alloy with iron and carbon, or as oxide of manganese with carbon, sound weldable steel was produced from iron which could not previously be employed for the purpose. Before the introduction of manganese into the crucible steel manufacture only the best Swedish brands of iron were used.

The manganese acts beneficially in several ways, mainly by its having a greater affinity than iron for oxygen and sulphur, which are thus removed from their combinations with iron, and are carried for the most part into the slag.

Since the introduction of the Siemens regenerative system,[1] furnaces built on that principle have been largely used in the manufacture of crucible steel. The melting-chamber is a long trench with overhanging sides, arched horizontally and vertically, to prevent them sinking in, should the pillars between the ports give way. It is divided

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[1] See chapter on 'Fuel,' p. 75.

into several compartments, each holding six pots, arranged in two rows. Each of these chambers communicates by flues with the regenerators, which are situated on each side of the melting-chamber. The gas and air meet at a point about 2 ft. from the entrance to the melting-chamber, into which they flow together, the gas being undermost, very little mixing of the gas and air taking place up to this point, so that the full heat of the combustion of the gas is developed around the crucibles.

Over each pair of pots is an opening in the arch, fitted with a fire-brick cover, which can be raised and lowered by a lever.

The economy of fuel by the use of these furnaces is said to be very great as compared with the old system, about ¼ cwt. of small coal doing work for which previously 3 tons of coke were required. The pots stand very much longer, owing to the absence of dust, which in the old melting-holes rapidly corroded them.

Case-Hardening.—Since in the *cementation process* the carburisation of the metal proceeds gradually from the exterior to the centre of the iron, it is obvious that, by stopping the process after a certain time, the piece of metal will consist of wrought iron coated to a greater or less thickness with steel, a combination extremely useful for purposes in which a hard surface in conjunction with the power to resist sudden shocks is required, as, for instance, in the case of the mandrils of lathes. Cementation applied in this way is known as *case-hardening*. The articles to be case-hardened are placed in a fairly air-tight box, which is then filled up with some substance containing animal carbon, such as leather, horns and hoofs, bone dust, &c., which has been sufficiently charred to make it capable of being reduced to a powder. The box and its contents are then very gradually raised to a red heat, at which they are maintained until the required thickness of *casing* has been obtained. About half an hour after the temperature has reached the proper point, the case-hardening will have proceeded to the depth of a sixpence, and so on. It is sufficient for most purposes to convert to the depth of $\frac{1}{16}$ in. The presence of alkaline substances, such as soda or lime, assists the process. When a hard surface is wanted, which has not to stand much friction, it may be produced by simply heating the iron to redness, sprinkling the surface with prussiate of potash, and then plunging the metal into cold water. In this way a very hard surface, but of hardly appreciable thickness, is obtained. Heavy armour plates are frequently case-hardened on one side to the depth of about an inch, by heating them uniformly for three or four weeks with that side in close contact with the carburising medium. The process is known as *Harveyising*. Very great care is required to ensure regularity. As soon as the action has proceeded sufficiently far, the plates are removed and chilled by means of a spray of ice-cold water, which gives intense hardness to the carburised portion.

Carburising and Decarburising Cementation.—The principle of cementation may also be applied to the softening of carburised metal. It is only necessary to reverse the conditions. It was formerly supposed that the production of malleable cast iron depended solely upon such a reaction. The more probable explanation of this phenomenon will be given later on. Under favourable conditions, however, white cast iron, maintained for a long period at a high temperature in a moderately oxidising atmosphere, loses carbon. Under such conditions, it is assumed that the oxygen acting upon the carbon at the surface of the metal, produces carbonic acid, which diffuses into the metal; and there, coming in contact with a further quantity of carbon, it is reduced to carbonic oxide, some of which gradually diffuses out again, to be again converted into carbonic acid at the expense of more oxygen, and so on. Were the character of the atmosphere too highly oxidising, the removal of the carbon would be attended by a partial oxidation of the iron.

At first sight it may appear difficult to reconcile the theories just put forward to account for the two opposite kinds of cementation. They are, however, perfectly in accord with the laws of chemical affinity and of dissociation. It has been supposed that in the carburising process carbonic oxide undergoes dissociation in the pores of the iron. It might not unnaturally be asked: Why does not the carbonic oxide produced by the reduction of the carbonic acid in the decarburising process also undergo dissociation, depositing carbon in the pores of the metal? The explanation of this apparent anomaly is that at any given temperature and pressure an atmosphere of carbonic acid, placed under conditions favourable to its reduction to carbonic oxide, will undergo a certain definite amount of change, the extent of the change being entirely dependent on the temperature and pressure.

The iron in the two cases under consideration has, probably, nothing to do with the matter, except in the sense that it furnishes the spaces in which the gases are placed, under the necessary conditions of temperature and pressure to initiate their dissociation.[1] If we assume as a working hypothesis that the conditions in the heated iron are such as to enable dissociation of both carbonic acid and carbonic oxide to take place, then all that happens in each case is easily explained. It must be borne in mind that in the dissociation of a gas a portion only of it is dissociated, the percentage being regulated entirely by the temperature and the pressure, and being independent of the actual amount of any other gas also present.

In carburising cementation the metal is surrounded with carbonaceous matter, and the conditions are therefore favourable to the maintenance of an atmosphere saturated in respect to carbonic oxide, but containing only a relatively small

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[1] Under similar conditions, carbon has been found to diffuse into porcelain. Still, it is possible that the tendency to form a carbide of iron may assist the dissociation of the carbonic oxide.

amount of carbonic acid, since any carbonic acid entering the region around the metal would be decomposed by the charcoal into carbonic oxide ($CO_2+C=2CO$), so long as the atmosphere remained unsaturated with the latter. At the commencement of the operation the interstices of the iron are charged with an atmosphere the nature of which will depend on the previous treatment of the metal during its manufacture. Unless this atmosphere not only coincide exactly in composition with that on the exterior, but also be at such a tension as to ensure dissociation not setting in, *diffusion* will commence in both directions. It may, then, be safely inferred that diffusion would take place. The atmosphere which would diffuse in would consist in great part of carbonic oxide, not only for the reasons already given, but also because the *diffusion equivalent* of carbonic oxide is greater than that of carbonic acid in the ratio of 1 : 0·8 ; so that supposing, for the sake of argument, the external atmosphere were saturated in respect both to carbonic oxide and carbonic acid, this equilibrium would be destroyed on their diffusing into the metal. The force of diffusion is inversely as the square roots of the densities of gases. Deville has shown that at the ordinary atmospheric pressure carbonic oxide is sensibly dissociated at about a bright red-heat. Now, the temperature is the same within and without the metal, and unless the pressure be too great in the interstices of the iron, the carbonic oxide will undergo dissociation therein also. Our hypothesis is, that the conditions in the iron are favourable to the dissociation of the carbonic oxide, and that the carburisation of iron in the cementation process is affected by this means. The next point to be considered, in order to prove or disprove this view, is what becomes of the oxygen liberated on the splitting up of the carbonic oxide. The oxygen cannot combine with the iron in the presence of an atmosphere saturated with carbonic oxide; but it can combine with carbonic oxide to form carbonic acid, since this latter gas will be stable. *i.e.*

cannot undergo dissociation, the quantity present being insufficient to form a saturated atmosphere. There will thus be a continuous dissociation of carbonic oxide, accompanied by a proportional formation of carbonic acid, which, however, can never form a saturated atmosphere, since it will gradually diffuse out from the metal, and, coming in contact with charcoal, be reduced to carbonic oxide, which, in its turn, will act as a carrier of a further quantity of carbon to the metal. The only limit to the reaction is that determined by the actual fusion of the metal at the temperature of the operation, owing to its fusing-point being lowered by its union with the carbon deposited in it.

Let us now turn our attention to what takes place in *decarburising* cementation. As already pointed out, the decarburisation is effected by the agency of carbonic acid. Dissociation in this case, in all probability, has nothing to do with the matter. For, in the first place, the quantity of carbonic acid existing in the atmosphere outside the metal must be very small, quite insufficient to constitute a saturated atmosphere ; and, secondly, the atmosphere in the interior could never become supersaturated with carbonic oxide, since its formation takes place *in situ*, and must of necessity stop when equilibrium of tension is reached. As in the case of carburising cementation, this state of equilibrium is never reached, owing to diffusion taking place continuously. There is, therefore, nothing to interfere with the complete removal of the carbon from the metal. Carbonic acid diffuses in and is reduced by the carbon, and the carbonic oxide thus formed diffuses out, and, in contact with oxide of iron or air, becomes converted into carbonic acid, and so on, the carbonic acid acting as a carrier of oxygen. The assumption that the iron does not take a primary part in the reaction in the carburising process is supported by its apparent inactivity in the decarburising process.

It was pointed out, above, that if the atmosphere were too strongly oxidising during decarburisation, an oxidation of iron would take place. This fact has recently been turned to practical account, it having been found possible to so oxidise the surface of the iron as to form a protective coating against the action of damp air, in other words, to prevent rusting.

Bower-Barff Process.—Professor Barff, several years ago, patented a process for the protection of iron surfaces by forming on them a film of magnetic oxide. This is effected by heating the iron to redness, and passing superheated steam over it. The iron decomposes the aqueous vapour, setting free the hydrogen, and taking its place.

The process is now carried out in the following manner: The articles to be coated are placed in a fire-brick chamber of suitable dimensions, and there heated by means of 'producer'-gas. When the temperature has been sufficiently raised, superheated steam is substituted for the producer-gas.

So far we have traced how certain methods for the manufacture of steel naturally grew out of the primitive process of extracting iron direct from its ore. It should now be clear that the difference between iron and steel is only one of degree, depending upon the amount of carbon present. It may safely be stated that iron has never been manufactured, on anything like a large scale, free from carbon; it always contains at least a trace under such circumstances. Until recently the term steel was only applied to carburised iron which had a high tensile strength, was elastic, and *would harden on being heated to a certain temperature and suddenly cooled.* This definition no longer holds good, for a vast quantity of slightly carburised iron produced by modern methods now goes by the name of steel. How this came about will be made clear in the sequel.

Development of the Blast-furnace.—It is necessary that we should now return[1] to the study of the processes by which iron can be extracted from its ore. The more impor-

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[1] Vide p. 160.

tant steps in early blast-furnace development were made in Carinthia and Styria. There the dimensions of blast-furnaces were gradually increased until the limit beyond which malleable iron could no longer be made was reached. Before this limit was arrived at, furnaces were in use in which either malleable iron or cast iron could be made by slightly altering the method of working. The same furnace was known as a *Stückofen* or a *Blauofen*, according to whether it was being worked for the production of malleable iron or cast iron. The height of the furnaces was from about 10 ft. to 16 ft.; in shape they commonly resembled two truncated cones placed base to base; sometimes, however, they increased in diameter regularly from top to bottom. Taking as an example a recorded case, we find that a furnace 16 ft. high measured $1\frac{1}{2}$ ft. at the top and $2\frac{1}{2}$ ft. at the bottom, the diameter at the widest part, or 'boshes,' represented by the junction of the bases of the two cones, being 4 ft. This furnace was worked with one twyer, made sometimes of copper and sometimes of clay, placed about 14 in. above the bottom. When malleable iron was being produced, the lump was withdrawn from the bottom of the furnace through an aperture 2 ft. wide, which was kept closed during the smelting, with the exception of a small hole through which the slag escaped. Much damage was often done to the furnace in withdrawing the lump of metal, owing to its adhering to the material forming the bottom, and tearing it away. From the description of the malleable iron obtained, it was evidently of a decidedly steely nature.

When it was desired to produce cast iron, the direction of the twyer was altered, and also the proportion of the *burden* (or ore used) to the charcoal, that of the latter being increased. When it was intended to make malleable iron, the blast was made to impinge as much as possible upon the lump of metal, to assist which the slag was tapped out often. These latter conditions would, therefore, be reversed in order to produce cast iron, and the metal would be exposed to the action of the charcoal for a longer time and at as high a temperature as could be obtained.

Even in some of the higher Indian furnaces cast iron was sometimes unintentionally produced in more or less quantity, much to the disgust of the workers, who looked upon this product as worthless. In making malleable iron in the blast-furnace, ores containing a considerable quantity of phosphorus might be employed, and yet the iron produced would be free from that objectionable element. If, instead of malleable iron, cast iron were made in the same furnace, the bulk of the phosphorus would pass into the metal.

The reason of this is that carbon has a greater affinity than phosphorus for oxygen. When smelting for cast iron, the charge consists largely of carbonaceous matter, therefore the phosphoric acid (P_2O_5) in the ore is soon deprived of its oxygen, and the phosphorus combines with the iron. Since carbon has a greater affinity for oxygen than phosphorus has, it also follows that, so long as the metal retains an appreciable quantity of carbon, the phosphorus cannot be removed to any great extent by oxidation.

When the blast-furnace was employed for making malleable iron, the conditions were favourable to the removal of phosphorus from the iron, the metal produced being sufficiently free from carbon to allow that portion of the phosphorus which had been reduced to reoxidise, and pass into the slag in combination with oxide of iron.

In consequence of the comparative ease and cheapness with which cast iron could be produced from the ore as compared with malleable iron, some simple means were naturally sought by which it could be converted into malleable iron. This was soon accomplished, in spite of the presence of phosphorus, and gradually cast iron became the sole product of the blast-furnace.

Use of Coke in the Blast-furnace.—In the furnaces we have so far considered charcoal was the only fuel employed.

In course of time charcoal began to get scarce, and people were forced to consider whether coal could not in some way be used as a substitute. At first it was used only for forging iron, but in time, after many failures, it was successfully applied to smelting in the blast-furnace. The first to do this was Dud Dudley, about the middle of the seventeenth century. What means he employed are not known ; he was greatly persecuted through the jealousy of other ironmasters, and he ended his days in poverty, his secret dying with him. There is not much doubt that his secret consisted in converting the coal into coke, and employing a good blast in his furnace. Although not absolutely lost sight of, the question of substituting coal for charcoal was not further practically developed until about a hundred years after Dudley's death. About the year 1730, Abraham Darby took the matter in hand, and achieved success by treating the coal in the same way as in making charcoal from wood, *i.e.* he converted the coal into coke.

Blowing Machinery.—With the introduction of coke commenced a new era in blast-furnace history. The bellows which had up to that time been employed were not equal to dealing with the more refractory fuel. This resulted in the introduction of blowing-cylinders worked by water power, and in due course of time by steam power.

At first single-acting cylinders were used, but in time double-acting cylinders were substituted for them. The arrangement is a very simple one. The cylinder, which may be of cast iron, is fitted with an air-tight piston, to which a reciprocating motion is imparted, causing air to be drawn in and forced out alternately, through suitably arranged valves in each end of the cylinder. The air forced through the outlet valves of the blower passes into pipes attached to both ends of the cylinder and connected with the blast main which supplies the furnaces. The arrangement of the valves and the attitude of the blowing-cylinder to the motive power have been varied in many ways; the principle involved must always remain the same. The blowing-cylinders attached to blast-furnaces of the present day are often required to discharge 50,000 cubic feet of air per minute, and sometimes even more, at a pressure varying from about 3½ lb. to 10 lb. per square inch, and even higher under special circumstances. In order to steady the blast a large chamber, equal in capacity to from twenty to fifty times the volume of blast passed into the furnace per second, was interposed between the blower and the furnace. The blast mains are now commonly so large that no other regulator is required. Valves are placed in the regulator or blast main to prevent the pressure of the blast rising beyond a certain fixed amount. The British system of supplying several furnaces from one blowing-engine is now being superseded, in America, by the provision of a separate engine for each furnace. The object of this change is to give greater control over each furnace.

Although the discovery that coke could be used for the manufacture of iron was a very important one in consequence of the increasing scarcity of charcoal, yet it must not be lost sight of that, owing to coke containing always more or less sulphur, it is really not so well suited as charcoal for the production of the best malleable iron. Even at the present day, where it can be obtained, charcoal is still used, notably in Sweden, and parts of America. The use of charcoal must, however, sooner or later come to an end.

Introduction of the Hot Blast.—One of the most important innovations which has ever taken place in blast-furnace practice is undoubtedly the introduction of *hot blast*. This took place in the year 1828. It was first carried into effect by Neilson, at the Clyde Iron Works, and notwithstanding that the idea was received with much derision at first, yet by about the year 1835 it had been universally adopted throughout Scotland. As a direct consequence of the use of a heated blast, it became possible to employ coal in the furnace, the heat being sufficient to cause the coal to coke to the necessary extent whilst still near the top. All coal cannot be used with equal advantage: a highly caking coal would be objectionable. The splint coal of Scotland is well suited for use in blast-furnaces; in the Staffordshire district coal is also used; in Wales and America anthracite is similarly employed, generally, however, in admixture with other coal; in Yorkshire, Durham, Cumberland, and some other localities, the blast-furnaces are fed with the best oven-coke procurable.

Irrespective of the nature of the fuel used, the effect of heating the blast was to cause considerable saving in fuel, and also to increase the actual *make* of a furnace; the latter being to a great extent the direct consequence of the former, for to decrease the proportion of fuel in the burden is equivalent to increasing proportionally the ore.

By blowing in hot air the temperature in the vicinity of the twyers is sensibly increased. With cold blast a *nose* of chilled slag forms at the end of the twyer, and extends itself to a greater or less distance into the furnace according to the temperature, thereby modifying the working and affecting the quality of the metal produced. With hot blast it is necessary to cool the twyers by passing a stream of water through a jacket surrounding them, to prevent their being fused. In the case of hot blast it is clear the conditions are more uniform and more under control; atmospheric influences can less affect the working of the furnace, and the zone of fusion is brought lower down in the furnace and concentrated within a smaller area. The importance of these considerations is apparent when we call to mind the conditions in the blast-furnace. A tall cylindrical chamber is filled with ore, fuel, and flux, in certain proportions; at the base air is blown in, which, coming in contact with incandescent fuel, combines with it, forming carbonic acid, which, however, is almost instantaneously converted into carbonic oxide by the excess of carbonaceous fuel. Cold blast pig-iron is still made at the celebrated Lowmoor Works, where they deal with exceptionally pure materials, on account of its containing less silicon than that made in the hot blast. Part of the carbonic oxide as it passes through the ore last introduced at the top of the furnace, reduces it, with formation of carbonic acid in the way already explained ; another part undergoes dissociation in contact with metallic iron, in the interstices of the partially reduced ore. Both the reduction and the carbon deposition take place almost entirely within the uppermost layers of the charge ; any carbonic acid formed in the lower part of the furnace is reduced again to carbonic oxide on coming in contact with more fuel, as it passes up ; so that a supply of carbonic oxide is maintained throughout the furnace. But above a certain level, the temperature is so low that the coke is unable to reduce the carbonic acid to carbonic oxide. When this point is reached there is a struggle for ascendency between the two gases, which results in a state of equilibrium. At suitable temperatures carbonic oxide is able to reduce oxide of iron, and carbonic acid can oxidise metallic iron. In certain proportions the one can neutralise the action of the other. Any change in temperature will give the advantage to the one side or the other, and a fresh equilibrium will result, to suit the altered conditions. For these reasons there must always be a considerable proportion of carbonic oxide in the gases issuing from the top of the blast-furnace.

It has been shown that, in the primitive blast-furnaces, the earthy matter of the ore was fluxed off by means of oxide of iron. In large furnaces producing cast iron this would be impracticable, for oxide of iron forms an easily fusible 'scouring' slag, which runs down into the *crucible* of the furnace, and meeting with the cast iron which is collecting there, decarburises it slightly, and removes a large proportion of silicon by oxidation, so that an inferior white cast iron is produced, instead of a grey iron rich in carbon. Besides, oxide of iron could not remain unreduced unless an insufficiency of fuel were employed. In modern blast-furnaces these difficulties are avoided by using lime (CaO) and alumina (Al_2O_3) as fluxing agents. They form a slag requiring a much higher temperature to render it fluid than is the case with oxide of iron, and, owing to the great affinity which calcium and aluminium have for oxygen, they are not reduced, except in very minute quantity, either by the carbonic oxide or by the carburised metal. In the higher zones of the furnace there exists, then, the following state of things: the ore has become reduced, and carbon, in a fine state of division, has been deposited throughout the mass; lower down, the earthy matter has combined with the lime to form a slag of pasty consistency; besides the reduced ore and slag there is also a considerable quantity of unconsumed fuel. All that remains to be done, then, is to raise the temperature of the charge in the lowest zone, so that the iron and slag may be rendered liquid, and thus enabled to separate one from the other by reason of the difference in their specific gravities. This is effected by burning the intermixed carbon by means of a powerful blast of air. It requires but a moment's reflection to see that, as the necessary temperature for fusion is obtained by means of air introduced into the furnace, there would be a great disadvantage in the fusion being effected *above* the point at which the air is introduced, for in that case the already fused metal would have to pass in front of the twyers, and in doing so would become to some extent decarburised. There is another point to be borne in mind, viz. that the carburisation of the metal is not effected merely by having carbon deposited in it. It will be recollected that when iron and carbon are brought together at a high temperature, the former dissolves the latter. It follows that, within certain limits, the higher the temperature brought to bear upon the mixture, the more highly charged with carbon will the metal become.

Until within the last few years, the blast was heated by passing it through iron pipes heated from the exterior;

recently, however, fire-brick stoves, heated by the waste gases of the blast-furnace, have come largely into use for the purpose. (See chapter on 'Fuel,' p. 85.)

At first, and for some years, the blast was only heated to a few hundred degrees, but since, the temperature has been gradually increased, until at present it is commonly employed at 600° C., and sometimes at 700°. The Cowper stoves are said to be capable of raising the temperature of the blast to 800° C., but they are not generally worked at their maximum power.

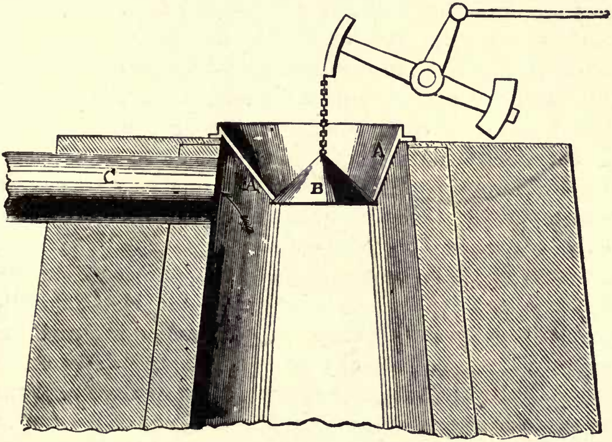

FIG. 34.—Cup and Cone for closing the Blast-furnace, in order that the waste gases may pass into the lateral flue, as shown by the arrow.

The Charging Mechanism of the Blast-furnace.—The utilisation of waste gases—a source of great economy—has only been carried into effect within the last half-century. At first it was only sought to utilise the sensible heat, a very small quantity as compared with that to be obtained by the combustion of the carbonic oxide and hydrogen contained in the gases passing out at the top of a blast-furnace, amounting in the case of carbonic oxide to 25 per cent. by volume on an average, the hydrogen varying up to 7 or 8 per cent. Various means have been tried with the view to collect the waste gases without interfering with the necessary arrangements for properly charging the furnace. That universally employed at the present day is the cup and cone (fig. 34), or some modification of it. The ore, fuel, and flux are tipped from barrows into the annular space or cup (A), and the cone (B), which is attached by means of a chain to a lever, is lowered, allowing the charge to fall into the furnace, after which it is raised again, so as entirely to close the top of the furnace. The gases are drawn off through the outlet (C). This arrangement has several great advantages. In the first place, it is very simple, and it can readily be altered without interfering with the body of the furnace; it distributes uniformly the burden in the furnace; and, by altering the dimensions of the cone, the arrangement of the charge can be regulated to suit the working of each furnace. As the charge descends more rapidly in the centre than at the sides, it is essential to the proper working of the furnace that the bulk of the larger material should be near the centre, so that the current of gases may ascend freely in that direction, and not creep irregularly up the sides. This the cup-and-cone accomplishes more satisfactorily than any other system which could be adopted. In one modification used on the Continent the exit tube for the gases is attached to the apex of the cone.

With the increase in height of blast-furnaces it became necessary to have resort to mechanical contrivances for raising the charge to the top. For this purpose inclined planes were commonly in favour. They consist in a staging reaching from the ground to the top of the furnace, supported at several points, and inclined to the horizontal at an angle of about 25° to 30°. On this incline travels a carriage, on which the barrows are sent up and down. In recently constructed works vertical lifts are usually put up. The motive power may be either steam, compressed air, or some hydraulic arrangement. Of these, the first is that most commonly employed. Perhaps the simplest method is that in which two drums are fixed on the same shaft, which is revolved by means of a small pair of reversing engines.

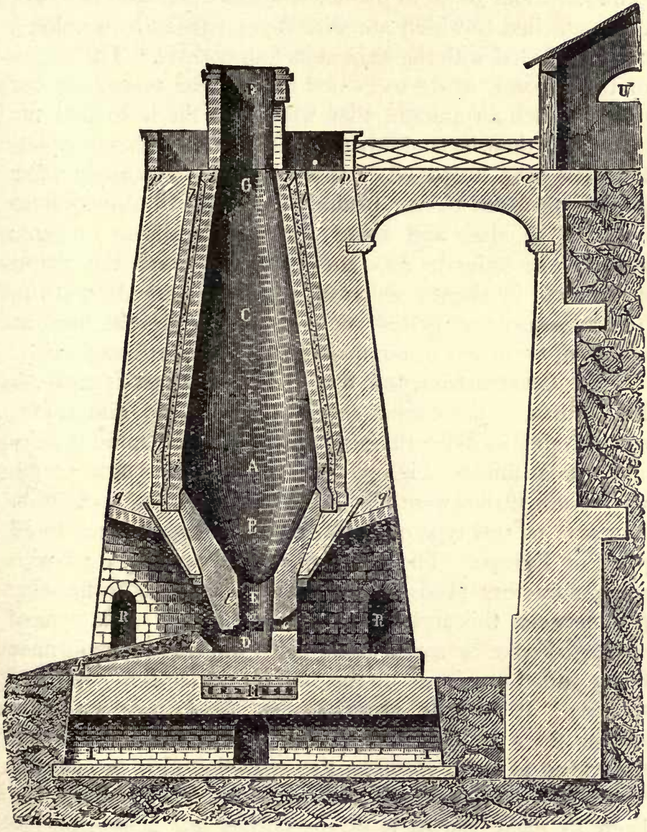

FIG. 35.—Obsolete type of Blast-furnace for Smelting Iron Ores.

Wire ropes attached to each drum pass over a pulley at the top of the furnace, and are connected with cages working between vertical guides. As one cage goes up the other is coming down, so that, to some extent, they balance one another. Amongst the pneumatic arrangements that of Gjers is most in favour in the Cleveland district. In a cylinder, about 36 in. in diameter, works a cast-iron piston or ram, attached to which are wire ropes, carried over pulleys, and connected with the cage at its four corners. The weight of the piston is made to exceed that of the empty lift, but only by such an amount that when the lift is loaded the latter shall then be somewhat heavier. Thus, when the platform has been unloaded, it is only necessary to apply a few pounds pressure to the piston in an upward direction to cause it to rise, and bring down the platform or *cage*; similarly, in order to raise the loaded platform, the piston is lowered by slightly exhausting the air from beneath it. The pressure and partial vacuum are readily obtained, as required, by means of pumps worked by a small engine.

The Construction and Shape of the Blast-furnace.—Blast-furnaces have been varied in shape and dimensions considerably in different localities, and in the same locality at different times. Fig. 35 will give a general idea of the way in which they were constructed up to quite recent times. Furnaces of this type of construction were to be seen in all parts of Europe. The body of the furnace is lined with some refractory sandstone, or more generally with fire-clay (*i*); between this and another similar layer (*l*) is a layer of powdered coke or sand, which helps to prevent the furnace being pulled to pieces by the unequal expansion and contraction. It will be observed that the furnace gradually widens for a certain distance, and then contracts. From the widest part (A) down to the crucible (E) is termed the 'boshes.' The tendency in more recent constructions has been to make the angle of the boshes less acute; and in some cases, water-cooled iron blocks are built into the furnace at this point to keep the lining cool. They do not, of course, penetrate as far as the inner surface. E is the *hearth* or *crucible*, and *o o* points at which the twyers, varying generally in number from 3 to 5, are introduced. Three sides of the hearth are occupied by the twyers; the fourth is arranged for the tapping-out of the metal and slag.[1] A heavy block of stone, called the *tymp-stone*, supported by a cast-iron *tymp-plate*, built into the masonry of the furnace, formed a kind of arch on the fourth side, the lower part being enclosed by the *dam-stone*, faced externally with a thick cast-iron *dam-plate*. Both the tymp-plate and the dam-plate are kept cool by a current of water circulated through them. The space beneath the tymp is termed the *fore-hearth*. The metal is tapped out through a hole at the bottom of the dam-plate, the cinder being allowed to flow through a notch at the top of the plate and down an incline into the cinder-tubs, where it solidifies, and is removed to the tip-heaps. The tap-hole for the metal is often placed at one side of the dam-plate, so that it can be easily raised, if the furnace should be working badly. It was customary after each tapping, to partially fill the fore-hearth with ashes, which floated on the metal and protected it; when the metal was tapped out the ashes and slag settled down to the bottom of the fore-hearth, necessitating much labour and loss of time in removing them each time. This difficulty was got over by covering in the top of the fore-hearth with clay, weighted down to keep it in place, a hole being made in it for the exit of the slag. It is more common now to do away with the fore-hearth altogether, the slag being allowed to flow out from the crucible, at a point 15 to 18 in. below the twyers through a water-cooled block, another hole being provided at the bottom of the crucible for tapping the metal out. Such a furnace is said to have a *closed hearth*. When it is desired to close the tap-hole, a lump of clay, held on the end of an iron bar, is forced into it. It is very important that the clay should not be too easily fusible, nor, on the other hand, be too refractory. In the former case it

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[1] From the Scandinavian *slagg*, dross.

would be liable to fuse out, whilst in the latter it would give rise to a 'hard tap'—*i.e.* great difficulty would be experienced in making a hole through it with the iron bar in

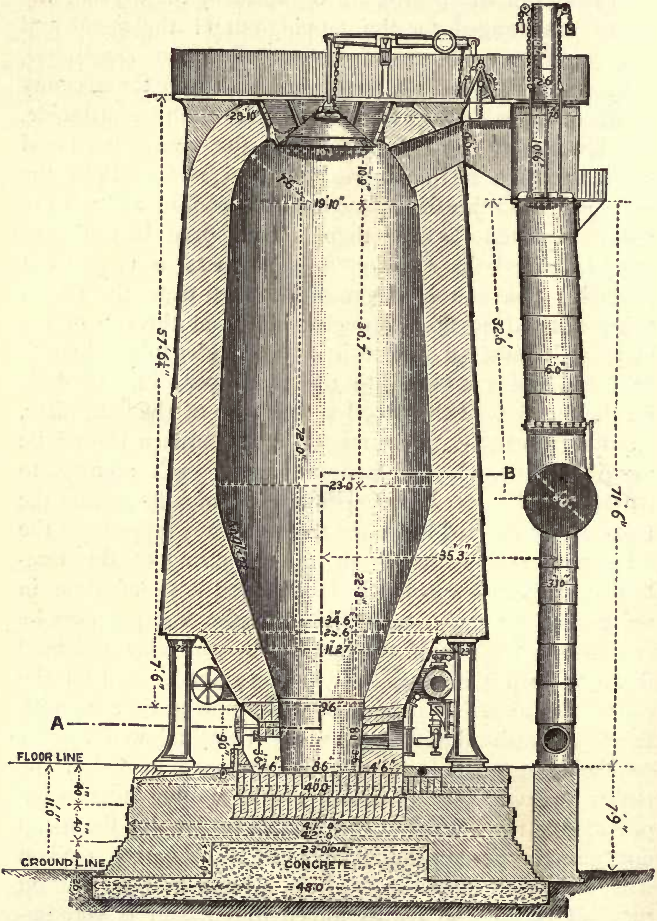

FIG. 36.—Modern Blast-furnace.

order to tap. A mixture of 2 parts of fire-clay and 1 of small coal, ground together, is said to answer well.

Fig. 36 illustrates a modern type of furnace, as constructed at Messrs. Bolckow, Vaughan & Co.'s in the Cleveland district. It will be observed that light iron columns are substituted for the massive brick structure in the older furnace, thus giving more working space, and enabling the twyers to be readily got at. A strong circular iron casting, made in segments, rests on the columns, and supports the body of the furnace, which is constructed of the best fire-bricks, and encased in wrought-iron plates, or braced with hoops. The waste gases pass from the top

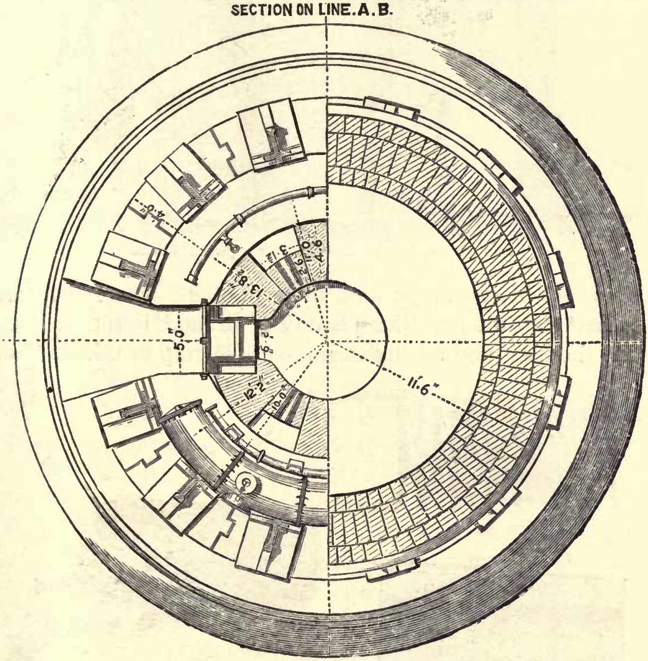

Fig. 37.—Section of Modern Blast-furnace.

of the furnace, through the 'gas box' into the vertical tube, called a 'down-comer,' and thence are drawn off into the main (shown in section at B), which may be connected with a number of furnaces, and from which the gases are led

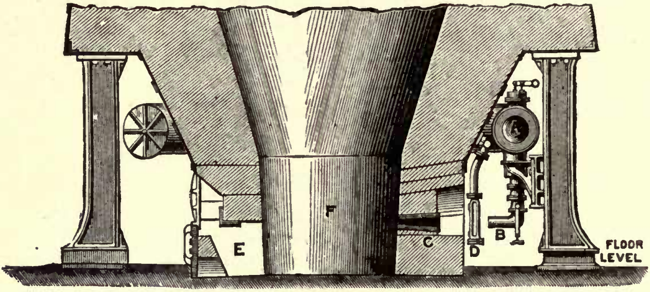

FIG. 38.—Enlarged Section of lower part of Furnace.

into hot-blast stoves, and under boilers, where they are mixed with the requisite quantity of air, and burnt for heating the blast and raising steam, &c. A trap or dust-catcher

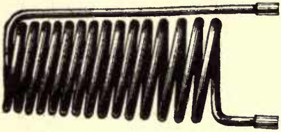

FIG. 39.

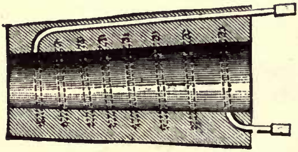

FIG. 40.

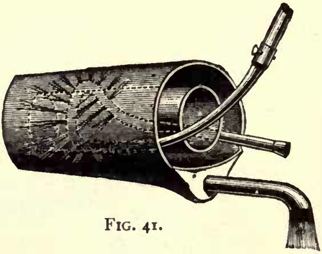

FIG. 41.

formed so as to change the direction of the gases sharply to a widened part of the down-comer is now frequently introduced, in order to intercept a portion of the dust which is always present in the waste gases and which would tend, otherwise, to clog the stoves. At C (fig. 38) is shown one of the *twyer houses*, in which rest the twyers through which the blast is conveyed into the furnace by means of the blast mains (B), connected with the 'horse-shoe' main (A). At the angle of the blast-main pipes a piece of mica is inserted, through which the temperature of the furnace can be observed. The twyers generally consist of a wrought-iron coil (fig. 39), encased either in clay or cast iron (fig. 40).[1] The only objection to this form of twyer is that, if the nose accidentally gets burnt off, the water, which is flowing through the coil under considerable pressure, is suddenly forced into the furnace, causing an explosion, which sometimes greatly deranges the working of the furnace, and occasionally does considerable damage. In Lloyd's spray twyer (fig. 41) this defect is got over. The only objection which has been raised to this system is, that the holes in the spray-tube are liable to become blocked up. This difficulty is easily overcome by filtering the water first through a copper tube with $\frac{1}{8}$ in. holes, which can be cleaned out, when necessary, by means of a simple sludge-cock arrangement. The size of the twyers varies very considerably; they must be proportioned to the volume of the blast, so that it may be forced well into the centre of the furnace, and not creep up the sides, which would cause irregular working. The average pressure of the blast is about $4\frac{1}{2}$ to 5 lb. at the twyer, in most districts in this country. When anthracite is used a higher pressure is required; with charcoal the pressure must be lower.

A steady improvement has been going on in the construction of blast-furnaces, since the time when they first began to make cast iron up to the present day. Instead of 10 ft. high, blast-furnaces may now be seen 100 ft. high, but in Great Britain it has been considered that these furnaces have passed the limit of economy to be obtained in that

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[1] This is the Scotch twyer; the Staffordshire twyer consists of a hollow truncated cone instead of a coil.

direction; in America, however, they are raising the height of furnaces smelting Lake ores to 100 ft. and increasing the number of twyers to about ten. The height of a blast-furnace must be regulated by the nature of the ore and fuel to be used in it. The furnace illustrated in fig. 36 is 72 ft. high, and the diameter of the boshes is 23 ft. The usual height, in England, for furnaces, working on Cleveland, Cumberland, Scotch, or Spanish ore, is from 70 to 80 ft., with 18 to 20 ft. diameter at the boshes; good coke, splint coal, or anthracite being used. If the ore or the fuel tend to crumble under pressure, the height of the furnace must be proportionately less. There appears, however, to be no necessity to reduce it below 50 ft. when coke or coal is used.

In order to combine a long period of reduction for the ore in a cool portion of the furnace, with the maximum rapidity in the descent of the reduced iron through the lower part of the furnace, and at the same time to assist in supporting the weight of the charge, furnaces have recently been constructed with a second set of boshes at the top. They are said to give good results.

Out-turn of the Blast-furnace.—About thirty years ago 150 to 200 tons of pig-iron was considered a good yield for a furnace. Now it is not uncommon for a single furnace to produce 1,000 or 1,500 tons of metal per week. In America the weekly make of a furnace in some instances exceeds 2,500 tons. This is to a large extent accomplished by increasing the diameter of the hearth, and the pressure and volume of the blast, whereby a greater consumption of fuel is obtained in a given time, and in consequence of this a more rapid passage of the charge through the furnace. Careful attention is paid to the quality of both the ore and the fuel, as well as to all details of management. Such rapid driving, however, shortens the life of the furnace lining very greatly, if not proportionately.

Calcination of the Charge.—In some cases the ore is calcined, and charged into the furnace whilst still hot. This is never done with the rich hæmatites of Spain and Cumberland, but only with those ores which contain water or carbonic acid in combination with the iron, such as, for example,

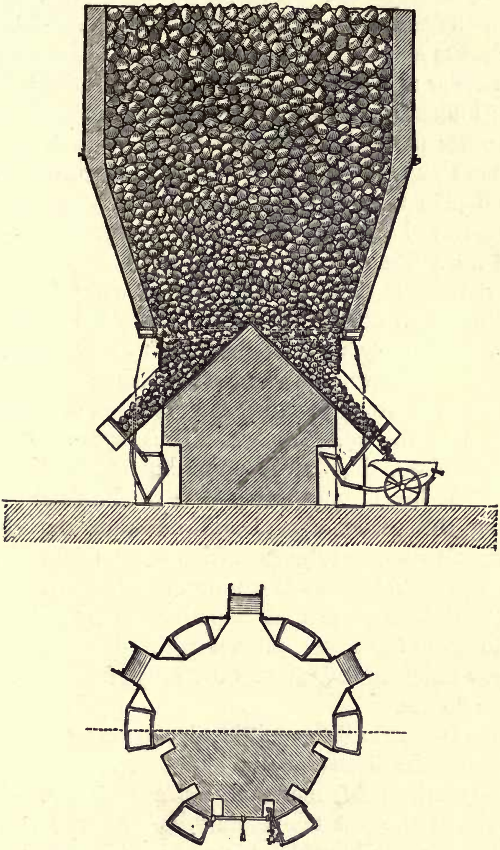

FIG. 42. - Calciner for Iron Ore.

the Cleveland stone and the Scotch ores. The effect of calcination is to drive off the carbonic acid and moisture, thereby rendering the ore more porous and easily acted upon by the reducing gas in the blast-furnace. Calcination formerly was always carried on in heaps. This method gives very irregular results, owing to the variable action of atmospheric influences, some of the ore being hardly affected, whilst other parts have actually become fused. Kilns of some kind or other are now almost invariably employed, in which plan there is great economy. The trucks which have conveyed the ore from the mines or the docks are carried on a line of rails over the kilns or calciners, into which the ore is dropped, a certain amount of small coal being thrown in at the same time. In fig. 42 is shown the calciner commonly used in the North of England. The calcined ore is drawn out, as required, at the bottom of the calciner into barrows, in which it is sent up, still hot, to be charged into the blast-furnace. Thus space and labour are economised, the ore is uniformly calcined, and but little heat is lost in transferring it to the furnace. Besides removing the carbonic acid and moisture, the effect of roasting is to convert the protoxide of iron into magnetic oxide and peroxide, thus lessening the tendency of the ore to fuse and become less easily permeable by the reducing gas. Protoxide of iron combines with silica at a comparatively low temperature, whereas the magnetic oxide and the peroxide do not.

There is practically very little advantage, and often none, in calcining the limestone, for although the carbonic acid is thereby driven off, more or less, according to the care taken, yet, at the low temperature which exists at the top of the furnace, the burnt lime is capable of combining with the carbonic acid with which it then comes in contact, so that it is brought back to a great extent, if not entirely, to its original condition. But the limestone for the charge is now sometimes mixed with the ore prior to the calcination of the latter, under which circumstances the cost of calcining the lime is reduced to practically nothing.

The use of lime has an additional advantage, beyond that of being a highly suitable fluxing agent; by its means a considerable proportion of the sulphur in the ore and fuel is retained in the slag. The most favourable conditions are a high temperature, plenty of lime, and plenty of fuel. It would appear that, under these circumstances, the carbon, the sulphide of iron, and the lime (calcium oxide) react upon one another, the oxygen of the lime passing to the carbon, whilst the sulphur, leaving the iron, unites with the calcium. The higher the grade of iron in any given brand, the less sulphur will it contain.

The Blast-furnace Charge.—The relative proportions of ore, fuel, and flux in the charge of a furnace must depend upon the nature of the ore and flux, and upon the dimensions of the furnace, the temperature of the blast, and the grade of iron it is desired to produce. It is customary to keep the weight of the fuel constant, and vary the proportion of the ore as required. For this reason, the ore and limestone are placed in one barrow and the fuel in another. A certain number of barrowfuls form a 'round' or 'charge.' Thus, for a furnace making Bessemer pig, the charge might consist of six barrows of hæmatite ore, weighing 9 cwt. each, with 1½ cwt. of limestone on each barrow, and six barrows of coke, averaging 5½ cwt. each. If much silica be present in the ore, there should be added to each barrowful about ¼ cwt. of aluminous ore. The presence of an unusual proportion of ash in the coke necessitates the use of an increased proportion of lime as flux.

Blast-furnace Slag.—The slag from blast-furnaces consists essentially of silica, alumina, lime, and magnesia. Taking the general run of cases in England, the silica varies between 30 and 40 per cent., being generally above 35 per cent. rather than below. The same figures will apply to the percentage of lime. The alumina ranges between 12 and

22 per cent., and the magnesia averages 5 to 7 per cent. In some cases these figures are considerably departed from. There is generally more or less manganese present: this varies greatly. The alkalis, potash and soda, generally amount to 1 or 2 per cent.; sulphur is always found in the slag, the amount depending on the quality of the ore and fuel, and on the working of the furnace.

The earthy matter, or *gangue*,[1] of iron ores usually consists mainly of clay, and it is therefore sufficient to add limestone alone to flux it. Occasionally, however, when a large proportion of silica is present, it is desirable to add alumina in some form or other, aluminous iron ore, such as that obtained from near Belfast, and other localities in Antrim, being commonly employed for the purpose. In order to form a satisfactory slag the lime should be present, at least, to the extent of one-third the weight of the constituents of the clay; and since limestone (carbonate of lime, $CaO.CO_2$) contains rather more than half its weight of lime (CaO), two parts of limestone should be employed for three parts of clay. It has already been explained that, in practice, in order to prevent sulphur from passing into the metal, more lime is used than is actually required as flux; it is, however, also essential for the removal of sulphur that the charge should contain a large proportion of fuel, and that the furnace conditions should not be favourable to the making of white iron.

The quantity of slag produced in the extraction of each ton of pig-iron will vary with the richness of the ore and with the weight of ash from the fuel under treatment; roughly speaking, it may be taken at from 10 to 30 cwt.

The colour of slag varies greatly according to the ore being used and the grade of iron being produced. A light burden, *i.e.* one in which there is a large proportion of fuel to ore and flux, is favourable to the production of a light-grey slag; whilst a heavy burden would tend to produce a slag

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[1] From the Northern word *Gang*, a mineral vein.

which, according to circumstances, might be yellow, green, brown, or black. To some extent the colour and consistency of the slag indicate the kind of iron being produced, but, to form a trustworthy opinion, it is necessary to be well acquainted with the general working conditions of the furnace.

The physical characters of the same slag vary greatly, according to the way in which it has been treated, just as is the case with glass. Quick cooling tends to produce a vitreous, more or less transparent slag, with a conchoidal fracture; slow cooling causes the same slag to be dull, opaque, and stony in appearance. Slags containing much lime or magnesia are the least fusible; they are stony-looking, whether quickly or slowly cooled, and soon disintegrate on exposure to damp air. The fluidity of slag is greatly increased by the presence of oxide of iron or of manganese, especially of the latter.

Utilisation of Slag.—Various means have been suggested for utilising blast-furnace slag; so far none of them have been taken advantage of to any great extent. Very excellent bricks, cement, concrete, and mortar are now made from slags, especially from those rich in lime, such as the slags from furnaces producing Bessemer pig, *i.e.* metal for subsequent treatment in the Bessemer converter. It is usual to mix some fresh lime or lime-cream with the granulated slag, say one part of the former to four or six parts of the latter, and then mould the mixture in some form of brick-making machine. By grinding the calcareous slag very fine, it may be used successfully without any addition of fresh lime. Bricks made by these methods, after having been exposed to the air for a few weeks, become as hard as stone. Highly calcareous slag has been employed to some extent in the manufacture of glass, its freedom from oxide of iron making it well suited for that purpose. For steam-packing, 'slag wool,' obtained by blowing air through the molten slag as it flows from the furnace, has been employed to some extent.

Slag wool also forms a useful filtering agent. Its want of elasticity, however, unfits it for many uses. There is one very important objection to the use of slag wool for many purposes for which it would otherwise be useful, viz. that the fine filaments are extremely brittle, and the material being very light, the needle-like particles are liable to become diffused in the air of a room, and pass into the lungs and eyes, where they would cause very serious mischief. It is perhaps most useful as a lagging for steam-boilers. Slag containing a large excess of lime falls to pieces on exposure to the atmosphere, and is therefore unsuited for the production of 'wool.' Attempts have been made to utilise blast-furnace slag for manure, on account of the large quantity of lime and potash it contains; its application to this purpose has not, however, been successful. It must be borne in mind that the lime is almost entirely in combination with silica; one might as well use bottle-glass, and expect it to improve the land.

The great cost of transport of slag, and of articles made from it, is the principal cause of the failure of attempts to utilise this waste product. Ironmasters would be only too glad to let anybody have it for nothing, on their undertaking to remove it from the works. Many millions of tons of slag are produced in this country annually.

The Pig-iron from the Blast-furnace.—For the sake of convenience, the carburised iron produced in the blast-furnace has hitherto been spoken of as cast iron. In practice, this term is only applied to the product of the blast-furnace after it has been re-melted, and *cast* in a foundry. Carburised iron which has not undergone this treatment is known as *pig-iron*, or in works as *pig*. Iron which has been smelted from ore alone is termed *all-mine pig* to distinguish it from *cinder-pig*, in the production of which a proportion of the rich ferruginous slag from the puddling—or other iron—furnace is introduced into the burden.

In the case of furnaces making hæmatite iron for conversion into Bessemer steel on the spot, the metal is now often tapped into a large ladle, supported on a carriage drawn by a small engine, and taken straight to the *converter*, to be treated whilst in a molten condition; or it is conveyed to a pig-mixer into which it is emptied, and where it is united with metal tapped from other furnaces. This ladle, as it forms part of the Bessemer plant, rather than that of the blast-furnace, will be described later on. When the metal is not required for immediate use in the liquid form, it is tapped out of the furnace into moulds made in a bed of sand, forming what are known as *pigs* of metal. The moulds are formed by pressing long billets of wood, **D**-shape in section, into the sand. They are arranged in parallel rows, each furrow being connected at one end with a main channel, called the *sow*, by which the metal is fed to them from the furnace. When the metal has cooled to a certain point, the pigs are easily detached from the sow by prising them up with a long iron bar. The pigs of metal are about 3 ft. long and 4 in. in section, and weigh about 1 to 1½ cwt. For particular purposes the metal may be cast in iron moulds; this is less common than it used to be.

From what has been said so far, it will have been gathered that the iron produced in a modern blast-furnace contains more or less carbon, nearly all the phosphorus originally in the ore, and a certain proportion of sulphur derived from the ore, and fuel. Besides the foregoing substances, pig-iron always contains more or less silicon, which has been reduced from silica at a high temperature, by carbon or carbonic oxide, and entered into combination with the iron. The higher the temperature employed, and the greater the proportion of fuel to burden, the more silicon will there be in the pig. The taking up of silicon by pig-iron is also greatly aided by the presence of a considerable quantity of alumina in the charge, as well as by the presence of alkaline silicates and an acid slag.

Ordinary pig-iron contains up to about 2 or 3 per cent. of silicon. The presence of silicon reduces the amount of carbon that molten iron can take up, and also tends, in moderate amounts, to decompose any combination that may exist of carbon with iron. For this reason the addition of silicon, or of a very silicious iron, to fused pig-iron may cause an immediate separation of carbon which floats to the top of the fluid metal in the form known as *kish*, whilst nearly the whole of the residual carbon will be found as graphite in the solidified metal. A silicious pig-iron is therefore usually grey. Besides this the silicon may exert a specific effect on the iron.

A soft foundry iron with the maximum tensile and compressive strength is obtained when there is about 1·4 per cent. of silicon in the cast metal. Silicon pig (or *ferro-silicon*) and *silicon-spiegel* are now made in considerable quantities for foundry purposes, both for cast-iron and for Bessemer and Siemens cast-steel. Although iron can without difficulty be made to combine with at least 30 per cent. of silicon in a crucible, it is not considered economical in blast-furnace practice to produce a pig with more than from 10 to 15 per cent., although sometimes pig containing as much as 17 per cent. is made. Such pig would contain, usually, up to about 2·5 per cent. of manganese, and less than that amount of carbon, and occasionally, when required for special purpose, 1·7 per cent. of phosphorus. In silico-spiegel there would be about 20 per cent. of manganese. The quantity of fuel required in blast-furnaces producing these materials is very great; in the case of the highest silicon metals it may be as high as two to three tons per ton of metal, and the 'make' of the furnace may be only one-tenth that of ordinary pig-iron.

Other substances (*e.g.* magnesium, calcium, copper, arsenic, cobalt, nickel, titanium, vanadium) may occur in pig-iron in small quantity; their influence in the quantities in which they would be likely to occur normally so far as is known is not of sufficient importance to warrant any special reference to them in this work.

Manganese is also a common constituent of pig-iron, in greater or less quantity according to the ore used and the conditions in the furnace. Manganese has been made to replace iron in pig-iron to the extent of 85 per cent. or more. Pig-iron containing from about 5 to about 20 per cent. of manganese is known as *spiegel-eisen*; with a greater percentage of manganese it is called ferro-manganese. These two alloys are now largely manufactured for use in the Bessemer and the Siemens processes.

With small amounts of manganese, beginning with about 7 per cent., the alloy crystallises with large brilliant facets: hence the name spiegel-eisen; the crystalline structure, after a certain point, becomes smaller with each increase in the percentage of manganese, finally becoming very fine grained. Ferro-manganese, at first, was made by smelting together carbonate of manganese and a small quantity of pig-iron in a Siemens furnace. Since the introduction of very rich manganiferous ore from the South of Spain, the conditions favourable to the production of ferro-manganese in blast-furnaces have been carefully studied, and all difficulties surmounted, so that now alloys containing 70 to 85 per cent. can easily be produced in this manner. There is no difficulty in reducing the whole of the manganese from an ore, but in practice it is found impossible, in that case, to work the furnace so as to produce a good spiegel, for, if all the manganese be reduced, the slag becomes 'dry' and infusible, unless a much larger quantity of fuel be used, in which case the metal would become grey, and useless for the purposes for which it is required. By adjusting the burden so as to have rather less lime than would form a basic silicate with the silica, and regulating the proportion of fuel, just sufficient oxide of manganese can be allowed to pass into the slag to render it liquid. The slag should be green and vitreous. There is a decided advantage in introducing the blast at high temperature and pressure. A greater quantity of coke is required than in making ordinary pig, the reduction requiring a higher temperature. The 'make' of a furnace is therefore very considerably less when working on rich manganese ore than when making ordinary grades of pig-iron.

Chromium pig-iron can be made in the blast-furnace by the use of chrome iron ore. With 10 per cent. the alloy is white and brittle, the fracture being close grained and irregular. With 16 per cent. of chromium the pig-iron may contain as much as 9 per cent. of carbon, and with 60 per cent. of chromium, even 11 per cent. of carbon may be present. Alloys of iron containing more than 40 per cent. of chromium are not usually produced in the blast-furnace, partly on account of their high fusing-point, and partly because it is not desirable to have so large a proportion of carbon as would thus be obtained in a material which is destined to be added to steel. The higher chromium alloys are therefore made in crucibles, and the carbon percentage is under better control. *Tungsten* can also be alloyed with iron in the blast-furnace by adding the mineral wolfram—a tungstate of protoxide of iron and protoxide of manganese.

Condition of the Carbon in Pig-iron.—When samples of grey cast iron are acted upon by acids (diluted sulphuric or hydrochloric) the iron is dissolved, but the black particles of carbon are left, and these are found to possess the same properties as the natural variety of carbon known as black lead or *graphite*,[1] of which pencils are made. But when white cast iron is dissolved in acids, very little black residue of carbon is left, because the greater part of the carbon is present in the state of chemical combination with the iron, and, on being treated with acid, is evolved in the liquid and gaseous forms.

The carbon, then, in pig-iron cast in the pig-beds in the ordinary way may exist in two distinct conditions, viz. the

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[1] From the Greek verb, *to write*.

uncombined, or *graphitic*, and the combined, the relative proportion of each depending mainly upon the proportions of other substances present. About 4½ per cent. is the maximum amount of carbon which iron is capable of taking up in the blast-furnace in the absence of manganese. With the maximum amount of graphite the pig exhibits a highly crystalline fracture, and on being pulverised scales of graphite can readily be separated; the colour of a fractured surface is bluish-grey; the metal has very little tenacity, breaking easily with a dead sound. As the amount of graphitic carbon decreases the grain becomes finer, the colour lighter, and the tenacity higher; but the fluidity of the metal when molten is diminished. With a still further decrease in the proportion of graphitic carbon the iron becomes mottled with dark spots on a light ground, or *vice versâ.* Below this point the iron becomes white, the greater part of the carbon then being in the combined condition. The presence of manganese enables iron to retain more carbon in combination, so that a pig-iron containing manganese may be white, although the carbon may amount to from 4½ to 5½ per cent. Nevertheless, it has been shown that iron containing as much as 16 per cent. of manganese, produced at a very high temperature, may be grey. The presence of sulphur very materially affects the colour and quality of iron. If sulphur be added to grey iron, it has the effect of throwing some of the carbon out from its state of combination. Thus, when about 3 per cent. of sulphur is melted with grey pig-iron, an extremely hard white metal is produced, some of the carbon separating in a sooty form from the molten metal, and floating up to the top. With less sulphur, say about ½ per cent., a strong mottled iron is obtained, possessing great strength. The conditions which are favourable to the production of a low grade of iron are also those which favour the retention of sulphur by the metal; on the other hand, the higher the grade the more silicon will there be present. Silicon and sulphur have evidently to some extent opposite effects. Both tend to reduce the solubility of carbon in liquid iron, and therefore to produce a pig-iron in which the percentage of total carbon is low; but silicon tends to separate the residual carbon as graphite, and so to produce a soft grey iron, whilst sulphur seems to favour its combination with iron, and thus to give rise to a white, hard, and brittle pig.

It has been observed, that in pig-iron which has been heated considerably above its fusing-point, and has therefore cooled more slowly in the mould, the carbon tends to separate in the graphitic form, whereas the same metal heated to a lower degree would, on cooling, retain more carbon in the combined condition. Two furnaces might be making from the same ore metal containing exactly the same total amount of carbon, yet the quality of the product in the two cases might be very different, owing to variation in the conditions of the carbon and iron, in consequence of the temperature not being the same in the two cases, with the result that different proportions of silicon and sulphur pass into the iron. From what has been said regarding the working of the blast-furnace, the difficulty there is in obtaining exactly the same grade of iron from a furnace for any length of time together will be understood.

Classification and Grades of Pig-iron.—In commerce, pig-irons are classified in certain grades according to their character, and to the fracture which they exhibit. Usually the various grades are known by numbers, thus: No. 1 is the softest, greyest, and most expensive, and Nos. 2, 3, 4-foundry, 4-forge, and mottled approach successively nearer to white iron, which is the last of the series. In any given brand of iron, made from the same material, the lowest number (No. 1) will have been prepared at the highest blast-furnace temperature, and with the smallest burden of ore, so that it may be expected to contain the most silicon and the least sulphur, and therefore the highest proportion of graphite in the series. In mottled and white iron, the percentage of silicon will be low, and that of sulphur comparatively high; a large proportion of the carbon present will therefore be in the combined condition. The result of this is that, whilst No. 1 pig is very grey, soft, and weak, with a very large, open grain, No. 2 will be stronger and of finer grain, and No. 3 will be even stronger and closer; No. 4 is much harder. In a few districts the old classification of numbers 1 to 10 is adhered to; and in America the grades are as follows: Silver-grey, No. 1 soft, No. 2 soft, Nos. 1, 2, and 3 foundry, grey-forge, mottled and white. The grades higher than No. 1 are more highly silicious.

Grey iron passes directly from the solid to the liquid state on being heated; but white iron, not containing manganese or much phosphorus, becomes pasty before liquefying. The difference in the condition and amount of the carbon is the cause of this. The higher the grade of iron the more malleable will the metal be; the most highly carburised grey pig may be considered to consist, practically, of a mixture of malleable iron and scales of graphite, for by crushing the pig, and levigating it with water, the graphite can be separated in a pure condition from the iron.

Since in grey cast iron a smaller proportion of the iron is in combination with carbon, and more of it in the true metallic state, this variety would be expected to exhibit more of the properties of metallic iron, whilst white iron ought to present the characters of the chemical compound of carbon with iron, described above. Accordingly, grey cast iron is much softer than white iron, and admits of being filed and turned; whereas white iron is so extremely hard that a file will not touch it, and a blow from a hammer, which indents a pig of grey iron, will break up one of white iron. The amount of combined carbon in the intermediate grades may correspond to that in steel; and the graphite plates are fewer and smaller than in very grey iron. For these reasons these metals are stronger. The larger proportion of metallic iron contained in grey cast iron causes it to require a higher degree of heat before it begins to exhibit signs of fusion, but it is capable of becoming very liquid at a sufficiently high temperature, so as to be easily run into moulds; white cast iron, on the other hand, is softened at a rather lower temperature, but does not flow well, assuming a somewhat viscid or pasty consistence. It *scintillates*, or throws off sparks or *jumpers*, as it runs from the furnace, to a much greater extent than grey iron. White cast iron is about $\frac{1}{20}$ heavier than the grey variety, its average specific gravity being 7·5, whilst that of grey iron is 7·1. Grey iron rusts more easily in air, and is more readily acted on by acids, than white iron, which may be ascribed partly to its containing more iron in an uncombined form, and partly to the acceleration of chemical action caused by the voltaic disturbance excited by the contact of the particles of graphite with the particles of iron, in the presence of an acid (in the case of air, carbonic acid). The properties of the irons lying between No. 1 and white iron correspond to the positions of their respective grades in the scale of classification.

Manganiferous and phosphoriferous pig-irons become fluid more easily than ordinary white iron, and do not pass through the pasty stage.

The effect of phosphorus in pig-iron being to render it more fluid, this is taken advantage of in selecting metal suitable for making fine castings. It may be observed, that although the effect of phosphorus is somewhat to lessen the actual strength of cast iron, yet the ultimate strength of a casting, as a whole, may be increased by its presence, owing to the ease with which the metal takes the shape of the mould, and the greater soundness of the casting. The object which a founder has to keep in view is to use the cheapest metal consistent with obtaining in the casting the properties requisite for the purpose for which it is to be employed. This he does by keeping in stock a certain number of pig-irons of different but known grades, which his experience enables him to mix in the best proportions for whatever work he may have in hand.

Structure of Pig-iron.—The rate at which cast iron is solidified affects its properties to as great an extent as differences in its chemical composition. Thus, if grey pig-iron be melted, and then rapidly solidified by cooling it in contact with a metallic surface, it may, to a greater or less depth, according to its thickness and that of the metallic surface, be converted into white iron. This treatment is known as *chilling*, the metal produced by it being termed *chilled* cast iron, and the mould a *chill*. This modification of cast iron is extremely hard, and possesses great tenacity as compared with the grey iron from which it is produced, but it is very brittle. This latter property does not, however, in practice materially interfere with the applications for which the other qualities of this metal render it particularly well suited, it being within the control of the founder to leave a greater or less depth of more or less tough grey cast iron to support that which has been chilled. This combination of chilled and ordinary grey cast iron is obtained by casting the metal in a mould having a cast-iron surface where the casting is to be chilled, the remainder of the mould being made of casting sand in the ordinary way. Very great judgment is required in selecting a metal to be cast in chill. An iron which is very grey cannot be chilled to any appreciable depth, whilst if too low a grade be used, the chilled layer will be so thick that the casting as a whole will be unduly weak. Usually the mixture is of such a character that, when cast in sand, the fracture will be slightly mottled ; the extent of the greyness or of the mottling depends upon the depth of chill required. The use of silicon as a controlling medium will be explained later. Rolls are generally cast so as to chill the surface to the depth of from half an inch to an inch. The head of large shot for artillery purposes is cast in chill to increase its penetrative power.

The rate of cooling modifies the properties of cast iron in another way, less within control. The more gradually the metal is allowed to cool on solidifying, the larger will be the crystalline structure developed, *i.e.* the coarser the grain ; from which it follows that the metal near the surface of a casting will be much finer in grain than that at the centre.

In castings of small thickness this is a matter of but little moment, the cooling of the whole taking place with sufficient rapidity to ensure the difference in grain between the centre and the circumference being too slight to be of consequence. In large castings, where, owing to the thickness and the mass of metal, the centre must of necessity cool slowly, the effect of the difference in the crystalline structure is of considerable importance, as it materially affects the strength of the casting. Large solid castings in which great strength is required are now usually made in steel, cast iron being reserved for such purposes as light columns, which are made hollow, and pieces of machinery, which either have not to bear much strain or have not so great a thickness as to cause the grain to vary much.

There is another point in connection with the making of castings which does not generally receive the attention its importance deserves. When any substance crystallises, the crystallisation always takes place at right angles to the surfaces at which cooling takes place ; in other words, the crystals will be formed so that their principal axes will be at right angles to the surfaces bounding the mass. The forms in which iron tends to crystallise are the cube and the regular octahedron : an eight-sided figure, with equal axes at right angles to one another, a figure which may be represented by two square pyramids placed base to base. The importance of this subject in practice may best be shown by a few examples. If a square bar be cast, and cooled uniformly in all directions, there will of necessity be regions in which the crystallisation, proceeding uniformly from all sides, will meet. Along these planes of intersection (fig. 44) there will be confused crystallisation, and lines of weakness in the casting will result. In a long rectangular bar the lines of weakness will be as shown in fig. 47. Now let us observe what takes place in a round cast bar (fig. 46). There are no lines of weakness. It is possible, then, by care in design to avoid many evils which might otherwise occur through ignorance of the laws of crystallisation. In fig. 43 is represented a part of the lower portion of the first hydraulic cylinder made for raising the tubes of the Britannia Bridge. It broke under the great pressure to which it was subjected, the sides giving way along the planes of confused crystallisation, as in fig. 48. A new cylinder was then made, the design being altered to that shown in fig. 45. This answered perfectly, although the same kind of metal was used, and no increase of mass was made. This points to the simple conclusion that abrupt changes of form should be avoided.

The foregoing considerations apply equally when a mass of metal, which has been cooled without very marked crystallisation having taken place, is subjected to such conditions as will enable the ultimate particles of the metal to rearrange themselves, as when the metal is heated beyond a certain point, more particularly if, at the same time, it be subjected to vibratory motion.

Remelting of Cast-Iron in the Foundry.—In order to melt the pig-iron for the production of castings, a *cupola furnace* is employed. The construction of this furnace varies in different foundries, but it is now commonly made of the form represented in fig. 49, being cased with thick iron plates strongly riveted together, and protected internally by a layer of binding sand about nine inches thick. A ring of twyers is arranged in the lower part of the cupola, as in the blast-furnace ; or, occasionally, at different heights up the sides of the furnace there are openings (G) for the introduction of blast-pipes, two or three of which

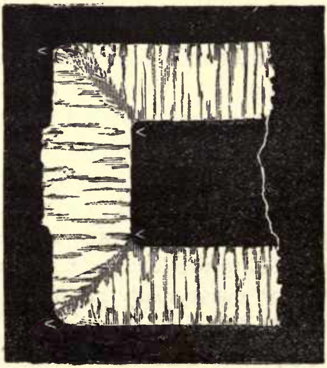

FIG. 43

FIG. 44.

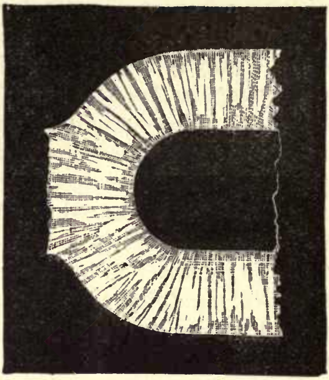

FIG. 45.

FIG. 46.

FIG. 47.

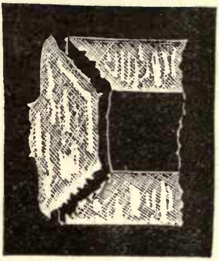

FIG. 48.

are employed at one time, the remaining openings being closed by iron doors. The cupola furnace is often about 9 ft. high, and $3\frac{1}{2}$ ft. in diameter, clear of the lining. The bottom is made to slope a little towards the gutter (E) by which the melted iron is run out. A conical iron hood (D) surmounts the furnace, connecting it with the chimney, and having an opening for introducing the metal and fuel. In some modern forms of cupola, the metal as it melts flows from the bed of the cupola through a closed channel into a separate chamber, placed at a slightly lower level, and known as a *fore-hearth.* In this it collects until sufficient has accumulated for the purpose required, when it is discharged through a tap-hole similar to that of the ordinary cupola. A current of hot reducing gas constantly passes from the cupola with the iron; and the gases, after traversing the fore-hearth, are returned through a separate small flue to the upper part of the cupola. A cupola of this type is illustrated in the Appendix. The blast is usually supplied by means of a fan worked by steam power. A wood fire is first lighted in the cupola, through the tap-hole, then a quantity of coke having been thrown in, and well ignited by the blast, the tap-hole is closed, and the pig-iron introduced in pieces of about 28 lb. each, together with one-fourth of its weight of coke.

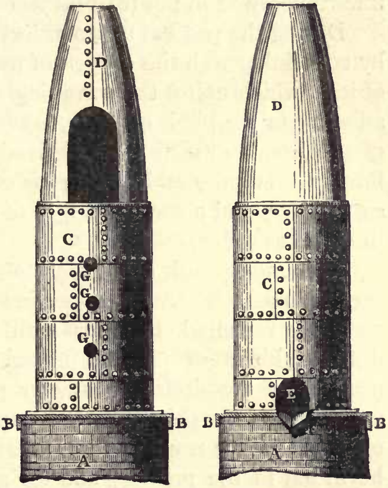

FIG. 49.—Front and Back Views of Cupola Furnace. A, Foundation of Masonry covered with Iron Plate B. (See also Appendix.)

A fresh charge is introduced about every quarter of an hour, until the whole of the iron is melted, when the tap-hole is unstopped, and the metal run, either into moulds sunk into the floor upon which the furnace stands, or into a casting-ladle, whence it is transferred to the moulds. The cupola is usually run for several hours continuously; a small ladleful of metal is withdrawn from time to time as required, and the tap-hole is then replugged with clay. Meanwhile the charging with pig-iron, coke, and flux is carried on uninterruptedly as in the blast-furnace.

During the process of remelting, a little iron is wasted by combining with the oxygen of the air to form an oxide of iron, which unites to form a slag with silica from the sand adhering to the pig-iron, with that from the silicon burnt out of the iron, and with some derived from the lining of the furnace. It is desirable to employ coke as free from sulphur as possible, and a small quantity of lime is introduced, with the iron, as a flux.

In foundry work one brand of iron is rarely, if ever, used alone. A large proportion of suitable scrap is generally remelted, together with variable proportions of different kinds of pig-iron mixed in such a way that a material of the desired character may be obtained. The nett effect of remelting iron in a cupola may be regarded as oxidising. The result of this is that a part of the silicon is burnt out in the process, and the grade of the metal that is run out is slightly lower than that of the iron charged. If the iron were very grey originally, the remelted metal would be stronger, but if a low grade pig were charged, the resulting iron might be mottled or white, and therefore weaker. To keep up the grade, a small proportion of a very soft or silicious (No. 1) iron is added to the charge. Scrap-iron, especially if any of it be oxidised or burned, has a special tendency to remove silicon, by reason of the oxide that it contains, and demands the use of a larger proportion of silicon than would otherwise be necessary.

In extreme cases a little *ferro-silicon* may be employed with advantage.

The mixture required is usually judged from the appearance of the fractures of the irons employed ; but it may generally be controlled more accurately by chemical analysis. Delicate castings of no great strength are best made of an extremely grey iron. Ordinary castings must be stronger and should have a finer grain ; they should therefore contain less silicon and more combined carbon, and are of a lower grade. For chill casting the amount of silicon must be watched carefully ; because an excess causes too much of the carbon to assume the graphitic form, and therefore tends to oppose chilling. On the other hand, given a material which chills to a certain depth, that depth may be increased or diminished by using less or more silicon in the mixture, and the change in the depth of chill is under these circumstances almost exactly proportional to the variation in the percentage of silicon.

In the following table is included a statement of the compositions which Turner has found to be most suitable for the various purposes indicated, and also of those which are preferred in the most recent practice in some parts of America.

	Turner's Iron, to resist			For General Strength (Turner)	American Practice ; for General Strength
	Tensile Stress	Crushing Stress	Transverse Stress		
	per cent.	per cent.	per cent.	per cent.	per cent.
Carbon, graphitic	2·9	2·4	2·7	2·9	2·75 to 3·52
,, combined	0·5	1·0	0·7	0·5	0·25 ,, 0·75
Silicon	1·8	0·8	1·4	1·4	2·5 ,, 3·75
Phosphorus	0·3	0·3	0·3	0·3	0·4 ,, 0·8
Sulphur	0·13	0·2	0·15	0·14	under 0·06
Manganese	0·3	0·5	0·4	0·4	0·3 to 0·7

Malleable Cast-Iron.—The possibility of producing a comparatively soft, tough, and yet strong material by heating white cast-iron for several days to a moderate red heat in chambers packed with hæmatite has long been known, but it is only within the past few years that malleable castings have been in great demand. Now, spanners, nails and many small tools, as well as parts of machinery and bicycles, are made by this process, which has the advantage that pieces of intricate shape, such as would be costly to make by forging, may be cast in moulds to the required shape, and then rendered sufficiently malleable for use. The iron employed is always white, and contains practically the whole of its carbon in the combined form ; it should be as free as possible from impurities.

The process was formerly supposed to depend only upon the removal of carbon from the iron through oxidation by contact with oxygen or carbonic acid, the atmosphere around the metal being maintained in an oxidising condition by the hæmatite which is present in excess. Although it is true that some oxidation usually occurs, and a portion of the carbon is removed superficially, and to a depth dependent upon the conditions of the experiment, very small articles frequently being quite decarburised, yet other materials, non-oxidising in character, such as bone ash, sand, and even charcoal, have been substituted for the hæmatite with success. The oxidation does not appear, therefore, to be absolutely necessary, and the explanation of the action, so far as data are at present available, is that, primarily, the compound of carbon and iron in the castings becomes gradually broken up at the high temperature employed, the carbon being deposited in the form of exceedingly minute grains of graphite, disseminated through the whole mass ; and, secondarily, that some of the carbon on the surface is, or may be, removed by oxidation. The material, therefore, may differ from grey iron only in the size of the graphite particles ; and its higher strength, frequently equalling that of pure weld iron, is due to the absence of the large plates of graphite which, lying in all directions in grey iron, must necessarily produce a weakening effect upon that metal. The extensibility, as might be expected, is more affected by the admixed carbon than is the strength, and while superior to that of even the softest grey iron, it is only from a quarter to a tenth that of weld iron or soft steel. For this reason thin castings, which may be required to withstand bending or twisting, are best completely decarburised.

In practice, the best iron to use is one that is only just white in the casting produced, and which would yield a very slightly mottled fracture in castings of somewhat greater thickness. Silicon, which tends to produce grey iron, must therefore be present in but small proportion. Sulphur, which helps to give a white iron, tends to retain the carbon in the combined form, and may therefore prolong the time of heating (or *annealing* as it is termed) if present in unduly large quantities. The castings are usually made of fairly uniform thickness, and are run in sand moulds. They are then packed in large iron pots, in a mixture of old hæmatite that has been used previously, with a small proportion of fresh material, both portions being present in fragments about the size of a pea. New ore used alone causes excessive oxidation or scaling of the castings, but after use it becomes partly reduced to lower oxides, and even in part to the metallic state, and there should finally be only a thin blue-black film of oxide upon the castings if they have been properly treated. The pots, filled with the mixture, are placed in a large brick chamber with a fire-place on either side, the flames from which circulate around them as in the hearth of a reverberatory furnace. In some instances the castings are packed in hæmatite directly upon the floor of the furnace, and the latter is even mounted occasionally upon car-wheels, so that no time may be lost through unpacking between successive heats. After the lapse of about a day, the temperature should be sufficiently high—a moderate red heat—and it is maintained at this for from two to four days according to circumstances, and the fire is then allowed to burn out, when the pots may be removed and unpacked. The castings after cleaning should be ready for use. The largest castings are heated for the longest period. In some cases gas or oil is used as a heating agent, in place of solid fuel.

Production of Malleable Iron and Steel from Pig-Iron. The production of malleable iron in the blast-furnace depended, we have seen, not merely on the power of carbon to deprive the iron ore of its oxygen, but mainly on the decarburising action of oxide of iron. It is absolutely impossible in the blast-furnace to prevent the partially reduced ore from becoming more or less charged with carbon, owing to its power to decompose carbonic oxide. The only way to get over the difficulty is to leave sufficient ore unreduced, and then to heat the mixture, by which means both the carbon and the oxygen are removed in combination with one another.

Since, at a red heat, oxygen and carbon have a greater affinity for one another than have iron and carbon, or iron and oxygen, it follows that if oxygen, either combined with iron, or in the free state as it exists in the air, be brought into contact with pig-iron in a molten state, the carbon will be removed from the latter. When pig-iron became the principal product of the blast-furnace, the fact that it could be decarburised by means of atmospheric air was soon discovered.

The process was carried out in a 'bloomery'—a term derived from the Saxon *bloma*, a lump, having reference to the *bloom*, or lump, of iron resulting from the operation. The term *finery* has also been applied to this furnace. It consists essentially of a shallow rectangular hearth, lined with iron plates 2 or 3 in. thick, protected on the inner side by a layer of 'brasque,' made of charcoal dust. There are one or more holes in the front plate, through which to tap out the slag. Several twyers were sometimes used, more commonly only one, the inclination of which was varied from about 5° to 16°, according to the nature of the pig being treated. The depth of the hearth measured from the nozzle of the twyer, varied between 6 and 10 in. in different localities, depending on the kind of pig-iron and fuel. Various improvements were made in course of time, such as the substitution of an iron bottom, cooled by water circulated through it, for a stone bottom, or one formed of cinder or small coal beaten down. The furnace in later times was enclosed, and the waste gases utilised for heating up the pig-iron ready for the next charge, thus economising time and saving fuel. Lastly, the blast was heated. This, however, was not done until about fifty years ago, and then only in a few localities. With slight modifications in working, this process is known sometimes as the *Lancashire*, or the *Charcoal-hearth* process, and sometimes as the *Walloon* process. One of these is still largely employed in Sweden for the manufacture of the high-class iron used in the cementation method of steel manufacture.

Supposing the furnace to be hot and in order, charcoal is thrown into the hearth, and on it pieces of iron, 2 or 3 in. thick, which are covered with more charcoal, and the blast is then let on. The metal slowly melts down, and as it drops to the bottom of the hearth it passes through the blast proceeding from the twyer, the result being that the silicon in the pig is more or less oxidised to silica, the carbon to carbonic acid, and a little of the iron to oxide of iron. The oxide of iron combines with the silica—besides that derived from the silicon in the iron, a good deal is introduced adhering mechanically to the pigs, in consequence of their being cast in sand—the liquid slag thus formed dissolves a further quantity of oxide, and being intimately mixed with the carburised iron, reacts upon it, removing the carbon. Rich oxide, remaining in the hearth from the previous operation, is also pressed into service. The now pasty mass is constantly broken up, the oxidising slag is pressed into contact with it, and it is lifted in front of the twyer, in order to expose the still unfined portion, or 'raw' iron, to the action of the blast. When the metal is considered sufficiently fined, it is removed from the hearth in the form of a spongy mass, or *ball*, charged with slag. Being still at a white heat, it is placed under the hammer, by which means the slag is squeezed out, and the iron welded into a rectangular slab or bloom. The operation requires in all about one hour and a half. The slag, which contains 70 to 80 per cent. of protoxide of iron, is returned to the finery. The bloom is subsequently reheated, and drawn out under the hammer into a bar.

White pig-iron is better suited than grey for conversion into malleable iron, owing to its becoming pasty, in which condition it can be thoroughly incorporated with the cinder rich in oxide of iron. The grey iron is not so well suited, for it passes directly from the solid to the liquid state, as already explained, and the cinder then simply floats on the top, exerting only a very modified deoxidising action.

The removal of phosphorus is effected in the finery in exactly the same way that it is in the blast-furnace, when making malleable iron, by the action of excess of oxide of iron on the carburised metal. The slag, which is highly 'basic,' *i.e.* one in which the metallic oxides predominate over the silica, first effects the removal of the silicon, then the carbon, and lastly the phosphorus. It is essential that the slag should be basic, for in the presence of free silica or of an 'acid' silicate the phosphorus would not be removed from the metal, the silica having a greater affinity than phosphoric acid for oxide of iron.

The Iron Refinery.—When it is desired to make grey pig-iron into malleable iron by the finery process it is first converted into white iron by treating it in a 'refinery.' The Germans call this process 'whitening' (*weiss machen*)—a better term than refining, which is misleading, since it would imply that the product is more highly purified than that attained by fining, which is not the case.

The effect of the refinery is to remove most of the

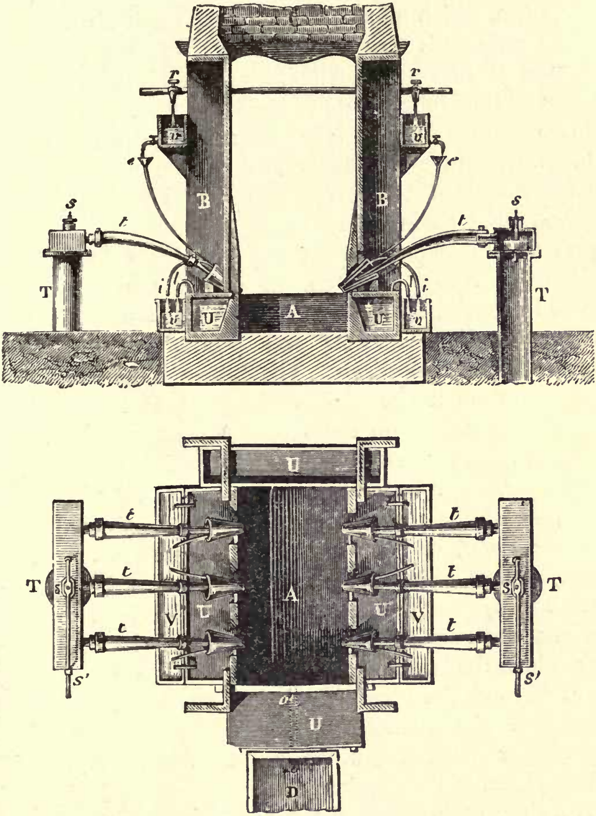

FIG. 50.—Hearth for refining Cast Iron, in section and plan. A, Hearth in which the fuel and pig-iron are placed. B, Hollow iron supports for the chimney C, which is about 18 feet high. D, Flat mould for the refined iron. *e*, Funnel-pipes for conveying water to the tuyères. *i*, Pipes for carrying off the heated water from the tuyères. *t*, Pipes for carrying off the heated water from the hollow walls U. *o*, Tap hole for running out the fine metal. *r*, Stopcocks for supplying water to the cisterns *v*. *s*, Valves for regulating the blast issuing from the pipes T.

silicon by oxidation, and thus to allow the carbon in the iron to remain combined, so that the metal is white. The extraction of the silicon facilitates the subsequent elimination of phosphorus in the finery, by removing one of the sources of the silica, which militates against dephosphorisation.

The refinery is now almost extinct, but the process is still used at Lowmoor preliminary to puddling in the production of the highest class of malleable iron. In its latest form it consists of a rectangular hearth (A), about 3 ft. long, 2 ft. wide, and 2½ ft. deep, enclosed on three sides by water-cooled iron blocks (U), and in the front by a solid cast-iron plate, having a tap-hole at the bottom of it. The twyers (*t*) are inclined at an angle of 25° to 30° to the horizontal. About 400 cb. ft. of air per minute are supplied to the hearth, at a pressure of from 1½ to 3 lb. per sq. in. The number and position of the twyers vary in different localities. The hearth is partially filled with coke; on it the pig-iron is piled, and more coke having been placed on the top, the blast is let on. In less than an hour and a half the charge melts down; it is, however, kept under the blast for about half an hour longer, according to the degree of purity of the metal. The *fine metal*, or *plate metal*, and cinder are tapped out into a shallow cast-iron mould (D), lined with loam, and kept cool by water circulated through it. The metal is thus cast into a plate about 10 ft. long, 3 ft. wide, and 2 in. thick, whilst the bulk of the slag runs off into a separate mould beyond, the remainder being easily detached from the surface of the metal. To assist the chilling, water is thrown over the metal, which can then be readily broken up into pieces of the required size.

Notwithstanding that the metal is kept covered with coke or charcoal, the process is a strongly oxidising one, owing to the inclination of the twyers and the pressure of the blast.

Practically but little phosphorus is removed in this process; a small quantity does, however, pass into the slag, although the carbon in the metal has only been reduced in quantity very slightly. The reason of this is that the proportion of silicon, carbon, and phosphorus present being very small in relation to the iron, they are too diffused to exert their individual influence throughout the mass. It thus happens that the carbon begins to oxidise before all the silicon has been removed, and, similarly, the phosphorus to some extent is affected, whilst carbon is still present. This is well shown in the case of the iron, which, though less oxidisable than either the silicon, the carbon, or the phosphorus, yet, owing to the greater surface exposed, is largely oxidised before these other bodies are removed. They are, in fact, removed by their depriving a part of the oxide of iron of its oxygen.

At the time metal made by this process was employed for making sheet iron for the best tin-plates, charcoal was used instead of coke, both in the refinery and the finery, in order to avoid introducing sulphur. The commoner plates were made from iron which had been refined with coke.

Subsequent Treatment of Finery Iron.—The metal from the finery, when intended for the best plates, undergoes a selecting process. The ball is shingled, and drawn into a bar 1½ to 2½ in. thick, which is then broken into lengths, called *stamps*, weighing about ¼ cwt. each. The stamps are carefully sorted, those which do not show a fine, bright, and uniformly crystalline grain being rejected, and returned to the finery with a subsequent charge. The selected stamps are made into a pile, reheated in a *hollow-fire*, and rolled down into sheets.

The hollow-fire consists of a deep rectangular hearth, the lowest part of which contains coke, kept at a strong heat by means of a blast from inclined twyers. The pile, supported on a *staff*—a long bar with the end flattened out—is held in the flame above the coke, so as to avoid contamination with sulphur by direct contact with the fuel.

The manufacture of charcoal- and coke-plates by this method has hitherto formed an important industry in South Wales; but it has now very generally given place to the Siemens process, by means of which plates can be produced superior in quality even to the best charcoal-plates.

Manufacture of Steel in the Finery.—By slightly modifying the process, steel can be produced in the finery instead of malleable iron, just as in the case of the Catalan forge and the primitive blast-furnaces. The method of conducting the finery process, for either iron or steel, will vary somewhat according to the kind of pig-iron and the locality in which it is practised. Each district has its own ideas as to the proper way of arriving at the best result, and besides the depth of the hearth, the slope of the sides and the inclination of the twyers have to be modified according to the character of the metal to be treated.

Broadly speaking, the chief difference between an iron finery and a steel finery is that the depth of the latter is less, and the twyer is both lower and more inclined. Steel and malleable iron are, however, sometimes produced alternately in the same hearth without difficulty.

When it is intended to make steel, the metal is not broken up after it has been melted down, but is kept covered with a layer of liquid slag. The process is conducted much more slowly, requiring about half as much time and twice as much fuel as in making malleable iron. The blast is used at lower pressure. The purest pig-iron and fuel alone should be used, as impurities affect the quality of steel much more than they do iron. This process has been largely used in Styria, Carinthia, and the Tyrol, very high-class steel being produced.

In the Siegen district a piece of pig-iron weighing from 50 lb. to 60 lb. is placed on the hearth, having been previously heated; the hearth is then three-quarters filled with burning charcoal; on it is placed a portion of the cake, which was produced in the last operation, and which has been kept hot in burning charcoal at the back of the furnace. The remainder of the hearth is then filled up with charcoal. The other six or seven pieces, into which the last cake was divided, are placed on the top. In this process the production of steel, and the reheating of that obtained in the last operation preparatory to working it under the hammer, are conducted together. The blast is turned on. The piece of pig-iron forms into a pasty mass ; cinder, rich in oxide of iron, produced in the latter part of the preceding operation, is then thrown in ; a second piece of pig-iron, weighing about 100 lb., is added, and afterwards four or five pieces of spiegel-eisen, weighing each about 100 lb., are successively added. The spiegel-eisen contains about four per cent. of manganese. If the metal be found to be too much decarburised, more spiegel is added. The cinder is usually allowed to rise 2 or 3 in. above the cake of metal, any excess being tapped off. There are several modifications of this process, but enough has been said to make the principle clear. In this, as in the Catalan process, it is impossible to obtain a homogeneous product, except in small quantity. The principle in both is essentially the same, viz. decarburisation by oxide of iron. In the finery process, in addition to the oxide added in the form of cinder, and scale produced during the working of the metal under the hammer, some is found to result from the reheating which we have seen is carried on at the same time. In this process manganese also plays an important part, and we shall see that in every process for the production of steel manganese is used with great advantage.

The Puddling Process.—All the processes which have been referred to in the foregoing pages are still in use in some parts of the world, though circumstances may have led to their being discarded in others, in which at one time they were in use. It thus happened that in England the finery process gave way to the *puddling* process. This was brought about by the increasing scarcity of wood for making charcoal. We have seen how coal, after being coked, came to be substituted for charcoal in the blast-furnaces of this country, though charcoal still holds its own where it can be obtained in sufficient quantity. In course of time, for the same reason, it was attempted to employ coal instead of charcoal in the manufacture of malleable iron. Neither coal nor coke could be used in the finery with satisfactory results, owing to the sulphur they contain. It was, therefore, sought to utilise the coal by burning it in a separate chamber, and only allowing the flame to come in contact with the metal being operated upon. In this way the sulphur in the fuel is converted into sulphurous acid gas before coming into contact with the iron, upon which it then has less action.

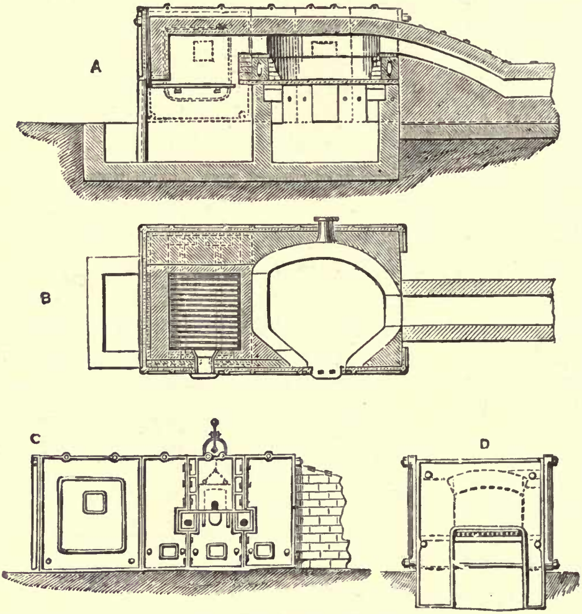

FIG. 51.—The Puddling Furnace.

The idea of manufacturing malleable iron in this way first began to take shape early in the eighteenth century; it was not, however, till towards the close of that century, about a hundred years ago, that it was actually carried into practice.

The most modern form of the furnace, in which the operation known as puddling is carried out, consists of a rectangular fire-place, a hearth or bed, and a flue connected with a stack or chimney. The hearth is separated from the fire-place and the flue by bridges, known as the fire-bridge and the flue-bridge respectively. The grate is formed by supporting wrought-iron bars on transverse bearers. The depth and area of the fire-place depends on the nature of the fuel employed, being least with highly bituminous coal, and greatest with anthracite. A dry, non-caking coal, burning with a long flame, is that to be preferred. The fuel is introduced about 10 in. above the grate through an opening which is kept closed with a few shovelfuls of coal when not in use. The bottom of the hearth is constructed of cast-iron plates, about 1½ in. thick, rabbeted together, and supported underneath by bars of wrought iron, resting on cast-iron standards, or some similar simple arrangement. The working bottom is formed by coating the iron plates with substances rich in oxide of iron, the slag produced in the furnace towards the end of the process itself, and hammer scale, *i.e.* the slag and scale squeezed out from the bloom of metal under the hammer, &c., being used for the purpose. These substances are strongly heated in the furnace, and then spread over the bed to a depth of 2 in. by means of a flat bar, or *paddle*. The hearth is enclosed by iron plates or hollow castings, backed with fire-bricks. These side plates are protected on the inner side in a similar way to the bottom. The material commonly used for lining or *fettling* varies in different districts and according to the nature of the pig-iron under treatment. *Bull-dog* obtained by roasting *tap-cinder*, the slag of the puddling furnace, is extensively used. Tap-cinder is essentially a silicate of protoxide of iron ($2\ FeO.\ SiO_2$). When this is strongly heated in the presence of air, the protoxide becomes partially converted into magnetic oxide and peroxide, which have no affinity for silica until broken up into protoxide again at a much higher temperature ; so that, instead of an easily fusible chemical compound, a mechanical mixture of two highly infusible substances is obtained. With the bull-dog is added one or more other oxides, such as hæmatite, calcined *pottery-mine* (a carbonaceous clay ironstone found in the pottery districts of Staffordshire), purple ore, and *best-tap*, which is a very pure cinder, consisting mainly of magnetic oxide, obtained from reheating furnaces constructed with a bottom of oxide of iron. The larger fragments are first thrown in, and are covered with the finer portion until all crevices are filled. Hammer slag, squeezed out of the puddled ball under the hammer, is frequently added as a flux which should melt rapidly and form a liquid bath to receive the first portions of iron that fuse from the pig. The fettling requires to be repaired after each heat, and as required the bottom is made up by throwing in about 1 cwt. of scrap iron, which is allowed to oxidise, and is then worked over the bed.

In the early puddling-furnaces sand bottoms were used. Owing to the great affinity of silica for oxide of iron, much waste of iron resulted from their use, and the elimination of phosphorus was rendered far more difficult. The introduction, at the beginning of this century, of the plan of making the bottom and sides of iron plates, and fettling in the way just described, was a great step in advance, and the weekly yield of the puddling-furnaces is said to have increased from 8 tons to 24 tons in consequence, mainly owing to the decreased wear and the greater facility for making repairs.

The fire and flue bridges are usually made hollow, so that they may be kept cool by circulating air or water through them. The sides of the hearth are sometimes also kept cool in the same way.

The working-door is generally made of fire-brick slabs, held in a cast-iron frame, suspended from a counterpoised lever, the lower edge being about 10 in. from the bed. At the bottom of the door is a notch called the *stopper-hole*, through which the tool employed in stirring or *rabbling* is introduced, in order to avoid admitting too much air, and cooling the charge by opening the door more than absolutely necessary. Immediately beneath the working-door is the tap-hole, through which the slag or tap-cinder is run out from the hearth.

The roof, which is made of fire-brick, forms a low flat arch, sloping slightly towards the flue. The sectional area of the flue varies according to the nature of the fuel employed, being greatest for highly bituminous, and least for anthracitic coal. The stack, with which the flue is connected, is usually from 30 to 50 ft. high when drawing only from one furnace, and about 20 in. square when the waste heat is not utilised for raising steam. If the stack serves more than one furnace, or the spare heat is utilised, it may be necessary to increase the height to 100 ft. or more. There is no advantage, beyond a certain point, in attempting to apply the waste heat to raising steam, as it is absolutely essential that a considerable quantity should pass up the stack, in order to create the necessary draught. The smaller the amount of heat allowed to escape, the higher must the stack be made. The draught has occasionally been assisted by closing in the underneath part of the grate, and forcing in a blast of air to increase the intensity of combustion. The regulation of the draught is effected by means of a damper placed at the top of the stack. On the proper use of the damper at different stages of the process depends, in a great measure, the success of the operation.

There are only two kinds of tools employed in ordinary puddling: the *rabble*, and the *paddle*. The former consists of an iron bar about 8 ft. long and $1\frac{1}{4}$ in. diameter, the working end being turned at right angles, and rather broader. The latter is a somewhat lighter bar, made at the end to a chisel shape. These tools are not allowed to remain in the furnace more than a few minutes, otherwise they would soften, and stick to the metal being worked. When removed they are immediately plunged into water.

The Siemens regenerative system has been applied to puddling furnaces, but the number of works where it is in use is very small.

There are two methods of conducting the puddling process : the one called 'dry' puddling, the other 'pig-boiling.' The former is the original process, the latter being that almost universally employed. For dry puddling, the iron must be white, or have been previously refined, so that on heating it may become pasty, and the oxide formed by exposure to the action of the air can then be incorporated with the metal, by which means the carbon, &c., are oxidised. The metal, which is never allowed to become fluid, is constantly broken up, and the oxide of iron worked in with it. When sand bottoms were given up, this method of puddling was performed on an iron bottom, thinly coated with cinder. There is less waste of metal and a smaller consumption of fuel in this process than in the boiling, but the quality of the iron produced from the same class of pig (excepting the best) such as Lowmoor, which containing but little silicon and phosphorus requires no fettling, would not be so good, the conditions of the operation not being so favourable to the removal of phosphorus and sulphur.

In pig-boiling, grey iron is used, forming a fluid bath, covered with a layer of slag, which protects it from the action of the air, and the decarburisation of the metal is therefore effected, practically, entirely by means of oxide of iron derived from the fettling, and from scale forming part of the charge. The only occasions when the air plays any part in the decarburising are during the melting down of the pigs, and after the metal has given up most of its carbon, when it becomes thick and pasty, and is said to 'come to nature.'

The charge of pig and hammer-slag, &c., having been thrown into the furnace, the damper is raised, and if a blast is employed, it is turned on. In about thirty minutes the metal has gradually melted down, and become covered with a thin layer of cinder. The temperature of the furnace is now sufficient to fuse the hammer-slag, which, by reason of its lower specific gravity, rises slowly through the metal, exerting a powerful decarburising effect. The charge is maintained for a few minutes longer at a high temperature, the rabble being well used, so as to complete the oxidation and removal of the silicon, which should have been effected mainly during the melting stage. The damper is now shut down, the blast turned off, and intimate contact between the molten oxide and the metal is promoted by stirring the charge with the rabble, worked with short quick strokes. It is advantageous to check the rise of the temperature at this point, otherwise the charge would become too liquid, and the cinder rise rapidly through the metal without exerting its full decarburising power. In about forty minutes from the commencement violent action sets in, the surface of the molten mass presenting the appearance of boiling, being agitated by the escape of carbonic oxide, formed by the union of the oxygen from the cinder with the carbon of the pig. The gas as it issues burns in small jets, known in the forges as puddlers' candles, having the characteristic blue colour of carbonic oxide undergoing combustion. During this stage, which lasts about a quarter of an hour, the metal, which has been rabbled vigorously all the time by the puddler, becomes less and less fluid, and ultimately, when the carbon has been reduced to about 1 per cent., becomes infusible at the temperature of the furnace, when it is said to have 'come to nature.' The temperature is now raised, and the pasty mass of metal and slag broken up repeatedly. When the puddler considers the iron to have been brought to a satisfactory condition, he reduces the temperature, and works the contents of the furnace up into balls of about 80 lb. weight, which are raised to a welding heat, and then taken from the furnace straight to the squeezer or hammer, where the spongy metal is consolidated into a slab or bloom, the cinder being squeezed out. This operation is termed shingling or nobbling. The puddled iron is never perfectly freed from carbon, the quantity remaining in varying up to about 0·25 per cent. To convert the charge of pig-iron into malleable iron by this process takes about one hour and a half, more or less, according to the character of the pig. Each complete operation is termed a *heat.* When pig containing an appreciable quantity of sulphur is being used, some manganese ore in the fettling is beneficial.

Phosphorus is, to a large extent, removed with the silicon and manganese in the melting period, but chiefly, perhaps, in the earlier stages of the boil. In puddling impure pig, it is, in some places, customary to cause a very sharp boil at first, so that a part of the impure cinder produced up to this point may overflow over the fore-plate and thus be carried out of the furnace. This slag is known as 'boilings,' to distinguish it from the tap-cinder removed through the tap-hole at the end of the operation.

The working of an impure pig-iron frequently affords a yield of puddled iron greater than the weight of pig employed owing to the fact that the removal of the impurities is effected by their combining with the oxygen contained in oxide of iron, and thus reducing metal from the melted cinder and adding it to the iron of the charge. The slag in turn takes up oxide of iron from the fettling.

In a few places double furnaces worked from both sides, and twice the size of the ordinary furnace, have been employed, but have not met with much favour. In Belgium, experiments, which so far (1896) have proved successful under the conditions obtaining there, have been made in the direction of connecting puddling furnaces with a reservoir communicating with a blast-furnace, and running the metal in the liquid state direct on to the hearth of the former. This is to some extent a revival, under new conditions, of experiments which have from various causes proved unsuccessful in England.

Subsequent Treatment of Puddled Iron.—Where the manufacture of iron is carried on in accordance with the most modern practice, steam-hammers alone are employed, the use of squeezers and tilt- and helve-hammers being mainly confined to countries in which less progress has been made. Nevertheless, there are many helves and squeezers in constant operation in England. In the helve, a hammer-head is placed at the end of a horizontal lever, the fulcrum of which is at the opposite end. By the action of a rotating cam, the hammer is raised at regular intervals to an uniform height, and, being then released, is allowed to fall by its own weight upon the mass of iron, which rests upon an anvil block beneath it. When not in use the hammer is supported by a temporary prop beyond the reach of the cam. The squeezers are generally rotary, the ball of iron being passed mechanically through a diminishing space, so that it is drawn out into a rough bar or billet, and loses most of its cinder during the compression. In single-acting hammers the steam is only employed to lift the head, which is then allowed to fall by its own weight. In double-acting hammers the steam is admitted alternately on each side of the piston, thus increasing the force of the blow which the hammer is capable of striking. These hammers have a great advantage over the old-fashioned helve- and tilt-hammers, inasmuch as the force of the blow can be accurately regulated by checking the exit of the exhaust steam, and can be increased, or decreased, from moment to moment at the will of the operator Thus, in treating a puddled ball, the blows at first should be light, and gradually increase in force as the mass consolidates. If heavy blows were applied at first the ball would break to pieces, whilst later on light blows would be equally objectionable, since they would fail to effect the object of the operation, viz. to render the metal as homogeneous as practicable, by squeezing out as much of the slag as possible. These hammers are made of all sizes, according to the nature of the work; hammers varying in weight from 30 cwt. up to 80 tons, and having a drop of 16 feet, have been employed. Steam is not generally used above the piston in hammers weighing more than 12 to 15 tons. Obviously the helve delivers blows which become heavier as the ball is flattened, because the head, being raised to a constant height, falls through an increasing distance as the iron becomes thinner; but the rate of increase is beyond control.

The shingled bloom, being still at a high temperature, is passed to the puddle-rolls, technically called the *forge-train*, which consists of two pairs of

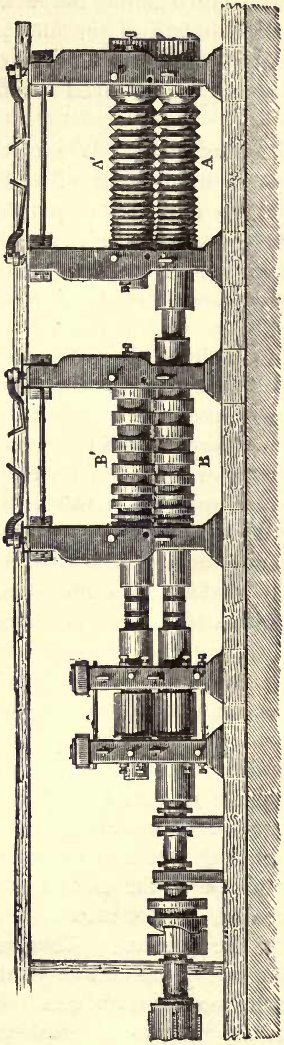

FIG. 52.—Forge-train, or Puddling Rolls.

rolls, the one (A A′), for *roughing down*, the other (B B′), for finishing. The roughing-rolls have on their surface angular grooves, which gradually diminish in depth from one end of the series to the other. The grooves in the finishing-rolls are rectangular, and also form a diminishing series. After passing through each groove the slab or bar is lifted on to the top roll, which, as it revolves, carries it back into position to pass through the next. In order to prevent the delay thus occasioned, either reversing engines or three-high rolls (fig. 53) are now frequently used, so that the metal is passed through the rolls first in one direction and then in the other, alternately. After it has passed once through the series of grooves in the roughing and finishing rolls, it is classed as No. 1 iron, or puddled bar. It will readily be understood that the iron thus produced will be far from homogeneous, being more impure in some parts than in others, and containing more or less

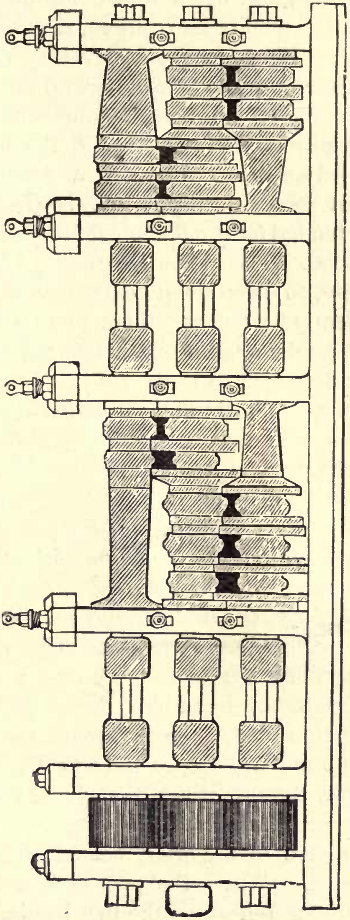

FIG. 53.—Train of Three-high Mill-rolls.

mechanically admixed slag. In order to obtain a better class of iron, the No. 1 bar is cut into lengths, *piled*, reheated, and again rolled, forming No. 2 iron, which, if a better quality be required, may be similarly treated, one or more times, to produce No. 3, or a higher quality. The shape of the pile will depend on whether bars, rails, angle-pieces, &c., are being manufactured. Sometimes a different quality of iron is placed in the interior of the pile to that used for the exterior. Thus a metal of high tensile strength, but somewhat brittle, may be placed in the centre of a pile intended for a rail, the exterior being composed of a tougher metal. The pieces composing a pile are tied together with wire, to keep them together until they have become sufficiently heated to adhere to one another. Very frequently the welding of a pile is effected partly under the hammer, and completed in the rolls ; or the pile, before going to the rolls, is put through a blooming-mill, consisting of a set of two pairs of horizontal rolls, with a pair of vertical-grooved rolls running between them. The rolling to which puddled bar is subjected after reheating is conducted in another train of rolls termed the *mill-rolls*, which are placed in the *mill*, and are capable of giving higher finish to the bar than is possible with the forge-train which works in connection with the *forge*, or puddling and shingling shops.

Reheating Furnaces.—The *reheating* or *mill furnace*, in which the piles are brought to welding-heat, in general appearance resembles the puddling-furnace, with the exception that the grate is smaller in proportion to the hearth, and the bed slopes towards the flue, where there is a tap-hole, through which the cinder (*flue-cinder*, or *mill-cinder*) formed during the reheating runs off. The bottom is constructed of fire-brick, coated with sand, rammed in while moist. When the pile cannot be rolled straight down without reheating, the first heating is sometimes given on a ‘dry’ bed of oxide of iron, to lessen the waste ; but, in any case, before the completion of the rolling of the bar or rail, it must receive a 'wash' heat, *i.e.* must be heated on a sand bed, in order that any oxide of iron may be dissolved out, leaving clean metallic surfaces, without which the pieces of which the whole is built up could not be properly welded together. For the same reason a blacksmith, when welding two pieces of iron, sprinkles sand over the surfaces to be united. The sand forms a fluid silicate ($2FeO. SiO_2$) with the oxide on the surfaces of the metal, protecting them from the further action of the air and being easily squeezed out when the two pieces are pressed together. Thus true metallic contact is produced, a condition which is absolutely essential to a good weld.

Reheating-furnaces, worked with gas on the Siemens system, with or without regenerators, are largely used ; and in several works the newer form of Siemens furnace described on p. 81 is being employed.

During the reheating, every precaution possible should be taken to exclude air from the hearth, the doors being well closed, in order to minimise oxidation.

Mechanical Puddling.—The labour involved in ordinary puddling is very great, requiring considerable physical strength and power of endurance. Many attempts have been made to perform the work of the puddler by machinery, but for various reasons none of the numerous arrangements which have been tried have remained in general use. There are only a very few works at which mechanical puddling is carried on at the present time. Machine puddling may be divided into two classes :

1. In which ordinary hand-puddling is imitated, the machine doing the greater part of the work, under the guidance of the puddler, who finishes the heat in the usual way by hand.

2. In which manual labour is dispensed with altogether, the ordinary process being reversed, rotary motion being imparted to the furnace, thereby bringing the charge to 'nature' without the aid of tools.

Fig. 54 will sufficiently indicate the nature of the appliances referred to under head No. 1. The cut is a cross-section of the furnace. It will be observed that the furnace is worked from both sides; in other respects it does not materially differ from an ordinary puddling-furnace.

Of the machines coming under head No. 2, the first to meet with any real success was that invented by Danks (fig. 55). A large number of these machines and various modifications of it have been tried in England, but at the present time there is not one in use in this country. The furnace consisted of an iron cylinder mounted on friction rollers, and capable of being rotated by the gearing shown in fig. 56. At one end was a grate with an air blast delivered beneath the bars, and also through a horizontal row of twyers at the end.

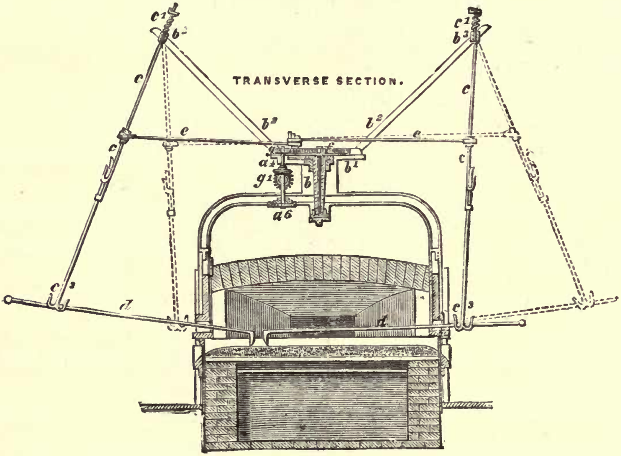

FIG. 54.—Mechanical Puddler. (Cross section through hearth).

By this means the temperature was kept under control. Opposite the grate end of the cylinder was a movable flue, communicating with the chimney and provided with a stopper-hole at the centre and a tap-hole. At the end of the operation the flue was detached to effect the withdrawal of the puddled balls. The joints at both ends of the cylinder were water-cooled.

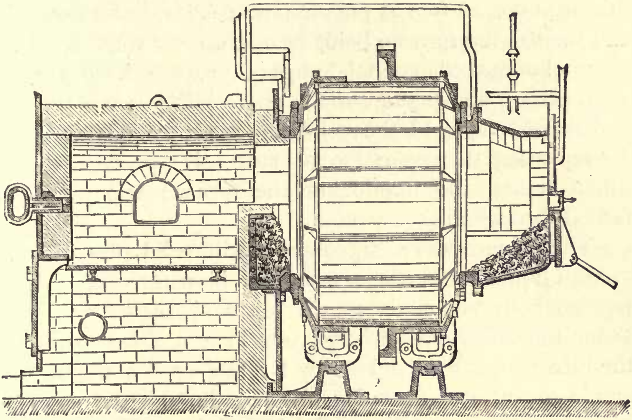

FIG. 55.—Cross section of Danks' Puddling-furnace.

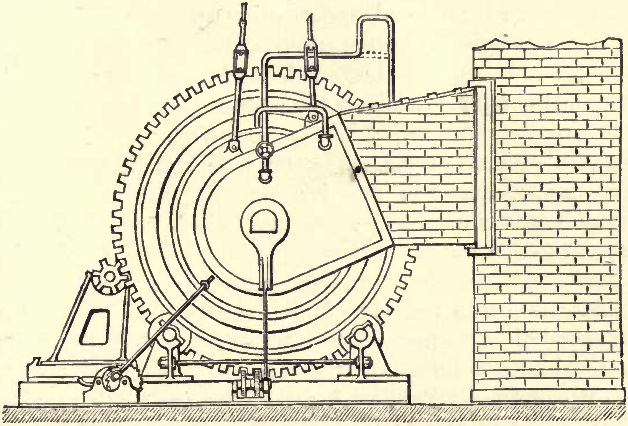

FIG. 56.—End-elevation of Danks' Puddling-furnace.

The metal casing, which had wedge-shaped recesses on the inner side, was first coated with a mixture of pulverised iron ore and cream of lime, made into a mortar, which soon set, and the furnace was then ready for fettling. To effect this, iron ore, as free as possible from silica, was thrown in and melted, the furnace being heated up and rotated. Into the pool of melted material, lumps of ore, of such dimensions as to project above the surface some inches, were thrown, and these being cold, the melted ore set and fixed the lumps. By repeating this operation on successive portions of the initial lining, the interior of the furnace was gradually fettled throughout.

The furnace was charged either with solid pigs of iron, or with liquid metal direct from the blast-furnace. About half an hour was required to melt a charge of solid pig. When the whole of the charge was in a molten condition, the furnace was revolved slowly for five or ten minutes, a gentle stream of water being injected through the stopper-hole upon the descending side of the lining, so that some of the cinder solidified, and was carried beneath the bath of metal where it remelted, and, floating up through the iron, materially assisted in decarburisation. The metal, after this period, rapidly thickened, and the cinder, made thoroughly liquid by raising the temperature, was run off by bringing the tap-hole just above the surface of the bath, and suspending the rotation. The tap-hole was then plugged, the temperature was raised again, and the furnace was rotated at about six to eight revolutions per minute, to effect the removal of the remaining impurities. Finally the speed was reduced to from three to four revolutions per minute, and with the aid of tools introduced through the stopper-hole, the spongy iron was worked into balls, which were withdrawn on a fork after removing the flue.

Production of Puddled Steel.—With one notable exception—the cementation process—the early methods for the production of steel were simply modifications of the methods for producing malleable iron. Accordingly, we find that the introduction of the puddling process, by which malleable iron is produced in a reverberatory furnace, was soon followed by a similar process for the manufacture of steel.

In order to produce steel the metal is only partially decarburised instead of being totally deprived of carbon, as in the manufacture of malleable iron. More time and labour are required to bring about anything like a satisfactory result than in making iron. There is great difficulty in determining the exact moment when steel of the required carbon-percentage has been produced, and moreover the impurities are less thoroughly removed then than when decarburisation is complete. The steel, too, being more easily fusible than malleable iron, has to be balled and welded at a lower temperature. This makes it more difficult to squeeze out the slag, which tends to thicken at the lower temperature. For this reason it is essential that manganese should form a constituent of the charge, as thereby the slag is rendered sufficiently fluid and also exerts a less decarburising action. It is very important that the slag should be removed from the spongy ball of steel as rapidly as possible. Even when charges of only 2 or 3 cwt. are worked at a time, it is practically impossible to produce a steel of uniform composition. The steel also has the drawback that it welds badly.

Early Steel-making Processes.—The same principle as that which regulates the production of steel by the foregoing methods was taken advantage of in the Uchatius process, which was patented in 1855. Pig-iron was first granulated by running it, while molten, into cold water. The granulated metal was then mixed with about 20 per cent. of roasted spathic ore, crushed fine ; the mixture, to which a little flux had been added, if necessary, was then fused in clay crucibles. If very soft steel were required, some wrought-iron scrap was added.

By all the processes we have so far reviewed good steel could be produced, but only in comparatively small quantity, and at great expense. The applications of steel were in consequence very limited; in fact, its use was practically confined to implements with a cutting edge.

Occasionally masses of steel weighing many tons were produced by melting the metal in a vast number of crucibles, the contents of which were poured simultaneously into a mould. This plan, although effective, was extremely laborious and expensive.

In 1845 Heath patented a process which, had it been successful, would have given him the power of producing steel in quantity. He proposed to melt scrap iron in a bath of molten pig-iron, in a reverberatory furnace heated by jets of gas. There were two conditions wanting in this method, which caused it to be a failure, viz. a sufficiently high temperature and the power to easily regulate the character of the gases employed. Nevertheless, in this suggestion is to be found the germ of one of the two most important processes of the present day. By the foregoing remarks it is not intended to imply that the idea of mixing wrought and cast iron together to produce steel was originated by Heath. On the contrary, as we should expect, the idea was a very old one; in 1722, Reaumur tells us that he succeeded in making good steel in a common forge in this way. It would appear, however, that Heath was the first to suggest the use of a reverberatory furnace and gas for the purpose, and that is the important point.

By the introduction, in the year 1856, of the regenerative system of heating,[1] the only remaining obstacle to the production of steel on a large scale by means of reverberatory furnaces was removed.

It is at once apparent that we have here the very conditions which were wanting to make successful the process patented by Heath in 1845, for not only have we the high temperature, which could not then be obtained, but it has become easy to create at will, by regulating the relative proportions of combustible gas and air, either a

[1] See article on 'Fuel,' p. 75.

more or less oxidising, a neutral, or even perhaps a reducing, flame.

Open-Hearth Steel-Making.—There are two methods now in use for the production of steel in the reverberatory furnace, or *open hearth*, as it is called. In France, pig-iron and scrap steel are fused together ; in England, pig-iron is decarburised by means of iron ore, some scrap, however, being generally added, for the sake of utilising it. The necessary amount of carbon is imparted to the metal at the end by means of spiegel-eisen or ferro-manganese.

This process has been largely employed for the production of ship- and boiler-plates. It has the great advantage that the metal can be kept fluid on the hearth, and its composition adjusted until it is exactly that required.

In the Siemens-Martin or pig-iron and scrap process, the percentages of carbon and silicon are decreased by the addition of soft steel scrap to the pig, but also to a large extent by the action of the air during the melting, whilst in the Siemens, or pig and ore, process the decarburisation is brought about mainly by the ore added, a part of which becomes reduced, thereby increasing the make of metal, the rest remaining in the slag.

A combination of these processes is generally employed, pig-iron, steel scrap and ore being used. The process is known as either 'acid' or 'basic,' according to the character of the hearth employed. In the former case the hearth consists of silica (sand) and is therefore acid and, as will be seen later, incapable of removing phosphorus from the charge ; in the latter case dolomite is employed.

In the acid process all the components of the charge must be practically free from phosphorus and sulphur, as neither of these elements can be eliminated. The proportions of pig-iron and scrap may be varied at will, within very wide limits, whilst the weight of ore used depends upon the amount of carbon to be removed. The actual proportions must be regulated for each charge, according to local circumstances and to the character and quantity of scrap available; but it may be generally stated that the scrap rarely exceeds 80, or is less than 20, per cent. of the whole charge, the maximum amount being used mainly when the pieces are of medium size. The furnace being hot from the previous charge, the bottom is repaired with sand wherever necessary. The metallic charge is then introduced, the scrap steel being commonly placed upon the bottom, where it is afterwards covered by the pig-iron, so that the latter, melting first, may trickle down over the less highly carburised material, and thus form an intermediate steely compound with lower fusing point than the original scrap. During the melting period superficial oxidation occurs, some carbon and much silicon and manganese, with some iron, are removed from the pig and scrap, forming a slag which floats upon the surface of the melted metal as it collects upon the hearth. The charge being melted, ore is introduced a little at a time; it dissolves in the slag and is well rabbled into contact with the fluid metal beneath, and reacting with the carbon forms carbonic oxide, which passes off through the layer of slag and thus gives to the bath an appearance of boiling. By continued introduction of ore, the proportion of carbon in the metal is commonly reduced to less than 0·1 per cent. The progress of oxidation in the bath towards the end of the boil is ascertained by removing a small sample in a ladle from time to time, hammering it flat, cooling it and breaking it across with the aid of an anvil and a heavy hammer. The character of the fracture at once gives the required information to an experienced eye. Sufficient carbon must now be restored to the bath to produce the desired grade of steel. This *recarburisation* is effected by adding to the charge the *physic*, which consists of a sufficient proportion of spiegeleisen and ferro-manganese, often mixed with ferro-silicon if the steel is to be run into castings instead of ingots. The ferro-manganese, and sometimes the ferro-silicon, may be thrown into the ladle as the metal flows into it from the furnace. A casting ladle, similar to that used in the Bessemer process (p. 264), is brought in front of the tap-hole, and a removable iron launder, or spout, lined with refractory material, serves to convey the metal from the one to the other. The tap-hole is then opened by forcing an iron rod through the stopping from without ; on the withdrawal of the rod, the metal flows freely into the ladle in a white-hot stream, and is followed by the slag which had been floating upon the bath in the furnace, and is therefore the last to arrive at the tap-hole, this being at the lowest part of the furnace bottom. The spout is at once taken away, and the slag flows into a space prepared for it in front of the furnace, that remaining in the hearth being removed with the aid of tools introduced through the working doors, which are on the opposite side of the furnace.

The casting ladle is usually mounted on a wide truck, which runs upon lines arranged above a long pit in which the moulds prepared to receive the metal are placed ; it is rapidly brought over each in succession ; a valve at the bottom of the ladle is opened, and the steel is allowed to flow out until the mould is full. By thus tapping the metal from the bottom, any slag, which may have passed out of the furnace with the steel, remains floating upon the surface of the liquid in the ladle, and cannot gain admission to the moulds until all the steel has been teemed. The residual slag is emptied into a rough sand bed by tipping the ladle sideways. The moulds for ordinary castings are made of a very refractory steel-moulder's composition, containing a large excess of sand, those for ingots are of iron, very thick, and tapering somewhat from the bottom to the top, to facilitate the removal of the ingot after solidification. As each ingot mould is filled, the surface of the fluid metal is covered with a thin iron plate, the space above this is filled with sand, and finally a heavy iron plate is firmly wedged over the top with the aid of lugs attached to two sides of the mould. This is essential when low-carbon steels are poured, because the metal on the hearth of the furnace dissolves large quantities of carbonic oxide, hydrogen, and nitrogen ; and although the bath may be well rabbled to expel the larger proportion of these gases by 'boiling' before the addition of the spiegel, yet a considerable volume remains in the charge. If the composition of the finished steel be such that these gases may remain dissolved until the moment of solidification, but no longer, the brisk evolution of gas in the midst of a pasty material will inevitably cause the metal to rise in the mould. This expulsion of gas might be so violent that much of the steel would be projected from the mould, and in any case the metal would be rendered worthless by the 'honeycombing' and blowholes that would result, if the covering process were omitted. Whitworth introduced a method of casting under pressure with the idea of preventing this escape of gas, and therefore producing sounder ingots. The mould is made of steel, and is of great strength ; when it is filled with the molten metal, a hydraulic ram is brought down upon the liquid with a pressure that may be increased, if desired, up to 20 tons per square inch, and may be maintained at any degree of intensity until the ingot is sufficiently solid. Considère, Jones, and others, with the same object in view, have applied high-pressure steam directly to the metal in a well-closed mould. When high-carbon steel, however, is properly made, all these precautions are unnecessary, the gases being retained by the metal even at the time of solidification, and the steel shows a tendency to 'pipe,' or to form a long cavity in the centre of the upper portion of the ingot. This is due to the contraction of the bulk of the metal while solidifying, for it remains fluid in the interior long after the outside portions have solidified and become rigid, by contact with the cool walls of the mould. To obviate this action, and so to reduce the size of the unsound top portion of such an ingot, which is necessarily wasted, a clay continuation of the iron wall of the mould is occasionally made ; the upper layer of metal, being unchilled, is fluid for a longer time, and 'feeds' the ingot, so that the formation of a cavity in the chilled portion is prevented. The presence of carbon in large proportion appears to favour the solubility of gases in the steel at the solidifying temperature. Silicon has a similar effect, and is therefore added to steel which is to be poured into sand-moulds that cannot be closed under pressure.

Elimination of Phosphorus in the Open-Hearth.—In speaking of the bloomery process, it was shown that a basic slag was essential to the elimination of phosphorus from the metal. On the acid hearth the slag must always be practically saturated with silica, as it rests in contact with the sand bottom. Hence no phosphorus can be removed by this process, and the materials composing the charge must be as free as possible from this element. By substituting a basic for an acid hearth, the proportion of silica in the slag may be kept under control, as it is derived mainly from the silicon in the pig and scrap, the sand adhering to the pigs, the silica in the ore, and that from the roof of the furnace, which is at present constructed of silica bricks. Basic open-hearth practice is very similar to that which has been described above, only the hearth is made of calcined dolomite or magnesian limestone (p. 103), or (rarely) of some other basic material ; the charge of pig and scrap is melted, and a quantity of lime is introduced upon the hearth before or after melting, to form the basis of the slag, so that the proportion of silica may not exceed about 20 per cent. Such a slag contains sufficient lime, magnesia, and oxide of iron to form compounds of phosphoric acid with three or with four molecules of base, which are not altered by contact with fused metallic iron. The phosphorus in the charge is thus absorbed by the slag as fast as it becomes oxidised. But if more silica were to enter the slag, it would combine with some of the base which had been previously held by the phosphoric acid, and a proportionate amount of a dibasic or monobasic phosphate would be formed (with two molecules and one molecule of base respectively), which would be attacked by the bath, so that a portion of the phosphorus would be reduced and reabsorbed by the metal. Basic slag is allowed to contain more iron than would be permitted in the acid process, because, although it involves a waste of metal, a ferruginous slag is found to act most efficiently as a dephosphoriser. With sufficient lime added originally, a large proportion of the phosphorus may be removed from the bath during the melting stage ; but much is left until the end of the operation. Basic slag is very valuable on account of the large proportion (generally over 15 per cent.) of phosphoric acid that it contains. It is usually crushed to an almost impalpable powder, and employed in that condition as a phosphate manure.

Removal of Sulphur in the Open-Hearth.—In the acid process practically no sulphur is eliminated, and in the basic process the removal is very uncertain. Saniter has introduced a process for desulphurisation on the basic hearth, which has been successful in several large works. About 30 to 40 lb. of crude chloride of calcium for every ton of steel melted is added to the slag, which must be very basic, soon after the bath has completely fused ; the mixture is well rabbled and the greater proportion of the sulphur is thus removed from the metal. He has found it possible to desulphurise pig-iron with the aid of the same material. The calcium chloride, in admixture with lime, limestone, and fluor spar, is placed on the bottom of a deep casting ladle, and the fluid iron is allowed to run in, when the mingling of the two as the calcium compounds float upwards, is sufficient to effect the desired purpose.

The material for treatment on the open-hearth should be as free as possible from sulphur (unless the Saniter process can be applied, which is impossible in the acid furnace) ;

and it should contain either little phosphorus or little silicon, according as the acid or the basic system is applied. A pig-iron containing much silicon with phosphorus is therefore unsuitable. To render such a material available, many processes have been attempted, most of them depending upon the fact that practically the whole of the silicon is removed during the melting stage. If a basic hearth were employed, the exceedingly silicious slag first formed would rapidly destroy the bottom ; and the bulk of the slag would be too great, if sufficient basic additions were made to render it dephosphorising. Hence the most feasible of the proposals consists in melting the charge on an acid bottom, tapping it at once into a ladle, where any intermingled slag would separate, and transferring it immediately, and without the slag, into a basic furnace, where it would be finished under a basic slag in the usual way. There are obvious objections to the system, but preliminary trials have been attended with some success.

Recarburisation in the Open-Hearth.—At first sight it will not be apparent why a metal of the desired character should not be produced by simply reducing the carbon to the necessary extent, and then tapping. This cannot, however, in practice be accomplished, it being found that under these circumstances a 'short' worthless metal is obtained. This difficulty can be got over by adding manganese ; but, then, manganese in the metallic state, uncombined with any other substance, is comparatively very expensive, whilst in the form of spiegel-eisen, or ferro-manganese, combined with iron and carbon, it is relatively cheap, so that it is far more economical in practice to wholly decarburise the bath of metal, and then impart to it the requisite amount of carbon by means of 'ferro' or spiegel. This plan further recommends itself on the score of simplicity, it being much easier to entirely decarburise, and then add a certain amount of spiegel or ferro, containing a known quantity of carbon, than to determine the exact point at which to stop the decarburisation. In a few exceptional cases, in which the pig contains two or three per cent. of manganese, and is free from sulphur, it is, however, practicable to get sound metal without the final addition of manganese, provided a hard metal, high in carbon, is being made. This can in no case be done in the ore process, as the manganese, having a greater affinity than iron for oxygen, rapidly replaces the latter in the slag, so that none is left in the metal at the time it would be required to exert its action. The fact that the metal, before the addition of manganese, is red-short is commonly attributed to the presence of oxygen in combination with iron, either mechanically mixed with, or in solution in, the mass of the metal. The probability of this is not difficult to realise, when it is remembered that the decarburisation is effected by oxygen, that iron has a great affinity for oxygen, and that at a certain stage of the process the carbon is reduced to a very small amount. This view is supported by the fact that only a portion of the manganese and carbon, introduced as spiegel or ferro, is subsequently found in the metal, even though the addition may have been made in the ladle after tapping. The beneficial influence of manganese may be considered as due, partly to its great affinity for oxygen, partly to its facilitating the separation of slag mechanically mixed, and partly to its power of neutralising to some extent the influence of sulphur, and of eliminating a portion of that element, which it appears to effect by carrying it into the slag as sulphide of manganese. The effect of manganese is, therefore, to produce a metal which is forgeable, instead of brittle and worthless, at a red-heat.

A method of recarburisation by direct solution of carbon in the iron has been introduced by Darby, and is now in use in many works. The addition of the carbon has been effected by allowing a gentle stream of fine particles of gas-carbon to fall into the molten steel as it flows into a receptacle with a perforation at the bottom, on its way to the ladle ;

or by throwing coke or anthracite dust in paper-bags, 50 lb. at a time, into the ladle containing the iron ; or by moulding coal-dust and lime into bricks, which after drying are placed at the bottom of the ladle prior to tapping the furnace.

The Use of the Open-Hearth Process.—By the Siemens-Martin and the Siemens processes metal of any desired composition can be produced ; in this country the Siemens process is, however, almost entirely confined to the manufacture of soft metal, very low in carbon (0·13 to 0·24), for boiler-plates, ship-plates, and angle iron ; almost all the rail metal being manufactured by the Bessemer process hereafter to be described. In France a good deal of rail metal is made by the pig and scrap process. The make of a furnace is about the same, whichever method is worked ; but rather more fuel is required for the ore process, owing to there being a greater quantity of slag, which, being a bad conductor of heat, causes the consumption of a greater amount of fuel to raise the metal to the proper temperature. A moderate proportion of slag, however, is essential, because, resting upon the bath of metal, it serves to regulate the heat, and to protect the metal from the effects of sudden but temporary changes of temperature. The consumption of fuel in the ore process may be taken at about 15 cwt. per ton of metal made. In consequence of the greater intensity of the heat required in the ore process, the wear of the furnace is greater, more particularly of the roof, in the destruction of which the slag splashed on to it also plays a not unimportant part. A roof made of good Dinas brick, will, however, if properly used, last from 150 to 200 charges. The tendency has been to increase the size of the furnaces. At first they were usually made for 5-ton charges, now furnaces which will take 20 tons are common, and many 40-ton acid furnaces are erected. So long as everything is working properly, there would appear to be rather an advantage than otherwise in using these large furnaces ; but should anything go wrong, the inconvenience and loss would be very considerable. In America some of the largest furnaces have been built on rockers in such a way that the whole furnace may be tilted up about its longitudinal axis. In this way the tap-hole is normally above the level of the bath. It has not, therefore, to bear any appreciable weight, and so may be closed more loosely, whereby the evils of a 'hard tap' on the one hand, and on the other hand all possibility of a 'break out' of the charge of melted steel are obviated.

DIRECT PROCESSES FOR THE MANUFACTURE OF MALLEABLE IRON AND STEEL FROM THE ORE

This is a convenient point at which to consider further the so-called 'direct processes,' because it is tolerably certain that whatever measure of success they may obtain will result from their use as an adjunct to the open-hearth processes. The following direct processes, which differ from those already described, only began to attract attention about 1837, when Clay took out his patent. Modern processes of this character may be classified as (1) those in which the ore is heated with solid carbonaceous matter, and (2) those in which gases alone are used to effect the reduction of the ore. They may also be classified as direct- and indirect-heating processes, according as the heat is applied internally or externally. Their primary object was to produce malleable iron without the intermediary of the blast-furnace. In effecting this economically, with one or two exceptions due to local conditions, they may be said to have failed, though, as so frequently happens, the attempt may produce important results in another direction. From the description of the Siemens process it will be seen that the modern open-hearth is to some extent a direct process, inasmuch as a considerable proportion of ore is caused to contribute its metal to the charge.

Clay's Process consisted in heating to bright redness in clay retorts hæmatite in lumps not larger than a walnut, intimately mixed with one-fifth of its weight of charcoal. The resulting sponge was subsequently balled in a puddling furnace with or without coke. The product was frequently red-short or slag-short, owing, probably, to the difficulty in rendering the cinder sufficiently fusible. But the heating of material in externally fired retorts is a comparatively long and costly method, to be avoided whenever possible ; various attempts have been made to apply the waste gases from the puddling furnace to the heating of these retorts, but without success commercially.

Chenot's Process.—In this process it was attempted to remedy one of the chief defects of all direct processes, viz. the re-oxidation of the reduced iron. The metal having been produced at a low temperature, and being in a porous or finely divided condition, it is difficult to prevent re-oxidation before it can be balled. Chenot's idea was to provide a sheet-iron chamber, cooled externally with water, below, and in continuation of, the fire-clay retort which was fired in the usual way. The ore and charcoal were charged at the top of the upper chamber, and some reduced iron was withdrawn daily from the bottom of the cooling-vessel ; but the rate of working was so arranged that the mixture remained three days in each chamber, and the iron was finally delivered at a temperature below its igniting point. The iron was either worked into balls in the puddling furnace, or mixed with sufficient carbonaceous material (with or without consolidation by pressure), and fused in crucibles. With the object of economising fuel this indirect- was changed to a direct-heating method by passing hot producer-gas through the column of ore. Long experience has shown that good iron may be made by these methods, but not economically.

Blair's Process.—The success of the open-hearth method of making steel caused Blair, about 1870, to experiment with the Chenot process at Pittsburg, with the intention of using the sponge in the open-hearth. He improved Chenot's arrangement by introducing a preheating chamber, in which the ore could be raised more rapidly and economically to the temperature necessary for its reduction by charcoal, than in the body of the retort. Thus the Blair system involves the use of a preheater, a reduction-chamber

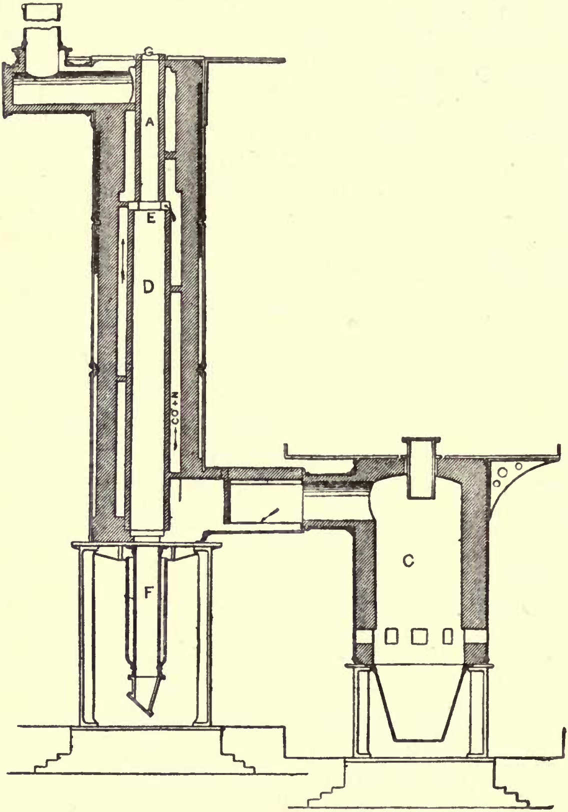

Fig. 57.—Blair's later (direct-heating) Sponge-making Furnace.

and a cooler. Fig. 57 shows the most advanced arrangement devised in this direction. Although its use has been discontinued, it is by no means certain that at no great distance of time it may not be revived. It will be observed that the reducing chamber D, is heated by the passage around it of hot gas from the producer C, which subsequently enters the preheating chamber A, by the annular space E, where it comes in contact with the ore and charcoal last charged at G, and heats it up for the reduction which takes place during its passage through D. The cold spongy iron, when taken out from the cooler F, still preserves roughly the original shape of the lumps of ore, and contains but little deposited carbon, the temperature apparently being rather too high for its deposition. It was found that the addition of about 5 per cent. of lime facilitated deoxidation, possibly by assisting in the formation of cyanogen. According to Blair 95 to 98, per cent. of the iron could be reduced, rich ores containing about 63 per cent. of iron being used. The bulk of the sponge was used to form part of the charge of an open-hearth furnace, whilst some of it was compressed into cylinders with about 8 per cent. of tar, and used instead of cast-iron scrap to melt with the ordinary sponge.

Siemens Direct Process.—Siemens, also, contrived a direct process, which, however, has been abandoned after an extended trial, mainly owing to the heavy loss of iron in the slag through the re-oxidation of the sponge, and the large consumption of fuel. It was found impossible to prevent the character of the furnace gases being too oxidising in the later stages of the process ; but it is to be observed that the large proportion of iron oxide in the slag led to the complete removal of phosphorus from the metal.

The design of the furnace recalls that of the Danks puddler. It was in the form of a short hollow iron cylinder rotating on a horizontal axis, as shown in fig. 58. At one end were three openings in the masonry, one below serving to admit heated gas direct from a producer ; the other two communicating with regenerators, through which by turns preheated air could be admitted to the furnace, or the gaseous products of combustion could be removed to the stack. Only the air, therefore, was regenerated. The lining of the furnace was composed of aluminous or bauxite bricks, covered on the inside with a layer of iron oxide produced by melting hammer scale and rich ore upon it while the drum was slowly rotated. At intervals, pipes (B) were buried under ridges in the lining, and through them water was constantly circulated with the aid of a trunnion joint at C. The ridges were thus kept cool, and served to roll the iron over upon itself as the cylinder revolved. About two tons of ore, mixed with fluxing and reducing materials, were charged through the working-door at the end of the drum opposite the gas- and air-ports. The door being then closed, the drum was rotated slowly. At a red heat the reaction between the ore and the solid reducing agent set in, and the temperature rapidly rose in consequence to such an extent that the supply of producer-gas could be greatly reduced for a time. The cinder fused, and after about one and a half hour from starting, the furnace contained a mass of very pure spongy iron. The rotation was then stopped, the tap-hole being in the lowest position, and after the bulk of the slag had drained off, it was resumed, but at a greater rate ; a

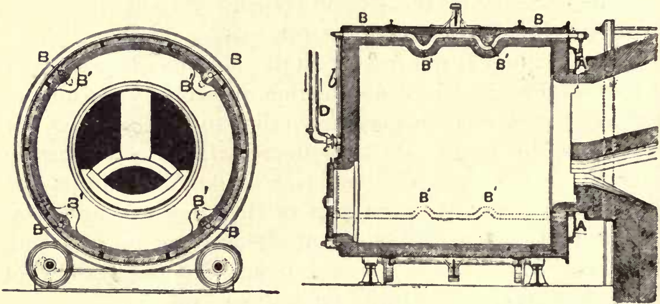

FIG. 58.—Siemens Rotating Furnace.

rabble was introduced to work the charge into two or three balls, which were removed through the door, rotation of course ceasing for the time. The balls were taken to squeezers to remove the excess of cinder ; and, being thus consolidated, were charged with pig-iron upon the hearth of a steel-melting furnace.

Eames and Adams Processes.—The abundant supply of natural gas in Pennsylvania led to the introduction of the Eames direct process in 1888, and that of Adams in 1890. The former was conducted in a furnace with a long hearth, fired at each end by gas, and provided with a central flue. The hearth was of anthracite and iron ore, faced with a layer of anthracite about 6 in. in thickness. Rich ore mixed to the consistency of a thick paste was spread over the hearth. After heating for an hour, the top layer became thoroughly reduced and was at a yellow heat. With the aid of an iron tool, flakes were dislodged from the top and worked into balls, which were turned over frequently upon the hearth, whence they acquired more iron by accretion, being bathed in fluid slag, and at a welding temperature the whole time ; fresh flakes were added until the balls were sufficiently large to be removed, squeezed, and either rolled, or re-melted upon the open-hearth. In the Adams process, the ore was charged into conical fire-brick chambers, where it was reduced by natural gas preheated by recuperation (regeneration), the gas being afterwards burned in the recuperating flues. Four of the reducing chambers were erected over a central hopper which was placed above the roof of an open-hearth furnace, so that by the opening of a door at the bottom of the hopper a sufficient quantity of the reduced iron could be introduced upon the hearth of the furnace, where it was rapidly dissolved by a bath of pig-iron already melted. Both of these processes, however, have been abandoned, at least temporarily, owing to the diminution in the supply of natural gas upon which they depended for fuel.

American Bloomery Process.—This may be classed as a modern adaptation of the Catalan process. It could only hold its own in outlying districts where there happens to be a supply of rich fine ore and charcoal, and where labour is relatively cheap. Such conditions have existed in certain localities in North America. The furnace is constructed of castings, and is about 20 to 30 in. wide, and 27 to 32 in. long, the depth being about 15 to 25 in. above the twyer, and 8 to 15½ in. below it. It has a single cast-iron twyer supplied with blast at a pressure of 1·5 to 2·5 lb. per square inch, heated to between 300° and 450° C. by passing through pipes placed in the path of the waste gases escaping from the furnace. The working-bottom is formed of charcoal-dust and hammer-slag well rammed. The method of working this furnace differs considerably in one respect from the Catalan, only fine ore—mostly magnetic—being used, intimately mixed with charcoal. The mixed ore and charcoal are charged at short intervals with some slag if the ore contain but little gangue. As in the Catalan process, some of the ore becomes reduced and carburised, and the carbon is subsequently removed by the slag, which is rich in oxide of iron. The quantity and quality of the slag, and the time it remains in the hearth, are regulated by the manipulation of the charge by the furnace men. The iron gradually forms into a ball or *loupe* weighing about 300 to 400 lb., which at the expiration of about three hours is withdrawn and forged into a bloom. These blooms are generally very pure, and are used in the open-hearth steel furnace.

Husgafvel's High Bloomery is a recent modification of the Stückofen, which economises fuel and enables work to be carried on continuously. The furnace is about 26 ft. high, and is 5 ft. wide at the boshes, and 4 ft. at the throat. The shaft is constructed of concentric shells of boiler-plate, with the annular space between them divided by a spiral partition. The bottom only, to a height of 5 ft., is lined with fire-brick. The outside is lagged throughout with 4 in. of fire-clay to lessen the radiation. The hearth is movable, being mounted on wheels, and supported on a platform that may be raised or lowered by means of a lever. It also has trunnions to facilitate turning it over for the removal of the bloom. Between the hearth and the shaft is a movable air-cooled ring, which protects the shaft proper by taking the wear, and can be renewed whenever required. The twyers, four in number, with telescopic pipes and goose-necks, are at two different levels in the movable hearth, which also has four cinder-notches, one above the other. The blast, at a pressure of from $\frac{1}{4}$ to $\frac{3}{4}$ lb. per square inch, is heated to from 150° to 250° C. by causing it to pass down through the spiral channel in the hollow iron wall of the shaft. The blast can be introduced into the casing at different levels and in different amounts, thus affording control to some extent over the working of the furnace.

The charge consists of fine ore, crushed tap-cinder and hammer scale, and charcoal. It is said that coke has also been used successfully. The reduction of the ore takes place in the manner already so often described, the reduced and carburised particles finally descending into the slag, which is rich in oxide of iron and so removes the carbon in greater or less degree, and facilitates their agglomeration. The slag is kept at the proper level by tapping it from time to time. When the bloom nearly reaches up to the lower twyers, the nozzles are raised to the higher level and the smelting continued until the bloom has risen to this height. It is then removed by lowering the platform and drawing out the hearth by means of a chain until the trunnions, by coming in contact with two stopping arms, cause the hearth to reverse, and to project the bloom into a truck beneath. At the same time a fresh hearth is run into place; thus no time is lost during the repair of the old hearth, and the process is practically continuous.

In 1876 a patent was taken out by Pernot, in which it was proposed to produce steel in an open-hearth regene-

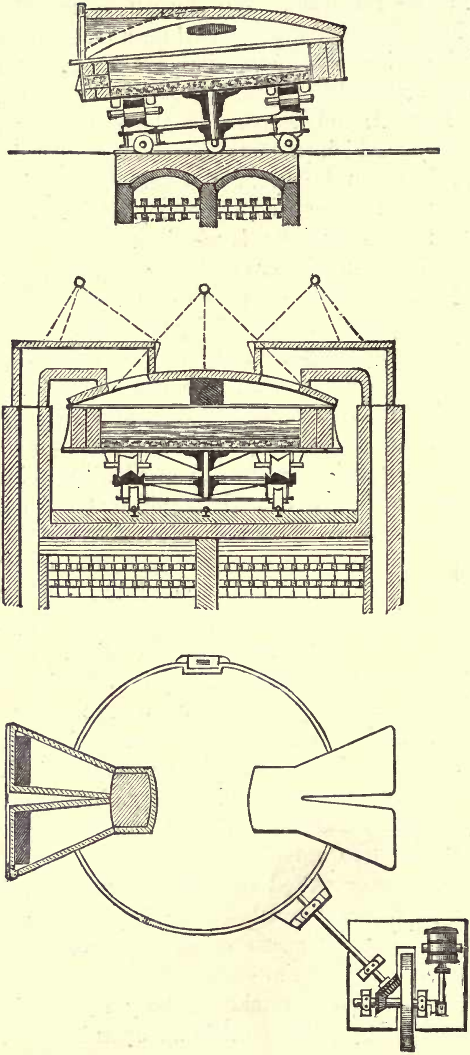

FIG. 59.—The Pernot Furnace.

rative furnace with a revolving bed, inclined at an angle of 5° or 6° to the vertical (fig. 59). Pig-iron, previously heated to redness, is placed on the bed of the furnace, and covered with scrap. The bed of the furnace is then made to revolve slowly, the pig gradually melts, and the scrap is alternately exposed by the motion of the furnace to the strong heat of the flame, and dipped under the molten pig-iron. In this way the fusion is comparatively very rapid, the whole mass becoming fluid in about two hours. The process is completed in the ordinary way.

When repairs are necessary, the bed on its carriage is drawn out.

In practice it is found that these furnaces require very frequent repairing. With the view to make this easier, Pernot arranged a movable roof, which had, besides, the additional advantage of reducing somewhat the strain on the structure occasioned by such great variations in temperature. The furnace has not, however, succeeded in establishing itself in this country. An enterprising firm in Scotland, who are working the Siemens process very largely, put up a Pernot furnace. They state that they gave it a fair trial, and were not satisfied until they had obtained as good a make from it as was said to be obtained in France. Yet they abandoned its use, giving as their reason that in the long run they found it had no advantage over the ordinary Siemens furnace in point of make, and the trouble in working it and the expense for repairs were greater. It is only fair, however, to point out that, in the case instanced, the furnace was employed for the ore process, and for soft metal requiring a high temperature to keep it molten, whereas in France, and also in America, where it is stated to have been successfully worked,[1] it is used for the pig and scrap method, for rail metal, containing about 0·4 of carbon. Herein lies an important difference, which should not be overlooked. There appears to be no reason to dispute that in

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[1] The use of this furnace has since been practically abandoned.

the Pernot furnace a charge can be worked off more rapidly than in the ordinary Siemens furnace, and that consequently, in addition to saving in time and labour, there is an appreciable saving in fuel; but it must be remembered that, in working at such extremely high temperatures, there are serious mechanical difficulties opposed to even the simplest construction of furnace holding together, and that these difficulties are enormously increased in dealing with a furnace of more complicated structure. Thus it may well happen that the time and interest on capital lost whilst the furnace is undergoing repairs, and the additional expense for repairs, may be greater than can be balanced by the advantages of the system. The wear and tear in the ore process, as already pointed out, is greater than in the Siemens-Martin process on account of the higher temperature and larger quantity of slag, and this difference may be about equal to or greater than the margin of advantage which there may be in favour of the Pernot furnace when working on pig and scrap without ore.

The Bessemer Process.—It will have been observed that the dominant idea in treating pig-iron for the production of malleable iron or steel has always been to refine the metal by the action of atmospheric air, and this was effected by causing a current of air to impinge upon the surface of the metal, by means either of blowing apparatus or the draught produced by a chimney-stack. What more natural than that it should occur to some one to refine iron by blowing air *into* it, instead of merely on to its surface? We find that this idea did actually occur to several persons in the year 1855, shortly before the introduction of the regenerative system, which we have seen has borne such important fruits. Not less important were the results destined to follow this, at first sight, not very important modification in the method of applying air to the refining of iron. The now world famed Bessemer process resulted from the attempt to carry out this idea. Until it demonstrated itself, it was not for a moment suspected by anyone—even by Bessemer himself—what an enormously high temperature could be produced by simply blowing air into molten pig-iron. He started with the idea of refining pig as a preliminary operation to puddling, and had no idea that the temperature produced would be sufficient to maintain in a molten condition the metal after it had been completely decarburised; a state of things, be it remarked, never before attained to. The discovery made by Bessemer was worked out by him in a most masterly manner, showing his great mechanical genius. The machinery invented by him for the carrying out of the process has remained in use ever since, only one or two appreciable alterations having been made, although hundreds of able engineers have since had to do with the process in various parts of the world, many millions of tons of forgeable metal having been made by it. Fixed *converters* were at first employed by Bessemer, but he soon superseded them in this country by converters movable on trunnions by hydraulic or steam power (figs. 61, 60), which are now universally adopted. The converter is a pear-shaped vessel, varying in size, but commonly about 8 ft. diam. × 15 ft. high, constructed of boiler-plate, lined to a thickness of about 1 ft. with ground ganister. In the bottom are arranged from 7 to 12 twyers, consisting of fire-clay cylinders, pierced with from 7 to 12 holes about $\frac{3}{8}$ in. in diameter. These twyers wear away more rapidly than the lining of the converter; and the bottom is now so constructed that, by turning the vessel on its side, the blast-box may be opened, and the defective twyer be replaced, even during the progress of a blow. The blast is stopped during the few moments required for the repairs. The twyer-box is connected by a curved pipe with one arm of the trunnion, which is hollow, and in its turn is connected with the blast main, so that air at a pressure of from 15 to 25 lb. can at will be forced through the twyers into the interior of the converting vessel. The other arm of the trunnion is solid, and

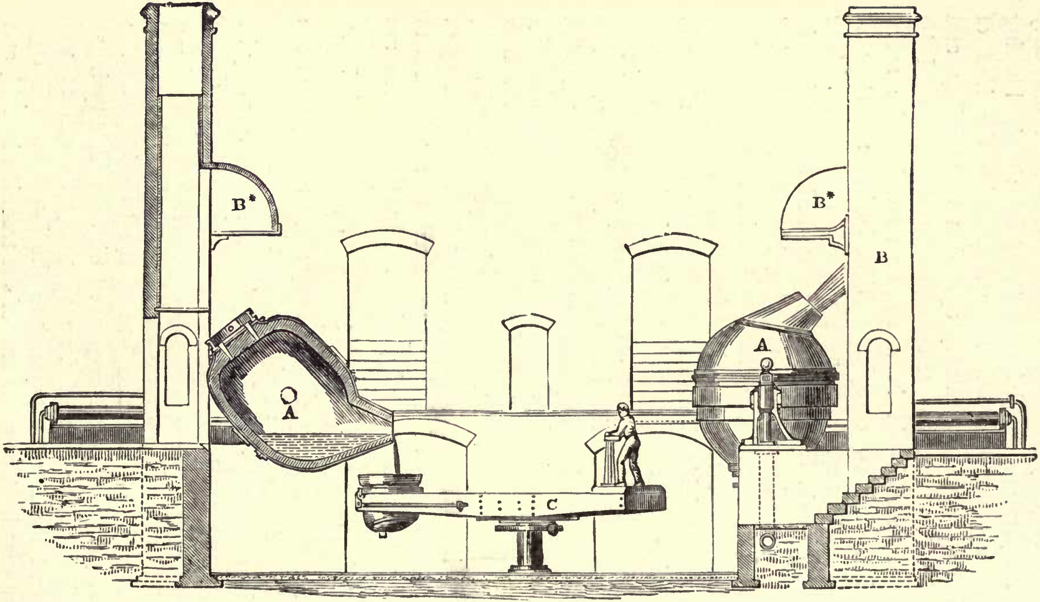

FIG. 60.—Bessemer process. A, Converting vessel. B*, Hood for carrying the gases into the chimney B. C, Crane for swinging the ladle under the converter. (Shallower pits than that shown in the figure are now used.)

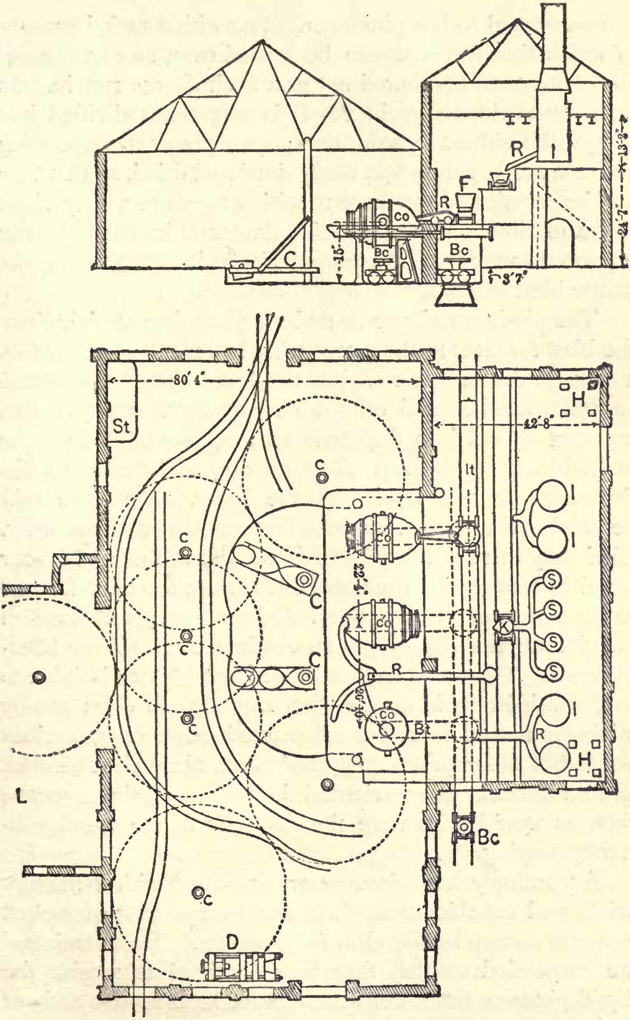

FIG. 61.—Bc, Bottom-car. Bt, Track for bottom-cars. C, Casting-crane. c, Ingot-cranes. Co, Converters. D, Sticker-press. F, Ladle for cast-iron. H, Hoists. I, Iron-cupolas. K, Ladle for spiegel-eisen. L, Room for repairing ladles. R, Runners. S, Cupolas for spiegel-eisen. St, Stage or pulpit.

has connected to it a pinion, engaging with a rack, by means of which the converter can be turned over, so as to enable the contents to be poured out or a fresh charge run in. In order to avoid delay, the vessel is sometimes divided into two parts besides a loose bottom : spare pieces corresponding to these are kept in stock, ready lined and dried, so that they can be substituted for those requiring repair in a very short space of time. Before charging the metal in, the converter is heated to redness by burning coke in it with the aid of a gentle blast of air.

The pig-iron to be converted may be taken straight from the blast-furnaces to the converter in large ladles mounted on a carriage drawn by an engine, the ladle being constructed so that it can be lifted off the carriage by a crane, and its contents tipped into the converter ; or pigs of iron may be melted in a cupola near the converter, and the metal run thence along a channel into the latter, or a ladle may be employed to transfer it from the cupola to the converter. Obviously there is a considerable amount of fuel and labour saved by transferring the metal direct from the blast-furnace to the converter ; but it can only be conveniently done in practice when a supply can be obtained from several blast-furnaces. The metal from a single blast-furnace is liable to vary considerably in composition from day to day ; but by mixing the metal from several furnaces in suitable proportions a metal of the required composition can always be obtained, and no difficulty is experienced in the converting process, such as would arise were the character of the metal constantly varying.

Accordingly large iron reservoirs, lined with refractory brick, and capable of holding 100 to 150 tons of melted iron, are now to be found in frequent use. These 'mixers' are suspended so that they may be tilted to receive the liquid pig-iron from the blast-furnace ladle at one end, or to deliver it into the ladle by which it is transferred to the converters at the other end. In this way, the product of several blast-furnaces is averaged, and as hot metal is frequently being added and the charge in the mixer is never allowed to fall below about 80 tons, whilst all apertures are carefully closed, except at the moment when iron is being introduced or withdrawn, there is no difficulty in maintaining the temperature of the metal. The use of mixers offers the additional advantage that, provided a portion of the iron contains a fair percentage of manganese, there may be a very marked elimination of sulphur, owing to the formation and removal of sulphide of manganese.

When the molten pig-iron is received at the converter a little is poured into a small mould, cooled quickly in water, and fractured. By the character of the fracture the quality of the pig and the treatment it will require can be sufficiently nearly judged. The metal having been run into the converter, the blast is put on, and the vessel turned into the upright position. The pressure of the blast must be sufficient not only to sustain the column of metal, but to force its way through it. The pig-iron, it will be remembered, contains, besides iron, the following substances in more or less quantity: silicon, manganese, carbon, phosphorus, and sulphur—all of which, when heated, are capable of combining with oxygen. At the commencement of the 'blow' the action of the blast is confined mainly to the silicon and manganese, only a little carbon and iron being burnt; consequently there is but little flame, the products of the combustion of silicon and manganese, viz. silica and oxide of manganese, being solids, which unite and remain in the converter as liquid slag, whilst the carbon which escapes is already oxidised to the maximum. Soon, however, the silicon and manganese are burnt out, and the carbon is vigorously attacked. The roaring of the blast, the rush of white-hot flame from the mouth of the converter, occasionally accompanied by slag, which is projected far into the air and falls in a golden shower, varied with scintillating particles of burning iron, are very impressive to witness, especially at night, when the dark shadows lend additional grandeur to the scene. This period, during which the carbon is being burnt out, is known as 'the boil'; the carbon is now only oxidised to carbonic oxide, the temperature being so high that carbonic acid would be decomposed; hence the flame at the mouth of the converter. The point at which the carbon has all been removed is recognised by the dropping of the flame. Phosphorus is not removed in this process to any appreciable extent, owing to the lining of the converter being silicious. Pig-iron free from phosphorus has therefore to be employed. The action of silica in preventing the removal of phosphorus has already been explained. Sulphur is but slightly affected and should therefore be present only in very small quantity, as a great loss of iron would attend its removal, and, if allowed to remain, the character of the metal would be deteriorated. Directly the flame drops, the converter must be turned down and the blowing stopped, otherwise the iron would be rapidly oxidised, and issue from the mouth of the converter as a thick brown smoke. It was soon discovered that workable metal could not be made by this process without the aid of manganese, no matter whether some carbon were left in or all were removed. The credit of suggesting the introduction of the manganese in the form of spiegel-eisen is due to Robert Mushet. We have seen how, afterwards, spiegel was employed with a similar object in the Siemens process. After the converter has been turned down, the carbon having been reduced to about 0·10 per cent. or less, 5 to 10 per cent. of melted spiegel is run in, causing a burst of flame, due to the action of the carbon in the spiegel on the oxygen in the blown metal. In some works the converter is turned up again, and the blowing continued for a few seconds; more commonly the metal is simply poured out into the ladle, whence it is run into the ingot moulds, it being considered that in this way the manganese becomes sufficiently and uniformly distributed throughout the iron. That a perfectly homogeneous metal is not always produced in this way has been proved beyond a doubt. It so happens that the want of uniformity of composition is rarely so great as to destroy the value of the metal for rails, and such like purposes, although the tests are severe; but for boiler-plates and cutlery steel the case is undoubtedly quite otherwise. Bessemer foresaw this so long ago as 1863, and provided a remedy, which consisted in agitating the metal by a mechanical stirrer after the addition of the spiegel. The expedient is simple and inexpensive, and has been found to be effective. The agitator is a rotating paddle constructed in iron or steel, and coated with loam or ganister. The ladle containing the metal, which has just been poured out from the converter, is carried under the agitator by an hydraulic crane, and then raised so that the agitator is immersed. The stirrer is then revolved at about 100 times a minute. Occluded gases are found to be expelled in great quantity, the metal finally becoming quite tranquil. The whole operation only requires two or three minutes, and at its completion the metal can be run into the moulds, where it will lie quietly, and solidify into sound ingots. The effect is exactly comparable with that of rabbling the open-hearth charge well, immediately before adding the spiegel. Delay is, however, caused at a critical moment, and the rapid teeming of the metal is seriously interfered with. When mechanical stirring has not been resorted to, the metal, after it has been teemed into the moulds, tends to rise and form unsound ingots. In order to prevent this, as far as possible, sand is thrown on the top of the metal directly the mould is full, and a plate of iron is wedged down in the manner already described (p. 243).

When the ingot has sufficiently cooled, the mould is lifted off by a crane; the ingot is then placed on a trolley and carried to a heating furnace, where it is allowed to attain the necessary temperature, when it is withdrawn and put through the cogging-rolls, after which it is transferred to a reheating furnace, and finally it is rolled into the required shape. In the manufacture of rails and similar material, of which large quantities are made of the same shape and section, and to which the Bessemer process with its treatment of small charges in rapid succession is especially well adapted, the ingots are frequently passed through the rolls without preliminary reheating. This is accomplished with the aid of *Gjer's Soaking Pits.* As soon as the ingot is sufficiently solid to be handled with safety, the ingot mould is stripped off. At this moment the core may be still liquid whilst the exterior is comparatively cool. It cannot be rolled in such a condition, for the ingot would be ruined, even if a serious accident were not caused by the bursting of the liquid metal through the crust. The ingots are therefore transferred to a pit lined with porous refractory material and still hot from a previous charge. Here they are left until the excess heat in the internal portion has 'soaked' into, or distributed itself evenly over, the whole mass. The mean temperature is sufficiently high to enable the ingot to be passed through the rolls without further expenditure of fuel; the process depends solely upon the equalisation of heat.

It will be of great interest and practical importance to trace to its source the very high temperature which we have seen is produced in this process. The substances which are burnt out are silicon, manganese, carbon, and a little iron. The last named may be left out of consideration, as it is not essential to the process, care being taken to avoid, as far as possible, the combustion of the iron. Of the three remaining substances, silicon is that which contributes the greatest amount of heat, manganese coming next, and carbon last. The carbon is seriously handicapped, owing to its product of combustion being a gas, causing a very considerable absorption of heat-energy, whilst in the case of the combustion of silicon and of manganese the whole of the heat of combustion is available for raising the temperature of the charge. Were silicon and manganese absent from the pig-iron, the temperature produced by the combustion of the carbon alone would not be sufficient to render the charge properly fluid. It will be shown presently that a too-high temperature, as well as a too-low temperature, may be obtained under certain conditions. Apart from the necessity of making the metal sufficiently fluid to pour clean from the converter, a moderately high temperature produces a metal of a homogeneous character and close texture, not otherwise obtained. There are three considerations by which the temperature is mainly regulated : the quantity of metal, its composition, and the rapidity of the blow. The quantity of the metal used in each blow and the rapidity of the blow are well within control ; the composition of pig-iron is very much less so. It thus happens that, in England, it is the constant aim of the Bessemer-steel maker to keep the percentage of the silicon in the pig as low as he can, whilst in Sweden and parts of Germany just the reverse is the case. This great difference depends solely on the fact that in the former case coke is used in the blast-furnace, and ores containing but little manganese, whilst in the latter charcoal is used, and manganese is commonly present. The coke contains always more or less sulphur, not uncommonly 1 per cent. It has already been pointed out that the conditions which yield the least sulphurous pig are those which favour the formation of a grey iron ; but the greyer the iron the more silicon is it likely to contain. Thus the Bessemer-pig maker using coke, so to speak, sits between two stools. On the one hand is sulphur, on the other silicon. If the grade of the iron be allowed to go too low, it will contain too much sulphur, which, not being removed, except to a very small extent, in the converter, will cause the steel to be red-short. If the grade of the pig be too high, there will be so much silicon in it that it would cause the blow to be too hot, to avoid which a quantity of cold scrap has to be thrown into the converter. There is no objection to the presence of silicon, so long as it is not in so great a quantity as to require more scrap than can be conveniently and economically supplied by the works. The difficulty can be conveniently got over in large works by mixing different grades of pig whilst still molten. If the metal be blown too hot, owing to an excess of silicon, too much of that element will remain in the finished product, causing its quality to be deteriorated; silicon in quantities exceeding about 0·50 per cent. tending to produce both red- and cold-shortness. The exact amount of silicon, however, which is permissible will depend on the relative proportions of carbon, manganese, phosphorus, and sulphur also present, and on the purpose for which the steel or ingot iron is to be employed.

If charcoal be used as the fuel in the blast-furnace, with ore fairly free from sulphur, and some manganese be present, the sulphur difficulty is got rid of; but when charcoal is used the conditions in the blast-furnace are unfavourable to obtaining a pig sufficiently rich in silicon. The difficulty could, probably, be most satisfactorily solved by mixing coke-pig, high in silicon and free from sulphur, with charcoal-pig. Charcoal-pig must, however, in the natural order of things, before many years have passed, become scarce in Europe and America.

Pig-iron, containing from 2 to 4 per cent. of manganese, can be worked by what is known as the direct process, when it is only desired to reduce the carbon to 0·3 or 0·4 per cent., as for rails; *i.e.* the blow is continued until the carbon is reduced to the requisite amount, the manganese still remaining in (0·1 to 0·3) being sufficient to render the metal workable. This method is in use in Sweden, and parts of Germany, where suitable pig is available. It would not pay to make pig specially for the purpose by introducing manganese into the blast-furnace. The exact moment at which the blow should be stopped can only be judged by the spectroscope, and by observing the colour of the slag and the forgeability of samples of the metal rapidly withdrawn from the converter on the end of an iron bar.

The average time required to blow a 7-ton charge in England for rails is about twenty minutes.

Notwithstanding the fact that phosphorus cannot be eliminated in the ordinary Bessemer converter, enormous quantities of metal have been made by this (the acid) process. Means have happily recently been devised by which this bugbear of Bessemer-steel makers has been overcome. The process is known as the Thomas-Gilchrist or 'basic' process.

The Basic Bessemer Process.—In the ordinary Bessemer converter we have seen that the lining is formed of ganister, a silicious (acid) material. Under these conditions phosphorus cannot be eliminated. We have already seen that, in the open-hearth process, this difficulty was overcome by the use of a basic lining. It must here be explained that in point of time the basic Bessemer process has priority. It was the success of the dolomite lining in the converter that led to its application to the Siemens process.

In selecting the basic material, the difficulty with which Thomas and Gilchrist had to contend was to obtain a lining which would hold together. After many failures and much patient labour, they found that magnesian limestone fulfilled the necessary conditions. By grinding it and mixing it with pitch, as patented by Mr. Riley, bricks can be formed which, after burning, are very refractory. In lining the converter it was impossible to cement the bricks satisfactorily together : they generally get a good deal curved in baking, and fit badly together, and the cementing material is easily washed out by the molten metal. In order to overcome this difficulty, the converters are now lined by placing a hollow tapered iron core in the centre, at the bottom of which a coke fire is lit, a liquid mixture, or 'slurry,' of tar and previously well-burnt limestone is run into the space between the core and the shell of the converter, which has had a layer of bricks placed flatwise against it. The lining consolidates with the heat, so to speak, into one solid brick. This method has proved to be very successful.

From an enemy, by judicious treatment, we may be said to have converted phosphorus into a friend. In the 'acid' process it is essential that about 2 per cent. of silicon should be present, for it is, to a great extent, due to the presence of silicon that the requisite high temperature can be obtained. In the basic process the less silicon there is the better, because it destroys the converter-lining by fluxing it away. Here it is that the phosphorus befriends us, for it, too, is capable of producing a high temperature by combining with oxygen; and that being the case, it becomes possible to work with about half the silicon necessary in the acid process, which practically means that we may employ a much lower grade of iron, for the lower the grade of iron the smaller will be the amount of silicon in it.

The slag must necessarily be highly basic, which is ensured by introducing a quantity of lime into the converter with the pig-iron. The basic-slag frequently contains well-defined crystals of a tetra-basic phosphate of lime, and always so much (15 to 18 per cent.) phosphoric acid that it is valuable as a manure.

The phosphorus is removed by continuing the blow after the flame has dropped, *i.e.* after the carbon has been all burnt out. This is called the 'after-blow.' The time the after-blow should last can only be regulated by experience gained by direct experiment with the particular class of iron being treated. The approximate time which the after-blow should last being known, the converter is turned down before that time has expired, and a small sample taken, which is hammered out and fractured. A little practice soon enables the workman to decide with great accuracy from these rapidly performed tests how many seconds longer the blowing should be continued in order to effect the entire removal of the phosphorus.

So appreciated has this hitherto despised substance become, that it is sometimes the practice to put back into the blast-furnace a great part of the slag from the converter, in order to increase the amount of phosphorus in the pig-iron subsequently to be converted into steel.

There is, however, a limit to the lowness of grade of iron which can be used, for although the silicon decreases, the sulphur increases, and only about half the sulphur present in the pig-iron can be removed in the converter. $\frac{1}{10}$ per cent. of sulphur suffices to prevent Bessemer or Siemens steel from rolling in a sound condition. As has already been pointed out, the way to counteract the influence of sulphur is to employ manganese in sufficient quantity, but this is not without a serious drawback, for manganese is expensive.

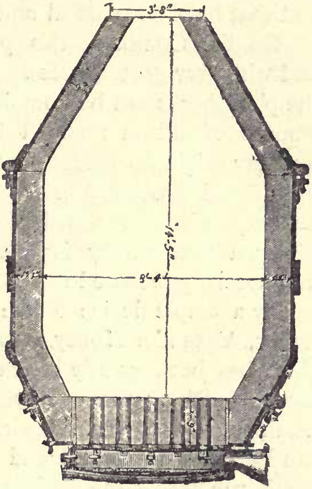

Fig. 62.—Basic converter.

In working out this process much difficulty was at first experienced owing to the mouth of the converter getting gobbed up, that is to say, stopped by projected slag. The basic slag, consisting as it does principally of lime, is very pasty. This inconvenience has been successfully got over by employing converters of the form shown in fig. 62. It was predicted by many that the slag and metal would be thrown out of the mouth of this converter, but that has not been the case, and this shaped vessel is now frequently adopted for both the acid and the basic processes.

The basic converters are usually more capacious for a given weight of charge than those of the acid process, and both linings and bottoms wear far more rapidly, the former lasting from 100 to 150 heats, the latter only from 20 to 30. The bottoms are made separately from the shell, so that they may be renewed without dismounting the whole converter. The best results are obtained with linings that have been stamped in place by hand, instead of by mechanical means, and that have been dried and fired very evenly.

On the Continent this process is being largely worked, and with very great success. Owing to the ease with which the phosphorus can be completely eliminated, and the small amount of silicon retained in the finished product, the quantity originally present in the pig being much less than in the acid process, a metal of remarkable malleability and ductility can be obtained, possessing, according to Kupelwieser, a conductivity for electricity only rivalled by pure iron specially prepared in a laboratory.

By a simple device of the well-known American metallurgist, Alexander Holley, now deceased, the make of a basic plant has been greatly increased. The arrangement consists in making the converter quite independent of the trunnion, so that, when repairs are required, the converter can be rapidly removed and another put in its place. A car is run under the shell, and raised by an hydraulic lift until it takes the weight of the latter off the trunnion ring, which is then disconnected by knocking out the cotters, and lifted above the shell. The shell is lowered and taken away to be repaired, another being raised under the trunnion ring, which is then lowered into place and cottered, the blast joint at the same time being screwed up.

Modifications of the Bessemer Process.—The capacity of the Bessemer converter is less open to variation than that of the open-hearth furnace, owing on the one hand to the difficulty in dealing with a large bulk of metal, and on the other hand to the danger of chilling a small volume.

In recent years attempts have been made to revive the use of quite small converters, holding only a few hundredweight of metal, for the manufacture of small castings, the chilling towards the end being obviated by the addition of from $\frac{1}{4}$ cwt. to $\frac{1}{2}$ cwt. of ferro-silicon after the carbon has been removed; and continuing the blow until the silicon also has been burnt out. It will be understood that the use of the silicon is to produce additional heat at the end of the blow, when it is most required; and it is equally obvious that the acid system must be employed, or else the phosphorus removed at first would be restored to the steel on the addition of the silicon, and the basic lining would be hopelessly destroyed.

It was pointed out that the first converters used by Bessemer were fixed; and although in England they have been entirely superseded by movable vessels swinging on trunnions, the older form has still survived in Sweden, and has been re-introduced into England and America by Clapp and Griffiths. It has one or two decided advantages: being fixed it is cheaper to construct, and is less dangerous in use than the more common form, with which serious accidents have occasionally happened owing to the failure during a blow of one of the teeth of the tilting-mechanism, followed by the stripping of the remaining teeth and the scattering of several tons of molten steel over the floor of the shops. But there are many disadvantages in this arrangement. Since the fixed converter cannot be tilted, so that the metal may rest on the side while the blast is shut off, the twyers must, almost of necessity, be placed around the sides instead of in the bottom; otherwise some of the melted pig would find its way through them during charging, and would cause stoppage through the solidification of metal in the air-way, or possibly even the breaking out of the charge. But a blast introduced through side twyers is apt to pass in undue proportion up the side of the converter instead of penetrating to the centre. The result is that, in spite of the circulation of the steel, one portion may be completely decarburised, and even some iron may be burned, with the production of red fumes, whilst other portions are by no means ready to receive the manganese additions. The blow once begun cannot be stopped without tapping the metal; hence an accident to a twyer during the operation may mean the loss of a charge; whilst if at any time a 'hard tap' be experienced, that is, if the tap-hole at the bottom of the converter cannot be opened at the exact moment required, the steel will be over-blown and oxidised, or in extreme cases even chilled and solidified in the vessel. By means of a differential piston, which allows sufficient air-pressure in the twyers, with the minimum of air passing, to prevent the passage of liquid metal into them when the blast is not fully on, the old objection that a full blast had to be maintained during the tapping is overcome. The metal is, therefore, in less danger of being over-blown in the Clapp-Griffiths converter. Witherow has still further improved this converter by adapting to it a movable bottom which can be readily removed for repairs and replaced by a new one.

A few years since a furnace was patented by Ponsard which aimed at combining the advantages of the Bessemer and open-hearth processes. It is a revolving reverberatory furnace supplied with twyers. By giving the furnace a half revolution on its oblique axis, the twyers may be brought either beneath or above the surface of the bath of metal. By these means the metal can be rapidly decarburised nearly entirely, as in the Bessemer converter, and then, by removing the twyers from beneath the metal, the final adjustment of the carbon can be made, as in the Siemens process. The chief difficulty experienced in working out this idea to a practical success appears to be the rapid destruction of the twyers. This obstacle is certainly a very great one, and so far has proved insurmountable. A further discouragement to the attempt to work in this direction is to be found in the success of the basic-Bessemer process, by means of which a metal, the character of which is well within control, can be produced.

Nomenclature and Classification of Iron and Steel.—In consequence of the extremely high temperature which we can command, either in the Bessemer or open-hearth processes, it is possible to obtain, in a molten state, metal practically free from carbon, or containing carbon to any required amount. It is sufficiently obvious that, having regard to the original and commonly understood meaning of the word steel, some other name should, strictly speaking, be applied to all metal manufactured by these processes which cannot be hardened and tempered. In practice, however, there are many obstacles in the way of this being done, and it has become customary in this country to designate by the term steel all the metal which has been produced by the Bessemer or open-hearth processes.

It thus has resulted that we speak of steel ships, steel boilers, and steel rails. The metal of which ship- and boiler-plates are made contains about $\frac{13}{100}$ to $\frac{24}{100}$ per cent. of carbon, while rails usually have about $\frac{4}{10}$. The first could not be appreciably hardened, and the second is considerably below what would formerly have been considered steel.

Although, then, metal possessing the true characteristics of steel can be made by these processes, yet that which is ordinarily made is not steel, but a metal called into existence by our recently acquired power of obtaining an extremely high temperature. It is most desirable that some uniform system of nomenclature should be adopted, and there is probably none better than that recommended by the International Committee of the American Institute of Mining Engineers in 1876, although it is now probably too late to introduce it. Of malleable metals only those which can be hardened by quenching from a red-heat in water should be called steel. Steel would be termed *Ingot-steel* or *Weld-steel*, according as it was a completely fused material such as is produced by the crucible, open-hearth or Bessemer processes, or was merely a consolidated sponge as in the case of Catalan or puddled steel. Material incapable of hardening by quenching would be known similarly as *Ingot-iron* or *Weld-iron*, according to the manner of its production. The presence or absence of slag thus becomes the test for the class (ingot- or weld-) in which malleable iron or steel is to be graded. Non-malleable metal remains to be classified as *cast-iron*.

Steel has properties far excelling those of wrought iron, except best Yorkshire iron, which is still used for chains and rivets on account of its fibre and softness, but which costs about four times more than mild steel, and it has only been a question of time to make this universally felt. At the present moment new iron rails are things of the past, and wooden sleepers have begun to follow in their wake. So with ships : the wooden walls of old England are no more. Nevertheless, for blacksmith's work wrought iron holds its own, mainly owing to the greater ease with which it can be worked and welded.

THE PHYSICAL PROPERTIES OF COMBINATIONS OF IRON WITH OTHER ELEMENTS

There are great practical difficulties in the way of studying the compounds of iron with each individual element. The knowledge which we at present possess is mainly derived from the observation of the effect of varying each element, when several are present.

Influence of Carbon on Iron.—By far the most important of all the combinations of iron with other elements, which we have to consider, is that with carbon in varying proportions.

The effect of the presence of carbon in iron is, up to a certain point, to increase the tenacity and decrease the ductility, and to cause the metal, when heated and then cooled more or less suddenly, to harden, the hardening being in direct proportion to the amount of carbon present and to the rate of cooling. Metal containing less than 0·75 per cent. of carbon is not usually employed in cases where it is intended to produce a very high degree of hardness. On the other hand, metal containing about 1·5 per cent. of carbon represents the maximum which can be safely worked; even then very great care is required to prevent its becoming overheated and burnt. Steel of this degree of carburisation is used for razors and tools for turning chilled rolls. In hardening it, it should not be heated above a dull cherry-red. Steel with about one per cent. of carbon is extremely useful, as it can be welded without much difficulty, and the unhardened portion of a tool made from it is sufficiently tough to withstand the blow of a hammer without snipping. Cold chisels and hot setts are made of this class of steel. Of the intermediate tempers between 1½ and 1 per cent. may be mentioned the following: 1⅜ per cent., temper for saw files: 1¼ per cent., tool temper, *e.g.* drills, turning and planing machine tools; it requires great skill to weld steel of this temper: 1⅛ per cent. is spindle temper, a very good temper for the largest size of turning tools, hot setts, mill-picks, circular cutters, &c. Steel containing from 0·8 to 0·9 per cent. of carbon has been found most useful for tools which are required to combine a high power of resisting shock with the ability to take a keen cutting edge.

The capability of being hardened by the addition of carbon is a property peculiar to iron; but the exact cause of the phenomenon is at present the subject of controversy. Many eminent metallurgists support Osmond's explanation that metallic iron is capable of existing in two allotropic modifications. His theory may be summed up in a few words: Pure iron when cold is always in the soft or *alpha* (α) modification, whilst on being heated to any temperature exceeding 855° C. the molecules become intensely hard (although the mass may be plastic), and the iron is said to have assumed the *beta* (β) modification, in which it remains until the temperature falls below 855°. As soon, however, as it cools past this point, pure iron reassumes the α or soft form. But the presence of carbon checks the reconversion into the soft variety ; so that if a sample of iron containing sufficient carbon be heated above the critical temperature, the iron being therefore in the β condition, and if it be then quenched in water, the rapid passage of the metal through the critical temperature, aided by the presence of the carbon, prevents to some extent the re-formation of the α modification ; and the iron remains hard. Yet, since the β variety is abnormal in the cold, any slight reheating—as in tempering—by giving greater molecular freedom, enables a further portion of the iron to revert to the α form, and the metal becomes proportionately softer. The carbon is considered to be in solution in the iron at all temperatures above the critical, but the elements combine at this special point and form a compound (Fe_3C). This substance has been separated by the action of suitable solvents upon annealed steel. The presence of the carbon lowers the critical point by from one to two hundred degrees.

Other metallurgists strongly oppose this theory, preferring to retain the older explanation that the water-hardening of steel is due to the existence of at least two compounds of carbon with iron. Their contention is that, of these two compounds (at least in steels with less than 0·9 per cent. of carbon), one can only exist in chemical equilibrium below, and the other above the critical temperature. On slow cooling or heating, the change is therefore complete ; but as the conversion requires an appreciable time, quenching, or very rapid cooling, from temperatures above the critical prevents more or less completely the re-formation of the ordinary carbide (Fe_3C) which is stable in the cold. Both carbides are hard ; but the lower carbide which is stable at the higher temperature is the more intensely so, and steel is therefore harder after quenching than after slow cooling because it contains a larger proportion of this lower and harder carbide. The carbon in the cold quenched steel is frequently said to be in the *hardening* form, and that in the annealed metal is termed *cement carbon*, because it is thus found in cementation-steel.

Whatever be the real cause of the hardening, it is certain that changes take place during thermal treatment, both in the condition of the carbon and in the condition of the iron. If a microscope be brought to bear upon a highly polished surface of steel, lightly etched with very dilute nitric acid or with tincture of iodine, so that it is magnified from 600 to 800 times, it will show the existence of certain constituents of the metal which are easily recognisable, and which by their presence or absence afford indications of the nature of the steel and of the treatment that it has last received. Pure soft iron, which has been heated to redness and cooled slowly, shows large crystals of iron (*ferrite*) which are even visible to the naked eye ; but as the percentage of carbon in the material is increased, there is seen to be a growing proportion of tracts, which, slightly magnified, resemble mother of pearl in their iridescent appearance. They occur intermingled with the crystals of ferrite, and, under greater magnification, are seen to consist of alternate parallel layers of two materials, of which one is hard, the other soft. When the carbon in annealed samples amounts to 0·89 per cent., as Arnold has shown, the iron crystals are absent, and the whole is made up of the pearly constituent (*pearlite*). With more carbon than this veins of a very hard and brilliantly reflecting substance are seen among the pearlite tracts, together it may be with small spots of graphite surrounded by ferrite, if the steel has been annealed for a long time.

The hard substance appears to be the compound Fe_3C, already alluded to, and known by the metallographic name *Cementite*. With the steel containing 0·89 per cent. of carbon, after heating to redness and quenching in water, Arnold was unable to detect any sign of structure under a magnification of 600. In samples of different composition the quenching process produces a similar homogeneity in some parts of the tracts which in annealed steels are occupied by pearlite, whilst the other portions of the steel show irregularly distributed patches of ferrite or of cementite, according as the steel has less or more carbon than 0·89 per cent. The metallographic name given by Osmond to the compound produced by hardening is *Martensite.* As Arnold has shown, the uniformity of this particular (0·89) material explains why it is so valuable for making tools that will take a cutting edge, and yet resist shock after hardening ; with less carbon there must be free soft iron present, which would spoil the edge ; and with more carbon there would be veins of hard cementite, which, although it will take an edge, will certainly increase the brittleness. He considers that this homogeneous material is a chemical compound, a sub-carbide of iron, the composition of which agrees with the formula $Fe_{24}C$. Osmond, however, considers that the uniformity points to the carbon being simply dissolved in the iron at high temperatures, and forming a saturated solution when it contains 0·89 per cent. of carbon at the critical temperature. On this assumption the separation of graphite in samples containing more than 0·9 per cent. of carbon would be due to the inability of iron to hold in solution more than that proportion at the temperature in question. Pearlite appears to consist usually of microscopically minute layers of cementite and ferrite ; but as any other two substances of unlike hardness or resistance to etching acids would give the same appearance, it is difficult of proof ; and Osmond has indicated his belief that laminæ of other compositions may sometimes be present.

The microscope has thus been able to amplify the knowledge of structure, which was previously based entirely upon the appearance of the fracture. Even the latter, however, especially in the case of high carbon steels, may be able to throw much light upon the heat-treatment that a sample of steel has received. Brinell, experimenting with steel containing 0·52 per cent. of carbon, found that all specimens when broken, after having been exposed to a low yellow heat and slowly cooled, showed a fine but hackly crystalline fracture, whilst if quenched in water at that temperature the grain was so fine that it resembled porcelain. After heating to a bright yellow and cooling slowly, the crystals were larger, and after bringing them to a bright white heat they were very coarse; but in both cases they were hackly. Quenching the bars at a low yellow gave a comparatively fine fracture; but at a white heat, even the sudden cooling failed to prevent the structure from being coarse, although it was still granular. The steel, in fact, had become *burned*, an expression which is used to describe the peculiarly rotten and worthless condition of a metal that has been overheated. The burning of the metal has been ascribed to various causes, such as oxidation; but it is probably due, in the main, to the purely structural alteration which the metal undergoes at high temperatures, and which is most readily observed in steels with the highest carbon percentage. It can to a large extent be remedied by working under the hammer whilst still red hot, and sometimes by reheating to a low yellow heat and then quenching in water. Brinell found that no change could be produced by quenching at temperatures below a low yellow, the character of the fracture being the same whether the bar was cooled slowly or suddenly; and if all the carbon were originally present in the form of cement carbon, it remained as such up to this temperature, in any case. But if the bar were heated above this point, practically the whole was found as hardening carbon after quenching, or as cement carbon after slow cooling. If, however, hardened steel were taken in the first place, as the temperature was raised to a low yellow, more and more of the hardening carbon present became converted into cement carbon, whether the specimen was subsequently quenched or annealed. But above a low yellow heat both hard and soft samples behaved alike.

It is clear that there is a critical point at which a great change occurs in the condition of the steel. And the effect upon the carbon is well marked by the Eggertz colour-test, which depends upon the proportion that exists between the amount of carbon present in a steel and the colour that it produces when dissolved in a given volume of nitric acid. All samples of the same steel which have been quenched at any temperature below the critical point show the same intensity of colour when dissolved in nitric acid under the conditions of the test; but as soon as this point is passed they give a much less intense colour than before, although the actual percentage of carbon present remains exactly the same. It was observed many years ago that, as steel was slowly cooled from a high temperature, a point was reached (when the metal was only just visibly red hot) at which it suddenly glowed and became distinctly hotter. This phenomenon is known as *recalescence*.[1] It was later found that at this particular instant the steel was momentarily much weaker, as though a profound molecular disturbance were taking place throughout it. This led, as soon as the introduction of the Le Chatelier pyrometer made a reliable measuring apparatus available, to a careful study of the rate at which bars of iron and steel cool.

If a red-hot bar of iron or steel be placed in such a position that it may cool slowly at a uniform rate, any disturbing cause due to the behaviour of the bar itself being absent, and if it be thus connected with a recording pyrometer, any rise of temperature or a retardation in the rate of cooling may be observed accurately. In this way it was found by Osmond that a retardation, of considerable magnitude, occurs with iron containing but little carbon at about 860° C., whilst a second but very slight check occurs at 750°, and a third, almost imperceptible if the proportion of carbon be very small, at about 660° C.

[1] From Latin words meaning 'to grow hot again.'

With increasing percentages of carbon the first of these breaks becomes less marked, but the second is more distinct and occurs at a lower temperature, whilst the third break is much more noticeable. With high carbon steels only one retardation can be observed, but that is of very great magnitude and occurs at about 680° C. Similar breaks are observed in the curve produced in heating the metal at an uniform rate, and the lowest of these being first observed was termed $\text{A}\textsc{r}_1$ (from the French *arrêter*, to stop), whilst the middle break was called $\text{A}\textsc{r}_2$, and that occurring at the highest temperature $\text{A}\textsc{r}_3$. These symbols have now been generally adopted in discussing the phenomena of recalescence, to indicate the breaks in the curves whether of heating or cooling. The points $\text{A}\textsc{r}_1$ and $\text{A}\textsc{r}_3$, however, occur at higher temperatures when the metal is being heated than when it is being cooled, as though the reactions, which they denote, take place but slowly. The retardation at $\text{A}\textsc{r}_2$ occurs usually at the same temperature both in cooling and heating.

These points, undoubtedly connected with some chemical or physical change in the metal, are at present differently interpreted by different schools of metallurgists. Osmond and Roberts-Austen consider that $\text{A}\textsc{r}_3$, which occurs in electrolytic iron, is due to the molecular change from β to α iron, whilst $\text{A}\textsc{r}_2$ indicates the change in the condition of the carbon to which allusion has already been made. Charpy, who has examined the mechanical properties and strength of steels that have been quenched at different temperatures, connects the break occurring at the lowest temperature ($\text{A}\textsc{r}_1$) with the change from hardening to annealing carbon (Martensite to cementite) or *vice versâ* ; whilst $\text{A}\textsc{r}_2$ is taken to indicate a change of some magnitude in the condition of the iron, and $\text{A}\textsc{r}_3$ a second change in the iron which is most clearly shown by the alteration in the magnetic properties of the metal, as iron becomes entirely non-magnetic at a temperature of about 865° C. The change in the iron which takes place in $\mathrm{A}\textsc{r}_2$ has also been studied by Charpy :—

In testing the tensile strength of a sample of iron that has been annealed, the extension is proportional to the load up to the elastic limit, but at this point a very sudden and great yield takes place, after which the metal recovers itself and the test proceeds normally ; the result is that the curve showing the relation of stress to strain during the progress of the test is indented with a deep notch just above the elastic limit. But if the load be entirely removed from the test-piece after this point is passed, and be then gradually reapplied, no such notch occurs when the elastic limit is again reached ; and the second test curve is quite smooth and regular. A bar that has been hammered, rolled, or otherwise worked in the cold also fails to exhibit any notch in the stress-strain curve. But the notch reappears if the bar be annealed at a fair red-heat and cooled slowly before testing. There is clearly a difference in the physical conditions of the cold-worked and annealed samples, and Charpy is inclined to consider that the former contains the iron in the β modification, more especially as the point $\mathrm{A}\textsc{r}_2$ is far less well-defined in the heating curve of a sample of cold-worked iron whilst being rapidly brought to a red-heat, than in that of an annealed bar. Conversely, a steel that has been quenched at temperatures above $\mathrm{A}\textsc{r}_2$ shows no notch, and thus appears to contain the cold-worked form. It has, however, been pointed out by Howe that there is nothing to prove that the cold-work hardness, which is common to most malleable metals, is due to the same (β) allotropic modification of iron that is seen in quenched steel, and he prefers to term it provisionally *gamma* (γ) iron. It should be remarked that, with a sample of steel containing 0·7 per cent. of carbon, the influence of the allotropic iron change upon the strength and extensibility of the specimen is far less marked than that of the change in the condition of the carbon.

The temperatures corresponding to the different points vary with the metal, the foreign substances present having a specific influence. The temperatures observed *on heating* are usually about 710° to 720° C. for AR_1, 735° to 740° for AR_2, and 800° to 860° for AR_3; whilst those noted *on cooling* are 640° to 690° for AR_1, 735° to 740° for AR_2, and 750° to 850° C. for AR_3. It is clear, therefore, that to harden steel the metal should usually be heated above 700° C. before quenching, whilst there is no gain, but possibly a great disadvantage, in allowing the temperature to exceed 800° or 850° C.

Since the hardening of steel apparently depends upon the persistence in the cold of an unstable condition of the material, the process of hardening or tempering may be varied at will. The steel being once heated above the critical recalescence point, the more rapidly it is cooled, the larger will be the proportion of the harder substance (be it β iron, subcarbide, or any other material) left undecomposed in the cold metal, and therefore the harder will be the metal. Thus quenching in cold mercury produces the most intense hardness because of the high conductivity and the low specific heat of mercury, which enable it to take up the heat from the steel almost instantaneously. In place of mercury dilute acids or salt solutions may be used, but the hardening effect is then less marked; and it is even less so in the case of water, which is the quenching agent usually employed. Warm water, cold oil, and warm oil produce less and less chilling, and oil hardening is frequently used to produce a combination of fair hardness with considerable toughness. For ordinary purposes hardened steel is too brittle, it is therefore *tempered* after quenching. This consists in raising the temperature of the hardened metal until sufficient of the hard constituent has become converted into the softer variety. This tempering effect may be observed even at 100° C., and at 200° it becomes very marked; the hardened steel, in practice, is therefore reheated to a certain temperature, which is regulated by the temper required, and is then allowed to cool slowly or is quenched again in water. This second quenching is preferable, as it stops the tempering when the exact degree of softness is reached, whilst it cannot reharden the metal because it is effected far below the critical recalescence point.

When reheated, as the temperature rises the surface of the steel passes gradually through a series of beautiful colours—due to films of oxide of iron. These colours indicate to the experienced eye of the workman the temperature at which the steel has arrived, and therefore the point at which to stop the reheating. The approximate temperatures corresponding to the various tints are shown in the following table :

Temp. C.	Colour	Temper
221°	Very faint yellow.	Lancets.
232	Pale straw.	Razors and surgical instruments.
243	Full yellow.	Penknives.
254	Brown.	Scissors and cold chisels.
266	Brown, with purple spots.	Axes, plane-irons, pocket-knives.
277	Purple.	Table-knives, large shears.
288	Bright blue.	Swords, watch-springs.
294	Full blue.	Fine saws, augers.
316	Dark blue.	Hand and pit saws.

During the hardening process the tool should not be removed from the water until it is quite cold, otherwise it is liable to crack. When it is intended to harden the edge of a tool only, the metal should be moved slightly up and down in the water, so as to avoid an abrupt transition from the hardened to the unhardened part, which would be likely to cause it to crack. Over-heating at some time or other is a common cause of steel cracking during hardening. It is also sometimes due to 'over-melting.' The same result may be traced to the presence of too much manganese or phosphorus. By hardening, steel is expanded from its original size when cold. After hardening in oil, the tempering stage is rendered unnecessary for some purposes.

Silicon.—This substance produces both red-shortness and cold-shortness. The quantity of silicon which may be present without having any very decided effect depends very much on the relative proportion of carbon. Thus, with the carbon about 0·10 per cent., silicon might be present to the extent of 0·50 or more, without causing the metal to be brittle; whereas with about 0·50 per cent. the same amount of silicon would cause the metal to be very red- and cold-short. Gautier states that metal containing only a trace of carbon may contain as much as 7 per cent. of silicon, and yet roll and weld. Metal containing much silicon cannot be coated with tin, owing to the silicon becoming oxidised during the operation and forming a protective coating of silica, which prevents the tin adhering. The presence of silicon may be detected during rolling by the behaviour of the scale, which either adheres to the rails or falls off in flat dry flakes, instead of leaving the metal freely and curling up, as is the case when there is only a trace of silicon.

Although, as we have seen, silicon under certain circumstances is an objectionable constituent of steel, yet in the production of sound castings it has proved itself very valuable. The addition of silicon, in the form of highly silicious pig-iron containing a large percentage of manganese, to the molten metal just before it is run into the mould, has the effect of preventing the evolution of gas during the solidification of the metal, the silicon reducing the carbonic oxide whilst it is still held in solution in the metal, forming silica, which combines with any oxide of iron present. The manganese serves the double purpose of removing any excess of oxygen in the metal, and of rendering more fluid the silicate of iron produced by the action of the silicon on the carbonic oxide in the presence of oxide of iron.

The character of the metal produced in this way is susceptible of considerable modification by special treatment after being cast. The cast metal, as it is taken from the mould, is on fracture found to be largely crystalline. By heating the metal to a cherry-red and cooling it more or less gradually, the grain becomes much more compact, the toughness and ductility are greatly increased, and the breaking load becomes slightly higher, whilst the proportion which the elastic limit bears to the breaking-stress is decreased. By reheating and cooling in oil the breaking-stress and the elastic limit are increased, whilst the toughness and extension are diminished. The fracture of the oil-cooled metal has a very fine texture.

Cast steel produced in this manner is characterised by great toughness, it being possible to bend it to quite as great an extent as the best wrought iron. It will have been seen that, within certain limits, the character of the metal can be varied, either by altering its composition or by modifying the treatment it receives after being cast. In general, the variation in breaking-strain among low-carbon steels of approximately the same grade does not exceed 6 tons per square inch, ranging from about 29 tons to 35 tons per square inch; the extension varies between 17 and 6 per cent. when tested on lengths of 8 in., the standard length at present in this country. The elastic limit is found to range from $\frac{1}{2}$ to $\frac{5}{8}$ the breaking-strain. Stronger qualities can of course be made, but at the expense of toughness. The working stress allowed to be put upon cast iron rarely exceeds 1 ton per square inch. Now, it has been stated on authority that there are hydraulic riveters, made in this cast steel, which are in daily use with a working stress of 14 tons per square inch. Another great advantage possessed by this form of cast steel is that it can be wrought under the hammer and welded with facility, not only to metal of a similar kind, but also to rolled steel and to wrought iron. The shrinkage of these steel castings is about $\frac{1}{4}$ in. per square foot.

Sulphur.—This element is very active in causing red-shortness, even so small a quantity as one tenth of one per cent. (0·10) being occasionally sufficient to make a rail roll badly. Its presence in such small quantity in steel used for tools and cutlery appears to be less objectionable, since it does not produce brittleness in the cold. The soundness of steel castings and the welding power of steel are both impaired by sulphur. The presence of manganese tends to neutralise the influence of sulphur on the properties of steel when worked hot.

Phosphorus behaves in exactly the reverse way to sulphur, producing cold-shortness especially under shock. A given quantity of phosphorus has about the same effect in producing cold-shortness that the same amount of sulphur would have in causing red-shortness. Phosphorus hardens iron to a greater extent than carbon, the ratio between them being at least as 2 to 1. The hardening effect of phosphorus, however, differs from that of carbon in that it is not influenced by the rate of cooling, since phosphorus cannot exist in iron in two conditions—the combined and the uncombined. As in the case of silicon, the amount of phosphorus which is admissible depends greatly upon the percentage of carbon. Thus, a rail might contain 0·25 of phosphorus, and yet not be dangerously brittle, provided carbon were nearly absent. But a rail containing only 0·10 per cent. of phosphorus and 0·30 to 0·50 of carbon would be useless. It is in steel intended for tools and cutlery that phosphorus is more objectionable than in any other, as it renders it extremely difficult to temper, and a fine cutting edge cannot be obtained if even so minute a quantity as twenty-five thousandths of one per cent. of phosphorus be present. As a result of many experiments, it appears to have been shown that the effect of phosphorus on ductility under a steadily applied load is practically constant and is independent of the proportion of carbon ; so that the effect of a given percentage of phosphorus is much more marked in high-carbon steels, where extensibility is low, than in the soft and ductile metals containing but a small proportion of carbon. In iron castings phosphorus in small quantity is beneficial (as already explained in speaking of foundry practice), owing to its causing the metal to cast sounder; and although the actual strength of the metal is slightly reduced, yet that of the casting may as a whole be increased, and the casting is sharper in outline by reason of the greater fluidity of the metal.

Arsenic.—It has recently been shown that arsenic is present in most samples of pig-iron and steel. Its effect upon the metal resembles that of phosphorus, in that it produces cold-shortness, and that its influence increases with the percentage of carbon present; but the effect is much less marked. In steels containing less than 0·2 per cent. of carbon the tenacity is increased, and the bending power and ductility are but slightly diminished, even by 1 per cent. of arsenic; but with crucible (high-carbon) steels, even 0·2 per cent. of arsenic may exert a slight, but quite distinguishable, bad influence. The hot-working properties are scarcely deteriorated even when 3 or 4 per cent. of arsenic are present, but the welding power of the metal is destroyed.

Manganese.—This is the trusted physic of the iron and steel manufacturer. It is to this element that he looks for the cure of all the ills that iron is heir to, with the exception of the hereditary disease, 'phosphorus,' which experience has taught him must be dealt with by more modern treatment of a radical nature. Its uses have been so often referred to in the foregoing pages that it is unnecessary to do more than summarise them here. Amongst the most important are the removal of oxygen and sulphur from iron, the neutralisation of the deleterious effects of sulphur, and the production of a fluid slag, promoting its complete removal from the metal. Manganese steel will be described hereafter.

Copper has generally been considered to cause red-shortness in about the same proportion as it is produced by sulphur; but the experiments of Herr Wasum appear to prove that with even 0·86 per cent. of copper, 0·23 of carbon, and 0·71 of manganese, ingot-iron will roll perfectly sound.

Hydrogen is very generally found occluded or absorbed by steel; it tends to make the metal hard and brittle. Electro-deposited iron has been found to contain as much as 240 times its own volume of hydrogen, and the metal was then so hard that it would scratch glass. Iron that has been over-pickled in acid in cleaning it is sometimes made brittle by the hydrogen evolved during the action of the acid upon the metal. The gas is expelled and its effects are removed during the process of annealing.

SPECIAL STEELS

The nomenclature of iron, already sufficiently unscientific, has been made more confusing by the introduction of a number of so-called steels, many of which are alloys of iron with other metals, and contain but little carbon.

Manganese Steel.—This remarkable material, discovered by Hadfield, was one of the first of these steels to be produced and investigated. Manganese is invariably and necessarily present in ordinary steel; but by adding larger proportions than usual of ferro-manganese to molten decarburised iron in the casting-ladle, metals are produced possessing properties which could never have been foreseen. As the proportion of manganese increases up to 5 per cent., the strength and ductility of the metal decrease rapidly, until at that point there is formed a very weak, brittle, and intensely hard alloy, useless for all ordinary purposes. But on increasing the manganese beyond this limit, the toughness and tenacity both improve, until they reach their maximum when 14 per cent. of that element is present; further additions of manganese cause a sudden diminution in the ductility, and beyond 20 per cent. of manganese a rapid decrease in the breaking-load also. With increasing proportions of manganese the material becomes less and less magnetic, until when 12 to 14 per cent. of manganese is present only very fine drillings are capable of being attracted by a magnet.

The castings of manganese steel are sound, but they show a great contraction, which may amount to $\frac{5}{8}$ inch per linear foot. They are crystalline, and, as cast, they are somewhat brittle, with low limit of elasticity and extensibility, combined with only moderate tenacity ; but by heating them to whiteness and quenching in water, both the tensile strength and the ductility are enormously increased, whilst the elastic limit is not greatly affected. Hammering or working in the cold rapidly renders the metal hard and brittle, but the good working properties are restored by re-heating and quenching—a process, therefore, that must be frequently resorted to in wire-drawing or similar operations. Whilst hot, all the manganese steels—even that which is most brittle when cold—are capable of being forged easily. After the peculiar toughening by quenching, a good specimen of the steel shows an almost unparalleled combination of tenacity and extensibility (60 to 70 tons per square inch, with an extension of 40 to 50 per cent.), and is capable of resisting violent shocks. It is this latter capacity which renders the material so valuable for the wheels of cars, or for other objects which may be called upon to bear exceptionally rough usage. Air-cooling from a white heat improves the metal distinctly, but the effect is not comparable with that produced by quenching, whilst cooling in oil gives an intermediate result. The steel cannot be welded, and is so hard in the cold that it is very difficult to work with ordinary tools, and it is advisable to shape the material as far as possible while it is hot. It is noteworthy that this extreme hardness was not found in a sample made by Hadfield with practically no carbon.

Chrome Steel.—Steel containing a small quantity of this metal has a fine texture ; a larger quantity produces hardness and brittleness. The application of this alloy has, so far, been very limited, but it has been used to some extent for armour-piercing projectiles, and they have shown a high penetrative power.

Chrome steel is stated to be manufactured at Brooklyn, America, in the following manner : the chrome-iron ore is finely powdered and reduced with charcoal in crucibles, the yield being about 45 per cent. of crude chromium, containing 30 per cent. of chromium and 3 per cent. of carbon. This chromium-pig is granulated and mixed with a suitable quantity of pure wrought iron. Six charges of 70 lb. each can be worked off in 24 hours. The percentage of chromium ranges between $\frac{1}{4}$ and 2. The effect of chromium in raising the elastic limit and increasing both the breaking-load and extensibility is most marked in the higher carbon steels. Chrome steel is unweldable, probably because the chromium oxide, which forms on the surface during heating, is infusible and cannot be fluxed by means of sand.

Tungsten Steel.—The effect of tungsten on steel is greatly to increase its hardness without the necessity for quenching ; in fact, tungsten steel cannot be hardened further except by the use of oil, and then only with great difficulty, the richer alloys inevitably cracking. Hence the term *self-hardening*, frequently applied to those containing about 5 or 7 per cent. of tungsten. They are sometimes known also as Mushet steel. The great hardness and fair ductility of tungsten steels and the fact that their temper is not drawn when doing rapid turning, as is the case with ordinary steels, render them very useful, especially for tools for turning very hard metal. For such purposes there is an increasing demand for this alloy. The fracture of tungsten steel is remarkably fine-grained, and is very beautiful. The power of steel to retain magnetism is greatly increased by the presence of 2 to 3 per cent. of tungsten.

Nickel Steel.—Important experiments on nickel steel were first made by Riley in 1889 ; and since that date its valuable properties have led to its adoption in structural work, more especially in naval construction. The alloy commonly employed contains from 2 to 4 per cent. of nickel and from 0·2 to 0·3 per cent. of carbon. Such a steel is far stronger and tougher than the corresponding carbon steel, and it has a much higher elastic limit, whilst it is slightly less corroded by the action of water. The working properties are greatly enhanced by rolling. Its power of resisting shock and its toughness, which minimise the disruptive effects of collision or of the penetration of a heavy projectile, render it especially valuable in the construction of warships, and of propeller shafts and parts of machinery that are liable to receive heavy blows. Armour-plates of this material subsequently Harveyised are now being largely employed, and there is no difficulty in producing a material with a minimum elastic limit of 23 tons and tensile strength of 36 tons per square inch, and an elongation (on an 8-inch length) of 23 per cent. The French navy are employing a chrome-nickel plate, containing about 0·4 per cent of carbon with 1 per cent. of chromium and 2 per cent. of nickel.

The nickel may be introduced into the steel in the form of grain nickel or of a high ferro-nickel alloy, after the steel is melted in the open-hearth furnace, and about an hour before it is ready for tapping; but more generally now nickel oxide is placed on the hearth of the furnace, so that the carbon of the pig-iron may reduce it to the metallic state, or it is enclosed in sheet iron boxes, and so added, the reduced nickel dissolving in the bath of iron. Owing to the readiness with which almost pure nickel may be applied to the bath, it is easier to produce a nickel steel than a manganese steel containing a low percentage of carbon. Although probably there is for most purposes but little gain in employing an alloy containing more than 12 or 14 per cent. of nickel, it is quite possible to produce one with 25 or 30 per cent., accompanied by only 0·2 or 0·3 per cent. of carbon. The hardness of the material increases with the proportion of carbon, and it is impossible to machine a specimen containing high percentages of nickel and carbon together. Steels containing less than 3 per cent. of nickel may be welded, but above this limit the difficulty increases with the proportion of nickel. The scale produced on the re-heated ingots and bars of this steel gives great trouble by the pertinacity with which it clings to the surface of the metal; so that, unless special precautions be observed in rolling, it is forced into the metal and thus produces rough sheets.

Nickel steel in many respects resembles manganese steel. Bars containing 25 per cent. of nickel are not ordinarily magnetisable. But it is singular that, when cooled to −50° C., they become magnetisable, and remain so at the normal temperature, and even if they be re-heated to nearly 600° C. But at this point the material becomes once more permanently non-magnetisable (unless cooled again to −50°), and this change is accompanied by a marked reduction in strength and increase in volume.

Aluminium Steel.—Like silicon, aluminium is frequently added in small quantities to melted steel after re-carburisation. Its enormously high affinity for oxygen renders it valuable as a deoxidising agent; and it can even remove carbonic oxide from solution in steel by combining with the oxygen and thus liberating carbon, which is at once taken up by the bath; and it appears also to increase the solvent power of the fluid metal for gases, and thus to prevent their evolution at the moment of solidification. Since aluminium may be obtained practically pure, it is a most valuable agent in the production of ingots which are required to contain the smallest possible proportion of carbon, inasmuch as it ensures soundness and overcomes red shortness without the addition of manganese, which latter material is almost of necessity carburised, and must therefore introduce carbon into the metal. It was at one time popularly supposed that the addition of a few ounces of aluminium to several tons of steel reduced the fusing-point of the latter by two or three hundred degrees, but this is undoubtedly a fallacy; the metal may perhaps flow more freely, but the fusing-point is for practical purposes unaltered. Aluminium is more readily removed even than silicon by oxidation. A very small proportion suffices to destroy the welding properties of steel. The addition of increasing percentages of aluminium to steel affords a more and more crystalline metal, which becomes very sluggish and thick on melting, and which is no longer forgeable when more than 5½ per cent. of aluminium is present.

Silicon Steels may be produced which in their characteristics resemble aluminium steels of similar percentage composition.

Boron Steel.—Moissan and Charpy have shown that a true steel may be made in which boron takes the place of carbon. It may be prepared either by heating a mixture of reduced metallic iron with pure amorphous boron in a current of hydrogen, or by throwing the boron into fused cast iron, when it unites with the metal and displaces a large proportion of the carbon, which floats to the surface in the form of kish. Iron may in this way be made readily to take up 10 per cent. or more of boron. A steel containing 0·58 per cent. of boron and 0·17 of carbon was found to forge and to roll well at a dull red heat, but to become brittle at higher temperatures. The tenacity of an annealed specimen was 29 tons per square inch, with an extension of 11 per cent. On quenching in water, the tenacity of the bar could be increased to over 80 tons, whilst the extensibility was reduced by over 70 per cent. In this respect the boron steel resembled ordinary carbon steel; but in spite of the effect on the strength, the material remained quite soft to the file after quenching, instead of becoming glass-hard, as carbon steel with similar properties would have been.

Retrospect.—In the foregoing pages it has been attempted to show in what progress has really consisted, and how it has been brought about. If we glance back for a moment, we see that the open-hearth processes embody the same principle as the first process by which steel was produced, viz. the mutual action of carburised iron and oxide of iron on one another, and the Bessemer process is, after all, though a fine offspring, the natural descendant of the finery process, the origin of which, as we have seen, was due to modifications in the primitive blast-furnaces. There is perfect continuity throughout, and what, after all, more natural?

Progress in the art of manufacturing iron and steel has been the joint work of the scientific chemist and of the engineer. As in the past, so in the future: success will depend on these two elements working harmoniously together.

COPPER

THE word copper has been derived from the corresponding Latin word *cuprum*. The Romans, who obtained their copper mainly from Cyprus, called it *æs Cyprium*; this term in time became shortened to *cyprium*, and finally to *cuprum*.

Ores of Copper.—*Native* copper, *i.e.* copper in the metallic state, does not occur in Cyprus, nor, indeed, in any other part of the world, except in the Lake Superior district and in New Mexico, in sufficient quantity to constitute a source of copper in itself. There is distinct evidence to show that the Romans reduced the ores of Cyprus (sulphides and carbonates) by methods which in principle are identical with our own.

Native Copper is sometimes found in large masses having a very curious branch-like appearance, each branch being composed of crystals of copper, somewhat deformed, united together. Such masses have been obtained from the southern shore of Lake Superior. Some of the blocks weigh as much as 400 tons, and since the toughness of the metal prevents it from being blasted with gunpowder, much time and labour are expended in cutting the blocks into portable pieces with steel chisels. Metallic copper is also found in veins disseminated in granite, in Cornwall and North Wales, and in many other parts of the world. A very remarkable form of native copper is the *copper sand* of Chili, or *copper barilla*, which consists of grains of metallic copper mixed with quartz. Native copper, especially that from Lake Superior, is of a very pure description, and is tougher than any but the best specimens of the copper extracted from the ores.

The following table exhibits the composition of the ores of copper :—

Ores of Copper.

	Composition		Copper in 100 parts of pure ore
Red Copper Ore	Copper, Oxygen	Cu_2O	89
Black Oxide	Copper, Oxygen	CuO	80
Copper Glance	Copper, Sulphur	Cu_2S	80
Indigo Copper	Copper, Sulphur		67
Copper Pyrites	Copper, Iron, Sulphur	$Cu_2S.Fe_2S_3$	35
Peacock Copper	Copper, Iron, Sulphur		56
Grey Copper Ore	Copper, Iron, Sulphur, Antimony, Arsenic		Variable
Malachite	Copper, Oxygen, Carbonic Acid, Water	$CuCO_3 + Cu(OH)_2$	58
Blue Malachite	Copper, Oxygen, Carbonic Acid, Water	$2CuCO_3 + Cu(OH)_2$	55

Copper Pyrites, *Chalcopyrite*, or *Yellow Copper Ore* is the most abundant ore of copper. The colour of pure copper pyrites is a fine brass-yellow, but some specimens are much paler, from the presence of iron pyrites. Copper pyrites is much softer than iron pyrites, and the richness of a sample may be in some measure inferred from this character.

Peacock Ore or *Variegated Copper Ore* is found at St. Austell and Killarney, and in considerable quantity in the Butte Mines, Montana. It is characterised by the most beautiful iridescent colours.

Grey Copper Ore is one of the most abundant and important ores of this metal, as well as the most complex and variable in composition. Like the preceding ores, it contains the copper in chemical combination with sulphur, but this latter element is also combined with iron, antimony, and arsenic, and generally with zinc and silver. The proportion of copper varies between 25 and 40 parts in a hundred, and silver is very commonly present in sufficient quantity to render its extraction a matter of importance. Cornwall and Freiberg furnish large supplies of grey copper ore. The term 'grey copper ore' is, in Cornwall, most commonly applied to the sulphide next to be described.

Copper-glance (*Chalcosite* or *Redruthite*), also a Cornish ore of great importance, is a chemical compound of copper and sulphur, which is generally free from any important foreign minerals.

Indigo Copper, so named from its dark blue colour, is found in Chili.

Red Copper Ore (*Cuprite*). Although as a rule not forming by itself ores of importance, it is frequently associated with other ores of copper.

Black Oxide of Copper (*Tenorite*) is found in Chili and in the United States ; it is not so common as the red oxide, but is sometimes more concentrated.

Malachite or *Green Carbonate of Copper* is a very fine green ore, some specimens being so beautifully veined that they are more highly prized for ornamental purposes than as an ore of copper. It is a very pure and valuable ore, found chiefly in Siberia, the Ural Mountains, and Australia.

Blue Malachite or *Azurite* or *Blue Carbonate of Copper* contains a larger proportion of carbonic acid than the green carbonate, and is generally found in the same localities. The mines of Burra Burra in South Australia are noted for malachite ores, which yield copper of excellent quality.

EXTRACTION OF COPPER FROM ITS ORES

The smelting of copper is more complex than that of iron by reason of the greater variety of the ores which have to be treated, and of the impurities that they contain. Sulphides and oxidised ores must be dealt with; the sulphur must be removed together with iron, arsenic, antimony, and other substances which are always found in certain ores; gold and silver when present must be recovered; and at the same time the percentage of the metal sought is lower than that in the ores of iron. The object of the copper-smelter is usually so to mix and treat his ores that he may obtain first a nearly pure sulphide of copper, separated, as far as may be, from the various other substances accompanying it in nature, and then to recover from this an impure or crude metallic copper, which is afterwards refined. The mixture depends upon the materials at his command; it may be treated in either reverberatory- or blast-furnaces, and the process may be conducted in few stages or in many. Usually the pure sulphide is not obtained in the first smelting operation, because the slag which would accompany such a product would contain a considerable

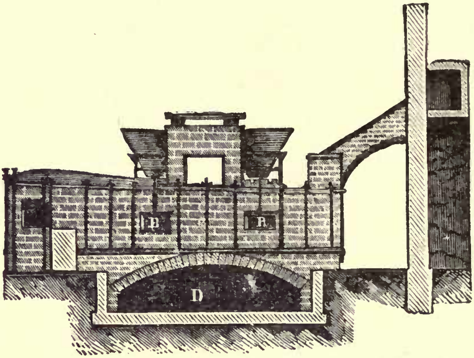

FIG. 63.—Furnace for roasting Copper Ores. B, B, Working doors. D, Vault for receiving the roasted ore.

proportion of copper; an impure sulphide containing about 30 per cent. of copper is therefore first made, and the earthy matters of the ore are fluxed away, forming a large bulk of slag which, in this case, contains so little copper that it may be rejected. The choice of the best method must be governed entirely by local conditions. In addition to the older types of furnace treatment, Bessemer practice has now been introduced into the metallurgy of copper ores; and the refining of crude copper is often accomplished in the wet way, or with the aid of electricity.

THE WELSH PROCESS OF COPPER-SMELTING

In England the reverberatory furnace has usually been preferred for copper-smelting; and the process is commonly conducted in six stages.

1st Process in Copper-smelting. Calcining or Roasting to expel Arsenic and part of the Sulphur.—The roasting is usually conducted in a reverberatory furnace, similar to those shown in figs. 26, 27 (pp. 134, 135), and in fig. 63.

Each calciner is charged with about three or four tons of the broken ore, which is spread evenly over the hearth, and roasted for twelve hours, being occasionally raked over through the working-doors (*p*) in order to expose fresh portions to the action of the air, and to prevent any part of the ore from being melted. At the low red heat of this furnace, the oxygen of the air combines with the metals and with the sulphur associated with them, the former being left in the form of metallic oxides, the latter passing up the flue as sulphurous acid. The roasting is stopped when it is only half completed, and much of the sulphide is therefore left in the product; it is chiefly the iron sulphide of the charge which is oxidised; nearly all the copper remains as sulphide, together with the residue of the iron. Arsenic becomes oxidised to arsenious acid (white arsenic), which passes with the sulphurous acid, in the form of vapour, into the chimney ; and on emerging into the air the mixture forms a grey cloud of *copper-smoke* which does much damage to the surrounding country.

At some works the sulphurous acid has been converted into oil of vitriol instead of allowing it to escape. The Gerstenhöfer, or some similar furnace, has been employed for this purpose.

2nd Process in Copper-smelting. Melting for Coarse Metal, to dissolve the Oxide of Iron as a Silicate.—It has been seen that the 1st process has had the effect of converting a large proportion of the sulphide of iron present in the pyrites into oxide of iron. It is the object of the process to remove, 2nd, this oxide of iron by causing it to combine with silica, to form a compound capable of being melted and separated from the rest of the ore. At this stage copper ores containing silica (quartz) can be introduced with advantage, provided that they are free from sulphur. It must not be forgotten that, during the process of calcining, a small proportion of the sulphide of copper in the pyrites has been converted into an oxide of copper, which resembles oxide of iron in its property of combining with silica at a high temperature, to form a melted silicate which would pass away in the slag, entailing a considerable loss of copper. This is prevented by the sulphide of iron which is still present in the calcined ore, and which exchanges constituents with the oxide of copper at the high temperature at which the fusion is effected, forming oxide of iron and sulphide of copper. The slag from the 4th process, to be presently described, is also conveniently introduced in this fusion, since it contains a considerable quantity of oxide of copper, which exchanges, as above, with the sulphide of iron still remaining in the calcined ore, furnishing more sulphide of copper to pass into the coarse metal, and oxide of iron to be removed in the slag. In some cases, the smelter adds some fluor-spar in order to facilitate the fusion of the charge.

The *ore-furnace* (figs. 64, 65), as it is called, in which the melting for coarse metal is effected, is also a reverberatory furnace, but its hearth (A) is much smaller than that of the calciner (usually about one-third of the size); also, the fire-grate is larger in proportion, generally about one-sixth the size of the hearth, because the charge has to be raised to a much higher temperature; the hearth is also slightly inclined on all sides towards a depression or cavity (B) at one side, which serves as a crucible in which the melted coarse metal collects. The bed of the furnace consists of an inverted fire-brick arch, carefully built and keyed; it is usually covered when hot with a 12-inch layer of a sand that will just *frit* (or cake together) at the highest temperature attainable in the furnace. It is calcined and rammed into the shape of a shallow basin with the aid of tools introduced through the doors; and then, all apertures being closed, the fire is urged to the utmost for several hours, and the whole is allowed to cool slowly to a very dull red heat. As the hearth so prepared is very porous, it is saturated with slag and low-grade matte before actual use, by melting first slag and then matte upon it until it will take up no more. After this treatment the loss of valuable regulus by absorption during the running of a charge is minimised. A second hearth of sand, about twice as thick as the former, is now carefully formed above it, and is saturated with sulphides and slag in the same way. Sometimes but one bottom is employed, and this is then of greater thickness than either of the above. But the latest English modification is to melt directly upon a fire-brick bottom, which must in this case be prepared with the utmost care.

Of late years, especially abroad, there has been a tendency to increase the size of the melting furnaces, and to alter the shape of the hearth from an oval to that of a rectangle with the corners cut off. In America furnaces have been built with hearths over 30 ft. long and 16 ft. wide; the grate is, of course, enlarged also, but not proportionately, the area being about 5 ft. by 6 ft. 6 in., whilst the flue area is about 16 sq. ft. The charge of such a furnace may exceed 12 tons. In many instances the air supplied to furnaces is preheated by circulation through flues or pipes embedded in the heated parts of the masonry, or built in contact with the walls of the chimney stack.

The following is a typical charge for a small furnace of this type, the materials being selected for the reasons above given, viz. :—

Calcined or roasted ore, about 18 cwt.

Ores containing oxide of copper and silica, 3 cwt.

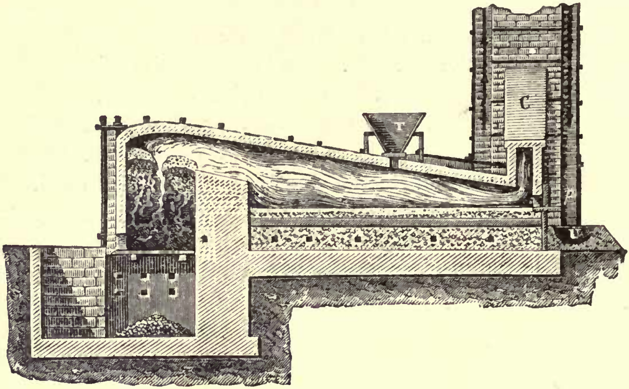

Fig. 64.—Section of Ore-furnace for smelting Copper Ores. T, Hopper for introducing the charge. *p*, Tap-hole for discharging the slag into the slag-moulds U. C, Flue leading to the chimney.

Metal-slag from process 4, containing oxide of iron, silica, and some oxide of copper, 6 cwt.

Fluor-spar, occasionally.

The roasted ore is most economically charged hot, and upon the regulus left from the preceding charge ; because it then distributes itself evenly and readily over the bottom.

The slag is the first to fuse, in about half an hour after the charge has been introduced, and by degrees the whole of the materials become liquid, and enter into violent ebullition, caused by disengagement of sulphurous acid gas, which assists the mixing of the melted charge.

After three or four hours the furnace-man stirs up the charge, and raises the temperature very considerably, to assist the separation of the coarse metal from the slag. About half an hour after, the tap-hole (*b*, fig. 65), which communicates with the cavity in the hearth, is opened, and the *matte*[1] or *regulus* of coarse metal is run out, through an iron gutter (*a*) into an iron box (G, fig. 66), perforated at the bottom, and standing in a cistern through which water is constantly running; the coarse metal is thus *granulated* or divided into small irregular grains, in order to fit it for undergoing the next operation. Very commonly the regulus is run into sand moulds, and subsequently crushed between rolls, or in a stone-breaker.

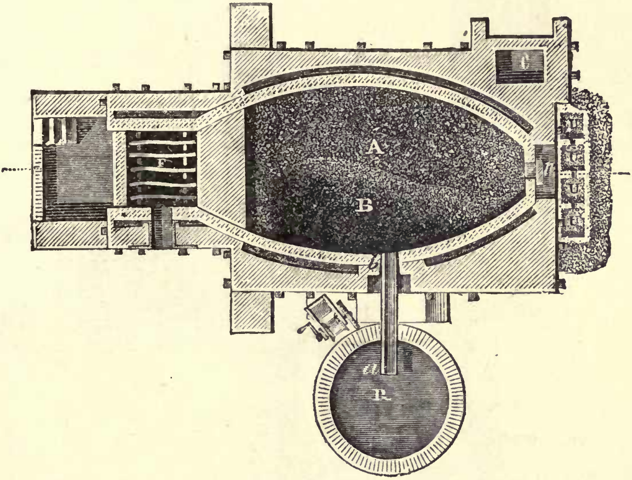

FIG. 65.—Plan of Ore-furnace for smelting Copper Ores. F The grate. R, Tank for granulating the coarse metal.

Sometimes the regulus from several operations is allowed

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[1] From the French *mat*, heavy.

to accumulate in the furnace before tapping, the slag alone being raked out before the introduction of a fresh charge.

The iron box containing the regulus is raised from the cistern by a winch (W), and its contents are carried to the calcining furnace.

This coarse metal should contain copper, iron, and sulphur in about the same proportion in which they are present in pure copper pyrites, so that the copper amounts to about 33 per cent., or nearly four times the proportion contained in the raw ore at the commencement of the process.

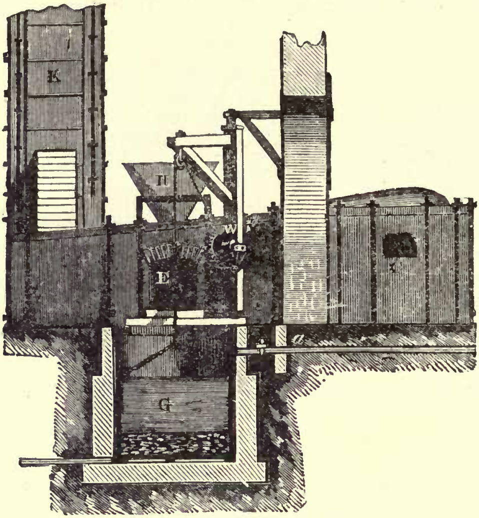

FIG 66.—Elevation of Ore-furnace for smelting Copper Ores. H, Hopper for introducing the charge. K, Chimney. C, Fire-door. *a*, Pipe for supplying water to the tank.

The slag (*ore-furnace slag*) is raked out into sand moulds (U, fig. 64 and 65), connected with each other by openings in their sides, where it solidifies into blocks of a black, somewhat glassy, appearance, interspersed with white fragments of quartz. It is used for rough building purposes in the neighbourhood of the copper works. The ore-furnace slag is composed essentially of oxide of iron (ferrous oxide) and silica combined in about equal proportions, as a *silicate of iron* or *ferrous silicate.* It is a waste product, but contains about one part in 140 parts of copper, which represents a loss that is apparently unavoidable. Occasionally a small quantity of regulus is found at the bottom of the blocks of slag, from which it is separated by hand-picking. Fig. 67 exhibits the general arrangements connected with the ore-furnace, and shows the furnace-man discharging the slag. In the larger reverberatory furnace provided with several working doors, the slag may be raked out of these simultaneously ; whereby a saving of time is effected, as in American practice.

3rd Process in Copper-smelting. Calcination of the Coarse Metal, to convert more of the Sulphide of Iron into Oxide.—Now that the earthy matter has been removed in the slag, it is far easier to oxidise the sulphide of iron than it was in the first calcining process. To effect this, three tons of the granulated coarse metal are calcined for 24 hours, the temperature being moderated at the commencement, to avoid fusion, and gradually raised in proportion as the removal of the sulphur diminishes the fusibility of the charge, which is raked over every two hours. The oxidising effects in this operation are the same as in the 1st calcining process, and the calcined coarse metal consists essentially of sulphide of copper, some oxide of copper, oxide of iron, and some unchanged sulphide of iron.

4th Process in Copper-smelting. Fusion of the Calcined Coarse Metal to remove all the Iron and to obtain Fine Metal.—The principles involved in this process are the same as in the 2nd process.

The fusion is effected in a furnace which does not differ materially from that employed in the 2nd process, except that there is no cavity in the hearth, which is made to slope from all parts towards the tap-hole (fig. 65). The larger furnaces may be used here also with equal advantage. The charge of a small furnace may consist of—

Calcined coarse metal (about one ton),
Roaster-slag from the 5th process
Refinery-slag from the 6th process
Ores containing oxide and carbonate of copper } About 12 cwt.

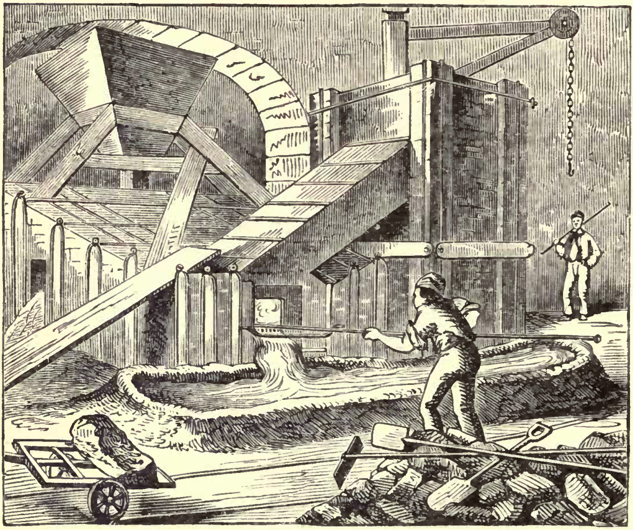

FIG. 67.—Copper-smelting Furnace.

(The roaster and refinery slags contain silica in combination with the oxides of iron and copper.)

These materials are fused together for about six hours, when they divide, as before, into a regulus or matte, and a slag, which remains above it. This regulus is called *fine metal*, to distinguish it from the *coarse metal* of the 2nd process; it may contain from 60 to 80 per cent. of copper, according to the amount of oxidised products and ores containing oxide and carbonate of copper added to the melting-charge. The different qualities are distinguished by specific terms ; thus, when an insufficient quantity of oxides has been added to the charge, the metal contains from 60 to 70 per cent. of copper, has a smooth, shining fracture and blue colour, and is called *blue metal* ; with from 70 to 78 per cent., the fracture is granular, the lustre greasy, and the colour greyish-white, it is then called *white metal*, and is nearly pure sulphide of copper ; when the percentage of copper is above 78, the surface of the metal is covered with pimples, and *moss* copper (metallic) is found in the air cavities, it is then called *pimple metal.* The pimples are formed by escaping sulphurous acid gas, produced by the reaction (shortly to be described) between sulphide and oxide of copper, which has yielded the moss copper ; such a product indicates a deficiency of sulphides in the charge.

When it is intended to manufacture *best selected copper* the fine metal is made to undergo a partial roasting ; some metallic copper is thus formed and those of the impurities present that have a weaker hold upon sulphur than copper has are displaced by a portion of the copper, and, being reduced, alloy themselves with the remainder of the copper, producing the impure metal, termed *bottoms*, which is formed in this process. The unreduced fine metal, which should now be comparatively free from impurities, is treated in the ordinary way for copper. The greater portion of the gold, silver, bismuth, tin, antimony and arsenic are removed in the bottoms ; but the elimination is never quite complete, owing, possibly, to the formation of double sulphides of copper and the other metals which are not decomposed by the copper.

In some smelting-works, where the fine metal is not obtained in so pure a condition, and contains only 60 per cent. of copper, it is again submitted to the two processes of calcining and melting, exactly as in processes 3 and 4, when it yields *black copper* or *coarse copper*, which contains from 70 to 80 per cent. of copper.

The *metal-slag*, as the slag from the 4th process is termed, is very crystalline and lustrous, and consists chiefly of silicate of iron, but it contains a considerable proportion of copper, partly as silicate of copper, and partly as small grains of metallic copper, disseminated through the mass. In some specimens of the metal-slag, the copper appears in very fine brilliant filaments, forming *moss copper*. This slag is usually employed as part of the charge in the 2nd process (melting for coarse metal).

5th Process in Copper-smelting. Calcining or Roasting the Fine Metal to remove Sulphur and obtain Blister Copper.—The manner in which this process is carried out is varied according to the degree of purity of the fine metal, but the chemical principles which it involves are the following: When a compound of copper with sulphur is heated in air, sulphurous acid gas and oxide of copper are formed. Further, when an oxide of copper is melted in contact with a sulphide of copper, the oxygen of the former combines with the sulphur of the latter to form sulphurous acid gas, and the copper is separated in the metallic state.

The pigs of white metal are introduced, to the amount of several tons (from 1½ up to 25 or 30 tons, according to the size of the furnace), into a reverberatory furnace, where they are heated, at a gradually increasing temperature so as to avoid fusion, for about four hours, in order that a part of the sulphide of copper may be converted into oxide of copper. When it is judged that this has been effected to a proper extent, the temperature is further raised so as to fuse the charge, which by this time has sunk down upon the hearth, the doors of the furnace being closed in order to avoid excess of air. As soon as the mass is fairly liquefied, the temperature is somewhat reduced, being again raised towards the close. During this fusion a violent effervescence is observed in the liquid mass, due to the escape of sulphurous acid gas, whilst metallic copper subsides, in a fused state, and is run out into sand-moulds, where it solidifies into ingots, which preserve a blistered appearance, caused by the escape of sulphurous acid during solidification. The duration of the process depends upon the degree of purity of the metal under treatment, but it varies between 12 and 36 hours.

Blue metal requires a prolonged treatment, and should be converted into pimple metal (containing about 88 per cent. of copper) before submitting it to the blister process. A small quantity of slag (called *roaster-slag*) is formed during the fusion, which resembles pumice in its porous texture, but has a dark red-brown colour, and consists of the oxides of iron and copper combined with silica, derived partly from the hearth of the furnace, and partly from the sand-moulds in which the ingots of white metal are cast. This slag contains about 16 per cent. of copper, and is used as a portion of the charge in the 4th process.

The roasting-furnace employed in this process is often constructed with an air-channel (fig. 68), traversing the whole length of the fire-bridge, open to the air at both ends, and communicating with the hearth of the furnace through two openings (*b b*) in the brickwork. This permits the introduction of heated air into the hearth, by which the roasting is much facilitated. The grate-area is still further increased to about one-fourth that of the hearth. The enlarged American furnaces are applied to this process equally with those previously described.

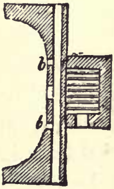

FIG. 68.

6th Process of Copper-smelting. Refining and Toughening, to purify the Copper.—The pigs of blister copper are far from pure ; they contain from 96 to 99 per cent. of copper, the remainder consisting of sulphur, arsenic, iron, tin, lead and other foreign substances, varying with the ore available. The furnace employed does not differ very materially from the melting-furnace used in the 2nd process (fig. 64), but the hearth should be saturated primarily with the highest-grade metallic copper, instead of with regulus. The blister copper to be refined is piled, in charges of 8 to 20 tons, upon the hearth, in such a manner as to allow air to circulate freely among the ingots. A moderate heat is applied at first, to allow the oxygen of the air to act upon the blister copper. The sulphur then becomes converted into sulphurous acid gas, and the arsenic into arsenious acid, which passes off in vapour, whilst the iron, tin, lead and other foreign metals, as well as a portion of the copper, are converted into oxides. After being roasted for about six hours, the metal is melted, when a thin layer of slag is formed upon its surface; after raking this off, a large sample of the copper is withdrawn and examined by the refiner, who can judge from the appearance of its surface if the oxidation has proceeded to the necessary extent. In order to toughen the metal, its surface is then covered with wood charcoal or anthracite, which is renewed from time to time so as to shield the copper from further oxidation, and the melted metal is stirred with a pole of young wood (usually birch), until a small sample, withdrawn in a ladle and cooled, and then half cut through with a chisel and broken, exhibits a fine close grain, a silky fracture, and a light-red colour; and a small bar, cast for the purpose and hammered when red-hot, is found to be soft and free from cracks at the edges. The cast ingot should show no depression on the surface, as this would indicate the presence of too much dissolved oxide. The copper is then said to be at *tough-pitch*, and is taken out in iron ladles lined with clay, and cast into ingots of *tough-cake* copper. The ingot moulds employed are also made of copper.

The effect of this process of *poling*, as it is termed, in toughening the copper depends upon the removal of oxygen from the metal. When the blister copper has been refined, as above described, by being very slowly melted in contact with air, it is found to have taken up a large proportion of oxygen, which is dissolved in the metal as an oxide (*suboxide*) of copper. The presence of the oxygen, though it does not amount to more than two or three parts in a thousand of copper, has the effect of rendering the copper brittle or *dry*, so that a small ingot of it is easily broken when hammered, and its fracture exhibits a deep red colour, and a coarse-grained, somewhat crystalline structure. When the pole is plunged beneath the melted copper, the combustible gases generated from the wood by the heat effect the removal of the oxygen from the metal, and bring it by degrees to tough-pitch, mainly by agitating the mass and bringing the copper into better contact with the anthracite. If, during the operation of casting the ingots, the surface of the metal on the hearth be not well covered with charcoal or anthracite, the copper will go *back*, or become brittle again, in consequence of the absorption of oxygen from the air.

If the process of poling be continued after the copper has been brought to tough-pitch, it may become even more brittle than before it was poled, an effect which was formerly ascribed to the combination of the copper with a little carbon from the wood ; but analysis has failed to prove the presence of carbon. The way in which the small quantity of oxygen, which it is necessary to leave in (even in the case of the purest metal produced), acts beneficially is as yet unknown. If oxygen be entirely removed, the copper will be *overpoled*, exhibiting a brittle character, due to some of the above named impurities. On the other hand, if too much oxygen has been left in the metal, the copper is dry or *underpoled*. The effect of overpoling upon the metal may be remedied by allowing air to act for a short time upon the melted copper, so that a small quantity of oxygen may be absorbed by it.

When the copper is intended for rolling into sheets, it is usual to add lead, in the proportion of about five parts to a thousand of copper, just before skimming the surface in order to ladle out the copper. The metal is well stirred after the addition of lead, in order that the action of the air may produce an oxide of lead, which combines with the oxides of tin, antimony, and other foreign metals, to form a liquid slag, which rises to the surface of the metal and is skimmed off before casting. It is necessary that the removal of the lead from the copper by oxidation should be as complete as possible, since its presence would prevent the scale of oxide of copper from being easily detached from the sheet during the process of rolling, and even 0·1 per cent. of lead in copper suffices to injure its quality.

This treatment of the metal with lead is called *scorification*, from the *scoria* or slag which forms upon the surface.

The *refinery-slag*, skimmed from the surface of the melted copper before commencing the process of poling, has a dull brown-red colour, with a purple shade, and consists almost entirely of suboxide of copper combined with silica derived from the hearth and from the sand-moulds employed in casting the blistered copper. It is utilised in the 4th process (fusion for fine metal).

The hearths of the copper-furnaces become strongly impregnated with copper in course of time, and are broken up in order that the metal may be removed from them.

Many modifications of these processes, some lessening, some increasing, the number of operations, are employed to meet the requirements of different districts or ores; and regenerative gas-firing has in a few places been applied with success to the copper-furnaces.

One of the most recent modifications is that of Nicholls and James, and the Cape Copper Company of Swansea; it is known as the *Direct Method* of copper refining. White metal crushed to pass a $\frac{3}{8}$-in. sieve is calcined to remove the bulk of the sulphur, and is then mixed with the right quantity of unroasted white metal, and charged on to the hearth of a reverberatory furnace. In a short time the charge begins to melt, the copper compounds react, much sulphurous acid is given off, and nearly pure metallic copper is left; the small quantity of slag is skimmed off, and the metal is refined at once in the same furnace. The proportions of the charge are ascertained by trial experiments in small crucibles, the object being to adjust the sulphur and oxygen so that they shall both be removed as SO_2.

Contrasting this process with the ordinary roasting process, James points out that in the former the oxidation takes place below the temperature of fusion of the regulus, whereas in the latter it is effected above it. He claims as the result of experiments that some compounds of copper formed during the oxidation, which are volatile at the higher temperature of roasting, are not volatilised at the lower temperature of calcination, whilst the conditions are still favourable to the removal of the more volatile compounds of arsenic and antimony; consequently there is a much smaller loss of copper. He also claims to have proved that there is no loss of silver in the various stages of copper-smelting up to the point at which metallic copper is liberated, and, as in the 'direct process' the reaction producing metallic copper is very rapid, the loss of silver is very greatly reduced.[1]

Mr. James states that complex copper ores which ordinarily produce leady mattes, entailing a considerable loss of silver in their treatment, may be smelted by the direct process without loss if silica be present in sufficient quantity. The silver passes into the copper, and the lead may be recovered from the slag by smelting in a blast-furnace in the usual way.

EXTRACTION OF COPPER FROM THE BITUMINOUS SCHISTS OF MANSFELD

At Mansfeld, an ore is extensively worked which contains not more than 4 per cent. of copper in the form of

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[1] Trans. Inst. Mining and Metallurgy, 1896–7.

crystals of copper pyrites, diffused through a clay slate containing a large proportion of bituminous matter. The consumption of fuel in extracting the copper from this ore is only one-third of that in the Welsh process.

The ore is first roasted in large heaps made up with alternate layers of brushwood, the bituminous matter also serving as fuel. A heap containing 200 tons of ore will go on burning for fifteen or twenty weeks. In this process, which corresponds to the first calcination in the Welsh method, a part of the sulphur passes off as sulphurous acid, and much of the iron is converted into an oxide.

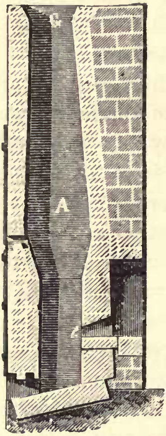

Fig. 69.—Blast-furnace formerly employed for smelting the Bituminous Schists at Mansfeld.

The next process is similar to the Welsh fusion for coarse metal, and consists in melting the roasted ore with some fluor-spar, some copper ore containing carbonate of lime, and some slags containing oxide of copper to decompose the sulphide of iron and remove the iron as a silicate (p. 304). Formerly this fusion was conducted in small blast-furnaces (fig. 69), which were about 14 ft. high, and 3 ft. in their greatest width. The blast was supplied by two twyers (*t*) placed side by side, about 2 ft. above the bottom of the furnace. The melted regulus and slag were conducted through two channels into two basins about 3 ft. in diameter and 20 in. deep, lined with a mixture of clay and charcoal dust, and filled alternately. The furnace was provided with a chimney (G) 30 or 40 ft. high. The fuel employed was either charcoal or a mixture of charcoal and gas-coke, which was charged alternately with the ore, as in an iron blast-furnace. The modern Mansfeld furnaces are circular and constructed like iron blast-furnaces, with a ring of twyers below, and a cup and cone charging apparatus above ; they use a blast heated to about 300° C. The height of the furnace is about 30 ft., and it is about 6 ft. wide at the twyers, gradually widening (without boshes) to 7 ft. at the top. The slag flows away continually from a cinder-notch, and the matte is tapped at intervals into moulds. The chemical changes which take place in the furnace resemble those in the Welsh process of melting for coarse metal, and the fused products which flow into the receiving basins divide into two portions, the lower layer consisting of the sulphides of copper and iron, and the upper layer of slag composed chiefly of silicate of iron containing but little copper. The slag is ladled out into moulds and employed for building, and the matte is then removed in crusts as it solidifies.

If the matte contain less than 30 per cent. of copper, it is again heap-roasted and treated as before, so as to remove more of the sulphide of iron ; but if it contain more than this proportion, it is at once roasted in stalls, or as is now more usual in kilns, the sulphurous acid being utilised by converting it into oil of vitriol. This operation of roasting corresponds to the *calcination of the coarse metal* in the Welsh process.

The roasted matte, containing oxide of iron and sulphide of copper, is treated as in the *melting for fine metal*, being fused in reverberatory furnaces with silicious slags or ores which dissolve the oxide of iron. The fine metal, which contains silver, is so roasted at a high temperature that this metal is converted into sulphate (see p. 131), which may be dissolved out in water for separate treatment, leaving the copper as insoluble oxide of copper, to be subsequently reduced and refined in reverberatory furnaces.

MODERN AMERICAN PRACTICE

Smelting in the Blast-furnace.—In America, copper ores are most commonly smelted in the blast-furnace, which is occasionally used to produce *black copper* (crude metallic copper) direct from oxidised ores, but more generally to concentrate the copper in mattes, from which it may afterwards be recovered. A mixture of sulphide and oxidised ores with slags from subsequent processes is so made up, by adjusting the proportions of silica, iron, sulphur, and copper, that the matte produced may contain the desired amount of copper—say 30 per cent.—and the slag a suitable amount of silica—about 33 per cent.—to render it fusible at the temperature of the furnace. The ores are commonly sorted over by hand, the richer lumps, containing massive pyrites, being separated for use without further treatment, the remainder being crushed and dressed by a washing process similar to that used in preparing gold ores (see p. 128). The heavier concentrates, consisting of pyrites more or less completely separated from the light gangue-stuff, are then charged into the blast-furnace ; the object of this preliminary treatment being the washing away of earthy matter, which contains no copper, but which would require fluxing, and would add to the volume of slag in the furnace. Very fine ore is frequently agglomerated with a little clay or lime, and is made into bricks or rough lumps before charging, in order to prevent the choking of the furnace by fine particles, and to lessen the loss due to the mechanical removal of dust in the waste gases through the action of the blast. When a high-grade matte (containing much copper) is to be produced, the ore may be calcined, as in the first stage of the Welsh process, prior to charging into the blast-furnace.

The furnaces were formerly built of brick, and resembled iron blast-furnaces. They were originally circular ; but as larger outputs were demanded, it became necessary to increase the area at the twyer-level, so that a greater volume of material might be constantly passing through the furnace. There is, however, a limit to expansion in this direction, owing to the difficulty in forcing the blast through any great thickness of charge with a reasonable blast-pressure ; and this limit is found in practice to be about 2 ft., which must therefore be the maximum *radius* of the hearth

If, then, the diameter of a circular hearth between the twyers exceed 4 ft., the centre portion will not be served by the blast from any of the twyers, for these are all placed at the circumference of the circle. In order to increase the make of a furnace beyond this limit, the shape must be altered; and this was accomplished in the *Rachette* furnace, introduced in 1862, by making the hearth rectangular. The extreme width being less than 4 ft., and there being twyers on all sides, the length of the rectangle is only limited by practical considerations connected with the structure and convenience of working the furnace itself. The length of such a furnace may be 10 to 12 ft.; it would have from three to six twyers on each long side, and one or two on each of the others; and two or three charging doors would be provided on one side at a height of 8 to 10 ft. above the level of the twyers. One cinder-notch and one tap-hole are sufficient, and the method of working is similar to that of a brick-furnace of the circular type. In the most modern Rachette furnaces, pipes are built into the brickwork just above the twyer-level, and a current of water is circulated through them constantly, to lessen the destruction of the brickwork through over-heating.

The majority of American copper-furnaces are now built of iron, of circular or oval section, or of the Rachette type, tapering slightly so that the upper part is slightly wider than the lower. They may be of cast iron, built in sections, or, better, of wrought-iron plates riveted together. An inner lining of the same metal is provided, and the space between the two casings (generally some 3 or 4 in. across) is kept filled with running water, of which from 1,000 to 3,000 gallons per hour may be passed while the furnace is in blast. When the furnace case is built in sections, pipes are provided to convey the water from one section to the next. In certain cases moist ores containing a little copper sulphate may be charged into blast-furnaces, and these rapidly corrode the iron lining near the charging door, iron dissolving and changing places with copper, which deposits as a loose film upon the plates. To prevent this, copper plates are sometimes employed instead of iron, as the copper sulphate solution is without action upon them. The plates are kept so cool by the water within that they are not destroyed, even in the hottest part of the furnace; and they require no lining except the chilled accretions which naturally form to the depth of a few inches in course of ordinary working, and which must be removed when they exceed this thickness. The water used must be fairly soft and pure, and lime-deposits must be carefully guarded against. The furnaces are from 6 to 10 ft. high from twyers to charging door, and are usually provided with a contracted flue above the charging platform, to carry away fume. The diameter is regulated by the pressure of blast to be employed as in brick furnaces. A blast belt surrounds the furnace, and from 6 to 12 twyers pass from this, water-tight, through the jacket to the interior. Fig. 70 represents a side view and fig. 71 an end view, partly in elevation and partly in section, of such a furnace. In this furnace there are five twyers (F) on each side and two at each end, all connected with the blast main E. H H are tap-holes, and M M cinder-notches. The charge is introduced through N, which is only a few feet above the twyers. The furnace is water-jacketed, as indicated, in two sections—the body and the boshes—and is supported on the pillars K K. In a few instances the matte is allowed to accumulate in the hearth of the furnace, and is tapped at intervals as in iron blast-furnace practice; but usually a fore-hearth is provided, and the matte constantly flows into this, in which it remains until a sufficient quantity has collected, when the tap-hole is opened and the charge drawn.

The fore-hearth is of very variable character, the simplest form being a plain rectangular box lined with clay. In the so-called *siphon-tap*, the slag and matte are allowed to fall together into a cast-iron box about 5 ft. square and 3 ft.

high, lined with fire-brick, and divided into two compartments by a partition of fire-brick. One compartment is about twice the size of the other, and they are connected by an aperture at the bottom of the partition; each has an overflow spout. The melted material from the furnace flows constantly into the larger compartment; and the connecting aperture is closed until this is nearly full. The matte and slag meanwhile separate, owing to their different specific gravities, and then, on opening the passage between the two receptacles, the level of liquid becomes equalised in the compartments, but only matte (which being heavier has sunk to the bottom) can pass into the smaller chamber. From this time the mixture separates automatically, the slag always floating on that portion of the matte which remains in the larger compartment, and matte alone passing into the smaller. When, at last, both divisions are full, matte constantly overflows from the spout of the small, and slag from that of the large, division. Owing to the time which is thus allowed for separation, the slag is obtained practically free from shots of metal. Most fore-hearths are mounted on wheels, so that they may be readily removed for repairs. The Herreshoff fore-hearth is itself water-cooled—as the furnace is—and is connected by a water-cooled opening with the hearth of the furnace; it is surmounted by a brick-lined cover, and is provided with a slag notch at the upper part, and with a tap-hole close to the bottom of one side. In one or two cases the matte flows from the furnace direct on to the hearth of a small reverberatory furnace, where it is stored in the melted condition until required for subsequent processes.

Water-cooled blast-furnaces of the type just described may treat from 40 to 150 tons of ore per diem according to size, using a blast pressure equal to about 1 or 1½ in. of mercury. It is impossible to give an accurate general estimate of fuel consumption, inasmuch as it varies with the conditions of use; but about 2 to 3 cwt. of ordinary coke are commonly required to smelt one ton of a charge consisting of ore and slag adjusted to be self-fluxing.

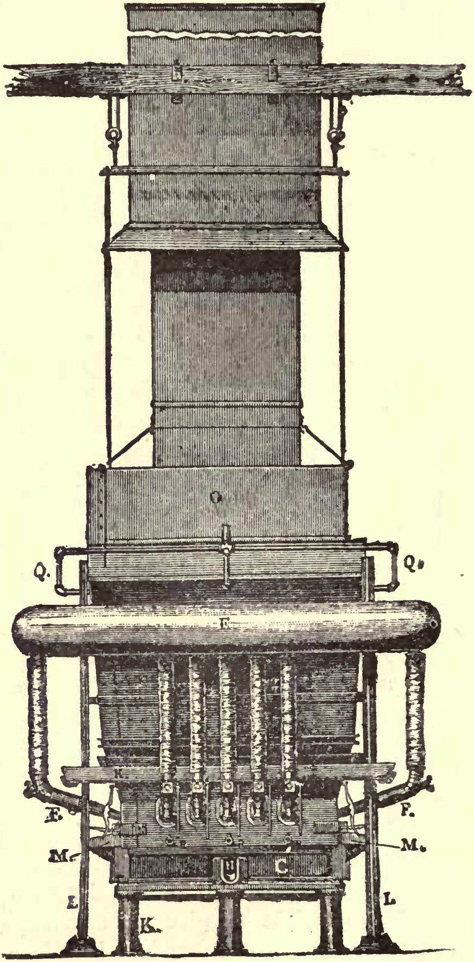

FIG. 70 —Water-jacketed Rachette furnace for copper-smelting (side elevation).

The degree of concentration of copper in the sulphide is by no means constant, matte containing from 20 to 50

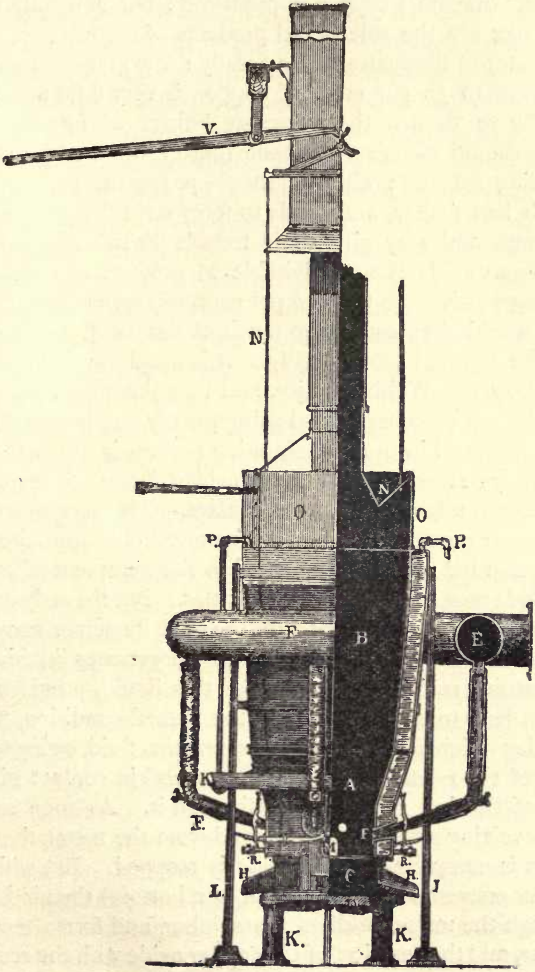

Fig. 71.—Water-jacketed Rachette furnace for copper-smelting (end view, part elevation, part section).

per cent. (or more) of copper being made. In a few furnaces, with rich ore and rapid driving, a small quantity of 'black' (metallic) copper is produced; but generally matte and slag are the sole liquid products of the furnace. The character of the matte varies greatly: low grade matte, with from 20 to 30 per cent. of copper, is very fluid and tends rapidly to destroy the refractory linings of furnaces, and these should therefore be made thicker when such material is being smelted; with 45 to 50 per cent. copper it is much less fusible, and tends to form solid deposits on cool surfaces, and may give some trouble for this reason in the fore-hearth. It is not advisable to produce a matte containing much more than 50 per cent. of copper, because the slag would then contain so much of the metal that it could not be rejected economically. It is usual, on this account, to follow the Welsh practice, and to make a medium grade which may be concentrated subsequently, as the quantity of slag produced in the concentrating process is much smaller, and may be readily returned to the blast-furnace for smelting.

Bessemerising of Copper Mattes.—The success of the Bessemer process in removing the metalloids from iron by oxidation led to its being applied to the treatment of copper sulphide ores, and afterwards to mattes. But the early experiments were not successful. In the steel Bessemer converter the air is blown at first through a homogeneous liquid, and, by burning certain constituents of this liquid, provides sufficient heat to keep the bath in the melted condition, whilst the slag which floats upon the top remains fluid, owing to the heat of the relatively large bulk of metal in contact with it, and of the hot gases passing through it. As soon as the heat-evolving substance is removed from the metal, the operation is complete and the blast is stopped. But with the copper converter (with twyers at the bottom) the air blown through the matte oxidises the sulphur and forms metallic oxides, and the reaction of the copper oxide with the remaining sulphide causes a reduction of metallic copper after the manner described on page 312. Thus there is produced a quantity of heavy metallic copper which sinks beneath the matte, and the cold air from the twyers has to pass through this copper before it can reach the sulphide. Some of the metal is thus oxidised, but the heat produced by its combustion cannot suffice to retain the metal in the fluid condition; the copper is therefore chilled rapidly by the cold air, and, solidifying, closes the twyers and stops the air supply. The failure of the original process was largely due to this cause. But in 1880, Manhès introduced the use of a converter with twyers at the side, and at a sufficient height above the bottom to ensure that the whole of the metallic copper produced should remain below the twyer-level. In this converter the oxidation of the matte, and the reaction between sulphides and oxides, provide sufficient heat to keep the whole charge fluid, and the copper, as it is reduced, sinks into the dead space at the bottom of the converter, where it is protected from the action of the blast.

A matte suitable for converting should not contain less than 45 per cent. of copper, or the proportion of iron would be unduly great, and would lead to the production of an unmanageable bulk of slag, and the silicious lining of the converter would be very severely attacked by the oxide of iron formed. On the other hand, it should not carry much more than 60 per cent. of copper, or there would be insufficient sulphur and iron to provide the necessary heat by oxidation. From 50 to 55 per cent. is usually preferred. Matte of the right grade is either provided direct from the blast-furnace or cupola, or may be concentrated by partial oxidation by a process of 'pyritic smelting.' It is usually delivered in the solid form, and is broken up into pieces of convenient size for charging into the small cupola in which the matte is obtained in a fluid condition at a temperature suitable for use in the converter. It is melted with the aid of coke, of which a little over 1½ cwt. may be required per ton of matte, and is then run into the converter. It is not expedient, usually, to bring matte in the molten condition direct from the original blast-furnace; but when a material of the right grade is either made or collected in a reverberatory furnace, it may be conveyed thence to the converters.

The converters are generally constructed in three sections, of either cast or wrought iron, and the shells are externally about 8 ft. in height and 5 ft. in diameter. They are suspended from trunnions, and in a general way resemble those used in steel practice, only the twyers are placed around the side instead of at the bottom. The lining, which is about 18 in. thick at the bottom, is made of a mixture of crushed quartz with a sufficient quantity (about 20 per cent.) of good plastic clay to make it bind; it is rammed into place, and carefully dried by a slow fire. The lining gradually tapers off, until at the bottom of the hood or covered part it is about a foot in thickness, and at the nose only one-third or fourth of this. The upper part is usually made of a less refractory mixture. The twyers are about $\frac{3}{4}$ in. in diameter, and vary from sixteen to twenty in number; they are formed opposite corresponding holes in the outside of the iron twyer-ring by driving an iron rod through the lining while it is still moist. When in use, the holes in the outer ring are closed with wooden plugs, and are of great service in enabling the workmen to clear any twyer that may have become stopped up during the progress of the blow.

Owing to the action of the oxide of iron upon the quartz, the lining of a converter is rapidly worn away; it rarely lasts more than nine blows, and the converters are therefore made readily interchangeable, as in steel practice. Basic linings have been tried, but have not proved successful, as silica is, in fact, necessary to flux the oxide of iron produced from the matte. A newly lined converter will rarely hold more than $1\frac{1}{2}$ ton of matte, whilst, owing to the destruction of the lining, the last charge run before re-lining may amount to four tons. The converter being placed horizontally, the charge is introduced through the nose, while a light blast is used; the full blast-pressure (about 11 lb. per sq. in.) is then let on, and the converter is brought to the vertical position, the blow being continued until practically the whole of the iron in the matte has been converted into oxide. The oxide thus formed combines with the silica of the converter lining, and produces a fusible slag, which is poured or skimmed off by turning down the converter; this slag may contain over 2 per cent. of copper, and is returned to the blast-furnace to be re-smelted. A small quantity of matte usually comes over with the slag, but collects at the bottom of the slag-pots in which the material is received, and is broken away by hand after cooling. The converter is then turned up again, and the blow is continued until practically the whole of the sulphur is oxidised, and a blister-copper containing 99 per cent. of the pure metal is obtained. Overblowing produces a 'dry' copper, containing oxide; but the ordinary condition may be restored by adding a small quantity of raw matte, which provides sulphur to act upon and reduce the oxide in the copper. The end of the blow is more difficult to observe than in the bessemerising of iron, for the flame indications are very uncertain. It is commonly judged by watching the behaviour of the small shots of material discharged against the wall from the nose of the converter. At first, these adhere tenaciously to the wall, but towards the end of the blow an increasing number rebound, and the operation is stopped when nearly all are observed to do so. The converter is then turned down, and its contents are poured into copper moulds brought successively beneath it. In normal work the time occupied in completing a blow is from one to two hours, of which approximately the half is taken up by the first stage, during which the bulk of the iron is removed.

Three converters are commonly worked together, being supplied with matte by one cupola, and their noses are placed under hoods communicating through dust-chambers with a stack, to carry off the intolerable fumes of sulphurous acid produced during the process. The appearance of the flame is even more beautiful than that of the ordinary Bessemer converter, owing to the volatile metallic impurities in the copper. In the earlier stages the flame is accompanied by dense clouds of zinc oxide ; as the zinc is removed, these clouds disappear, and the flame, which previously had been partly greenish and partly red, becomes first pure green, and then by degrees bluish. The end of the first stage is reached at this point ; and, after removing the slag, the flame, which is still bluish, slowly decreases in volume, and becomes red once more, and finally, taking a browner shade, is scarcely appreciable.

In Bessemer practice with side-blowing converters, one of the difficulties met with is the tendency of metal to enter the twyers as it flows over them when the converter is turned up or down. Unless this be carefully guarded against, there is danger of the melted metal finding its way to the blast box, and even melting a passage through it. Converters have been devised with the object of overcoming this difficulty, and among them is a trough-shaped vessel employed in Italy, and in a modified form introduced into America, with twyers on one side alone, so that by tilting sideways in one direction or the other, the depth of the twyer below the surface is variable at will ; and in charging or teeming all the twyers may be permanently above the level of the fluid charge.

Pyritic Smelting.—The blast-furnace and cupola are generally but slightly oxidising in their effect, owing to the presence of coke and to the atmosphere of carbonic oxide which exists even at the twyer level ; and in the mere melting of copper matte with sufficient coke to supply the necessary heat, the resulting product may have practically the same composition as the original charge. But since sulphides are used in the copper blast-furnace, and these are capable of combustion, any reduction in the weight of coke employed involves the oxidation of matte in its place; and as it is the iron sulphide which oxidises first, the residual matte should contain practically the whole of the copper originally present. By carrying this principle to its utmost limit, we can imagine a blast-furnace, in which the whole of the heat necessary for the melting of the matte and its accompanying slag is derived from the combustion of a portion of the matte. This is the process known as pyritic smelting, and there is some prospect that it may take a prominent position in the metallurgy of copper, although at present it is mainly employed in the extraction of gold and silver from complex ores containing variable proportions of copper in addition to other metallic substances.

Treatment of Poor Copper Ores.—In some instances, very poor copper sulphide ores are treated in blast-furnaces or cupolas in such a way as to afford a high degree of concentration. In a few districts in Spain, where the devastating fumes of sulphurous acid may be permitted to pass freely into the air, the ore if it contain more than 20 per cent. of sulphur, and less than that amount of silica, is roasted in large heaps, called *teleras*, usually containing about 400 tons of fairly large-sized lumps of ore. The temperature is so controlled that the copper shall be converted into copper sulphate (see page 131), which may be dissolved out by treating the material with water after cooling.

An interesting process of concentration, known as *kernel-roasting*, has been practised for more than a century in several parts of Europe. A poor copper pyrites, free from gangue, is roasted in nodules with a limited supply of air, at a temperature sufficiently high to make sub-sulphide of copper plastic without melting the whole. As oxidation proceeds, the iron sulphide, forming the bulk of the pyrites, becomes attacked, and is converted into oxide which remains infusible on the outside of the nodule; and (adopting Howe's probably correct explanation) the copper sulphide in the outer layer becoming enriched by concentration is at last half fused and tends to remain attached to the pyrites that is still unattacked within. The action thus gradually proceeds towards the centre, the oxide of iron remaining as an ever-thickening fringe outside, and a portion of the copper retreating inwards, until at last an irregular lump of ferric oxide is produced with a central kernel of a valuable mixed sulphide. The latter may be readily detached by hand, and smelted by ordinary processes. More than half of the copper, however, remains in the oxidised portion, and of this about one-half exists in the form of copper sulphate, which may be extracted by washing the ferruginous residue with water.

Several wet processes are in use for treating copper ores, and among them may be mentioned Henderson's, which is used in the extraction of the 2 or 3 per cent. of copper contained in the Spanish pyrites that has been roasted at the vitriol works for the sake of its sulphur. These residues contain a very small quantity of silver and a small proportion of residual sulphur. They are mixed with a sufficient quantity of sodium chloride (common salt) and heated in a muffle furnace (p. 143) to a very moderate red-heat. A muffle furnace is heated externally so that the products of combustion from the fuel cannot gain admission. Air is allowed free access to the mixture, and any fumes evolved are withdrawn by flues. The copper sulphide present becomes copper sulphate, and this reacts with the common salt, forming copper chloride and sodium sulphate, whilst the silver is simultaneously converted into silver chloride. On withdrawing the charge it is transferred to large vats fitted with false bottoms covered with brushwood to serve as a filter; it is there treated with water which dissolves the chloride of copper and the common salt, and the brine thus produced dissolves the silver chloride also. The solution is then filtered off into a separate tank and treated by Claudet's process, which consists in mixing it with a solution of iodide of zinc containing just sufficient iodine to combine with all the silver present; silver iodide is thus produced, containing small quantities of gold and some lead, and as it is insoluble in brine, it separates out in the solid state and sinks to the bottom. On filtering the liquid again, a solution of chloride of copper free from silver is obtained; and the solid iodide of silver, being carefully collected, is treated with metallic zinc, which decomposes it, re-forming an iodide of zinc that may be dissolved in water and used to separate the silver from a fresh batch of ore, whilst the silver, now in the metallic state, is melted and refined. The working loss of iodine is made up by adding iodide of potassium.

The solution of chloride of copper obtained in this way, or that of sulphate of copper recovered from ores that have undergone a sulphating roast (see page 132), may be made to yield their copper in a powdery but metallic form by placing fragments of scrap iron in the liquid in large tanks, or as it flows through long channels. The iron exchanges places with the copper, because its combining power for sulphuric or hydrochloric acid is greater than that of copper. It gradually dissolves into the solution, and a precipitate of copper separates in the form of *cement copper*, which is rarely sufficiently pure to be used direct, and is therefore subsequently refined in furnaces or electrolytically.

Electrolytic Refining of Copper.—The improvements which have recently been made in electric generators have led to their application to the refining of copper by an electrolytic process similar to that employed in electroplating. If a current of electricity pass between two copper plates immersed in a solution of sulphate of copper, the *anode* (that is, the plate by which the current enters the liquid) gradually dissolves, whilst an equivalent weight of copper is deposited on the other plate, which is termed the *cathode*. If, then, an impure copper plate be used as the anode, the copper will be dissolved, and with it some of the impurities, such as iron, nickel, cobalt, and zinc;

but so long as there is a good excess of copper in the solution, and the right strength of current is employed, only the copper, among the metals named above, can be deposited, because the copper compounds are so much more easily decomposed by the current than are those of these other metals. Too strong a current, or too weak a solution, however, would lead to the deposition of small quantities of the other metals with the copper. Of the remaining impurities in blister copper, platinum, gold, lead, slag, and (if the solution be acid) silver, cannot dissolve in the liquid, and are therefore left on the anode in the form of an insoluble slimy deposit. Bismuth, tin, antimony, and arsenic remain in part insoluble, and in part pass into the liquid, where they tend to deposit as basic compounds. With a suitable current strength and a good solution, a copper, as nearly as possible pure, may be regularly obtained as a massive deposit on the cathode, whilst the more valuable impurities are concentrated in the anode slime, from which they may be afterwards recovered.

The crude copper is cast into cakes, which are suspended one behind the other in large wooden vats lined with lead, all of them being connected with the positive pole of the generating dynamo. Alternately with them are hung the thin copper sheets, upon which the pure copper is slowly built up while the current is passing, and these are connected with the negative pole of the dynamo, and carefully insulated from the anodes. These cathodes are sometimes rubbed over with graphite to prevent the deposited copper clinging to them too firmly. The application of a slight force suffices to strip off the fresh copper when it has been deposited to a sufficient thickness, and the sheets may be used again. In some of the most recent installations only one anode plate is used, and the end crude copper anode alone is connected with the positive pole of the source of electricity. This acts as an anode, and dissolves, the equivalent of copper being deposited on the back of the next anode, whilst its face is at the same time dissolving and passing the current forward through the solution. Thus each copper plate after the first acts as cathode to the plate behind it and anode to the one in front, until the whole of the original copper has been dissolved, and its place taken by pure electrotype copper. The last plate of the series is of pure copper, and serves only as a cathode, conducting the current back to the negative pole of the dynamo.

The bath originally employed may contain from 1½ to 2 lb. of crystallised sulphate of copper (blue vitriol) and 5 to 10 oz. of sulphuric acid to each gallon of water; the electrodes should hang 1½ to 2 in. apart, and the current employed may range from 0·1 to 0·6 ampere per square inch of plate surface exposed. Usually the weaker currents give the purer deposits; but with care the higher limit may be safely attained, although it is not usual in this country to employ more than half that volume of current. The electromotive force required is usually about 0·3 volt between each pair of plates placed in series.

The action is very slow, and it would require nearly three months, working continuously, to dissolve or deposit a plate of copper 1 in. in thickness; and it is the amount of capital locked up in copper and solutions, and the floor space required to conduct works of any magnitude, that have militated against the universal introduction of this process of refining. The means of applying water-power to drive the dynamos have caused the system to be used widely in America, but both there and in England steam power is being employed with satisfactory results. It must be remembered that, although electro-deposited (*electrotype*) copper should be almost absolutely pure, it is not necessarily so; and it is unwise to trust to the purity of a sample of copper merely because it is known to have been produced electrolytically.

Various Descriptions of Commercial Copper.—*Cement Copper* is obtained by precipitation with iron in the manner above explained. It was first accidentally extracted from the *blue water* naturally produced by the action of rain upon pyrites which, by long exposure to the weather, had become oxidised to sulphate.

Rosette Copper or *Rose Copper* was formerly made at Chessy, in France, by throwing water upon the surface of the melted copper, and removing the solidified metal in layers, which were covered with a beautiful red film of suboxide of copper, formed by the action of the oxygen of the water upon the metal.

Japan Copper resembles the preceding in colour, and is cast into ingots weighing only six ounces each. It is coloured by being cast under warm water on canvas.

Copper is sometimes cast into thin plates by pouring into the mould enough metal to form a single plate, which is allowed to cool before pouring in a fresh quantity, when a film of suboxide of copper is formed upon the surface of the first plate, and this prevents it from adhering to the next, so that the plates are easily separated when the moulding-case is removed.

Bean-shot Copper is made by pouring melted copper through a perforated ladle into a vessel of hot water, when it forms round fragments like shot. When cold water is used, the metal is obtained in flakes, which are termed *feathered shot.*

Electrotype Copper has already been described.

In order to remove the scale of oxide from rolled copper plates before sending them into the market, the somewhat inexplicable course is adopted of washing them with urine, then heating them in a reverberatory furnace and plunging them while hot into water, when the scale detaches itself. The sheets are then smoothed between rollers.

Effect of the presence of Foreign Matters upon the quality of Copper.—From the circumstance that the refiner tests the quality of copper by forging a *hot* sample, it will be inferred that the effect of impurities upon its malleability and tenacity is more perceptible at a high than at a low temperature. The foreign matters which commercial copper is liable to contain are arsenic, sulphur, antimony, tin, bismuth, lead, silver, iron, and nickel. Of these, sulphur and antimony are generally considered the most injurious in diminishing the malleability and tenacity of the metal. Arsenic is very commonly found in copper, amounting, in some of the Spanish coppers, to as much as one part in a thousand, and was formerly supposed to be as injurious to the quality of the copper as antimony is, but modern experience has shown that copper may be easily rolled and drawn into wire even when it contains a considerable proportion of arsenic. A small proportion of tin is believed to increase the toughness of copper, but bismuth and nickel have the opposite effect.

The conducting power of copper for electricity is reduced in a most striking manner by the presence of foreign matters, so that, in the construction of telegraph wires and electrical apparatus, it is important that the purest attainable copper wire should be employed. This wire is frequently known in commerce as *conductivity copper.* Pure copper is scarcely inferior to silver (see p. 120) in its conducting power, and the conducting power of the native copper from Lake Superior, which is almost pure, stands to that of pure copper in the proportion of 93 to 100, whilst the Australian (Burra Burra) copper, also very pure, has a conducting power of 89, and the Spanish copper, which contains much arsenic, has a conducting power only one-seventh of that of pure copper, or in the proportion of 14 to 100.

Phosphor-copper, containing from 5 to 10 per cent. of phosphorus, may be readily made by melting copper, and adding phosphorus to it when it is in the molten state, an operation which requires great care, owing to the dangerous character of phosphorus. This rich phosphor-copper is sold for use in making phosphor-bronze, and for adding in small proportions (about five parts in a thousand) to copper, as it is found to harden it and somewhat to increase its tenacity; it is also said to render it less liable to corrosion when exposed to the action of sea-water.

By adding arsenic to copper, in about the proportion of one to ten, a white somewhat malleable metal is obtained which is not easily tarnished by air, and is much harder than copper. This compound, which is employed for clock dials and for thermometer and barometer scales, is made by heating, in a covered earthen crucible, five parts of copper clippings with two parts of white arsenic (arsenious acid) arranged in alternate layers and covered with common salt.

TIN

THIS metal is scarcely, if ever, found in the metallic state, but is extracted from the ore known as *tinstone*, which is an oxide of tin. Cornwall has been noted for its tin mines from a very remote period; tinstone is also found in Australia, Bohemia, Saxony, Malacca, and Banca, the *straits tin* obtained from the last-named localities being much valued on account of its purity. Siberia, Sweden, and North and South America also furnish tin ore, though in smaller quantity. Tinstone is found either as *stream tin ore* or *mine tin ore.* The former is also called *alluvial*[1] *tin ore* from its occurrence in the mineral matter deposited by torrents in the valleys adjacent to the veins of mine tin ore, and is much purer than the latter, because it has been mechanically separated, by the action of the stream, from the foreign minerals which were associated with it in the vein. Occasionally, it is found in well-formed prismatic crystals which are perfectly pure oxide of tin. The mine tin ore occurs in veins traversing rocks of quartz, granite, or clay-slate; it is commonly associated with arsenical

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[1] *Alluvio* (Latin), an inundation.

pyrites, copper pyrites, specular iron ore, and a remarkably heavy crystalline mineral called *wolfram* (tungstate of iron and manganese), which consists of tungstic acid (an oxide of the metal *tungsten*) combined with the oxides of iron and manganese. In order to obtain the tinstone in a sufficiently pure state for smelting, the ore is stamped to powder, washed, and calcined.

The processes which are put in operation in order to obtain marketable tin from the raw ore may be summed up under the following heads :—

1. Mechanical preparation of the ore.
2. Calcining.
3. Washing the roasted ore.
4. Smelting.
5. Refining.

1. **Mechanical Preparation of Tin Ores.**—The mine tin ore, as it is raised from the mine, is roughly separated from earthy matters by washing it upon a grating under a stream of water. It is then picked over and broken with a mallet, the pieces of copper pyrites being placed aside to be smelted for that metal, and the iron and arsenical pyrites rejected. The tin ore is then crushed by stamps until it will pass through a sieve with 40 holes to the linear inch. The water which flows through the stamp boxes carries the powdered ore into a series of reservoirs, in which the ore settles down, whilst the water flows away. Since the tinstone is much heavier than the other substances present in the ore (its specific gravity being 6·5), the greater part of it is deposited in the first reservoir, the successive deposits becoming poorer as the stream flows on, and the rock, which has a specific gravity of about 2·7, being in great measure carried away. Various mechanical contrivances are adopted for effecting a further purification of the *slimes* deposited in the reservoirs, in all of which advantage is taken of the high specific gravity of the tinstone. The rack and the buddle are very commonly employed.

2. **Calcining the Tin Ores.**—The arsenical pyrites and copper pyrites are too heavy to be entirely removed by stamping and washing, so that the ore is next calcined in order to expel the arsenic and sulphur. This is effected in calciners which have settling chambers between them and the chimney for the deposition and recovery of the arsenious acid. A great portion of the sulphide of copper in the copper pyrites will also combine with oxygen to form sulphate of copper, a change which is completed by allowing the calcined ore to remain exposed to the air, in a moist state, for some days.

3. **Washing the Calcined Tin Ore.**—If sufficient copper be present, the next process consists in leaching the calcined ore with water, in a wooden tank, when the sulphate of copper is dissolved by the water, and is drawn off after the ore has settled down, cement copper being obtained from the solution by bringing it in contact with iron. By washing upon the rack, or some similar arrangement, the lighter oxide of iron produced by the roasting of the pyrites is removed, and the prepared tin ore or *black tin*, containing above 60 per cent. of tin, is ready for smelting.

4. **Smelting the Prepared Tin Ore.**—The furnaces (fig. 72) generally employed in the *smelting-houses* of Cornwall are reverberatory furnaces, having a low arch, with air channels under the fire-bridge and hearth, to prevent injury from the high temperature. About a ton of the prepared ore (oxide of tin) is mixed with one-fifth to one-eighth of its weight of ground anthracite coal, and with a little lime which is intended to flux the small quantity of silica still mingled with the ore. Occasionally fluor-spar is added with the same object. The mixture is damped with water, to prevent it from dusting, and thrown upon the hearth of the reverberatory furnace. The doors are closed, but the temperature is kept low at first, for otherwise the oxide of tin would combine with the silica and the lime to form a glass or slag, causing a great loss of tin. The tem-

perature is gradually raised for about five hours, by which time it should have reached its maximum. The charge is then well rabbled, and some culm having been thrown on the surface, the door is closed again, and heat applied for a further period of about three-quarters of an hour, at the expiration of which time the charge is again rabbled and then left at rest for about fifteen minutes to regain the proper temperature for tapping. There are three principal products resulting from this smelting operation, viz. metal, glass, and slag. The 'glass,' which is the true slag, being perfectly fluid, is tapped out of the furnace with the metal into a clay-lined basin, called a float, placed in front of the tap-hole. Alongside the float is a second receptacle called a *kettle*, made of cast-iron and heated by an independent fire-place beneath it. It is used in a subsequent operation. The glass is essentially a silicate of iron, but contains also any earthy matter from the ore, or added as flux, and a variable amount of tin as silicate. After it has been run from the furnace into the basin, it separates into two layers. The one called *bottle-slag*, resembling bottle-glass, is thrown

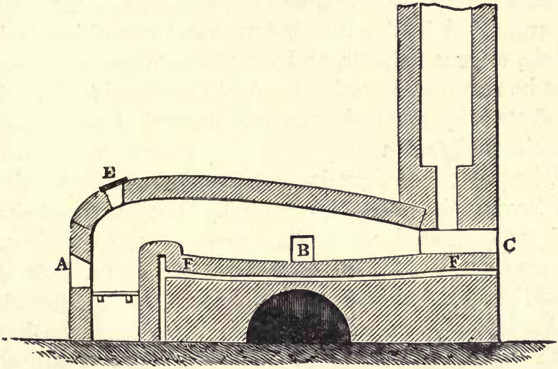

FIG. 72.—Furnace for smelting Tin Ores. A, Fire-door. B, Charging-door. C, Working-door. E, Door for moderating the draught whilst charging the furnace, lest the ore dust be blown into the flue. F, Air-channel under hearth.

away; the other, a heavy black slag, is subsequently, when sufficient has accumulated, remelted. The *slag*, so called, is a scoriaceous pasty substance, consisting of anthracite, shots of tin, and 'glass.' The greater part of it remains behind on the hearth after the metal has been tapped; it is removed through the end door, and subsequently stamped and washed to separate the tin.

5. **Refining the Metallic Tin.**—The ingots of tin, as obtained from the smelting-furnace, contain various impurities. Not only are particles of slag, and of the oxide of tin, entangled in the metal, but small quantities of iron, arsenic, copper, sulphur, and tungsten are present in it, and must be removed in order to obtain marketable tin. This is effected by successive operations, which are known as *liquation* and *poling*.

The process of liquation consists in melting out the tin and leaving the impurities behind. The ingots of tin are moderately heated upon the hearth of the reverberatory furnace employed for smelting the ore, when the bulk of the metal liquefies and is allowed to flow out of the furnace into the kettle, leaving a residue of impurities upon the hearth. Fresh ingots are introduced from time to time, until about five tons of tin have collected in the kettle, which is the case in about an hour after the commencement of the process.

The *poling* consists in plunging into the tin contained in the kettle, and kept heated by its separate fire, stakes or logs of wet wood, which are held down under the metal by a lever-arm fixed above the refining-basin.

The heat of the melted metal causes a brisk evolution of steam, which throws the metal up, exposing a large surface to the action of the air, whereby the impurities become oxidised, and are removed from the surface in the form of dross. Sometimes *tossing* is substituted for poling, that is, the tin is well agitated by raising a ladleful of the metal to a considerable height, and pouring it into the bath. The duration of the poling is determined by the state of purity of the metal and by the grade required, *i.e.* whether it is to be 'common' or 'refined' tin. In the latter case the metal might be poled for several hours. The tin is then ladled out into moulds, either of granite or cast iron, and cast into ingots weighing about 3 cwt. each. Refined tin is very brittle at a temperature somewhat below its melting-point, so that when ingots are heated and allowed to fall from a height, they break up into irregular prismatic fragments, which are called *grain tin.*[1] The refiner tests the purity of the tin by casting a small quantity in a stone ingot mould, when the refined tin remains bright and smooth after cooling, the common tin becomes partly frosted on the surface, and the impure tin is frosted all over.

The metallic residue left upon the hearth in the process of liquation allows tin of inferior quality to melt out when a stronger heat is applied; this is run out into the float. The portion finally left on the hearth is a white brittle alloy, known as 'hardhead,' containing tin, iron, and other foreign metals.

The temperature at which tin is melted before casting is said to be of importance, its malleability being injured if it be cast at too low a temperature.

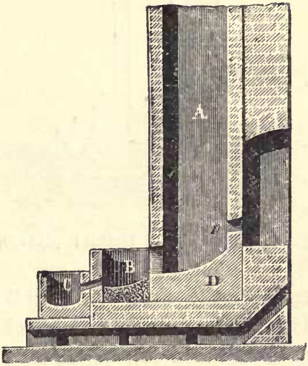

FIG. 73.—Blast-furnace or Blowing-house for smelting Tin Ores.

Reduction of Stream Tin Ore in the Blast-furnace or Blowing-house.—This operation is attended with greater consumption of fuel and loss of tin than that practised in England, but it has been largely employed in the tin-works of Saxony. The blast furnace (A, fig. 73) is only ten feet

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[1] Only the best tin from specially pure ores is sold in the market as grain tin.

high, cylindrical in shape, and surmounted by a conical hood divided into compartments for collecting the dust carried up by the blast, which is forced in by a blast-pipe at *o*, near the bottom of the furnace. The sides and bottom of the furnace are built of granite, the bottom (D) being a single block hollowed out for the reception of the tin which flows out, together with the slag, into a basin of granite (B) lined with a coating of clay and charcoal. If the tin ore contains much oxide of iron, some quartz is employed as a flux ; but if much silica is already contained in the ore, lime or finery cinder (p. 218) is employed to form a fusible slag.

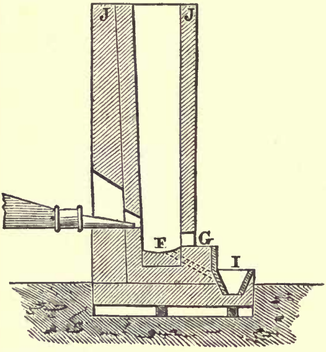

FIG. 74.—Blowing-house at Altenberg. F, Crucible. G, Inclined plane for slag. I, Fore-hearth.

The prepared tin ore and wood charcoal are constantly charged in at the top of the furnace, so as to keep it full, when the carbonic oxide, produced by the combination of the carbon with the oxygen of the air, abstracts the oxygen from the oxide of tin (see p. 180), and the metallic tin, accompanied by a small quantity of slag, runs out into the *fore-hearth* (B), from which the slag is removed, the tin remaining liquid in the basin. When the latter is full of tin, it is discharged, through a tap-hole, into an iron basin (C), where it is further treated like the tin obtained by liquation (p. 342). The loss of tin in the blowing-houses is twice to three times as great as in the smelting-houses, and is due to volatilisation of the metal.

At Altenberg, in Saxony, where the ores contain bismuth, they are treated, after roasting, with hydrochloric acid, for the extraction of that metal. The Saxony tin generally contains a little bismuth.

In the Malay peninsula, blast-furnaces are also frequently employed to smelt tin ores.

Treatment of Tin Ores containing Wolfram.—Since wolfram is even heavier than tinstone, its specific gravity being 7·5, and that of tinstone 6·5, the tin ore cannot be freed from wolfram by washing. When the prepared tin ore contains any considerable proportion of wolfram, the quantity of this latter is ascertained by chemical analysis, and enough sulphate of soda (salt-cake from the alkali-works) is added to furnish a little more soda than is necessary to form tungstate of soda with the tungstic acid which is present. Some coal dust is added to the mixture, which is then heated on the cast-iron hearth of a reverberatory furnace, when the carbon removes the oxygen from the sulphate of soda, leaving a combination of sulphur with sodium (sulphide of sodium). A little air is then allowed access to the heated mass, when its oxygen converts the sulphur into sulphurous acid gas, and the sodium into soda, which combines with the tungstic acid to form tungstate of soda. The furnace is so constructed that the flame from the grate, after passing over the hearth of the furnace, may return underneath it, and thus heat the charge uniformly. The mass is transferred from the furnace into tanks of water which dissolves the tungstate of soda, to be afterwards obtained in crystals by evaporating the solution. Tungstate of soda may be used for rendering muslin, &c., uninflammable. The oxides of iron and manganese derived from the wolfram are still contained in the tin ore, but they are so much lighter that they can easily be separated from it by washing, when the tin ore is ready to be smelted in the usual way.

Tin is remarkable for its property of *creaking*, or producing a peculiar grating sound, when bent. It has been noticed, in the general consideration of the properties of metals (p. 120), that tin is more easily melted than any other simple metal in common use, and that it is possessed of a high degree of malleability, which is turned to advantage in the manufacture of tin-foil, by rolling and hammering the metal into extremely thin leaves.

Tin is so little acted upon or corroded by air or by weak acids, that it is employed as a coating to protect the surfaces of other metals, such as iron, copper, and brass. Tin-plate is iron covered with a thin coating of tin, and, since its manufacture is an important branch of English industry, an outline of it may be here given.

Manufacture of Tin-plate.—The sheet iron employed for the manufacture of the best tin-plate was formerly refined with charcoal (p. 221), though iron refined with coke was sometimes employed, the tin-plate being distinguished accordingly as *charcoal-plate* and *coke-plate*. The latter term, however, now usually refers to plate which has been made from puddled iron, whilst the former is commonly applied to low-carbon steel plates made by the open-hearth process.

In order to obtain iron plates of the required gauge, bars, $\frac{3}{8}$ in. thick, are cut into pieces 15 in. long and 6 in. wide. Each of these, having been heated to redness, is rolled until its width is increased to 15 in. It is then again heated, and rolled in the opposite direction until it is $5\frac{1}{2}$ ft. long. The plate is next doubled, having been first sprinkled with a little coal-dust to prevent the surfaces from adhering, and it is then heated again, and passed between very smooth rollers until the original length of the doubled plate ($2\frac{3}{4}$ ft.) has been increased to 5 ft. After being again doubled and heated, the four-fold plate is rolled out from 30 in. to 43 in. It is then cut to nearly the proper dimensions (not exceeding 18 by 13 in.), and the plates having been separated, are prepared for tinning. At this stage they are termed *black plates*.

The plates must be rendered perfectly clean and bright, for the slightest impurity would prevent the proper adhesion of the tin.

(1) They are therefore pickled in warm diluted sulphuric acid for about twenty minutes, which dissolves part of the

black oxide of iron from the surface and loosens the remainder, the cleansing being completed by scouring them with sand and water.

(2) The plates are annealed by being heated to redness, for twelve hours, in an air-tight cast-iron box placed in a reverberatory furnace; they are allowed to remain in the box till quite cold, when they are found to have acquired a deep purple colour, from a thin coating of oxide, and are said to be *black annealed.*

(3) They are *cold rolled* between very hard polished rollers to polish them. They are thus expanded to their full size.

(4) They are annealed as before for about six hours. Air is very carefully excluded, and the plates, being polished, remain comparatively bright, and are said to be *white annealed.*

(5) The plates are again immersed in warm sulphuric acid, weaker than that employed in process 1, and are finally washed and scoured with wet sand. They may be stored for use without rusting, in water containing fresh slaked lime.

Tinning.—In order to tin them, they are transferred into a cast-iron pot containing melted tin covered with 3 or 4 in. of tallow or palm oil, and heated over a fire to nearly the inflaming point of the grease. The plates are passed through the oil, one at a time, into the tin-bath, where they are caught by a fork and guided to a pair of rollers working with very light pressure in the melted fat. In passing through these rollers the excess tin, which is still melted on the surface, is squeezed off the plates and returned to the tin-bath.

In this operation of tinning, an alloy of iron with tin is formed upon the surface of the plate, and a firm adhesion of the tin coating is thus secured.

After the grease has been removed by rubbing the plates with bran, they are ready to be packed in boxes. About 3 lb. of tin are sufficient to cover 112 plates of iron measuring 14 by 20 in.

Tin-plate is very durable as long as the coating of tin is perfect, but if any portion of the iron surface beneath should be exposed, it is corroded by rusting even more rapidly than untinned iron plate, because the iron and tin, in presence of the film of moisture containing carbonic acid which is deposited by the atmosphere upon the surface of the plate, form a galvanic pair of which the iron is the metal attacked by the water and acid, so that the plate is speedily eaten through. An alloy of tin and lead is sometimes employed in lieu of pure tin, and plates so prepared are known as *terne* plates.

Tin-plate moiré.[1]—The beautiful variegated appearance known as *moire métallique* is produced by wiping the surface of tin-plate with tow or sponge dipped in warm dilute nitric acid mixed with hydrochloric acid, common salt, or sal-ammoniac, and well washing with water. The acid liquid dissolves away the smooth surface of the tin and discloses the crystalline structure beneath, the variegated appearance being apparently caused by the reflection of the light in different directions by the minute faces of the crystals. The moiré may be greatly diversified by heating the plate before applying the acid, and cooling it irregularly by sprinkling water over it, or by directing a blow-pipe flame over its surface before wetting it with the acid. The surface is afterwards covered with a transparent coloured varnish.

Tinning of Copper.—If copper used for cooking utensils be not kept perfectly clean it is liable to become oxidised and pass into food with injurious effects. For this reason saucepans, stewpans, &c., are usually tinned on the inner surface. That this is not generally necessary, and is only a safeguard against carelessness, appears to be shown by the statement that the highest class of preserves is made in untinned copper in order to avoid discoloration by the action of the tin. Fortunately it is much easier to tin copper than iron. The

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[1] Wavy-like mohair, having reference to the peculiar changing sheen of the surface.

copper surface, having been smoothed by rubbing it with a fine sandstone, is made pretty hot, and rubbed over with powdered sal-ammoniac, which has the property of removing the oxide from the surface, and leaving the copper perfectly bright. A little tin is placed upon the bright copper, together with some powdered rosin, which is intended to form a varnish when it melts to protect the copper from oxidation by the air. On heating the copper plate the tin melts, and is spread with tow over the surface, to which it firmly attaches itself. 200 gr. of tin are commonly employed to cover a square foot of copper. The tin employed for this purpose is sometimes alloyed with lead; but this practice is dangerous in the case of cooking utensils.

Phosphor Tin.—By adding phosphorus cautiously to molten tin, as much as 20 per cent. may be introduced into the metal. Large quantities of phosphor tin are made containing from 4 to 6 per cent. of phosphorus. The material in appearance resembles cake zinc more than tin. Its fracture shows very large crystals, which are soft, somewhat flexible and very inelastic, so that they may be detached and bent to a right angle by gentle pressure from the blade of a penknife. These properties serve to distinguish the material at once from zinc.

Alloys of Tin and Copper.—The alloys of tin and copper are known by the generic name *bronze.* When fluid, copper and tin can mix in all proportions, forming a series of mixtures with very diverse characteristics. For coinage purposes, and for medals, an alloy, containing 4 per cent. of tin and 1 per cent. of zinc, is sufficiently hard to withstand the wear to which it will be subjected, while it is yet soft enough to be rolled into sheet and struck in the coining press with facility. Up to a comparatively recent date cannon and heavy ordnance were, for the most part, made of a bronze containing from 8·5 to 10 per cent. of tin, and this mixture, which is widely employed in engineering work, still retains the name of *gun-metal.* It is much harder and more elastic, and decidedly stronger than good copper, and it is also more fusible, but it is far less extensible under stress. The strongest alloy of the whole series is that containing about 18 per cent. of tin, its tenacity being about 17 tons per square inch. Among the ancients, axes and other implements were sometimes made of this mixture, which possesses the peculiar property of hardening when it is heated to redness and cooled slowly. The softness and malleability may be restored to the metal by heating and quenching it in water. Many of the older swords and weapons contained 10 per cent. of tin, or even less, as these alloys would be less liable to break in use than the more brittle mixture containing 18 per cent. A further increase in the amount of tin, up to 20 or 22 per cent., adds greatly to the hardness, closeness, and sonorousness of the metal; and as these mixtures are employed in the casting of bells, they have received the name of bell-metal. As the tin is increased beyond 18 per cent., the strength falls off very rapidly. The alloy containing about 67 parts of copper to 33 of tin is intensely hard, and will break under a tensile load of a little over half a ton per square inch. It is as brittle as glass, and a bar dropped from the height of a couple of feet upon a stone pavement may break into fragments. Its intense hardness enables it to take a brilliant polish, and as its colour is nearly pure white, it is used for the reflectors of telescopes under the name *Speculum metal.* There is much evidence in favour of this alloy being a chemical compound, with the formula Cu_4Sn. The addition of further quantities of tin impairs the hardness of the material, and both strength and softness gradually increase; but these alloys are not employed in practice.

In the casting of bronze there are three principal difficulties to be contended with: oxidation during melting; segregation or separation into different alloys or mixtures, leading to the formation of *tin spots*; and absorption by the liquid metal of oxygen and other gases, which may be given off during solidification and so produce unsound castings. The oxidation must be checked by using, as far as possible, a reducing atmosphere ; because tin combines more readily than copper with oxygen, and the result of oxidation is that the alloy contains less tin than was originally intended. For small castings the metal may be kept covered with charcoal to protect it from oxidation during the period of fusion. The difficulty introduced by absorbed oxygen and other gases may often be met by adding a small proportion of phosphor copper or phosphor tin, immediately before pouring the metal into the mould. The phosphorus, having a great attraction for oxygen, combines with the oxygen dissolved in or combined with the metal in the crucible and forms phosphoric oxide which floats to the top of the liquid alloy. *Phosphor-bronze* is thus made, and it should be remembered that the object of the phosphorus is to purify the metal : it is not necessary, and may indeed be undesirable to employ an excess of this material ; and as the phosphorus is used up in playing its part, it is not uncommon to find only a trace of the element in samples of good phosphor-bronze. Other substances, such as silicon or manganese, may be substituted for phosphorus, but in the case of these alloys generally with less satisfactory results. Segregation takes place chiefly in large castings, and there is no way of obviating the difficulty, except by pouring at low temperatures and cooling as quickly as possible.

Bronze is made by melting copper in crucibles, and then adding the tin, stirring well and pouring ; scrap bronze is usually added to the charge in melting, and it is then that the greatest loss of tin occurs through oxidation. For heavy castings, the metal is melted in reverberatory furnaces, or cupolas, copper and scrap being employed, and the excess of tin required to bring the metal to the required composition being added after fusion, either as metallic tin, or in the form of *hard metal* (which is practically identical with speculum metal) prepared beforehand.

Britannia-metal.—Tin constitutes the chief part of this and some similar alloys which are employed for the manufacture of spoons, tea-pots, &c., being hardened for such purposes by the addition of antimony and copper. Lead and bismuth are also sometimes added.

The following are a few out of many modifications of bronze employed for particular purposes :—

	Wheel boxes or sockets	Stop-cocks and pump-valves	Nails for ships' sheathing
Copper	80	88	87
Tin	18	10	9
Zinc	2	2	4
	100	100	100

Complex alloys of copper, with a high percentage of zinc and a small proportion of tin and other metals, are now commonly termed bronzes also.

ZINC

METALLIC zinc is not met with in nature, and though its combinations with other substances are abundant in certain localities, they are by no means universally diffused over the earth's surface. England is not particularly rich in ores of zinc, and the extraction of the metal is carried out in this country to a very limited extent, most of the zinc required in the arts being imported from Silesia, Belgium, and America.

The Ores of Zinc.—The ores of zinc from which the metal is commonly extracted are enumerated in the following table :—

Ores of Zinc

	Composition		Zinc in 100 parts of pure mineral
Blende	Zinc, Sulphur	ZnS	67
Red zinc ore	Zinc, Oxygen	ZnO	80
Calamine	Zinc, Oxygen, Carbonic Acid	$ZnCO_3$	52

Blende derives its name from the German *blenden, to* *dazzle*, in allusion to its lustre. It usually occurs in black shining crystals which owe their colour to the presence of sulphide of iron, since the pure compound of zinc with sulphur is white. Blende is also met with of a brown or yellow colour. Black blende is sometimes regarded as a definite compound of sulphide of zinc and sulphide of iron, containing 52 parts of zinc in the hundred. The miners often call it *Black Jack*. It is found running in veins through limestone or sandstone, and is commonly associated with galena (sulphide of lead) and with iron and copper pyrites. Blende occurs in Cornwall, Devonshire, Cumberland, Derbyshire, Ireland, Wales, and the Isle of Man ; also at Freiberg, Aix-la-Chapelle, and in North America. In the Broken Hill district of New South Wales it occurs in a vast deposit, in very intimate association with argentiferous galena, constituting an ore which is very difficult to treat. Blende sometimes contains a considerable proportion of cadmium.

Red Zinc Ore (*Zincite*) is the oxide of zinc, which would be white in the pure state, but is coloured in this ore by the oxides of iron and manganese. It sometimes forms red translucent prismatic crystals, and is found chiefly in New Jersey, in the United States, where it is associated with *Franklinite*, a mixture of the oxides of zinc, manganese, and iron, which may contain from 5 to 20 per cent. of zinc, and is first smelted for that metal, and afterwards for manganiferous iron.

Calamine appears to be so called in allusion to the columnar structure of some specimens of the ore, which gives them some resemblance to a bundle of reeds (*calamus, a reed*). It is a compound of the oxide of zinc with carbonic acid, which would be white if pure, but is usually of a buff or brown colour, due to the presence of oxide of iron, which is objectionable, because it corrodes the clay vessels employed in smelting the ore. Calamine occurs in veins, commonly traversing limestone rocks, and is associated with blende, galena, and *electric calamine*, which resembles calamine in appearance, but shows electrical polarity when heated. The electric calamine is a compound of oxide of zinc, silica, and water (hydrated silicate of zinc). Calamine is found in Flintshire, the Mendip Hills in Somersetshire, Alston Moor in Cumberland, at Lead Hills in Scotland, at Aix-la-Chapelle, at Tarnowitz in Silesia, in Sardinia, in the north-west of Spain, in Greece, in the United States of America, and in many other places. It sometimes contains more than two per cent. of cadmium. In Spain, the carbonate of zinc is found in combination with the *hydrated oxide* of zinc, so that the ore contains as much as 57 per cent. of zinc.

In order to extract zinc from its ores, reduction is effected by means of carbon, but as this reduction can only take place at a temperature of 1,320° C., and as zinc boils and distils freely at 1,090° C., it is evolved from its oxide in the form of vapour, and requires, therefore, to be condensed to the liquid state. It is this fact which imparts such a distinctive character to the metallurgy of zinc. The ores having been calcined so as to obtain the zinc in the form of oxide, or to drive off carbonic oxide and water, and render them more porous and easily attacked, are mixed with carbon and distilled, when the oxygen passes off in combination with the carbon as carbonic oxide gas, and the zinc is given off in vapour which is condensed. The mode in which the operation is carried out varies in different works, but the principle of the process is always the same.

A very thorough calcination of the blende is indispensable, because sulphide of zinc is not attacked by carbon, and all the zinc contained in blende which has escaped conversion into oxide would be lost.

In order to save the clay vessels in which the distillation is effected, those ores which contain much oxide of iron and lime are mixed with others containing clay, which is attacked by those substances, instead of the material of the distilling vessels.

The old English method of effecting the distillation is now obsolete, either the Belgian or Silesian process having been adopted in the larger zinc works, but the process is sufficiently interesting to merit a short description.

Obsolete English Method.—The roasted ore was distilled with coke in crucibles (fig. 75) made of Belgian fire-clay (nearly pure silicate of alumina), furnished at the bottom with iron pipes in which the zinc was condensed. The crucibles were made of a mixture of equal parts of fire-clay and old crucibles ground to powder, and each crucible commonly lasted about four months, in which period it distilled two tons of zinc. The crucibles were 4 ft. high and 2½ ft. wide, and the iron pipes which passed through the bottom of each crucible were 7 in. wide. These pipes were made in two pieces, the shorter length being cemented into the bottom of the crucible, the other (*h*), about 8 ft. long, being made to fit on to it. Six of these crucibles were usually set in one furnace around a long fireplace and under a dome: the flame played around the crucibles, and then, through apertures in the domed roof, into a wide conical stack like those used in glass-melting houses. Each crucible was placed over an opening in the floor, through which the iron pipe *h* passed into a vault below.

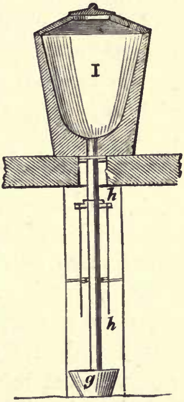

Fig. 75.—Crucible for extraction of zinc by the obsolete English method.

The top of the short length of pipe having been loosely plugged with a lump of coke to prevent the charge from passing into it, each crucible was charged, through an opening above it in the dome, with 4 or 5 cwt. of the calcined ore and 2 or 3 cwt. of broken coke or anthracite.

The covers were then cemented on and the fire applied. In a short time, a blue flame appeared at the mouth of the tube, beneath the furnace, which was due to the combustion of the carbonic oxide formed by the combination of the carbon with the oxygen of the oxide of zinc. After a few hours, the flame became greenish white, from the combustion of the vapour of zinc; it was then extinguished by attaching the longer piece of iron pipe, in which the metal condensed and dropped into a vessel containing water; the tube (*h*) was removed occasionally in order to clear out the zinc which obstructed it. The distillation occupied about sixty hours, and the ore yielded rather more than a third of its weight of zinc, a considerable proportion of the metal being left in the form of silicate of zinc, which cannot be made to yield up its metal at the low temperature attainable in this process.

The zinc collected in the receivers owing to the way it was distilled was, of course, not in the form of a compact mass of metal, and it was intermingled with some oxide of zinc formed as the heated metal dropped through the air into the receiver. It was therefore remelted in an iron pot set over a furnace, and well skimmed, the dross being introduced into the crucibles with a fresh charge. The zinc was cast into flat cakes or ingots, and sent into commerce under the name of *spelter.*[1]

When cadmium is present in the zinc ore, it passes over in vapour before the zinc, for cadmium boils at about 770° C., and its presence is indicated by the brown fumes of oxide of cadmium which rise from the flame (*brown blaze*). The metal which then distils over consists of zinc containing a large proportion of cadmium, and is collected separately.

Belgian Process.—This process is now that most employed in England. The distillation of the mixture of ore and coal is effected in cylinders which are made usually in

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[1] The name *spelter* is also given to an alloy of equal weights of zinc and copper employed for soldering brass.

the zinc-works themselves, from a mixture of raw and hard-baked fire-clay (often with a few parts per hundred of coke-dust in addition). This mixture, to prepare it for use, is dried, ground, and kneaded. The cylinders are now made, generally, by forcing the clay into steel moulds with the aid of an hydraulic ram, working under a pressure of about a ton per square inch, or they may be made by hand with copper moulds. They are about 8 in. in diameter, and about 4 ft. 6 in. long, and are closed at one end. The walls of the cylinder are about an inch in thickness. A large number of these cylinders, varying generally from 40 to 80 for a single grate, are arranged in tiers (*a b c d*, fig. 76), so that they may be heated by the same fire (F), the mouths of the cylinders being placed a little lower than the closed ends. The furnaces are usually built back to back in couples.

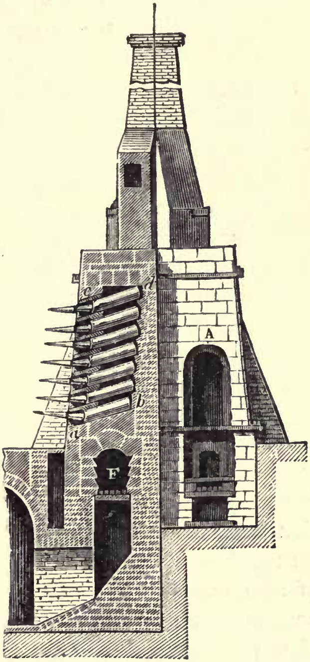

FIG. 76.—Belgian Furnace for distilling Zinc from its Ores.

The flame passes into the furnace through openings in the arch beneath the lowest tier of cylinders. Gas recuperative firing is now much used with satisfactory results for all types of zinc furnaces. Of course the lower cylinders are raised to a higher temperature than the upper rows, and a larger charge, or a more refractory ore, may be used in them. Before the cylinders are charged for the first time in a new furnace, they are brought to a very bright red or white heat, an operation which requires from two to four days.

The mixture of about a hundredweight of ore and coal, slightly moistened to prevent dusting, is introduced into each cylinder, to the mouth of which is luted a tube of fire-clay, shaped as shown at *g*, fig. 80, about 2 to 3 ft. long. In a short time, the flame of carbonic oxide gas is perceived at the mouth of the tube, and soon afterwards acquires the brilliant greenish-white appearance which indicates that the zinc is beginning to distil over. In order to condense any vapour of zinc which has passed the condenser, a conical pipe of sheet iron, the smaller opening of which is only two-thirds of an inch in diameter, is now attached. After the lapse of two hours, this is removed and cleared out, the mixture of zinc and oxide of zinc which it contains being worked again with the next charge. The bulk of the zinc is found in the fire-clay condensers, and is drawn out by the workmen into a large iron ladle. The sheet-iron cones are again attached, to exclude the air, and after another interval of two hours the condensed zinc is raked out as before. About a day is required to distil the zinc from a single charge of ore, after which a fresh charge is at once introduced, so that the furnaces are kept in continual operation until it becomes necessary that they shall be stopped for repairs ; 100 lb. of the ore furnish, on an average, 31 lb. of zinc, but a considerable proportion of zinc still remains, combined with silica, in the residue, since the extremely high temperature required to extract it would soften the clay cylinders and cause them to collapse. On account of the high price of coal, clay, and labour, ores containing much less than 40 parts of zinc in the hundred cannot be worked in Belgium.

The zinc collected in the iron ladle is freed from dross by skimming, and cast into ingots weighing from 40 to 80 lb. each.

Silesian Process.—In Silesia, ores which contain only

18 or 20 per cent. of zinc are worked with profit. The calcined calamine is distilled with coal or coke in large *muffles* (*l*, fig. 77), 4 or 5 ft. long by 6 in. wide and 20 or 24 in. high. They are made of fire-clay mixed with ground pots, like the cylinders already described, but their flat bottoms being well supported throughout their whole length, the muffles will sustain a higher temperature than the cylinders without bending, so that the distillation of the zinc is much more completely effected. The calamine is calcined in reverberatory furnaces, which are sometimes heated by the waste heat of the smelting-furnace. It is broken up into grains about as large as a pea, mixed with

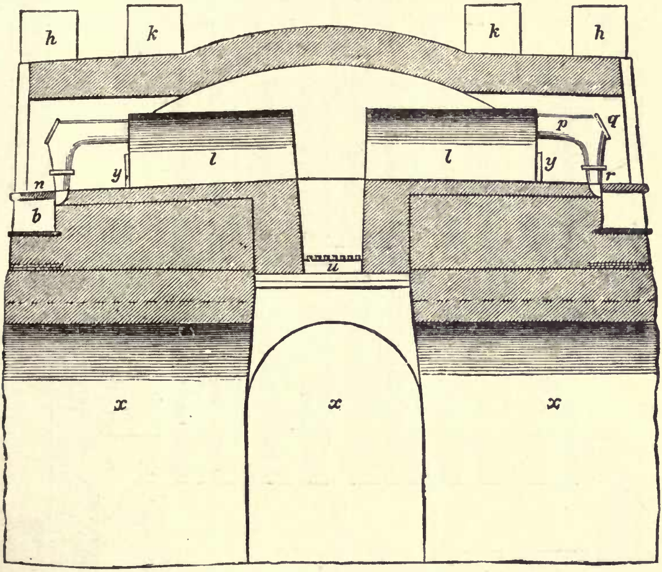

FIG. 77.—Silesian Zinc-furnace; section. *l*, Arched retorts. *y*, Door for removing the exhausted ore. *q*, Door for charging the retorts. *p r*, Tube for condensing the zinc. *b*, Receptacle for condensed zinc. *h k*, Flues. *u*, Fire-grate. *x*, Vaults.

about an equal bulk of broken coke or fine cinders, and introduced into the muffle through an opening which is afterwards closed with a fire-clay stopper. The muffles were formerly provided with rectangular clay tubes (*p*), prolonged by a cast-iron cone and a sheet-iron tube, for the passage and condensation of the vapour of zinc, an opening (*q*) being provided through which the tubes might be cleared from obstruction. The condensed zinc dropped from the earthen tube through an opening corresponding to it in the fore-hearth of the furnace, and was collected in a small chamber (*b*) beneath. In a few works the condenser is replaced by

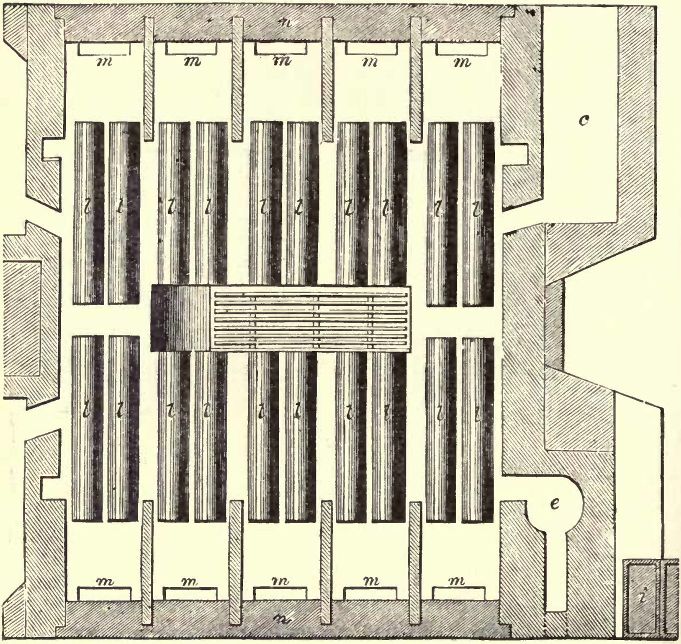

FIG. 78.—Silesian Zinc-furnace; plan. *l*, Arched retorts. *c*, Space for heating the retorts before setting them in the furnace. *e*, Pot for re-melting the distilled zinc. *i*, Iron ingot-moulds for casting the zinc.

a long rectangular tube placed horizontally, and closed with a movable tile at the outer end. It has a short arm turned upwards close to the tile, and the top of this tube is fitted with a grate on which a small coal fire is kept burning, to prevent the access of air to the condenser. The bulk of the zinc is deposited in the long tube, and the waste gases pass upwards through the side-tube and grate to the air. In the majority of works, however, the condenser consists of three long horizontal tubes placed one above the other with connecting apertures at alternate ends, so that the vapours pass through them one after the other. Any uncondensed zinc is burned to oxide at the orifice by which it escapes from the uppermost tube; and the oxide formed is drawn off with the air and gases by flues connected with the hood, or recess in front of the retort (shown in fig. 79); the gases are afterwards passed through depositing chambers on their way to the chimney, so that the bulk of the oxide of zinc may be recovered. The condensed zinc is withdrawn from the tubes by opening the movable tiles, by which their entrances are usually closed. Thirty or more of these muffles are arranged in each furnace, so that the flame may pass well round the top and sides of them, and the firing is very gradual, to avoid all risk of splitting them. The muffles

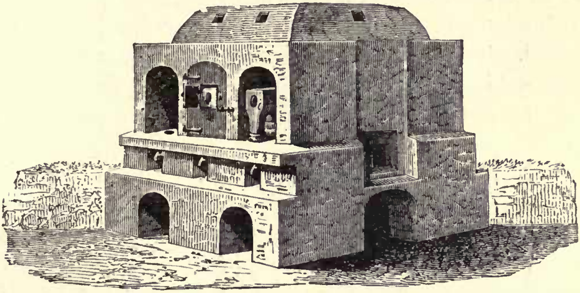

FIG. 79.—Silesian Furnace for distilling Zinc from its Ores. *i*, Condensing tube. *t*, Openings beneath the hearth for receiving the condensed zinc.

are charged afresh every 24 hours, and last about 27 days. The residue left in the muffle does not retain more than $\frac{1}{50}$ of its weight of zinc. The zinc is remelted in iron pots lined with clay, since, if the melted metal be in direct contact with the iron vessel, the latter becomes corroded, and the zinc contaminated with iron, which injures its quality.

Owing, partly to the escape of uncondensed zinc vapour into the air, partly to absorption of zinc by (or to the escape of vapours through) the retorts, and partly to the occasional breakage of a retort in the furnace, with the consequent loss of a charge, as well as to mechanical waste, the total loss of zinc in the Belgian process usually exceeds $\frac{1}{10}$, whilst in the Silesian process it may even exceed $\frac{1}{4}$, of the amount charged. To smelt 1 cwt. of zinc from the ore, the coal consumed is, in Belgium, from 3 to 4 cwt., and in Silesia about 10 cwt., whilst for the old English process it was 25 cwt.

In the Belgian-Silesian furnaces, as they are called, which are used principally in Rhenish Prussia, two or sometimes three tiers of retorts are used, the flame playing freely around those in the upper rows, and then being carried down past the sides of those in the lower row to a flue running beneath them to the chimney. More than 200 muffles are commonly built in each block, one half being placed on each side of the firing-space, which runs lengthwise down the block, as indicated in fig. 80. The condensing-tubes (*g*) have a depression at the under side, and are sometimes provided with tapping-holes through which the zinc may be run off into ingot-moulds. Other forms of condenser may, of course, be used.

The only substantial advance in zinc-smelting in recent years has been the introduction of gas-firing with or without recuperators.

When very poor ores have to be smelted it has sometimes been found economical to charge the roasted ore into a cupola or small blast-furnace, in alternate layers with fuel, when the zinc is given off in vapour, which becomes partly re-oxidised by the carbonic acid in the furnace-gases ; the *grey oxide of zinc* produced, which is a variable mixture of oxide and very finely divided metallic zinc, is collected in condensing-flues, and distilled in the usual way with coal for the production of metallic zinc. The advantages of this process consist in the greater yield of zinc in the distillation, and the absence of the oxides of lead and iron, which do so much damage to the clay vessels.

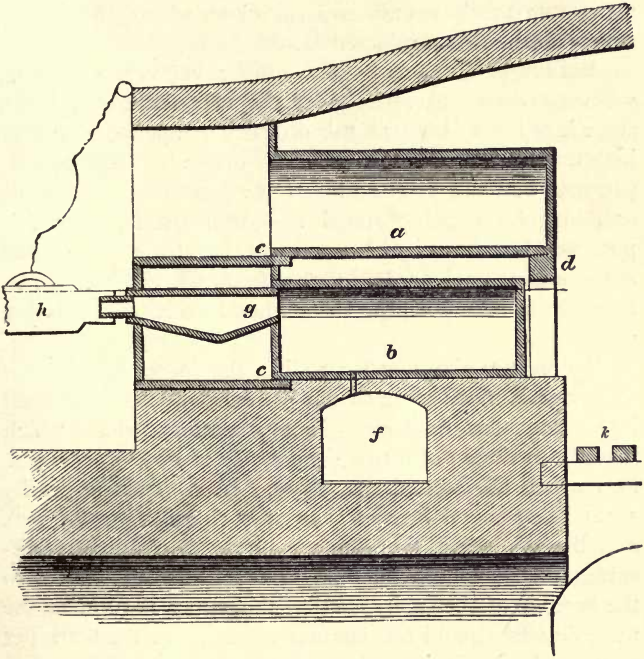

FIG. 80.—Belgian Silesian Zinc-furnace. *a b*, Arched retorts. *c d*, Their supports. *f*, Flue. *g*, Condensing tube. *h*, Receiver suspended by iron-wire. *k*, Fire-place.

At Bleiberg, the *zinc-dust*, or mixture of finely divided zinc with oxide of zinc, which is first collected during the distillation of the ores, is melted in fire-clay tubes set upright in a furnace ; clay pistons attached to iron rods are thrust into the tubes, the pressure causing the finely divided zinc to run together, so that it may be tapped out from the bottom of the tubes. The metal so obtained is very impure, containing much arsenic and cadmium, which always pass over with the first portions of distilled zinc.

Rolling of Zinc into Sheets.—Before the year 1812, zinc was used almost exclusively for the manufacture of brass, since it is brittle both at the ordinary temperature and at high temperatures, but it was then discovered that a temperature between 100° and 150° C. rendered it malleable and capable of being rolled into thin sheets. For this purpose, however, it is necessary that the zinc should not contain iron or lead ; the former it acquires when remelted in iron pots, the latter when lead is present in the ore.

To prepare the zinc for rolling, the ingots of spelter if they contain much more than 1 per cent. of lead are refined by melting upon the hearth of a reverberatory furnace, which is made to slope down to a deep cavity or *sump* at one end, into which the melted zinc flows. Lead (specific gravity 11·4) being much heavier than zinc (specific gravity 7·1), and the two metals having very little disposition to dissolve in each other, the bulk of the lead settles down to the bottom of the cavity, so that the upper portion of the melted metal should not contain much more than 1·1 per cent. of lead. It is useless to attempt the refining of a sample containing less than this amount of lead. Iron cannot be removed by this process, but if it greatly exceed $\frac{1}{4}$ per cent. the metal will not roll well. The metal is ladled out of the furnace and cast into ingots of convenient size for rolling, and after these have been again heated to about 150° C. by the waste heat of the furnace, they are passed between cast-iron rollers and reduced to the required degree of thinness.

After being rolled, the zinc always retains a great deal of its malleability, even after cooling, whereas cast zinc may be broken by laying it across an anvil and striking it with a hammer. The fracture of an ingot of zinc presents a very beautiful crystalline appearance and great lustre, and if it contain iron, minute grey spots are visible on the bright facets of the crystals. At temperatures above 200° C. zinc is even more brittle than at the ordinary temperature, and it may be obtained in extremely fine powder by pouring melted zinc into an iron mortar, and well stamping it with the pestle as it solidifies. Powdered zinc has been employed as a metallic paint for protecting iron from rust. A zinc powder very suitable for this purpose may be obtained by treating the 'grey oxide' from the blast-furnace, or from the condensers of the distilling furnace, with very dilute hydrochloric acid, which dissolves the oxide, and leaves the metallic particles nearly pure.

Since the discovery of the malleability of zinc at suitable temperatures, this metal has been extensively employed for gutters, rain-pipes, cisterns, baths, chimney-pots, and roofing, purposes for which it is eminently fitted by its lightness and by its resistance to the action of air and moisture; for although a bright surface of zinc soon tarnishes, from the formation of a film of oxide and carbonate of zinc upon it, this film serves to protect the metal beneath from any further corrosion. Zinc sheets exposed to the action of the atmosphere should not be joined with soft solder, nor be kept in place by copper nails, as a galvanic action would be set up between the different metals whenever they were wetted, and the zinc, being the more oxidisable metal, would be corroded rapidly. Thoroughly 'galvanised' iron nails may be used.

In casting zinc, it is important to avoid employing too high a temperature, not only because zinc may be lost in vapour, but because *burned zinc* is produced; that is, the zinc becomes very much harder, and difficult to cut with a file or chisel, probably because it has dissolved some oxide of zinc.

Galvanised Iron is sheet iron coated with zinc, and is made in a similar way to tin plate, by thoroughly cleansing the surface of the iron, and immersing it in melted zinc which is kept covered with powdered sal-ammoniac (muriate or hydrochlorate of ammonia), this salt having the property of dissolving the oxide of zinc from the surface of the bath. The zinc probably alloys with the iron plate to a slight depth. A small quantity of iron is dissolved by the melted zinc, and a very brittle alloy is deposited in pasty masses at the bottom of the zinc-pot, whence it is removed occasionally with a perforated ladle. This alloy has been found to contain 6 per cent. of iron and 94 per cent. of zinc. In some large galvanised-iron works, where much of this alloy is obtained, the zinc is partly recovered by distilling this hard spelter in clay retorts like those employed in gas-works. A process recently devised for treating this alloy consists in melting it in iron pots, and cooling it slowly, from the bottom upwards, when an alloy of 9½ parts of iron with 90½ parts of zinc is deposited in crystals, which are removed by a perforated ladle, and the liquid zinc is left much purer. The crystallised alloy is distilled, to recover the zinc. The zinc coating adheres more firmly if the iron be previously tinned. Iron articles can be coated with zinc by electro-deposition. When any portion of the iron surface is exposed in consequence of the abrasion of the zinc, the adjacent portion of the latter metal will protect the iron from corrosion, because the two metals form a galvanic pair of which the zinc only is attacked by the moisture and carbonic acid of the air. It will be remembered that, in the case of tin plate, it is the iron which is attacked.

Galvanised iron is ill-adapted for situations where it is much exposed to the acid vapours sent into the air by some factories, or to the sulphuric acid found among the products of combustion of coal and gas, because zinc is among the metals most easily attacked by the acids. It is often called *corrugated iron*, from the practice of ridging and furrowing the plates in order to strengthen them for building purposes. Vessels of galvanised iron are not well fitted for cooking utensils, since many articles of food are liable to become contaminated with zinc to a hurtful extent.

The low temperature at which zinc melts (417° C.), and its perfectly liquid condition, render it suitable for casting statues, since it runs easily into the very finest lines of the mould. The colour is unsuitable, but this objection may be removed to some extent by 'bronzing' the surface. The beautiful effects due to the *patina* of real bronze surfaces are, however, in that case never attained.

Electro-Metallurgical Treatment of Zinc Ores.—In order to separate a metal by electrical means, it is essential that it should be in solution. The most abundant ore of zinc is blende, which, as already mentioned, on being roasted is converted partly into sulphate and partly into oxide, some of the sulphur going off as sulphurous acid. The sulphurous acid may be collected and converted into sulphuric acid in the ordinary way, and used to dissolve the oxide of zinc, or it may be made to act directly upon oxide of zinc or carbonate, causing the formation of sulphite of zinc, which is also soluble, though much less so than the sulphate. Having obtained the zinc in solution, it only remains to separate it by means of an electric current and suitable electrodes. For this purpose a positive electrode of lead and a negative of zinc may conveniently be used. Oxide of iron separates at the former and falls to the bottom of the tank, whilst the zinc separated at the latter adheres, and may be removed from time to time, when sufficient has accumulated, by taking out the electrode and putting in another. The appliances required are simple, but they are costly, and the process is very slow and up to the present time unsatisfactory. Where a cheap source of power for the generation of the current can be obtained, and the zinc is obtainable as a by-product, the electrolytic method may possibly be worked at a profit. The electrolytic refining of zinc has also been practised, and has produced a very pure metal, but at considerable cost.

Electro-deposited zinc is generally very difficult to melt, owing to the particles being more or less coated with oxides causing further oxidation in melting and considerable loss of metal.

ALLOYS OF ZINC AND COPPER

Brass.—Brass is usually described as an alloy of zinc with twice its weight of copper, but the proportions employed are varied to suit the particular purpose for which it is intended.

Before the year 1780 brass was always made by strongly heating copper in contact with calamine and charcoal or coal. Three parts of bean-shot copper, 3 of calcined calamine, and 2 of charcoal were heated to bright redness in a covered crucible, when the zinc, reduced from the calamine by the action of the carbon, instead of passing off in vapour, as in the extraction of zinc from the ore, entered into combination with the copper, producing brass, which was found in a melted state at the bottom of the crucible. Hence the name of *Calamine brass*, once so well known in commerce.

When it is required to make brass from the pure metals, the copper is melted first, in clay or plumbago crucibles or a reverberatory furnace ; meanwhile the cakes of spelter (zinc), broken into fragments of a convenient size, should be warmed by allowing them to rest upon the hot top of the furnace. They are then added, piece by piece, to the molten copper ; each piece being held firmly by a large pair of iron tongs and plunged beneath the metal in the crucible until it has melted and alloyed. The crucible is then removed from the fire, the dross on the surface of the metal skimmed off, and the contents of the crucible poured into a mould. Such a process is necessarily very wasteful of zinc, but the loss cannot be avoided when making very large castings of brass or its alloys, *e.g.* for propellers, bed-plates, sheathing, &c.

The boiling-point of zinc is so near to the melting-point of copper that, by the time the copper has attained so high a temperature that the whole of the comparatively cold zinc might be added without lowering the mass to the solidifying point, a large proportion of the zinc first introduced is boiled off as vapour with considerable violence. But brass has a much lower melting-point than copper has, and by mixing scrap brass of suitable character with a little copper, and melting the mixture in a crucible, the extra zinc required may be added with the minimum of loss. This is usually done in making small castings when the maximum strength obtainable is not of prime importance. Some loss, however, is inevitable, partly through the oxidation of the zinc in melting and partly through volatilisation ; and both the blue flame which plays over the brass pot, and the dense white clouds of oxide of zinc, produced by the vapour of zinc burning when it comes in contact with the air, are evidences of this loss, which, however, with due care, need not be excessive. For many purposes scrap brass is simply remelted without additional copper, and a little extra zinc is added, usually after the pot has been drawn from the fire, to make up for the unavoidable loss, which may vary from 1 to 5 per cent. according to the conditions of working. Fluxes are not generally employed.

Ordinary brass castings are made by pouring the melted metal into cavities of the shape required, prepared in sand, which has been pressed into iron frames or boxes, technically known as flasks. But brass which is to be rolled into sheet or drawn into wire is usually poured into strip or sheet-moulds, made of cast-iron, in two parts, which may be clamped together, enclosing a space of the size and shape of the ingot required. The faces of these moulds are prepared by painting them over with oil and charcoal, or oil and rosin ; and they are heated to about 200° or higher before the brass is poured into them.

The presence of much iron in brass that is intended for rolling is very objectionable, as it greatly impairs the malleability.

The colour of the alloy of zinc and copper is of course dependent upon the proportions in which the metals are employed. Those alloys which contain more than 80 per cent. of copper exhibit a reddish-yellow colour, in which the red predominates as the quantity of copper increases, the colour becoming yellow when less than 80 per cent. of copper is present. If the amount of copper be less than 30 per cent. the alloy is no longer yellow, but approaches more nearly to the colour of zinc.

The various alloys used to imitate gold before the art of electro-gilding was introduced were all modifications of brass. The alloy termed *gilding-metal*, which is used for cheap jewellery, because its colour is so similar to that of gold that a mere wash of the precious metal upon the surface suffices to complete the illusion, consists of copper containing 10 to 20 per cent. of zinc. *Dutch metal* or *Dutch leaf gold*, which is one of the most malleable of alloys, is composed of 11 parts of copper and 2 parts of zinc. It is cast into thin plates and rolled into sheets, being occasionally annealed (p. 114). When these are very thin, several are passed through the rolling-press together, and they are eventually cut up, and beaten out to extreme tenuity in piles of 40 and 80, under a hammer making three or four hundred strokes per minute. *Bronze-powder* (or at least one kind of it), used for decorative purposes, is made by stamping the thin leaves of Dutch metal to a fine powder. Such powders are made of different shades, from dark copper colour to pale gold, by varying the proportion of copper. They are finally ground with a very little oil to prevent the metal from being tarnished by oxidation.

Ordinary brass contains from 30 to 38 per cent. of zinc, that used for wire commonly ranging from 30 to 33, and that for sheet from 30 to 35, per cent. There are many different names by which brass alloys are known, but the corresponding compositions are variable. A few of these are noted in the appendix.

The alloy containing about 33 per cent. of copper and 67 of zinc (which corresponds to the formula Zn_2Cu) would appear to be a chemical compound. It is as brittle as glass, and white, and corresponds exactly to the speculum metal containing 67 of copper and 33 of tin. It will be observed from these numbers that the hardening effect of tin upon copper is about twice as great as that of zinc.

A little tin is added to the brass intended for engraving, since it causes it to break up more easily under the action of the graver. The addition of a little lead (about 3 oz. to 10 lb.) much facilitates the working of brass at the lathe and with the file, since it prevents the shavings and filings from *greasing*, or adhering to the tools.

Brass is liable to be rendered very brittle when placed in situations where it is exposed to continual vibration. This seems to be due to the development of a crystalline structure in the metal, and has occasionally caused the snapping of the suspending chains of chandeliers.

The *lacquering* of brass, in order to protect it from being tarnished by the air, consists simply in varnishing it with shellac dissolved in spirit and coloured with saffron, annatto, dragon's blood, &c., so as to give it a golden hue. Considerable experience is, however, required in setting the lacquer by slightly heating the article either before or after the lacquer has been applied.

Brass has been *bronzed* by coating it with a film of arsenic, mercury, or platinum, the last being used only for small articles, such as instruments, on account of its high price. A solution of white arsenic (arsenious acid) in hydrochloric acid, or of corrosive sublimate (chloride of mercury) in vinegar, is brushed over the brass, previously warmed, when the zinc in the brass chemically displaces the arsenic or the mercury from the liquid, and deposits it as a coating upon the brass. In bronzing with platinum a solution of chloride of platinum is applied in a similar way. There is much art in obtaining a durable bronze coating of any desired shade of colour. A mixture of chloride of platinum, corrosive sublimate, and vinegar was used for bronzing the *sights* of guns.

A 'bronze' commonly employed now is obtained by immersing the brass in a solution of carbonate of copper in carbonate of ammonia of suitable strength. When properly applied, the deep, almost black, deposit is very durable and adherent.

Pins made of brass wire are tinned by boiling them with granulated tin, water and cream of tartar (bitartrate of potash), when the latter, being strongly acid, slowly dissolves the tin, which is afterwards displaced from the solution and deposited upon the brass by galvanic action.

Malleable Brass, or *Muntz Metal*, or *Yellow Metal Sheathing.*—This is an alloy of from 60 to 62 parts of copper and from 38 to 40 parts of zinc, which differs from common brass in being malleable when hot. It is, of course, cheaper than ordinary brass, on account of the predominance of the cheaper zinc, and can be more easily rolled into thin sheets. When used for sheathing ships it keeps cleaner than copper.

The nails employed for securing the sheathing contain, in 100 parts, 87 copper, 4 zinc, and 9 tin, the latter giving them hardness.

Aich Metal, or *Gedge's Metal*, is an alloy of zinc and copper in nearly the same proportions as are contained in

Muntz metal, but it contains also a little iron. A sample has been found to contain in a hundred parts

Copper	60·0
Zinc	38·2
Iron	1·8

This alloy is very malleable at a red heat, and may be hammered, rolled, or drawn into wire, with the additional advantage of being readily cast. It was at one time employed in Austria for casting cannon, and some Chinese cannon have been found to consist of a similar alloy.

Sterro-metal[1] is another very strong and elastic alloy It contains copper, zinc, iron, and tin, in the following percentage proportions, the composition varying within the assigned limits according to the purpose for which it is required :—

Copper	55 to 60	Iron	1 to 2
Zinc	34 to 41	Tin	1 to 2

Good specimens of sterro-metal have been found to offer far more resistance than gun-metal to transverse fracture, and it is only two-thirds of the price.

Manganese bronze, in addition to the above-named metals, contains manganese. It is an alloy possessing great tensile and transverse strength, and it can be worked hot.

A very hard white alloy, of 77 parts of zinc, 17 of tin, and 6 of copper, is sometimes employed for bearings of the driving wheels of locomotives ; and another alloy, containing 90 of copper, 5 of zinc, and 5 of antimony, is used for sockets in which the steel or iron pivots of machinery are to work.

Brazing Solder.—Iron or copper sheets may be united by placing their edges so that they slightly overlap, sprinkling a small quantity of brazing solder in fine grains, together with a little borax, along the joint, and then directing the flame of a blowpipe on to it. The borax first melts, and

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[1] Named from the Greek adjective, *strong*, *firm*.

acts as a flux, dissolving any film of oxide upon the metal, and, at the same time, helps to protect it from further oxidation. At a higher temperature the grains of solder melt, and the metal running between the clean surfaces of the joint, on solidifying, firmly holds them together. It is obvious that the solder must have a lower melting-point than that of the metal sheet to be treated. For iron or copper, an alloy of 43 per cent. of zinc and 57 per cent. of copper may be used. Brass sheet may also be brazed, but, in order to allow a sufficient margin of safety, an alloy of equal parts of copper and zinc is used. This has a lower melting-point than the other ; and a little silver added to the mixture renders the alloy even more fusible.

[For alloys of zinc and copper with nickel, see NICKEL.]

CADMIUM [1]

CADMIUM is found, in small quantities, not exceeding 2 or 3 per cent., in the ores of zinc, and distils over, together with the first portions of zinc, during the smelting of the ores of that metal, the period of its distillation being known as the *brown blaze*, because its vapour imparts a brown colour to the flame. If these first portions of metal, containing some oxide, be mixed with charcoal and distilled again, the metal which passes over first will contain a still larger proportion of cadmium, this metal being much more easily converted into vapour than zinc is. To obtain pure cadmium, the mixture of zinc and cadmium is dissolved in diluted sulphuric acid, and sulphuretted hydrogen gas is conducted into the solution, when the sulphur combines with the cadmium to form a bright yellow sulphide of cadmium, which is deposited.

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[1] From *cadmia* (Latin), *brass-ore*, referring to its connection with the ores of zinc.

This is washed, dissolved in strong hydrochloric acid, and converted into carbonate of cadmium by adding carbonate of ammonia. The carbonate of cadmium being washed, dried, and distilled with charcoal, yields metallic cadmium in a pure state. When zinc containing cadmium is treated with hydrochloric acid, the zinc dissolves first; and if the operation be checked at the right moment, a residue is obtained containing the greater part of the cadmium with but little zinc. The residue may be distilled, and thus separated from the lead and other impurities with which it may be mixed.

Cadmium is usually found in commerce in small rods or sticks. It resembles tin in colour and appearance, as well as in the property of *creaking* when bent. It is a malleable and ductile metal at the ordinary temperature, but becomes brittle at about 80° C. It melts at the remarkably low temperature of 321° C. It boils and may be distilled at a temperature of 770° C. An alloy of one part of cadmium, four of bismuth, two of lead, and one of tin fuses at 61° C.

Cadmium is harder than tin, and possesses greater tenacity. It is also somewhat heavier, its specific gravity being 8·6.

NICKEL AND COBALT

THESE two metals almost invariably occur in the same ore. They are so closely allied in nature that their separation from one another is attended with a considerable amount of difficulty. Their properties very nearly resemble those of iron. Both are slightly more fusible than the latter substance; they are magnetic, but much less so than iron. In respect to tenacity, malleability, and ductility, they rival it to the extent that, with our present knowledge, it cannot be stated which possesses these properties in the greater degree. Nickel and cobalt are both whiter than iron; nickel has a slight yellowish tinge, whilst cobalt has a bluish shade in it. The atomic weight of nickel is given as 58·7, and that of cobalt as 59·4.

The following specific gravities were determined in the author's laboratory:—

	I.	II.	III.	Mean.
Grain nickel (*a*)	7·942	8·044	—	7·993
Malleable cast nickel (*b*)	8·364	8·375	8·333	8·357
Malleable nickel, rolled and stamped (*c*)	8·77	8·688	—	8·729

(*a*) Two specimens of same sample.
(*b*) Three ,, ,,
(*c*) I. a spoon; II. a fork.

The specific gravity of cobalt after fusion is stated to be 8·7. Rammelsberg gives its mean specific gravity as 8·957. Nickel and cobalt behave towards carbon in the same way that iron does. The principal ores of nickel are: *Garnierite*, a hydrated silicate of nickel and magnesia, free from arsenic, sulphur, and cobalt, and containing on an average about 7 to 10 per cent. of nickel, found in New Caledonia; and a nickeliferous pyrites, or pyrrhotite (magnetic pyrites), found in Canada and Norway. The extensive Canadian pyrrhotite deposits contain on an average about 2½ per cent. of nickel, with about an equal amount of copper in the form of copper pyrites. *Kupfernickel*, or *Niccolite*, an arsenide of nickel, and *Millerite*, or nickel pyrites, a yellowish sulphide of nickel found in delicate hair-like crystals (*capillary pyrites*) are also to a small extent sources of the metal.

The cobalt ores are essentially the same as those of nickel, with the exception that some of the New Caledonian ores are practically free from cobalt.

Extraction from the Ores of New Caledonia.—The processes employed for extracting nickel may be classified broadly into dry and wet methods. Originally the silicate ores of New Caledonia were smelted on the spot in blast-furnaces with the aid of coke, and yielded a crude pig nickel containing about 66 per cent. of nickel, 25 of iron, 2 of sulphur, and 4 of carbon, with other impurities; but there was a considerable loss of nickel in the slags, and the refining of the metal in Europe from iron and sulphur, which was attempted in the open-hearth furnace, was not satisfactory. Attempts were then made to refine the pig nickel by first converting it into matte, by fusing it with gypsum and coke or with 'alkali waste,' but the process as a whole proved unremunerative, mainly owing to the limited and uncertain market for the product. The nickel ore has since been shipped and then concentrated into a matte, which is subsequently refined by a series of processes resembling those used in copper-smelting in Swansea. In the first place the ore is mixed with calcium sulphate and coal, or with alkali waste (calcium sulphide), and pressed into bricks, which are smelted with coke in small blast-furnaces. The sulphur of the calcium sulphide (either added as such or resulting from the reducing action of the coal upon the calcium sulphate) exchanges with the oxygen of the nickel and iron oxides, and produces a matte containing sulphides of nickel and iron, and a slag in which the lime is combined with the silica and other materials in the ore. The matte is then roasted, and afterwards fused with sand, twice in succession, to eliminate iron and concentrate the nickel. Nickel sulphide containing less than 1 per cent. of impurities being thus obtained, it is 'dead'-roasted (*i.e.* free from sulphur), and should then consist of nickel oxide with less than 0·5 of sulphur or iron. The oxide is finally mixed into a paste with flour or oil, and moulded into grains, cubes, or discs, dried, and heated to a white heat with charcoal, when fragments of reduced metallic nickel result, unfused, but fritted together, and quite solid. These pieces are known as *grain* or *cube*-nickel, according to their shape. The reduction was formerly effected in crucibles, but now in iron pots placed in reverberatory furnaces, a final heating being given in crucibles to ensure that the reduced nickel is thoroughly coherent. In some works the mixture is treated for several hours in long fire-clay cylinders, open at both ends, and heated to about 1,200° C. in regenerative gas furnaces, the mass at the end of this time being forced out into air-tight cylinders, in which it is cooled. It is obvious that in this process copper would concentrate with the nickel, and cupriferous ores would yield an alloy of the two metals. A pyrrhotite or pyritous ore may be similarly treated; but in this case, instead of introducing sulphur, it is necessary to remove a portion of the excess of that element by roasting.

Extraction from Canadian Ores.—The Canadian ores are commonly roasted in heaps of about 1,000 tons until they contain only about 7 per cent. of sulphur. The roasted material is then melted with coke in a water-jacketed blast-furnace, such as that described on p. 321. The resulting matte, containing some 20 to 25 per cent. of nickel and 20 per cent. of copper (more or less, according to the ore), is run into moulds, and the slag is rejected. The matte may be remelted and 'blown' in a silica-lined Bessemer converter, by which much of the sulphur, and practically the whole of the iron, is removed, as in the copper converter, and by similar reactions. In this process, iron, having the strongest attraction for oxygen, is first oxidised, together with the sulphur which had been combined with it as sulphide. But, as nickel is more oxidisable than copper, a continuation of the blow after the iron has been removed would involve a loss of nickel in the slag and a concentration of copper in the remaining regulus. The operation should therefore be stopped when there still remains some 14 or 15 per cent. of sulphur associated with about 40 per cent. of nickel and 44 per cent. of copper. A rich regulus is thus obtained, which may be used for the production of a rich alloy of copper and nickel by roasting it very thoroughly and then reducing the mixed oxides at a bright red heat with the aid of carbonaceous material. When pure nickel is required, and as there is no cobalt worth separating, the matte is ground, mixed with sulphate of soda and coal, and melted. The resulting matte separates on cooling into a nickel matte containing much less copper than the original matte, and a copper matte comparatively free from nickel. This operation is repeated until nickel and copper mattes are obtained free respectively from copper and nickel. A pure nickel sulphide is thus produced, which may be dealt with in the manner already described.

The Mond Carbonyl Process.—The remaining dry process to be noticed is, perhaps, one of the most interesting in the whole field of metallurgy. When carbonic oxide is passed over recently reduced metallic nickel at a temperature below 150° C. a curious compound, known as *nickel carbonyl*, is formed, which has the formula $Ni\ (CO)_4$, and is a liquid, boiling at 43° C., and forming a vapour, which is decomposed again into nickel and carbonic oxide when heated to 180° C. Of the other metals, only iron is capable of forming an analogous compound, and that in but small quantities. A method is thus obtained for completely separating nickel from associated metals, and even from cobalt, which is in other respects so similar to nickel that a perfect separation is very difficult. In practice, an oxidised ore or a thoroughly roasted pyrites is heated to 400° C. in water-gas (see p. 69), whereby the nickel is reduced to the metallic state ; it is then conveyed through air-tight tubes, and is introduced into the top of an iron cylinder, in which it is caused to fall gradually over a series of shelves until it reaches the bottom. In this cylinder the temperature is never allowed to exceed 80° C. Through the cylinder ascends a current of pure carbonic oxide, of which a portion combines with nickel, and the resulting nickel carbonyl, mingling with the excess of carbonic oxide, passes out above, and is conveyed to a series of tubes heated to 180° C., whereby the carbonyl is decomposed, and nearly pure nickel is deposited upon the hot walls of the tubes. The carbonic oxide thus set free is returned with the aid of a blowing fan into the bottom of the volatilising cylinder. After a short time the reduced nickel fails to combine with carbonic oxide ; the material which falls to the bottom of the cylinder is therefore mechanically conveyed along gas-tight tubes to the reducing plant, where it is revivified and returned to the volatiliser. Thus there are two circuits constantly in progress : ore is reduced and continuously circulated through the reducer and volatiliser, whilst carbonic oxide is passed through the volatiliser, where it combines with nickel, carries it to, and leaves it in, the depositing tubes, and then returns to the volatiliser. This is continued until most of the nickel has been extracted, when the process is stopped, and the residual copper oxide and other substances are treated for the extraction of their valuable constituents. Since the nickel carbonyl forms explosive mixtures with air, great care must be taken that air is rigorously excluded from all portions of the apparatus. It is premature to predict whether this process will ultimately be commercially successful.

Wet Extraction Processes.—In using the wet processes, a concentration of nickel, either in the form of matte or as *speise* (which is an impure arsenide of nickel), may be first effected ; the final treatment depending on the complexity of the matte.

The following is a general description of the treatment of speise at the works of the well-known nickel and cobalt refiners, Messrs. Henry Wiggin & Co., Birmingham. The arsenide, or sulphide, is roasted in reverberatory furnaces, in order to drive off, in the form of arsenious acid, as much as possible of the arsenic, which is condensed in coke-towers, and subsequently used up in the works. The calcined ore is treated with hydrochloric acid in large earthen receptacles, and the solution, containing nickel, cobalt, copper, iron, arsenic, and, perhaps, lead and bismuth, &c., is ladled out into wooden vats. The residue is again calcined and lixiviated and finally resmelted, as it still contains 1 or 2 per cent. of nickel. The solution is diluted and sesqui-oxidised by the addition of chloride of lime (bleaching-powder), the quantity added having been adjusted to the iron by analysis. Milk of lime is also added in suitable proportion, to throw down the whole of the sesqui-oxide of iron, which at the same time carries the arsenic with it in combination as basic arseniate of iron. The precipitate is transferred to a filter, consisting of flannel strained over a wooden frame, and there well washed. It contains sufficient arsenic to make it worth while to use it in smelting operations on the works. The solution is next treated with sulphuretted hydrogen, which precipitates the copper, bismuth, and lead as sulphides. Only nickel and cobalt remain to be dealt with. The cobalt is thrown down at a higher temperature as sesqui-oxide by the addition of bleaching-powder, and the nickel subsequently as hydrated oxide by means of milk of lime.

Some of the New Caledonian ore contains cobalt and much peroxide of manganese, and is treated in France by a wet process. The powdered mineral is mixed with a solution of ferrous sulphate (green vitriol) by means of a current of steam, whereby the manganese, cobalt, and nickel are dissolved, and the iron in the solution is deposited as peroxide, together with the insoluble residue of silica and alumina. This residue is separated in the form of cakes with the aid of a filter-press, and the clear liquid which filters through, and contains the nickel, cobalt, and manganese, is transferred to stone basins and mixed with a solution of sulphide of sodium. The whole of the nickel and cobalt separate in the solid condition as sulphides, which are removed from the liquid by filtration under pressure. The manganese for the most part remains in solution, and the trace which is left in the cakes obtained in the filter-press is removed by treating them with a solution of ferric chloride. The purified sulphides of nickel and cobalt are so roasted at a low temperature in reverberatory furnaces that both metals may be converted into sulphates, which dissolve readily in water. After washing the roasted matte with boiling water, to dissolve the sulphates, a solution of chloride of calcium is added, with the result that calcium sulphate—a comparatively insoluble substance—is formed, together with the chlorides of cobalt and nickel, which remain dissolved in the solution. A portion of this clear solution is then mixed with lime, which causes the nickel and cobalt to separate as a solid precipitate, chloride of calcium being formed at the same time and passing into solution. The two oxides are filtered, washed well with water, and then treated with water, chlorine, and air under pressure. The nickel and cobalt thus become converted into peroxides. A further quantity of the original solution of the nickel and cobalt chlorides is now mixed with the solid peroxides. The result is that the nickel in the precipitate exchanges with the cobalt in the solution; peroxide of cobalt separates out and mixes with that already present, whilst an equivalent quantity of nickel passes into the liquid as chloride. The added liquid is used in quantity just insufficient to extract all the nickel from the solid peroxides, so that the whole of the cobalt in the solution is deposited, and only nickel is left dissolved. The pure nickel solution is then run off, and the nickel is recovered from it as oxide by adding lime in the usual way, the oxide of nickel being filtered off, dried, mixed with carbonaceous matter, and heated. The peroxide residue, consisting mainly of cobalt, is now treated with a fresh quantity of the mixed chloride solution, with the result that the small residuum of nickel is extracted, and the pure cobalt peroxide has only to be washed and is then ready to be converted into any required cobalt compound. The final solution is used to treat a fresh portion of the mixed peroxide, and the cycle of reactions is continued.

Malleable Nickel.—Formerly nickel was only used in alloy with other metals as a whitening agent. The reason of this was that it could not be obtained in a workable form. The metal resulting from the fusion of grain nickel is always wanting in malleability and ductility, behaving in a similar way to wrought iron which has undergone fusion, and probably for a similar reason. Nickel may be rendered malleable by adding to it, whilst in a state of fusion, a small proportion of magnesium, introduced through a hole in the top of the crucible, a few lumps of charcoal having been previously added. In this way it is possible to produce malleable nickel, which can be welded to iron or steel at a white heat and rolled into thin sheets without separation. Nickel and cobalt may also be rendered malleable by means of manganese. Commercial manganese (about 95 per cent.), or any ferro-manganese, may be used for the purpose, the presence of iron not destroying the malleability of the nickel or cobalt. Thus the analogy between the treatment of nickel and cobalt and iron which have undergone fusion is perfect. The manganese is added little by little to the fused nickel or cobalt, which is kept well stirred during the time, and finally poured out into moulds when tranquil. The metal is considerably agitated by the escape of gas during the addition of the manganese. For most purposes the addition of 2 per cent. of metallic manganese is sufficient; but when the maximum degree of malleability and ductility is required the quantity added may be increased to as much as 5 per cent., beyond which there is no gain under ordinary circumstances. Malleable nickel anodes are sometimes used instead of cast anodes in nickel-plating. The former certainly have a great advantage in their uniformity of structure, which not only prevents their being eaten away irregularly, but also avoids loss of energy through secondary currents. On the other hand, the cast anodes are more readily soluble in the plating liquid, and, moreover, the manganese in the malleable nickel leads to a black deposit of binoxide of manganese, which causes a 'back electro-motive force' that has the effect of practically increasing the resistance of the bath, and so adding to the expense of current.

Alloys of Nickel.—Zinc can be successfully alloyed with nickel by reducing their oxides in a state of admixture. By rapidly fusing the alloy thus obtained, a tough, malleable, and ductile metal can be made. The melting-point of nickel is too high to admit of zinc being introduced into it after the nickel is molten. The addition of $\frac{1}{10}$ per cent. of magnesium is said to improve the working properties of this alloy.

The principal remaining alloys of nickel are those with copper, nickel steel having been already referred to. A few continental coins are made of nickel alone, but both in America and in Europe much of the smaller currency consists of an alloy of nickel and copper. The alloy used contains from 20 to 25 per cent. of nickel. The *cupro-nickel* used for the sheath of the leaden bullets employed in the new magazine rifle consists of 80 parts of copper alloyed with 20 of nickel. The alloy is cast in strip-form in iron moulds, the ingots are rolled into thin sheets, discs are stamped out of these sheets, and are then drawn down into the required shape with the aid of punches and dies. For other purposes than the above zinc is commonly added to the copper and nickel, and *German silver* is thus formed. It is used as a substitute for silver and as the basis of electro-plated ware. The varieties of German silver are numerous; abroad, alloys are occasionally made with as little as 6 per cent. of nickel, but in England the percentage of nickel usually ranges from 15 to 25, that of copper from 55 to 60, and of zinc from 17 to 24, according to quality, those containing most nickel being the whitest; but there is apparently no gain in increasing the proportion of nickel beyond 25 per cent. The latter proportion is often used in alloys for the fittings of lavatories or the furniture of doors. Under the name of *maillechort*, a German silver containing about 15 per cent. of nickel and a small proportion of iron has been used as the basis of electro-silvered ware. Other metals with high percentages of nickel are even used as a substitute for plate, their whiteness rendering a coat of silver unnecessary. The substitution of 2 or 3 per cent. of cobalt for a like amount of nickel is considered to improve the colour of the alloy. German-silver wire is very largely used by electricians for standard electrical resistances, because it has a low conductivity, and because the conductivity is not greatly affected by moderate differences in temperature. *Platinoid*, the electrical resistance of which is singularly constant through a considerable range of temperature, is a German silver containing about 2 per cent. of tungsten.

German silver is made by fusing nickel and copper together in crucibles, usually in equal proportions, the excess of copper required for any alloy being added after the mixture has melted, and finally the zinc. The zinc may most conveniently be introduced in the form of brass. Other alloys of nickel are noticed in the appendix.

Cobalt.—The greater rarity and consequent higher price of cobalt as compared with nickel precludes its general use in the solid metallic state. It is, however, being used for electro-plating, the articles coated with it being sold as superior nickel-plate.

Oxide of cobalt imparts a fine azure-blue colour to glass, pottery, and enamels, even $\frac{1}{1000}$ part producing an appreciable amount of colour. It is largely employed in the form of *smalt*, a silicate of cobalt and potash. Great care has to be exercised in the manufacture, any impurities deteriorating the quality of the colour. When iron and copper are present, in order to separate them advantage is taken of their greater affinity for oxygen; whilst nickel can be removed by reason of its having a greater affinity than cobalt for arsenic, so that the cobalt can be obtained as silicate and the nickel as speise in two distinct layers.

LEAD

Ores.—Whether lead in the metallic state has ever been found as a true natural product appears to be doubtful, since the small quantities which have been found associated with the ores of lead may have been accidentally reduced.

Although minerals containing lead are pretty abundant, there are only two which are found in sufficient quantity to serve as sources of the metal on the large scale.

Ores of Lead

	Composition		Lead in 100 parts of the pure ore
Galena or Sulphide of Lead	Lead, Sulphur	PbS	86½
White Lead Ore or Carbonate of Lead	Lead, Oxygen, Carbonic Acid	$PbCO_3$	77½

Galena is by far the most abundant of the compounds of lead. It forms extensive veins, traversing limestone in Derbyshire and Cumberland. It is also found in Flintshire (Holywell), Scotland (Leadhills), and the Isle of Man. Spain yields abundance of galena in Catalonia, Grenada, and at Linares in the Sierra Morena, where it occurs in granite. This ore is also abundant in the Upper Hartz, at Freiberg in Saxony, Przibram in Bohemia, Pontgibaud in France, and in the United States of America, particularly in Colorado, Idaho, Montana, Nevada, and Utah. Few ores are so easily recognised at once as galena; it is distinguished by its lustre, which is almost metallic, its dark grey colour, and its great weight (specific gravity, 7·5). It can generally be easily split up into rectangular fragments, and often occurs in distinct cubical crystals of large size.

Galena almost invariably contains silver, which takes the place of a part of the lead in its combination with sulphur without producing any alteration in the crystalline form and general appearance of the ore. A galena containing two parts of silver in a thousand would be spoken of as an *argentiferous galena*, because even that small proportion of silver can be profitably extracted from the lead after smelting it from the ore.

Antimony is also found in many specimens of galena as a sulphide of antimony, and its presence has a serious influence upon the quality of the lead extracted from the ore. The minerals commonly associated with galena in the vein are blende (sulphide of zinc) and copper pyrites, whilst *cawk* or heavy spar (sulphate of baryta), calc-spar (carbonate of lime), and fluor-spar (fluoride of calcium) are often found adjacent.

White-lead ore or *carbonate of lead* (*Cerussite*) is a much less important ore, often occurring in veins of galena, and apparently produced by a chemical alteration of this ore. When pure, it is a white crystalline mineral, but it has often an earthy appearance, and it is so unlike galena that miners have been known to reject it as worthless. Sometimes it has a dark colour, from the presence of a little galena intermixed with it. Carbonate of lead is found in considerable quantity near Aix-la-Chapelle, as well as in Spain and in the valley of the Mississippi. This ore is so seldom smelted apart from galena that it will not be necessary to describe its treatment separately.

Sulphate of lead (composed of lead, sulphur, and oxygen), or *Anglesite*, is very rarely found in any quantity. Australia furnishes some of it, containing a considerable proportion of silver.

In New South Wales large quantities of lead are produced from the Broken Hill ore, of which there are two kinds, the upper portion being mainly a carbonate of lead associated with manganiferous iron ore, and the lower portion an exceedingly refractory mixture containing from 20 to 25 per cent. of lead with a somewhat smaller percentage of sulphide of zinc, and a small proportion of silver, ranging from say 6 to 40 oz. in different deposits.

In order to prepare the lead ore for smelting, it is sorted by hand, the worthless pieces being rejected, and then crushed between rolls preparatory to washing it in order to separate, as far as possible, the foreign matters. The differences in the ore have led to the adoption of different methods of conducting the operation of smelting; thus in Derbyshire and Flintshire, where the lead ores are rich and contain very little quartz (silica), the galena is smelted in reverberatory furnaces, whilst at Alston Moor, and generally in the lead-works of the North, small blast-furnaces are employed.

The English Method of Smelting Galena in the Reverberatory Furnace.—The chemical principles upon which metallic lead is separated from galena are in the main similar to those involved in the last stage of the extraction of copper (roasting the fine metal for blister copper, p. 312), the sulphur being finally expelled in the form of sulphurous acid.

The galena is first roasted until a part of it has become converted into oxide and sulphate of lead. The charge is then melted, when much of the sulphur is converted into sulphurous acid, and a corresponding amount of lead is left in the metallic state. But a considerable proportion of lead still remains as oxide and sulphate in the slag; and some is carried up the chimney in the form of fume. Sulphide of lead appears to be volatile under certain conditions.

A reverberatory furnace in which the smelting of galena is effected is represented in figs. 81, 82. The hearth (B) is about 8 ft. by 6 ft., and is separated from the grate (F) by a fire-bridge which rises to within about 18 in. from the arched roof (AA′). The roof gradually descends, as it approaches the chimney, until it is within about 6 in. of the hearth. The flame and products of combustion, after passing over the hearth, are conducted by two openings into a flue about 18 in. wide; and thence into a chimney between 50 and 60 ft. high. The flue is so constructed that it may be readily opened to clear out the deposit of lead fume. The fire-door (P), for throwing the coal upon the grate, and the ash-pit (F) are on opposite sides of the furnaces; that upon which the fire-door is situated is called the *labourer's side*, whilst that opposite is the *working side*.

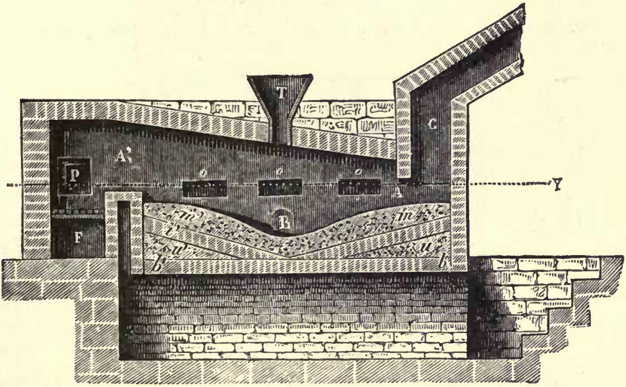

FIG. 81.—Reverberatory Furnace for smelting Galena.

On each side of the furnace there are two and often three doors about 6 in. high by 10 in. wide, which can be closed by iron plates. On the working side there is a tap-hole for the lead and another for the slag.

The furnace is now frequently built somewhat larger and trapezoidal in shape, being from 9 to 10 ft. long by 8 to 9 ft. wide at the flue end, increasing to about 10 ft. in width near the fire-bridge. The hearth, also, is frequently solid, without the vault beneath.

The hearth of the furnace is lined to an average depth of from 6 to 12 in. with grey slag from previous operations and sand, which are spread over it while in a semi-fused state, and fashioned to the proper shape, as shown in fig. 81. This operation is repeated several times until a layer of sufficient thickness has been formed. On the labourer's side it is nearly up to the level of the working doors, but on the opposite side it is hollowed out so as to form a well 18 in. below the middle door; this being the lowest part of the hearth, where the melted lead collects, a tap-hole is provided for running off the metal, and at some distance above it is the aperture for the escape of the slag. Adjacent to the tap-hole there is a cast-iron basin outside the furnace for the reception of the lead. The Derbyshire ores commonly contain heavy spar (sulphate of baryta), which, owing to its high specific gravity, cannot be separated from the galena by washing. If the ore does not already contain it, fluor-spar is added to flux the heavy spar.

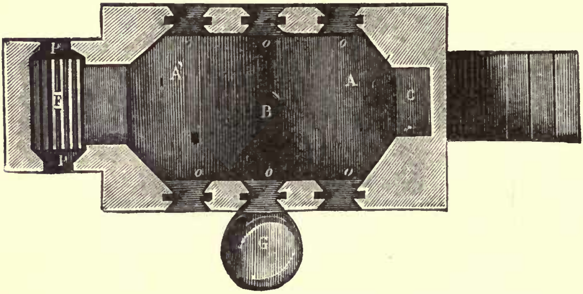

FIG. 82.—Plan of Reverberatory Furnace for smelting Galena.

The operation of smelting galena in the reverberatory furnace consists of four consecutive stages, distinguished as first, second, third, and fourth *fires*.

First fire.—As soon as the lead smelted in the preceding operation has been tapped into the outer basin, and while the furnace is still hot, the fresh charge of about a ton of ore is introduced through a hopper (T, fig. 81) in the arch of the furnace. No regular fire is made up, but only a little coal is thrown into the grate to keep up a moderate temperature, for if this were raised at first above a just visible red heat the galena would fuse, and the roasting would be rendered impossible. A workman stationed at the labourer's side spreads the ore uniformly over the surface with a rake, taking care that as little as possible enters the well, after which the doors are closed and the draught moderated by lowering the damper. Since there is little fuel upon the grate, a considerable quantity of unconsumed oxygen of the air passes over the hearth of the furnace, so that some oxide of lead and sulphate of lead are soon formed. The ore is stirred with a paddle from time to time.

After the roasting has been continued for some time the skimmings from the lead, run into the outer basin at the end of the last smelting, are thrown into the hearth. These skimmings consist chiefly of lead containing a small proportion of sulphur, the mixture being less fusible than lead. This dross is speedily acted on by the oxide and sulphate of lead, with separation of metallic lead, which runs down into the hollow, and is drawn out through the tap-hole into the basin. This first portion of lead contains a larger proportion of silver than that tapped at a later period of the process. About an hour after the commencement a large quantity of lead may be run off, being chiefly derived from the action of the skimmings upon the roasted galena.

After an hour and a half from the commencement, all the doors are thrown open, and the ore is well turned over by two workmen placed on opposite sides of the furnace, after which the doors are closed. At the end of two hours, the first fire is completed, a sufficient proportion of the galena having been converted by the roasting into oxide and sulphate of lead.

Second fire.—The damper of the furnace is partly raised, and more coal is thrown into the grate, so as to bring the temperature up to a bright red heat, which causes lead to run out in abundance. The workman stationed on the working side thrusts the pasty slags out of the basin, whilst the man on the labourer's side spreads them over the rest of the hearth ; a little quicklime is now thrown in to assist in stiffening the unreduced portion. Were the stiffening effected at this stage entirely by means of lime, the unreduced portion would be rendered too infusible for subsequent operations, so it is made sufficiently pasty partly by opening the fire door and lowering the temperature. The charge is well worked and calcined for about an hour. The thickening of the charge not only allows any reduced lead to drain out, but also – and this is the main object—prevents the galena from sinking below the slag, and being thus removed from the action of the air.

Third fire.—The doors are all shut; and the damper opened entirely, more fuel being thrown upon the grate so as to raise the hearth to a still higher temperature for about three-quarters of an hour, when the doors are again opened, the slags spread over the hearth, and a further small quantity of lime thrown upon them. The lime enters into combination with any silica which may have united with the oxide of lead, and sets the latter free to act upon any portions of unaltered sulphide of lead. The lime also acts advantageously by diminishing the fusibility of the mass, and thus facilitating the contact between the sulphide of lead and the oxide. This third fire also occupies about an hour.

Fourth fire.—The grate is again charged with fuel and the doors closed for about three-quarters of an hour, the furnace being thus raised to its highest temperature. The tap-hole is then opened to allow the lead to run into the outer basin (G, fig. 82), and some lime is mixed with the slags in order to *dry up* or partly solidify them, when they are raked out through the openings on the labourer's side, and the furnace is ready to receive a fresh charge of ore. A little small coal is sometimes thrown upon the hearth at the conclusion of the fourth fire, to remove the oxygen from some of the oxide of lead which still remains.

The iron of the tools employed in stirring the contents of the hearth is seriously corroded by the sulphur in the ore.

The whole operation of smelting in the reverberatory furnace lasts about five to six hours, and the coal consumed is about 12 cwt. for every ton of ore.

The rich scum which forms on the metal in the pot contains a considerable quantity of lead mechanically intermixed, to effect the separation of which the workman agitates the lead vigorously with a paddle, at the same time throwing some coal slack into the pot and igniting, by means of a shovelful of hot cinders, the gases thus generated. In this way the dross is prevented from solidifying, and the greater part of the entrapped lead separated. The dross is at once returned to the furnace.

The slag amounts to about one-fourth of the weight of the ore, and sometimes contains as much as 40 per cent. of lead, so that it is smelted in the *slag-hearth*, to be described hereafter.

In some of the Continental furnaces, metallic iron is added to the charge in order to combine with the sulphur in the galena, and separate the lead in the metallic state.

When galena containing much antimony is smelted in the reverberatory furnace, a portion of the oxide of lead combines with the oxide of antimony to form a compound which can only be decomposed by the coal at a very high temperature, so that the first portions of lead obtained contain much less antimony than those at the end of the process.

Smelting of Lead Ore in the Scotch Furnace or Ore-hearth.—The reactions which occur in the ore-hearth appear to be identical with those of the reverberatory furnace, although the reduction takes place in less time, and in a single operation. But since a blast of air is used in the hearth, the ore may with advantage be used in fragments the size of a small nut, in order to minimise mechanical loss. There is probably a further gain in the use of these comparatively large pieces, for they are less liable than fine dust to become oxidised to sulphate by the action of the air. Usually a richer and purer ore must be employed in the ore-hearth than in the reverberatory furnace.

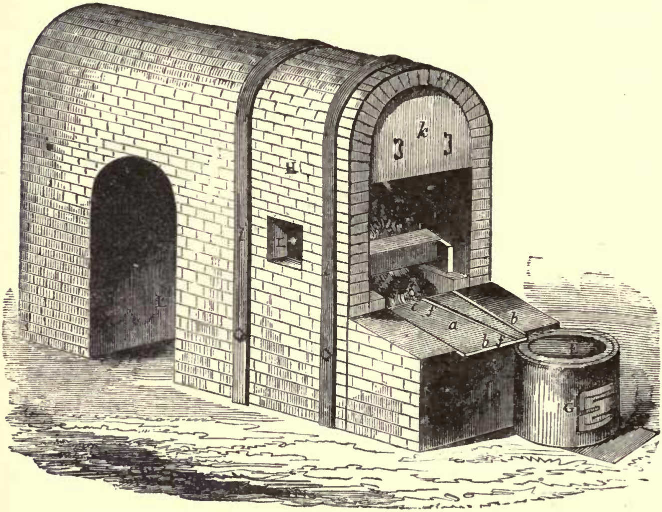

FIG. 83.—Scotch Furnace or Ore-hearth for the extraction of Lead.

The ore-hearth (fig. 83) is a small forge or blast-furnace about 2 ft. square. It is arched over at the top, so that the *lead fume* may be conducted into a long flue, sometimes 5 ft. high and 3 ft. wide, in which a large quantity of oxide of lead and sulphate of lead is deposited. At some works, this flue is carried up the side of a hill for two or three miles before it terminates in the chimney, in order to secure perfect deposition of the lead fume, which would otherwise involve very considerable waste; the flue dust is afterwards heated in the calcining furnace till the particles can be made to stick together, and they are then smelted in another furnace called the *slag-hearth.* A *rain chamber* is often provided, in which the condensation of the fume is assisted by water; and the great length of flue renders it necessary to assist the draught by large exhausting pumps. More elaborate arrangements have been made for the condensation of fume, depending in some cases upon the action of water, used either by sprinkling it through the gases, or by causing the fume to pass through the liquid; but they have not in most cases been successful. Better results have been obtained by forcing the flue gases, after cooling, through coarse sacking bags or screens, which serve to filter off the dust; or by passing them through spacious flues in which their velocity is greatly reduced, and there causing them to take a devious course, by the judicious arrangement of screens and baffles, and in some cases finally passing them through water. The resulting retardation of the current greatly facilitates the deposition of the dust, which may afterwards be collected from the bottom of the flue.

Since a very moderate temperature suffices in the ore-hearth, the sides and bottom are lined with cast-iron plates, and in front of the furnace, where there is an opening about a foot high, a sloping iron plate *a b* (*work-stone*) is fixed, upon which the materials can be raked out when necessary, for examination and manipulation by the smelter. The bottom of the furnace, upon which the melted lead collects, is about 4½ in. below the upper surface of this iron plate, in the edge of which there is a groove cut, near to the side of the furnace, through which the melted lead may overflow when it rises to a sufficient height, into a gutter (*f*) which conveys it into a cast-iron pot (F) heated by a separate fire, and called the *melting-pot.*

The blast-pipe enters at the back of the furnace, about 11 in. from the bottom. Although coal is now used in many districts, peat is still commonly employed in the form of square blocks, with which the furnace is filled at the commencement, some judgment being required in their arrangement. The fire is lighted by placing one of the blocks, already kindled, in front of the blast-pipe, when the combustion soon spreads throughout the furnace. In English practice the first charge introduced into the ore-hearth does not consist of the roasted ore, but of the residue from a previous smelting operation, which is called *browse*, and consists of partly reduced ore mixed up with cinders; before this is thrown in, a little coal is put on the fire to raise the temperature, and in a short time the charge is raked out upon the work-stone in front of the furnace, and examined, in order that the *grey slag*, a shining glassy mass, may be picked out and thrown on one side. This grey slag contains a quantity of silicate of lead, with silicate of lime, &c., and requires a higher temperature for the extraction of its lead than is attainable in this furnace; it is therefore smelted in the *slag-hearth*, to be presently noticed.

The browse cleaned from slag is thrown back into the furnace, and its behaviour observed; should it appear to melt too readily, owing to the presence of very fusible silicates, it is rendered less fusible by adding a little lime, lest it should run down to the bottom of the furnace with the metallic lead; on the other hand, if it does not become soft enough to permit the lead to separate, owing to an excess of silica, lime must also be added to soften it.

A peat is now placed before the opening of the blast-pipe, in order to prevent any dust from entering it, and a quantity of roasted ore with a little coal is thrown in. After about twenty minutes, the charge is again raked out on to the work-stone, the grey slag picked out, the remainder thrown back into the furnace, and a fresh charge of roasted ore and coal added.

These operations are repeated during 14 or 15 hours, in which period one or two tons of lead will have collected in the outer basin, according to the richness of the ore, and the proportion (varying from $\frac{1}{10}$ to $\frac{1}{15}$ of the whole) which has been removed in the grey slag. The hearth being lined with solid cast-iron, the English furnace cannot be run for longer than this period, without risk of overheating. In America the back and sides of the hearth above the twyer level are now made of hollow iron blocks cooled with air or water, and the process may therefore be carried on continuously. Below the twyer level the hearth is of cast-iron plates, but the cavity is filled with metallic lead, and as it is not exposed to the action of the blast it is sufficiently protected.

Smelting of Slags, &c., in the Slag-hearth.—In this operation the object is to extract as much of the lead as possible from the slags and other residues, without reference to its purity, by the employment of a very high temperature, so as to completely liquefy the slag. The general construction of the furnace (figs. 84, 85) is not very different from that of the ore-hearth, but it is larger, being 3 ft. high, and 26 in. by 22, internal area. The sides are built of sandstone or fire-brick, in order to resist the much higher temperature of this furnace. The fire is lighted with peats as in the ore-hearth, the blast being forced through a nozzle at the back of the furnace, about 4 in. above the layer of cinders. Some coke is then thrown in, and about six hours after, when the temperature is sufficiently high, it is followed by a charge of the slags, &c., which are to be smelted. Coke and slags are thus added in alternate charges, as in the iron blast-furnace, until the furnace requires repair.

The bottom (A) of the furnace consists of a cast-iron plate, and is covered with a layer, about 16 in. thick, of porous cinders tightly rammed down, which serves as a strainer to separate the lead from the slag, since the melted metal easily percolates through the porous cinders, which protect it from being oxidised again by the air, and runs thence into a receptacle (B) outside the furnace, which is also filled up with similar cinders, and has an opening at the bottom through which the lead flows into an iron pot (E) kept hot over a separate fire. The slag runs off the surface of the layer of cinders, both in the furnace and in the receiving basin, and falls into a tank containing a gently flowing stream of water (C), where it breaks up, so that the lead entangled in it is easily separated by washing.

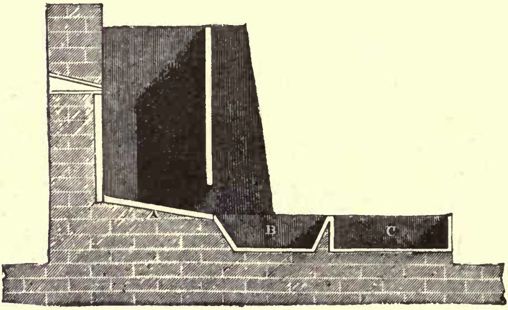

FIG. 84.—Slag hearth for extracting Lead.

The following is an example of a charge:—

100	parts	of slag from the reverberatory furnace;
20	,,	coal-ashes;
13	,,	clay-hearths of old furnaces, impregnated with lead;
5	,,	rich slag from a previous operation.

The silica and alumina present in the clay and in the coal-ashes combine with the lime and oxide of iron in the slag from the reverberatory furnaces, and form an easily fusible slag. The lead is reduced to the metallic state mainly by the action of the heated carbon, which removes the oxygen from the oxide of lead. The coke is piled up towards the front, and the charge towards the back of the furnace, and a *nose* or prolongation of the twyer is allowed to be formed by the solidified slag, so as to carry the blast up the centre of the furnace. When a cold-blast is employed, this nose is apt to become too long, so that air heated to about 150° C. is found to answer better, besides effecting a considerable saving of fuel. If the blast is too hot, the slag will not be chilled so as to form a nose.

A very inferior description of lead (*slag-lead*) is obtained from the slag-hearth.

In some parts of Spain, lead is extracted from the slags of the Roman lead-furnaces.

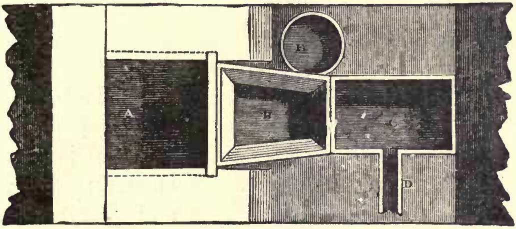

FIG. 85.—Plan of Slag-hearth.

Lead-smelting in Blast-furnaces.—In many parts of the Continent, and in America, as well as in Great Britain, the blast-furnace is now used in the smelting of lead. The furnaces were formerly built of every conceivable cross-section ; but in Europe they are now usually circular, and in America rectangular, of the Rachette type. Originally built entirely of brick, the lead was in some cases allowed to collect in the hearth, and was tapped from time to time as in iron blast-furnace practice ; in other cases the bottom of the furnace sloped downwards to one side, at the lowest point of which was a tap-hole that might be left open, if desired, so that the liquid products of the furnace should constantly flow into a basin placed in front to receive them ; and, lastly, a fore-hearth was sometimes built, communicating beneath with the internal hearth of the furnace, so that the melted lead could be ladled out as it accumulated.

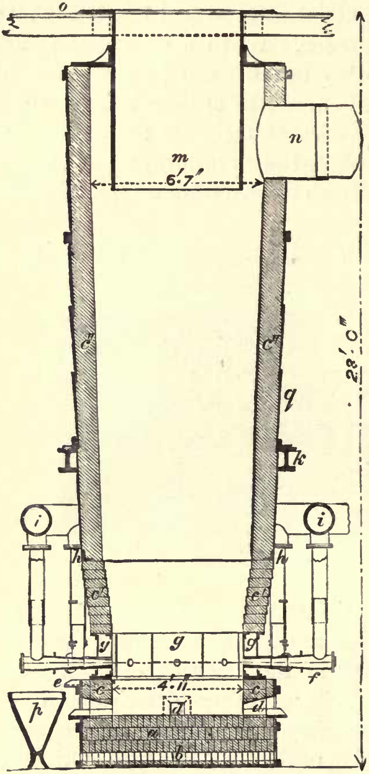

Fig 86.—The Piltz Furnace.

The modern blast-furnace is in many respects similar to that used in copper-smelting, and is commonly applied to the treatment of complex minerals, such as cannot be satisfactorily treated in the reverberatory furnace. In Germany the *Piltz* type of furnace (fig. 86) is commonly erected ; it is circular and very wide, but tapers from a diameter of about 7 ft. at the charging platform to about 5 ft. in the crucible, but is almost without boshes. At one side is the flue, about 20 ft. above the twyer level, and about 4 ft. above this is the charging platform. The throat is open, but is provided with a cast-iron charging tube 5 ft. in diameter, penetrating downwards into the furnace to a point just below the position of the flue, so that the entrance to the latter is an annular space unblocked by ore. Eight twyers are provided, spaced at equal distances around the hearth. There are four tap-holes placed equidistantly at the lowest level of the furnace, and two slag-notches close together immediately below the twyer-ring. The whole furnace is of fire-brick enclosed within an iron casing, excepting a zone of about 20 in. in width at the twyer level, which is water-jacketed to prevent overheating at this, which is the hottest point in the furnace.

The American Rachette furnace (fig. 87) is not quite so high, the charging door being frequently only some 15 ft. above the twyers. The hearth may be from 8 to 10 ft. long by from 2 ft. 6 in. to 4 ft. wide, with five 3-in. twyers on each of the long sides. The whole of the twyer-belt and the boshes is usually water-jacketed (*e*); and the blast-pressure may range from 2 to 3 lb. per square inch. The daily capacity of such a furnace depends upon the quality of ore used, but generally ranges between 30 and 40 tons of ore, with a consumption of about 2½ cwt. of charcoal per ton of ore. In place of the ordinary tap-hole a *siphon-tap*, as it is wrongly termed, is sometimes used. In this case, a channel (*a*) some 3 or 4 in. square is cut in a slanting direction in the solid masonry from the lowest part of the hearth (*b*) to a small basin (*e*) outside, the top of which is almost on a level with the slag notch. As metal begins to accumulate in the hearth, the level of the lead in the outside basin rises; and this level is always slightly higher than that of the liquid in the furnace by reason of the blast pressure within. With the siphon tap there is no need to tap the furnace, necessitating stopping the blast, because the lead is removed from without, a ladleful at a time, as fast as it collects, and the bed of fluid metal constantly within the furnace obviates all risk of forming permanent accretions on the masonry of the hearth, such as are sometimes caused in the older type of furnace by the falling of pasty material when the lead is suddenly withdrawn in large quantities. Mixtures containing as low as 7 or 8 per cent. of lead can be successfully smelted in furnaces fitted with the siphon-tap. The siphon is built as close to the well as possible, and both are enclosed by brickwork about 30 in. thick to minimise the loss of heat. The siphon-tap may not be suitable when the lead produced is so impure that its fusing-point is raised considerably, as for example when much copper is present.

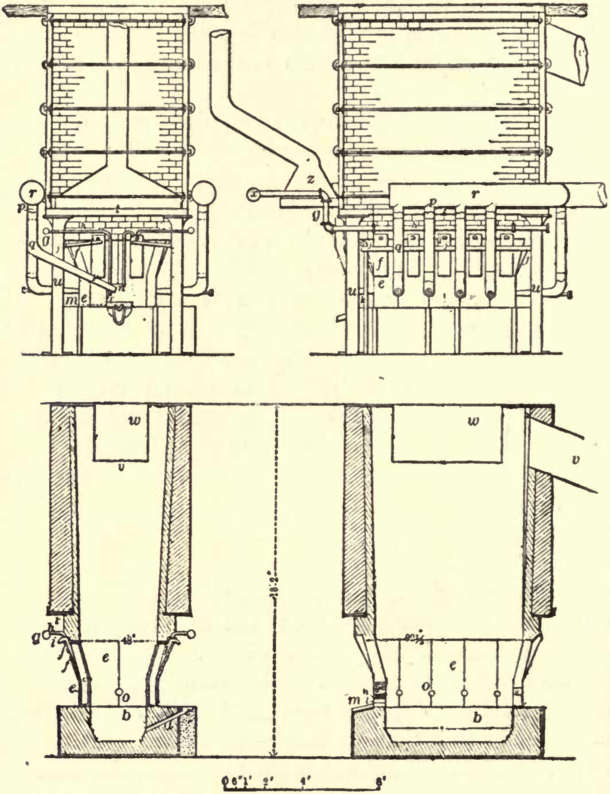

FIG. 87.—Blast-furnace for Lead Smelting.

The ores smelted in the blast-furnace are usually partially roasted if they contain more than 12 to 15 per cent. of sulphur ; this is done in reverberatory furnaces, which are sometimes 50 to 60 ft. long, with a wide hearth and working doors on either side ; the grate is at one end, and the charge is admitted at the other, so that the roasting may commence at the lowest possible temperature. The ore is gradually turned over and worked through the furnace up to the hottest end, fresh material being introduced in its place as it is advanced. In working very poor ores, the temperature at the fire end is intentionally raised so high that the mass fuses, and is drawn off as a slag, which may be charged conveniently into the blast-furnace, without fear of mechanical loss by 'dusting' ; in this case a well is provided close to the fire-bridge of the roasting furnace for the purpose of collecting the fused materials ; or in some American furnaces a separate hearth is provided for the fusion stage. But with better ores, fusion entails a loss of lead and silver, and the material must be only fritted, whilst with rich ores the temperature should be maintained so low throughout that the material is still dry and powdery when it is withdrawn.

When oxides alone are dealt with, carbon is a sufficiently good reducing agent, and the blast-furnace charge consists only of the ore and fuel—usually coke or charcoal—and fluxes. But when sulphur is present, as in raw or imperfectly roasted galena, carbon would not produce the desired effect, and iron is added. Iron ore or rich oxide of iron is generally preferred, as these, under the reducing conditions of the furnace, yield metallic iron, which attacks the sulphide of lead, forming sulphide of iron and metallic lead. The calculation of the charge, which is based on careful analyses of the materials, must be made very carefully, especially in smelting complex ores. When copper is present, it is separated in the form of matte, and to ensure this there must be sufficient sulphur in the charge to combine with all the copper as subsulphide (Cu_2S) and so prevent its reduction to the metallic state. Usually there is an excess of sulphur present, and then iron (or oxide of iron and carbon) must be added in sufficient quantity to combine with it, and carry it into the matte as sulphide; if this were not done a considerable proportion of lead would accompany the copper in the matte. In the presence of arsenic, a further amount of iron is added, in sufficient quantity to form a *speise*, approximating Fe_5As in composition, which is the most fusible of all the possible mixtures of the two elements. Zinc is one of the most troublesome ingredients of a lead ore. Sulphide of zinc considerably reduces the fusibility of matte; it can only be removed by roasting it to oxide and passing it into the slag, the melting-point of which is thereby raised. About 8 per cent. is the most that is permissible in a slag. Even then the amount of fuel required is considerably increased, and accretions are liable to form on the walls of the upper part of the furnace owing to the reduced zinc being volatilised and redeposited as oxide. In the blast furnace sulphide of zinc divides itself about equally between the matte and the slag, and it invariably carries some silver into the slag with it. With any appreciable amount of zinc, an increase in the proportion of copper in the matte is desirable, and great attention must be paid to the condition of the slag.

The four main products obtainable from the lead blast-furnace in addition to the gases are lead, or *base bullion*, matte, speise, and slag. The lead contains the greater proportion of the precious metals, with from 1 to 5 per cent. of metallic impurities which tend to harden it. It is either drawn off constantly by a siphon tap, or is tapped at intervals from the hearth of the furnace, and is then refined to recover the gold and silver and to prepare market lead. The matte contains a little silver, together with iron, copper, zinc, and other metals as sulphides, and still retains some 10 per cent. of lead. It is usually partially roasted in heaps, stalls, or reverberatory furnaces, and is re-smelted with rich lead slags, by which means the lead is reduced, together with the precious metals, and the copper is gradually concentrated in the remaining matte, so that it may be worked ultimately as a copper regulus. The speise contains little lead, but carries most of the nickel and arsenic, with iron and a little silver ; it is sometimes rejected, and sometimes re-melted and mixed with about one-quarter of its weight of melted lead, which dissolves out the precious metals ; after cooling, the resulting base bullion is separated from the purified speise, which may be thrown away, unless it contain sufficient nickel to make it worth treatment for the extraction of that element. The slag, which usually contains about 30 per cent. of silica, and 30 to 40 of oxide of iron, with less than 1 per cent. of lead, may be discarded. The slag, speise, and matte are caused to flow together from the slag-notch into conical slag-pots, in which they are allowed to settle ; they are afterwards separated by hand after cooling at the slag-tip.

In charging the blast-furnace, the fuel is commonly thrown towards the centre, and as in copper-smelting, care must be taken to prevent the formation of crusts or scaffolds which impede the working of the furnace. If these or wall-accretions should form, they are broken down with the aid of a stout iron bar, and if necessary the composition of the charge is altered in order to guard against their recurrence. In this, as in other lead-smelting operations, long flues must be used to collect the dust and fume, which frequently amounts to $\frac{1}{20}$ of the weight of the charge, and would otherwise constitute a very serious loss.

Softening of Lead in the Calcining or Improving Furnace.—The lead obtained by either of the above processes sometimes contains appreciable quantities of silver, antimony, copper, and iron, which harden the metal and render it unsuitable for some of its applications.

When the lead contains any notable proportion of silver, it is treated by a special process to be described hereafter, but when the hardness is due to the presence of antimony, &c., the lead is softened or improved by exposing the melted metal to the action of the oxygen of the air, which converts the antimony, copper, iron, and a considerable portion of the lead, into oxides ; these collect as a dross upon the surface, and are skimmed off at intervals, until the lead is found to be sufficiently softened.

A modern form of improving- or softening-furnace is shown in figs. 88 and 89. The fireplace is at one end, the flame, passing over a hollow air-cooled fire-bridge, traverses the hearth, and the products of combustion escape at the opposite end by an opening in the centre of the roof (fig. 88) communicating with a side-flue shown in fig. 89. The hearth is built as solidly as possible of fire-bricks supported by an external wrought-iron pan, about $\frac{3}{8}$-in. thick, indicated by the thickened line at A. The hearth in this instance is 22 in. deep at the fire end, and slopes downwards so that it is 23 in. deep above the discharge spout. The lead to be softened is charged through the working doors, of which one is shown in half-elevation in fig. 88, and at the end of the operation is run off through the spout at the flue end. In most furnaces the hearth is somewhat trough-shaped in

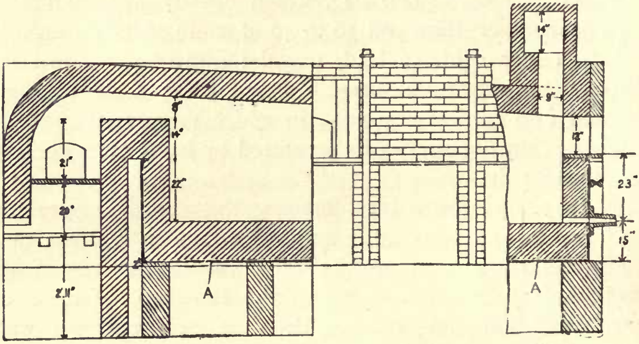

FIG. 88.—Calcining Furnace for softening Hard Lead.

cross section; and the practice of surrounding the upper part of the containing-pan with a water-jacket has recently been adopted in America.

Formerly, the charge of an improving-furnace was only 15 tons; but at present the furnaces are built to treat from 30 to 150 tons at one operation. That shown in the illustrations is a 37-ton furnace. During this process the bulk of the lead liquates out from the less fusible metals, which float to the top in the form of a metallic dross, and mingle with oxides formed through the exposure of the metal bath to the air, and if the operation be conducted sufficiently slowly (that is, at the lowest possible temperature), nearly the whole of the sulphur, copper, nickel, and cobalt, with some arsenic, may thus be separated. It is essential that this dross should be removed as fast as it forms, or the metals will gradually re-dissolve in the molten bath of lead. On raising the temperature of the metal after removing the metallic dross and exposing the bath to the air, the more oxidisable of the fusible metals which cannot be separated by liquation combine with oxygen and form an oxide dross. Tin becomes oxidised first, together with some lead and antimony, and

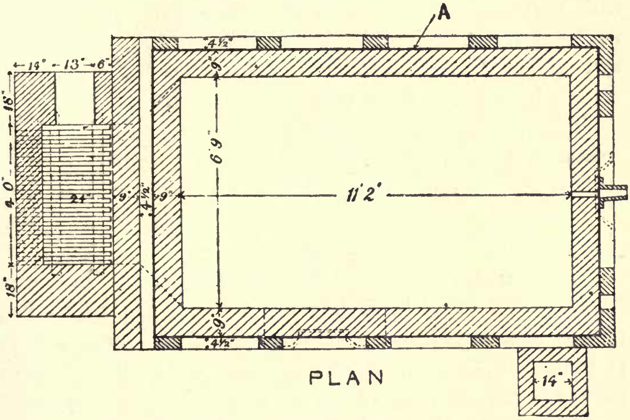

FIG. 89.—Calcining Furnace for softening Hard Lead.

forms the powdery *tin skimmings* which are drawn off; the heating is then continued, with an occasional period of cooling to solidify the crust of oxides, which are then raked off the surface. The remainder of the arsenic and antimony are thus oxidised, a part remaining in the dross, and a part passing into the chimney with the gases. After the space of a few hours, or in the case of a very hard lead it may be of some days, a sample withdrawn and judged by its appearance will show if the lead be sufficiently softened, and if it prove to be so, it is tapped off. The pure metal, if skimmed in the mould before solidifying, should cool with a deep blue film upon the surface, due to oxidation, whilst if it contain much arsenic or antimony, the surface will appear dull greyish white, and, if cooled slowly, will show a bright crystalline spot upon its surface.

The refiner sometimes judges that the lead is sufficiently softened if a rainbow or iridescent film is formed upon the surface when a rake is pushed over it from the working door. The softened lead should not form round globules when poured upon a heated iron plate.

In some works the softening is effected by 'bessemerising,' which consists in blowing air into the metal kept melted in a large iron pot holding about 20 tons. The air is passed in through a tube inserted from above. Some care is required in supporting the pot, which has to be heated from beneath. The softening is a very slow operation, in some cases requiring ten days or more. If it were hastened by raising the temperature, too much lead would be oxidised.

The dross, which consists chiefly of the oxides of antimony and lead, is smelted either in a blast-furnace or in a small reverberatory furnace, the hearth of which gradually slopes down towards the chimney, where there is a cavity for the reception of the metal, which constantly flows out through the tap-hole into an iron pot, to be afterwards transferred to the pig-moulds. The hard lead thus obtained is either again calcined with a fresh portion of metal, or if it contains a very large proportion of antimony (of which some specimens contain a third of their weight), it is sold to the type-founders.

Refining of Lead containing Silver by the Pattinson Process.—This very simple process was introduced in 1829, and not only greatly improved the quality of lead, but very much increased the production of silver. Previous to that date no process existed by which the silver could be removed so as to leave the lead in the metallic state, and it was necessary to convert the whole of the lead into an oxide in order to separate the silver, this oxide being afterwards smelted to recover the lead. Since this could not be made to pay unless the lead contained at least eight to eleven ounces of silver in the ton, any smaller quantity of silver was left in the lead sent into the market, the lead being thereby hardened, and the silver entirely lost for all useful purposes. After the introduction of Pattinson's process, much of the old lead was eagerly bought up for the sake of the silver which it contained.

The process depends upon the formation of the eutectic alloy (p. 124) of lead and silver. If lead containing less silver than is necessary to form this alloy (about 800 oz. of silver to the ton) be cooled slowly from fusion, crystals of comparatively pure lead will separate first, and the silver will tend to concentrate in the remaining liquid, until this has practically the composition of the eutectic alloy ; beyond this all excess of silver would separate with the lead. This is, therefore, the theoretical limit to the Pattinson process, but the practical limit is reached earlier, and it is rarely expedient to pattinsonise lead containing more than about 500 oz. of silver to the ton.

To carry out this principle, a series of melting-pots was originally employed. The number of pots as well as their form and general arrangement varied somewhat in different establishments, but for the sake of illustration, a *desilverising* plant containing five pots may be taken (fig. 90). These pots were made of cast iron and set in masonry; the *working-pots*, 1, 2, 3, and 4, were oval in shape, their mouths being 40 in. by 26 in., and they were shaped at the bottom like the small end of an egg. 5 is the *market-pot* for melting the desilverised lead before casting it into pigs; it was smaller than the others. The smallest pots (about 2 ft. in diameter), between 1 and 2, and between 3 and 4, are the *temper-pots*, containing melted lead to warm the perforated ladle (fig. 91), which was used for fishing out the crystals of lead. This was an iron ladle about 18 in. wide and 5 in. deep, with an iron handle of 4½ ft. and a wooden handle of about 5 ft. in length; the holes in the ladle were ½ in. wide and ¾ in. apart. Each pot was heated by a separate fire.

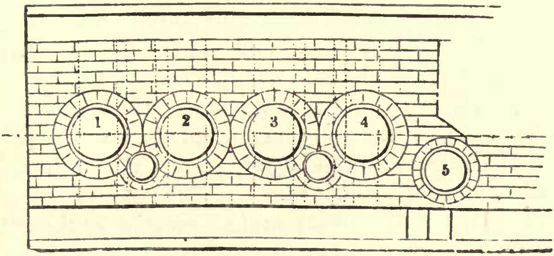

FIG. 90.—Pattinson Pots for desilverising Lead.

The process consisted in melting about 4 tons of the pigs of lead to be refined in pot 1; the fire was then drawn, the metal skimmed, and allowed to cool until crystals began to form, the cooling being often hastened by sprinkling water over the surface, or by adding a little cold lead, and by scraping down the metallic crusts as they formed at the sides. The metal was then well mixed and the ladle was introduced; with the aid of the long handle used as a lever, and with the assistance of the crane, the bowl of the ladle was next raised above the bath and shaken vigorously, the portion still fluid drained back into the pot, and the residual crystals were transferred to pot 2. This process was continued until only about 1 ton was left in pot 1, and this was richer in silver than was the lead originally operated upon. The crystals next withdrawn were thrown upon the ground, as they contained more silver than those first extracted, until only half a ton was left, and this was cast into pigs.

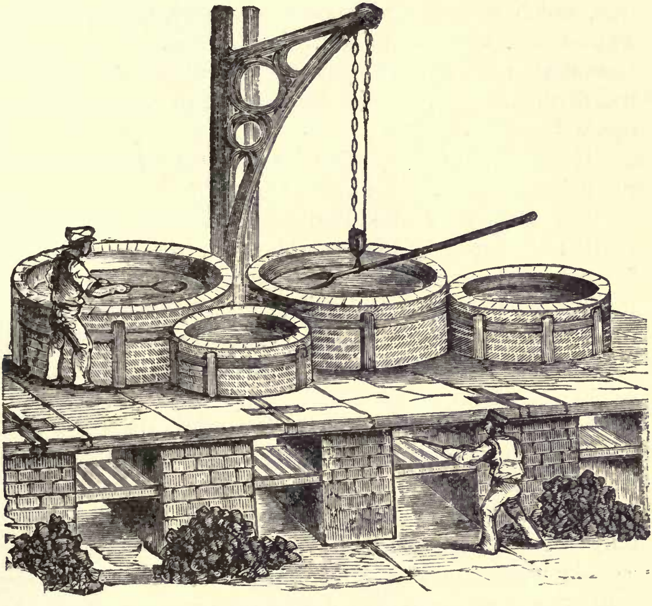

FIG. 91.—Desilverising Lead by the Pattinson Process.

The half ton of crystals on the ground were then re-melted with more lead in pot 1, and were treated in the same way.

The three tons of crystals of lead poor in silver, which were transferred to pot 2, were made up to four tons by adding lead of the same richness in silver, and submitted to a repetition of the same treatment, about three-fourths of it being transferred, in crystals, to pot 3, one-eighth of it, in the form of richer crystals, being thrown upon the ground to be re-melted in pot 2, and the remainder, which was left in the liquid state at the bottom, was ladled out into pot 1.

The crystals in pot 3 were treated in the same way, the portion remaining liquid being transferred to pot 2, and the poorer crystals melted in pot 4. Finally, the crystals of poor lead formed in pot 4 were ladled into pot 5, to be cast into pigs, which were treated again if necessary, until the silver was at last reduced to ½ oz. in the ton. By a single operation in the four pots, as just described, the silver in the marketable lead might be reduced to one-tenth of its original amount.

The process of cupellation for extracting the silver from the rich lead is described under 'Silver.'

The quality of the lead was greatly improved by Pattinson's process, not only because the bulk of the bismuth, antimony, and copper remained with the silver in the liquid portion, but because these and other impurities which tend to harden the lead were converted into dross by the oxygen of the air, precisely as in the improving or calcining process.

The description just given refers to an operation with Pattinson's process, upon the *low system*, as it is termed, in which seven-eighths of the contents of each pan are removed in crystals, whilst according to the *high system* only two-thirds are removed.

The high system was preferred for the treatment of the leads richer in silver and of otherwise impure quality, as many as fifteen pans being sometimes employed, so that there was a greater chance of oxidising the impurities. Both systems were combined in some establishments, in order to suit the different descriptions of lead. In working the high system, it was generally found that the crystals taken out of a given pot contained about half as much silver as the original alloy; thus nine tons of a silver-lead assaying 10 oz. of silver to the ton would yield six tons of crystals with only 5 oz. to the ton, and three tons of liquid alloy containing 20 oz. to the ton.

Where many pans were employed, they were commonly hemispherical, being about 5 ft. wide and $2\frac{1}{2}$ ft. deep.

If the lead contained as much as 60 oz. of silver in the ton, the third pan was selected for melting it, but if it contained only 7 oz. in the ton, it was melted in the 7th pan, an intermediate pan being selected in other cases.

As much as twelve tons of lead were sometimes melted, to begin with, upon the high system, and two-thirds of it were ladled out in crystals into the next left-hand pan—an operation requiring about two hours. The liquid alloy was then chilled into a pasty condition by throwing water upon it, and ladled out into the next right-hand pan, the melting-pot being again charged with twelve tons of the original lead. A supply of lead of the right tenour in silver was then added from stock contained in the works to the pans right and left of the first, and these were then crystallised, and so with the whole series, the crystals being passed always to the left, and the liquid richer in silver to the right. In a series of eleven pans there might thus be metals of the following composition, of which No. 1 would be passed on to the silver refinery for cupellation, and No. 11 would be cast into pigs of *market lead.* In working up fresh stock, the metal would be introduced into the pot of corresponding silver percentage.

No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
448 oz. per ton.	224 oz. per ton.	112 oz. per ton.	56 oz. per ton.	28 oz. per ton.	14 oz. per ton.

No. 7.	No. 8.	No. 9.	No. 10.	No. 11.
7 oz. per ton.	$3\frac{1}{2}$ oz. per ton.	$1\frac{3}{4}$ oz. per ton.	$\frac{7}{8}$ oz. per ton.	$\frac{7}{16}$ oz. per ton.

The Luce-Rozan Process.—A modification of the Pattinson, known as the Luce-Rozan process, in which hand-labour is largely superseded by the use of machinery, has now taken the place of the original cumbrous system wherever the

Pattinson process has survived. In this process the agitation of the metal during crystallisation is effected by means of steam. Two pots only are required, one placed at a higher level than the other; the lower one, which has a capacity of about 36 tons—at least double the upper one—is raised above the floor about 12 in., and each is heated by means of a grate beneath. The lower pot is covered in at the top with doors, and communicates with condensers. A crane is so placed that it can command the two pots and the ingot moulds.

The lead to be desilverised is charged into the top pot by means of the crane; when it has melted, the door is removed, and the lead run into the lower pot among the crystals resulting from a previous operation; the crystals melt; the pot is then drossed, and a jet of steam introduced. The steam is uniformly distributed by means of a baffle-plate placed above the nozzle. To hasten the formation of crystals, small jets of water are at first made to play on the surface of the lead; the cooled portion sinks into the molten mass, and gradually lowers its temperature to the crystallising point, the action taking place uniformly, owing to the mixing effect of the steam-jet. This part of the operation is carried on until two-thirds of the charge have crystallised; the one-third remaining liquid is then drained

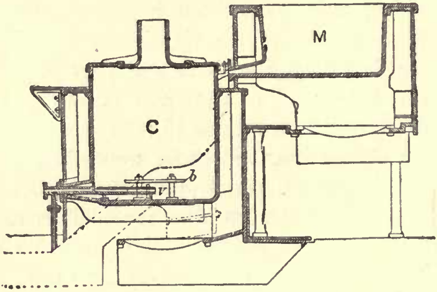

FIG. 92.—Section of the Pots used in the Luce-Rozan Process.

off through two pipes, controlled by valves, the crystals being retained in the pot by means of perforated plates. A 36-ton pot can be worked off in about an hour. After the lead has been tapped out from the working-pot, a fresh charge of lead is run in, having the same richness as the residual crystals from the last operation, and so on. In some works two melting-pots are used side by side, each holding about 7 tons of lead, in conjunction with the crystallising-pot, which has a capacity of about 20 tons. With this arrangement one batch of lead may be melted whilst another is being crystallised, and six charges may be worked off in 24 hours.

By the use of this process subsequent softening of the lead is rendered unnecessary, such impurities as antimony, arsenic, copper, zinc, and iron being removed by the poling action of the steam ; zinc and iron being directly oxidised with liberation of hydrogen. There is admittedly a saving in fuel and labour in this process, and the cost of softening is avoided. These advantages are, however, about counterbalanced by the original outlay for plant and the expenses for repairs.

The Parkes Process.—The Pattinson process has of late years been entirely superseded in many districts by that introduced by Parkes. This process depends on the two following facts :—

1. That lead and zinc, however intimately mixed, do not alloy, and on being slowly cooled almost completely separate from one another into two layers.

2. That silver and gold have a greater tendency to alloy themselves with zinc than with lead. Consequently, if zinc be melted and well stirred in with lead containing silver, on slowly cooling the mixture the zinc will rise to the surface, carrying with it the silver.

The charge of lead to be desilverised may amount to from 15 to 30 tons. If it is very hard, it is usually softened first to remove arsenic and antimony, the presence of which would prolong the process and necessitate the use of a larger proportion of zinc. It may then be run direct from the calcining furnace into the almost hemispherical cast-iron or steel pan in which the zinc is added. This pan, which is about 6 to 9 ft. in diameter, and rather over an inch in thickness, is set over a fireplace, and is heated nearly to the melting-point of zinc (417° C.) before introducing the fluid lead; it may be coated with whitewash first to prevent the alloying of the iron with the added zinc. The lead is then heated to a temperature above 417° C., and the zinc is added, either in the form of cakes which melt in the lead bath, or in the liquid state after fusion in a separate furnace. The molten zinc is then stirred thoroughly into the lead with the aid of large iron paddles, so that it may be forced below the surface of the lead and, floating up through it, may take up the precious metals. The stirring is now usually effected by the injection of a current of dry steam into the bottom of the bath, which ensures the circulation of the liquid. After about half an hour the fire is damped, and the pot is allowed to cool until the zinc begins to solidify, when the crust of crystals is removed with the aid of a flat iron skimmer, the current of steam materially assisting the cooling. The crusts of argentiferous zinc are transferred to a shallow liquation-pot, built beside the other, and over a separate fireplace.

The quantity of zinc added is regulated by the amount of silver contained in the lead; for lead containing about 50 oz. of silver to the ton the zinc required would be about $1\frac{1}{2}$ per cent. of the charge.

The zinc is added in two or more portions, according to the character of the lead, the silver being most easily extracted from the inferior grades. When copper or gold are present, they are for the most part removed in the first zincing; and in treating auriferous lead, the first crusts may be kept separate from the others and worked up by themselves. The lead is finally obtained almost free from silver, but containing about one per cent. of zinc, which must be removed by calcining in a refining or softening furnace. The zinc crusts in the liquating-pot are slowly heated to slightly above the melting-point of lead, when the excess of that metal flows away and is caught in a separate kettle, to be subsequently liquated again. The residual zinc is then broken into fragments, whilst still hot, mixed with a little charcoal, and charged into bottle-shaped refractory retorts, in which it is melted in charges of 5 to 6 cwt., the temperature being then raised to the boiling-point of zinc, to effect which coke equal to 50 per cent. of the metal is required. The zinc vapour which distils over is caught in condensers and is used again, whilst the residue in the retort, containing lead, silver, and gold, is melted and cupelled for the extraction of the precious metals. The zinc crusts are sometimes treated in blast-furnaces, giving a rich base bullion that may be cupelled at once, but the collection of the zinc is always troublesome in blast-furnace practice. In this process the cost of plant and the expenses for labour are small, the lead can be rapidly treated, and only a small working stock is required. There is, however, a considerable loss of zinc amounting to from 40 to 45 per cent.

Uses of Lead.—Many of the uses of lead result from its softness and plasticity, properties which it possesses in a higher degree than any other metal commonly used in the metallic state. Under a pressure of about 33 tons per square inch, lead will behave like a viscous liquid, and may be made to flow through comparatively small apertures. The ease with which it may be rolled into sheets recommends it for lining sinks and cisterns, &c., particularly since it can be easily adapted to any shape with the aid of a mallet. Again, its softness enables it to be made into pipes, either by casting a very thick cylinder round an iron core and drawing it through progressively diminishing steel dies, or by forcing the metal, at the moment of solidification by hydraulic pressure, through a steel cylinder with a core, from which the solidified metal issues with the required form and dimensions. This process is known as *squirting.*

The poisonous nature of the compounds of lead renders it dangerous to use the metal for cisterns and pipes with which water, and especially soft water, is to remain in contact for any considerable period, for although lead itself is not acted upon by water, the oxygen and carbonic acid of the air, some of which are always held in solution by water, readily convert a portion of the lead into carbonate of lead, which dissolves in small quantity ; even if only a very minute proportion of lead be dissolved in the water, repeated doses of it will give rise, in the course of time, to the most painful symptoms. Leaden pipes coated internally with tin, to resist the action of water and air, are made by drawing out two concentric cylinders of lead and tin. The use of lead in connection with cider-vats and presses is highly blameable, for the lead is dissolved in large quantity in contact with the acid liquid, and a moderate draught of such cider may easily contain a poisonous dose of the metal.

The want of tenacity exhibited by lead prevents it from being drawn into thin wire.

The easy fusibility of lead adapts it to the use of the type-founder, but it is far too soft to be employed alone for this purpose, and is therefore hardened by the addition of antimony.

Type-metal may be an alloy of lead with $\frac{1}{3}$ to $\frac{1}{4}$ of its weight of antimony. But commonly, type-metal contains tin and sometimes a little copper in addition, an alloy of 70 parts of lead with 18 of antimony, 10 of tin, and 2 of copper being made by some founders. Other alloys contain zinc.

The high specific gravity as well as the fusibility of lead recommend it for making bullets and small shot, where great momentum is required in a small mass. The Snider rifle-bullet was made of pure lead, in order that it might take the grooves of the rifle ; the metal for the longer and narrower Martini-Henry bullet required, however, to be hardened by the addition of $\frac{1}{12}$ of its weight of tin; whilst for the narrow bore and high velocity used with the new magazine rifle, even this alloy is too soft, and the leaden bullet is enclosed in an envelope of cupro-nickel.

The bullets employed in shrapnel shells are made of an alloy known in the service as *mixed metal*, which is composed of four parts of lead and one part of antimony, partly for the sake of penetration, and partly that they may scatter better, bullets of soft lead being liable either to be jammed together by the force of the explosion, or so distorted as to make a very short flight when the shell bursts.

Small shot for fowling-pieces are composed of lead containing from three to six parts of arsenic in a thousand, which has the effect, not only of hardening the lead slightly, but also of enabling it to take a nearly spherical form when the melted metal is dropped through a colander into water. Another condition for securing spherical shot is the proper cooling of the drops before they fall into the water, for if they are suddenly chilled and solidified externally long before the inner portion solidifies, the shrinking of the latter, as it cools, causes the outer layer to collapse, and the shot becomes deformed.

Probably the effect of arsenic in securing the spherical shape is due to its diminishing the contraction of the still liquid lead as it cools after the outer portion has solidified.

In order to cool the drops before they enter the water, they are commonly allowed to fall through the air from a considerable height, or the same object is sometimes attained by employing a rapid blast of air, when a high fall may be dispensed with. The larger the size of the shot, the more preliminary cooling will they require, so that large shot are allowed to fall through 150 ft., and small shot through 100 ft. In order to prepare the metal, it is usual to alloy a quantity of lead with a large amount of arsenic, and to add this to melted lead in the proper proportion. A ton of soft lead is melted in an iron pot, and 40 lb. of arsenic added to it; the pot is covered with an iron lid, and the joints cemented with clay to prevent the arsenical vapour from escaping; the metal is kept melted for three or four hours, then carefully skimmed, and cast into pigs. The arsenic is added sometimes in the metallic state, sometimes as *white arsenic* (arsenious acid, composed of arsenic and oxygen) or as *orpiment* (sulphide of arsenic), the last two being decomposed by the lead, and converting a portion of that metal into oxide or sulphide. Two or three tons of inferior lead having been melted, five or six pigs of the arsenical lead are added, and well stirred up with it; a small sample is allowed to fall from a height, through a perforated ladle, into water; if the drops become flattened, too much arsenic has been added, if they are pear-shaped, there is too little. The colanders are wrought-iron bowls about 10 in. wide, perforated with smooth holes varying in size with the description of shot required. In order somewhat to delay the passage of the melted lead through the holes, the colanders are lined with the *cream* or scum of oxide which forms upon the surface of the metal. The temperature of the lead when poured into the colanders is scarcely high enough to scorch straw. The drops then fall from the top of the shot-tower into a vessel of water at the bottom. They are afterwards dried on a hot plate, sifted into different sizes, the deformed shot rejected by gently shaking on a slightly inclined table, when only the spherical shot roll down, and these are polished in a revolving cask containing a little plumbago.

Lead is extensively employed in the construction of vessels for various chemical manufactures, since it resists the action of sulphuric, hydrochloric, and hydro-fluoric acids in a far higher degree than iron, copper, zinc, or tin. Even nitric acid, if strong, scarcely attacks lead, though the diluted acid readily dissolves it. The large chambers in which sulphuric acid is manufactured are built of leaden plates weighing 5 or 6 lb. per square foot. Here the fusibility of the metal becomes an advantage, for they have to be united by being *burned together*, that is, by directing a hydrogen flame along the edges of the plates so as to unite them without the intervention of solder, which would soon be corroded by the acid. This is sometimes called *autogenous* soldering.

Notwithstanding that lead is unacted upon in the cold by strong acids, it is very soon extensively corroded when exposed to the action of air in the presence of carbonic acid, and becomes eventually converted into a mass of *white lead* or basic carbonate of lead. Since carbonic acid is produced abundantly by the decay and putrefaction of animal and vegetable matters, metallic lead is much affected when kept in contact with such substances in the presence of air. The lead of old coffins is sometimes found to have become almost entirely converted into an earthy-looking mass of white lead in this way, a very thin plate of lead remaining in the centre. The oldest process for the manufacture of white lead depends upon the corrosion of lead by oxygen and carbonic acid.

In breech-loading cartridges, where grease is employed as a lubricator, the bullets have been known sometimes to become partly converted into white lead, and have thus increased so much in bulk as to burst open the copper case of the cartridge and render it useless.

Alloys of Lead and Tin.—*Pewter*[1] is an alloy of four parts of tin with one part of lead; it is harder, possesses more tenacity, and melts more easily than either of the metals separately, and provided that the lead does not exceed this proportion, the alloy may be used for drinking-vessels without any danger of lead-poisoning. Since, however, lead is far cheaper than tin, a larger proportion than $\frac{1}{5}$ of lead is often employed, when the lead is apt to be

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[1] Probably corrupted from the French; *potée*, pot. *Potée d'étain* is the French for pewter.

dissolved if left in contact with the acetic acid always present in beer. Pewter made with the above proportions has the specific gravity 7·8, so that specimens having a higher specific gravity than this will be known to contain more lead.

The solder employed by the pewterer is a very fusible alloy of tin, lead, and bismuth. The solder used for tin-plate is an alloy of lead and tin. *Common solder* contains equal weights of the two metals; *fine solder* contains two parts of tin and one of lead; *coarse solder*, two parts of lead and one of tin. In making solder, the proportions of the metals can be judged from the appearance of the alloy. When it contains a little more than $\frac{1}{3}$ of its weight of tin, its surface, on cooling, exhibits circular spots due to a partial separation of the metals; but these disappear when the alloy contains $\frac{2}{3}$ of its weight of tin. These alloys melt at a much lower temperature than either of their constituent metals. Common solder melts at about 240° C., and fine solder at 180° C., whilst the melting-point of tin is 232° C., and that of lead is 327° C.

Soldering is scarcely to be regarded as a merely mechanical adhesion, but depends probably, in part, upon the formation of an alloy between the solder and the surface of the metal to be soldered. Hence it is absolutely necessary that the surfaces to be united by the intervention of solder should be perfectly bright and free from oxide. Several substances are employed to ensure this at the moment of applying the solder; one of the commonest is muriatic (hydrochloric) acid *killed* with zinc, that is, in which a lump of zinc has been dissolved to form a chloride of zinc which melts over the surface of the work, dissolving any oxide, and protecting the metal from the oxidising action of the air. Sal-ammoniac or sal-ammoniac and chloride of zinc are sometimes used. Resin in powder is often sprinkled over the metal to be soldered, when the heat melts it and forms a varnish to protect its surface from the oxygen of the air.

SILVER

The Ores of Silver.—This metal, being, in general, a far less chemically active metal than the preceding—that is, being less likely to enter into and remain in a state of chemical combination with other substances—is much more frequently met with in the metallic or native state.

Native silver is usually crystalline, but often has the appearance of metallic twigs and branches, which are sometimes composed of crystals of silver attached to one another. The silver-mines of Potosi exhibit such specimens. Native silver commonly occurs with other ores of silver; it frequently accompanies the native copper of the Lake Superior district, and it has also been found in comparatively large quantities at Kongsberg, in Norway, in the Hartz, in Saxony, in Hungary, in Mexico, and in various parts of the United States.

The native metal generally contains small quantities of gold and copper. At Kongsberg a yellow alloy is found which contains silver with more than $\frac{1}{5}$ of its weight of gold. An amalgam of silver with mercury is found in large quantity in the silver-mines of Coquimbo, Chili.

Argentite, *Sulphide of Silver*, or *Silver-glance* (Ag_2S), containing, in its pure state, 87 parts of silver combined with 13 of sulphur, is one of the commonest forms of combination in which silver occurs in nature. It has been found, in a pure state, in Cornwall, Norway, Hungary, Saxony, Bohemia, Mexico, Peru, and the United States. It has a slight lustre, and a dark grey colour, possessing also, which is remarkable in an ore of this description, a good deal of malleability and flexibility, and it is so soft that it may be cut with a knife. It is also distinguished by its fusibility, being easily melted even in an ordinary flame. Sulphide of silver is more abundant in association with the sulphides of other metals ; thus, in argentiferous galena, with sulphide of lead ; in grey copper ore, with the sulphides of copper, antimony, arsenic, iron, and zinc. Blende, iron pyrites, mispickel, and some other minerals sometimes contain a small proportion of silver, which may be extracted with profit, incidentally to other processes.

Pyrargyrite, *Ruby Silver*, or *Dark-red Silver ore* ($3Ag_2S. Sb_2S_3$) is a deep red ore, sometimes almost black, which is a sulphantimonide of silver, found in Saxony, Hungary, and in other silver districts, and abundantly in California and Mexico. When pure, it contains nearly 60 per cent. of silver. In a similar ore of lighter red colour, called *Proustite*, arsenic takes the place of antimony ($3Ag_2S.As_2S_3$). It is therefore a sulpharsenide of silver. It is found associated with pyrargyrite, and contains, when pure, 65·5 per cent. of silver.

Stephanite, or *Brittle Silver ore* ($5Ag_2S.Sb_2S_3$) is a richer antimonial ore, containing 68·5 per cent. of silver in the pure state. It is iron-black in colour, and is sometimes known as *black silver*.

Horn-silver, or *Chloride of silver* ($AgCl$) contains, when pure, 75 parts of silver united with 25 parts of chlorine. Good specimens of this ore exhibit, as its name implies, some resemblance to horn in appearance and softness. It is found abundantly in Chili, Peru, and Mexico, and in many parts of the United States and the Continent of Europe, sometimes in large fragments, but more commonly in very small cubical crystals disseminated in a ferruginous rock.

The *butter-milk ore* of the German miners contains chloride of silver mixed with a large proportion of clay.

Chloride of silver has been found, in small quantity, in Cornwall. *Bromide* and *iodide of silver* are also found in Mexico and Chili.

In consequence of the high price of silver, it admits of being extracted with profit even from ores which contain a very small proportion of the metal, especially if some other useful metal can be extracted at the same time. In many instances, therefore, the metallurgy of silver is intimately associated with that of other substances ; and ores of the most complex description are now worked by processes specially designed for the extraction of the precious metals as well as the commoner metals they may contain. Thus, to take a very simple case, silver may be profitably obtained from galena containing only two parts of silver in a thousand, and even a smaller quantity than this is extracted from some copper ores. In these cases, the lead and copper respectively are extracted by the ordinary smelting processes, and are then subjected to special treatment for the extraction of the silver. It may be well to describe the principal methods in use for this purpose before considering the metallurgic treatment of the ores of silver with the sole object of extracting that metal.

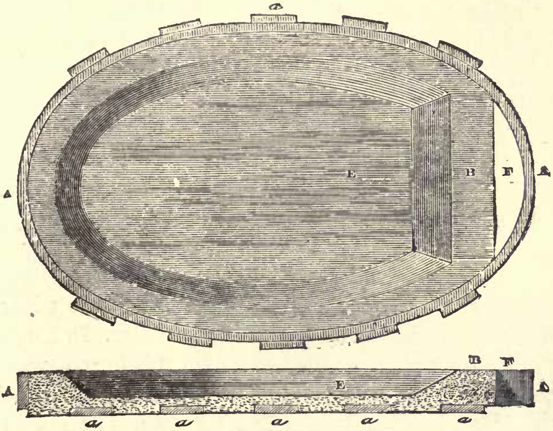

FIG. 93.—English Cupel or Test.

Extraction of Silver from Lead by Cupellation.—Most of the silver produced in this country is extracted by this process from the rich lead obtained in the Pattinson or Parkes concentration process (pp. 409, 415).

The process of cupellation derives its name either from the German *kuppel*, a *cupola* or *dome*, in allusion to the shape of the German cupellation furnace, or from a diminutive derived from the Latin *cupa*, a cup, referring to the concave hearth upon which the process is carried out.

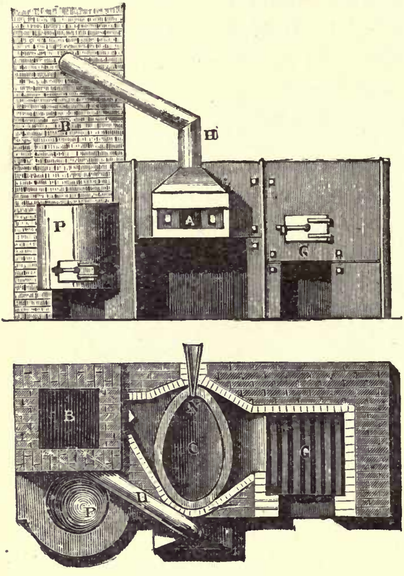

FIG. 94.—English Furnace for the cupellation of Lead.

The extraction of silver from lead by cupellation depends upon the facility with which the latter metal is converted into an oxide by the action of air at a high temperature, whilst silver is almost entirely unaffected ; the oxide of lead, being easily melted, is partly removed from the surface in a liquid state, and partly absorbed by the porous hearth upon which the silver remains. In England, this hearth, which is called the *cupel* or *test*, is an oval or rectangular frame of wrought iron (A, fig. 93), 4 ft. long and 2½ ft. wide, which is crossed by iron bars (*a*) 3¾ in. in breadth. This frame was formerly filled with finely powdered bone-ashes moistened with water, in which a little pearl-ash (carbonate of potash) had been dissolved ; this was well consolidated by beating, and scooped out until it was about ¾ in. thick over the cross bars, leaving a flat rim of bone-ash all round, about 2 in. wide, except at one end (B), the front or *breast* of the cupel, where it was 5 in. wide; through this a channel (F) was cut, to allow the melted oxide of lead to flow off without coming in contact with the iron, which it would corrode very seriously. The test is now made in many places of a mixture of clay with about twice its volume (more or less, according to the character of the clay) of limestone, or with some similar mixture, cheaper than bone-ash. The cupel rests upon a car, in order that it may be wheeled into its place under the reverberatory furnace (fig. 94), of which it forms the hearth (C), where it is arranged so that the flame of a coal fire (G) passes directly across it to the two flues, which run into a chimney (B), about 40 ft. high. A blast pipe or twyer (N) enters the cupel at the end opposite to that through which the oxide of lead escapes, and projects a blast of air over the surface of the metal at the rate of about 200 cb. ft. per minute. Opposite to the twyer is a hood with a pipe (H) for carrying the fumes into the chimney. The cupel is dried thoroughly and is then very gradually heated nearly to redness, and almost filled with the lead to be treated, which is either charged upon the test in solid pigs, or is ladled in from an iron pot (P), in which it has been previously melted. From 500 to 600 lb. of lead, or more according to the size of the furnace, are introduced at once. In a short time, the surface of the metal becomes covered with oxide of lead, and when the temperature has reached about 950° C., this oxide, or *litharge*,[1] will become fused; the blast is then turned on, and drives the litharge in wavelets off the surface, through the channel made for its escape, into a cast-iron pot outside the furnace. When this channel is very much corroded, it is closed, and another is cut. In proportion as the lead upon the hearth diminishes, fresh portions are introduced so as to keep the lead at about the same level. The process is continued for sixteen or eighteen hours, in which time four or five tons of lead will have been added,

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[1] From two Greek words, signifying *stone* and *silver*.

and an alloy containing about eight per cent. of silver will be left in the cupel. A hole is then made in the bottom, through which the metal is run out and cast into pigs. A fresh charge is introduced into the cupel, and the operation continued; one bone-ash cupel should last 7 to 10 days, and is capable of treating 5 cwt. of lead per hour, with a consumption of 1 cwt. of coal. The lime-clay test has a much longer life, especially if a water-jacketed rim be substituted for the plain iron. When about 3 tons of the rich alloy (containing 8 per cent. of silver) have been obtained, it is again subjected to cupellation in the same furnace, but in a cupel which has a concavity at the bottom intended for the reception of the cake of silver, which will weigh about 500 lb. This second operation is necessary, because the litharge which is formed from this very rich alloy contains a considerable proportion of silver, so that the lead obtained by smelting it (p. 429) and by smelting the cupel, which absorbs a large proportion of litharge, contains 30 or 40 oz. of silver in the ton, and must be treated for that metal.

The appearance of the metal in the cupel, as the last portions of lead are removed in the form of litharge and absorbed into the bone-ash, is very beautiful. When the film of oxide becomes so thin that the bright silver beneath can reflect the light through it, a decomposition of the light into its constituent colours takes place, and the most brilliant rainbow tints are seen upon the metal, their beauty being enhanced by the rapid rotation of the film. As soon as this film of oxide has been absorbed by the cupel, the splendid surface of the melted silver shines out—termed *brightening.*

During the cooling of the cake of silver, some very remarkable phenomena are observed. When a thin crust of metal has formed upon the surface, the silver beneath it assumes the appearance of boiling, and the crust is forced up into hollow cones about an inch high, through which the melted silver is thrown out with explosive violence, some of it being splashed against the arch of the furnace, and some solidifying into most fantastic tree-like forms several inches in height. This behaviour of silver has been shown to be due to its property, at a temperature above its melting-point, of absorbing mechanically (*occluding*) oxygen, which it gives off as it approaches the point of solidification, the escaping gas forcing up the crust of solid silver formed upon the surface.

A considerable proportion of lead and silver is carried off by the blast, in the form of vapour, and is partially recovered, as silver-bearing lead-oxide, from the flues of the furnace.

In America, the lead is frequently treated on the first test, until it contains about 60 per cent. of silver, and the final purification is then effected on a separate hearth, a few shovelfuls of nitre being sometimes added towards the extreme end of the operation to expedite the refining by the oxygen evolved.

The litharge produced in the English cupellation furnace is reduced to the metallic state in a reverberatory furnace with a hearth measuring 8 ft. by 7 ft., which is lined with bituminous coal; this soon becomes converted into a porous coke, which protects the clay hearth of the furnace from being corroded by the melted litharge, and forms a filter through which the lead runs towards the opening from which it is tapped. About 3 tons of litharge mixed with 6 cwt. of small coal are charged at once; the carbon of the coal removes the oxygen from the oxide of lead composing the litharge, and reduces the lead to the metallic state. The lead thus obtained usually contains 30 to 40 oz. of silver in a ton, and is treated by either the Parkes or the Pattinson process.

The *German cupellation-furnace* (figs. 95, 96) differs from the English in having a fixed instead of a movable hearth (A), covered with an iron dome (C) lined with clay, which is capable of being lifted off by a crane (G). The hearth is usually circular, but sometimes rectangular, about

10 ft. wide, and is lined with marl, or with an intimate mixture of clay and lime well beaten and hollowed out like

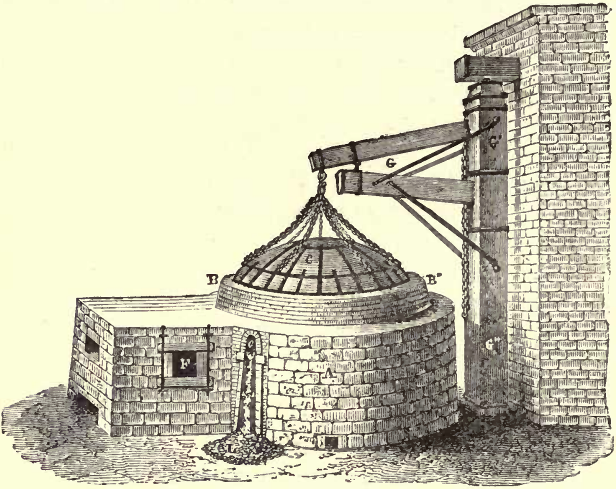

FIG. 95.—German Cupellation-furnace.

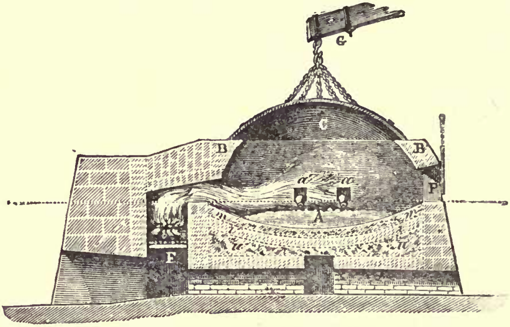

FIG. 96.—Section of German Cupellation-furnace.

a saucer, with a circular cavity about 20 in. wide and ½ in. deep, in the middle, for collecting the cake of silver. Two or more twyers (*a*) direct the blast across the hearth, and are provided with butterfly-valves for guiding the blast over the surface of the metal. The fire-place (F) is supplied, when practicable, with wood, which gives a longer and clearer flame than coal.

From 4 to 25 tons of lead can be cupelled at once, according to the size of the hearth, the pigs being placed upon a thin layer of straw. The heat is gradually raised so as to melt the lead, no blast being employed for the first three hours. When the metal is in a state of tranquil fusion, the surface is skimmed to remove the dross, and a very gentle blast is turned on, in order to renew the air over the surface, so as to promote oxidation. In about two hours, a stronger fire is applied, and the crust of oxide and of various mechanical impurities is skimmed off the surface through the opening (*o*) provided for the escape of the litharge. About an hour and a half is occupied in thoroughly cleansing the surface of the lead.

The blast is now freely directed upon the melted metal, so as to produce litharge abundantly, and to drive it in waves through the outlet (*o*), which is deepened by the workman in proportion as the level of the lead falls. The litharge flows out on to the floor of the shop as at L. After continuing the process for a period varying between seven hours and sixty hours according to the amount of lead, the removal of the lead is complete so far as it can be effected in this furnace, and the phenomena described at p. 428 as indicating the termination, are witnessed. A wooden spout is then introduced into the charging-door, through which water is carefully poured upon the surface of the silver to solidify it into a cake, which undergoes a subsequent refining to complete its purification.

The first portions of oxide which form upon the surface in this process contain, beside the oxide of lead, oxides of antimony, and iron and other impurities, and yield, when reduced, a very impure lead, fit only for making shot or type-metal. The last portions of litharge, amounting to about $\frac{1}{20}$ of the whole, are set aside to be reduced separately, when they furnish a lead rich in silver. When bismuth is present in the lead, the last portions of litharge have a green colour. A certain quantity of the intermediate portion of litharge (containing less than half an ounce of silver in the ton) is sent into the market as such, being useful to the manufacturers of glass and earthenware, of sugar of lead, &c. In the market, it finds a readier sale when in reddish-brown scales or flakes, which are produced by running it out, when melted, into large iron vessels, and allowing it to cool in a draught of air. When these vessels are inverted, the mass of litharge is easily turned out and broken into a flaky powder. Impure litharge cannot be converted into red litharge, so that the colour is evidence of its purity.

The cupel, which is largely impregnated with litharge and contains some silver, is broken up, that portion which is saturated with litharge is smelted in order to extract those metals, and the remainder is crushed and used over again for the making of hearths.

At Andreasberg and Freiberg, silver ores have been melted with the lead (already containing some silver) upon the cupel itself, when any sulphide of silver which they contain is decomposed, its sulphur combining with oxygen to form sulphurous acid, and the silver being dissolved by the lead.

The silver obtained by cupellation is liable to contain small quantities of lead, bismuth, antimony, copper, and gold, the first three of which render it brittle. It is therefore generally subjected to a refining process, which consists in exposing it in a melted state to the action of the air, when the foreign metals, with the exception of the gold, are oxidised and absorbed by the test. The operation is performed either in an ordinary cupellation furnace, or in another constructed upon the same principle.

Roessler, in 1889, introduced a process of refining in large plumbago vessels resembling crucibles, and containing about 6 cwt. of metal. The silver being melted, the top is covered with a pure sand; and a small quantity of sulphate of silver is introduced and stirred in; the lead which was alloyed with the silver to be refined exchanges places with the silver of the sulphate; lead is therefore removed from, and an equivalent amount of silver is added to, the charge. When the whole of the sulphate of silver is thus decomposed, the slag is withdrawn in a pasty state, and another smaller quantity of sulphate is added, and the operation is repeated until the silver is completely refined. After the whole of the lead has passed into the slag, bismuth becomes removed in the same way; the slags from successive treatments are therefore collected separately, in order that the bismuth may be kept apart from lead, and be recovered economically. The slags, too, are not completely freed from silver, and require therefore to be smelted subsequently.

Electrolytic Refining of Silver.—Many processes have been proposed for the electrolytic refining of the silver from the cupellation hearth, but the only one to which reference need be made here is that of Moebius. In the earlier form of apparatus, which has been used in many works in America and Germany, the crude silver to be refined is cast into anode-plates about $\frac{1}{4}$ in. thick, and these plates are enclosed within muslin or linen bags and suspended in a very dilute solution of silver nitrate or nitric acid. They are supported by hooks from metallic rods resting across the top of the vat, and are thus electrically connected to the positive pole of a dynamo, whilst the negative pole is connected to thin cathode-sheets of fine silver hung opposite to the anodes in the solution, but insulated from them. As soon as the current is started, silver, copper, and some other metals begin to be dissolved from the anodes at a rate proportionate to the strength of the current; in this way the solution tends to become richer, but at the same time an equivalent quantity of metallic silver is deposited on the pure silver cathodes. Gold being insoluble remains as a powder upon the surface of the anodes, and as it accumulates becomes detached and is caught in the anode-bags. A strong current is used in order that the action may be rapid, because silver is a costly metal, and it is desirable that the period during which it is being treated should be as short as possible. But the result of this is that the silver is deposited in the state of a fine powder, and the crystals that form tend to grow until they make a metallic connection between the anode and the cathode. To prevent this, wooden scrapers are caused to move backwards and forwards over the cathode-plates, and a tray is placed at the bottom of the vat to receive the crystals that are brushed off. As the action proceeds, more and more copper passes from the anode into the solution, and although silver is much more easily deposited by the current than copper, there would in course of time be danger of the latter metal being deposited to a small extent, thus defeating the object of the process. The copper gradually accumulates in the solution, and bears an increasing ratio to the silver present, because the latter is being deposited at the cathode at a greater rate than it is being dissolved at the anode, owing to the fact that other metals besides silver are undergoing solution, whilst only silver is precipitated. To prevent the deposition of copper, a little more nitric acid is added to the solution as the electrolysis proceeds, whilst the strength of current is somewhat reduced. The tray containing the silver is removed from time to time, and the powdery crystals of metal are melted together in crucibles after washing and drying. The copper solution at the end of the operation is treated by precipitation methods to recover the silver and the copper that it contains ; and the gold from the anode-bags is filtered, washed, dried, and melted. The whole operation should last about two days. In 1895 Moebius introduced a modified form of apparatus in which the cathode is an endless band of sheet-silver travelling horizontally through the bath. A belt, which moves obliquely through the vat, and comes into contact with the silver-band at one end, serves to convey the deposited silver out of the solution, where it is detached by fixed scrapers and transferred to a receptacle beneath. The principle of the process is identical with that of the earlier method of working.

Extraction of Silver from the Ores of Copper.—The ores of copper containing silver were formerly smelted at Mansfeld, by extracting the copper in the form of *black copper*, from which the silver was removed by the process of *eliquation*, which consisted in alloying it with from two to four times its weight of lead, and casting it into round cakes, 18 in. in diameter, and 3 in. thick, and then melting out the lead by a moderate heat, when it carried all the silver with it, to be afterwards extracted by cupellation. The copper was left in a skeleton form, and still retained a little lead. It was therefore re-melted in an oxidising atmosphere, which caused the separation of most of the lead as litharge. The liquation was effected in the hearth, shown in fig. 97.

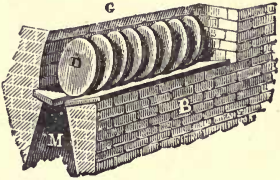

FIG. 97.—Liquation-hearth.

Extraction of Silver from the Ore by Melting with Lead.—At Kongsberg in Norway, where the ore contains its silver in the metallic state, it is extracted by simply melting the dressed ore with its own weight of lead, when an alloy containing about one-third of its weight of silver is obtained, which is submitted to the process of cupellation. When ores containing sulphide of silver are melted with lead, this metal removes the sulphur in the form of sulphide of lead, and the liberated silver is dissolved by another portion of lead.

Amalgamation Process for the Extraction of Silver from its Ores.—The process of amalgamation is so called because the silver is extracted in the form of an *amalgam* with mercury, and there are two modes of carrying it out, the choice being regulated by the cost of fuel in the locality. Thus, the amalgamation process employed in Mexico and Chili, where fuel is dear, is very different from that in use in places where it is relatively cheap.

Mexican Process of Amalgamation.—In Mexico and Chili, where the silver ores obtained from the western slopes of the Cordilleras are treated, the thorough pounding of the ores and of the materials added to them, by the comparatively inexpensive agency of water-power, or mules, is employed to facilitate the chemical changes which would be promoted by the action of fire, if fuel were more abundant. Time is also an important element in this process, which consists essentially in converting the whole of the silver into chloride of silver, to be afterwards brought to the metallic state by the action of mercury, and dissolved by the latter, in the form of an amalgam.

The ore sometimes contains only 35 oz. of silver in the ton, partly in the metallic state, and partly as chloride and sulphide of silver, and is carefully picked over in order that the worthless portions may be rejected. It is then crushed with crude, iron-shod, wooden stamps weighing about 200 lb. each. The crushed ore is ground with water into a mud, under granite stones, which are made to revolve on a granite bed by the labour of mules. This mud is transferred to the *amalgamation-floor*, or *Patio*, an enclosure about 300 ft. by 240 ft., paved with stone. It is there mixed, with wooden shovels, with a proportion of common salt, varying from one to five parts for every hundred parts of ore, and, in order to effect a thorough intermixture, a number of mules are made to trample the mud in the enclosure, after which it is left at rest for some hours.

On the following morning, the mules are again turned into the amalgamation-floor for an hour, after which, copper pyrites which has been roasted to the form of sulphate and ground to powder (when it is called *magistral*) is added in the proportion of $\frac{1}{50}$ or $\frac{1}{100}$ of the weight of the ore. The mud is then once more trampled for five or six hours by mules.

The mixture is now ready for the amalgamation with mercury, which is sprinkled upon it from a bag of coarse canvas, in quantity about twice that of the silver present in the ore. It is then trodden again by mules, and well turned with wooden shovels, these operations being repeated every other day until, on washing a small sample in a bowl, it is found that all the mercury which has been added is in combination with the silver, as an amalgam, no globules of mercury being visible.

The following appear to be the principal reactions upon which this process depends: The copper sulphate of the magistral acts upon the sodium chloride (common salt), forming cupric chloride and sodium sulphate; the sulphide of silver reacts with the cupric chloride, and yields chloride of silver, which is attacked by mercury, forming chloride of mercury and metallic silver, and the latter amalgamates with the excess of mercury. A certain amount of cuprous chloride is also formed, which reacts with sulphide of silver, as in the case of cupric chloride. This secondary reaction takes place at the moment double decomposition is occurring between the cupric chloride and the sulphide of silver; it is brought about by the copper of the chloride concerned in the reaction reducing to a lower chloride a further quantity of cupric chloride, in preference to combining with the sulphur of the sulphide of silver, so that, in the result, chloride of silver, cuprous chloride, and free sulphur are produced. This secondary reaction can, however, only take place to a limited extent.

The examination of the amalgam shows whether too much sulphate of copper (in the form of *magistral*) has been added. If this be the case, a quantity of the mercury will be found to be so finely divided as to form a dark-coloured mud, and occasional brown spots of metallic copper will be visible. A great loss of mercury would ensue if the magistral had been added in excess, because the chloride of copper formed from it would be decomposed by the mercury, yielding a chloride of mercury (calomel) and subchloride of copper.

If it be found that this error has been committed, a little lime is added to the contents of the amalgamation-floor to decompose the chloride of copper (forming chloride of calcium and oxide of copper) and prevent any further waste of mercury.

It sometimes occurs, on washing the sample, that globules of mercury are perceived, showing that it has not entirely united with the silver. This is due to an insufficient supply of magistral, in consequence of which the amount of chloride of copper formed has not been sufficient to convert the whole of the silver into chloride of silver, a form in which it is much more readily acted upon by the mercury than when it is in the state of sulphide of silver, because the chloride of silver is capable of being dissolved by the strong solution of common salt existing in the mud, and is thus presented to the mercury in the condition most favourable to chemical action. If necessary, a further addition of the roasted copper pyrites is made before proceeding with the amalgamation.

After about a fortnight, a fresh quantity of mercury is added (rather less than one-third of the first addition) and the operation of trampling is repeated. When this mercury has also been taken up, a third portion, about half as large again as the second, is added, in order to dissolve the amalgam of silver in an excess of mercury. After a thorough incorporation by trampling, the mixture is at once shovelled into barrows and taken to the washing-vat, which is a circular cistern 8 ft. wide and 9 ft. deep, in which the mud from the amalgamating-floor is well stirred up with water, by an agitator worked by four mules, fresh water constantly running into the cistern, and carrying off the earthy matter over the side.

The liquid amalgam left behind is thrown into a leather bag with a canvas bottom, through which the excess of mercury is strained off, leaving a pasty amalgam containing about $\frac{1}{5}$ or $\frac{1}{6}$ of its weight of silver, which is subjected to pressure in order to squeeze out more mercury and convert it into a hard solid mass. This is moulded into wedge-shaped masses of about 30 lb. each, which are built up into a circular tower on a copper stand having a hole in its centre through which a pipe passes in order to conduct the mercurial vapours into a tank of water placed beneath. The pile of amalgam is covered with an iron bell, the opening of which fits tightly upon the copper stand, any crevices being carefully filled up with a cement. A temporary furnace is built with bricks around the bell, and kept full of burning charcoal for about twenty hours, when all the mercury is converted into vapour, which condenses in the water beneath, and the silver is left as a hard mass; this is broken up, melted, and cast into bars weighing about 1000 oz. each.

The period occupied by the amalgamation process varies greatly according to the nature of the ores, extending sometimes over little more than a fortnight, and sometimes requiring six or eight weeks.

The loss of mercury in the process is very considerable, being due, in great part, to the *flouring* or fine division of the metal, which is then carried away in the process of washing, together with all the silver which has been dissolved in it.

The *hot amalgamation*, applied for extracting the silver from rich ores which contain it either in the metallic state or as chloride, bromide, or iodide, only occupies five or six hours, and entails less loss of mercury. It consists in boiling the finely powdered ore with water, common salt (10 to 15 parts for a hundred of ore), and mercury, in pans with copper bottoms, when the chloride, bromide, and iodide of silver are decomposed by the copper, forming a chloride, bromide, or iodide of copper, and liberating the silver, which is dissolved by the mercury.

The extraction of silver (and of gold) by amalgamation is very much facilitated by adding a minute proportion of *sodium* to the mercury employed, for it is found that mercury so treated attacks and dissolves silver and gold much more readily than pure mercury, and that it is very much less liable to assume that finely divided state in which it is so readily washed away and lost.

Silver ores containing complex sulphides, galena, blende, &c., cannot be successfully treated by the ordinary patio process : only a small portion of the silver being extracted. Such ores have been satisfactorily dealt with in Chili, by a process invented by Krölinke. He employs cuprous chloride, prepared by heating a solution of sulphate of copper and common salt with metallic copper. The amalgamation is effected with zinc and mercury, in closed barrels, in the same way as the Freiberg amalgamation process presently to be described. The process is complete in a few hours.

Amalgamation in Pans.—Another process, which has been introduced to deal with *Free-milling*[1] ores in Nevada, Colorado, California, &c., is known as the *Washoe* process.

In this process, the ore is crushed by stamps, and the mixture of ore and water is allowed to flow into a series of settling tanks, in which the solid portion subsides. When a sufficient quantity has been collected, the stream is diverted into a second series of tanks, and, the water being run off from the first, the mud is dug out and transferred to amalgamating pans. The pan (fig. 98) is a circular iron box about 4 ft. in diameter and 2 ft. high, the working bottom of which consists of a cast-iron plate, that may be easily re-

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[1] *Free-milling* is a term applied to ores which yield their gold or silver satisfactorily by amalgamation without previous roasting.

placed when worn, with a central cone projecting upwards above the level of the charge in the pan. Usually this bottom plate is made in radial sections, each of which is known as a *die*. Passing through the central cone is a shaft, rotated by means of gearing beneath the pan, and carrying an iron ring, termed a *muller*, which exactly covers the die on the bottom. Beneath the muller are fixed a number of removable blocks or *shoes*, and by suitable lever or screw mechanism the height of the muller and shoes above the die may be adjusted with accuracy. The shoes may thus be caused to revolve at the rate of 60 to 80 revolutions in a minute, and may either grind the ore between them and the dies under the weight of the muller, or they may be lifted clear of the dies, so that they rotate without any grinding action. The paste of ore and water which is placed in the pan in quantities ranging from 10 cwt. to 2 tons, according to the size and capacity of the apparatus, finds its way through central apertures in the support of the muller, into the space between the shoes and the dies; then, as the muller is rotated, the pulp tends to pass outwards towards the side of the pan, and is assisted in this movement by the shape given to the shoes, and by slots in the dies. Emerging from the outer edge of the muller, the ore is impelled upwards by the fresh ore that is following it. But as the mass is pasty, it tends to partake of the rotation of the muller, and the resulting motion is utilised by attaching curved wing-plates to the sides of the pan, which intercept the ore particles and direct them to the centre, where they again find themselves drawn downwards and passed between the grinding surfaces. After this manner a constant circulation of the ore is maintained. There are many modifications of the amalgamator, but the principle is the same in all. The Wheeler and the Patton pans are among the best-known types, and the construction of the latter is shown in fig. 98.

In all of them arrangements are made for heating the ore under treatment, either by means of a separate steam chamber beneath, or by the direct admission of steam into the pan itself.

In use, the fine ore is introduced together with a sufficient quantity of water, and, the muller being raised at first until it runs free of the bottom, the rotation is commenced; it is continued for a couple of hours, the muller being gradually lowered, so that the ore is at last thoroughly crushed to a fine pulp. A little copper sulphate and common salt are sometimes added during the grinding stage, with the object of facilitating subsequent amalgamation. When the ore has been reduced to the right degree of fineness, the muller is raised somewhat, and from 60 to 100 lb. of

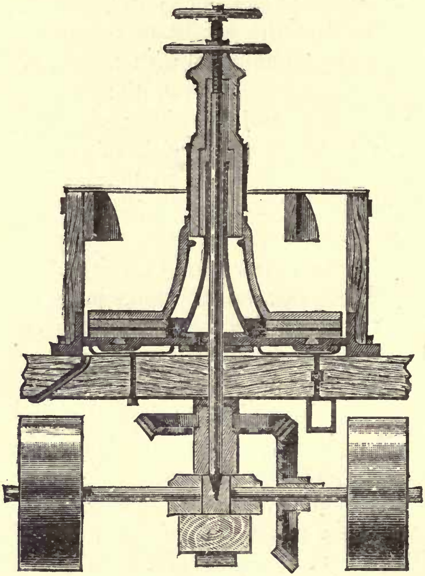


FIG 98.—The Patton Amalgamation-Pan.

mercury are sprinkled over the contents of the pan, and the rotation is continued for two or three hours with the muller raised. The intimate contact of mercury with every particle of ore is aimed at, in order that all the silver or gold may be completely extracted. To ensure this the consistency of the pulp must be carefully attended to. If too much water be present, the mercury will sink freely to the bottom and will not mix properly ; if too little, the mercury will be split up into such fine globules that some of it may be mechanically lost, afterwards, as *floured* mercury ; but if the proportion be correct, the quicksilver will be well distributed through the mass of ore in globules of moderate size, which will readily re-unite under favourable circumstances. The silver which existed as sulphide or chloride in the ore will have been set free by means of the iron of the pan (by exchange), and will thus readily dissolve in the mercury. Owing to the corrosive action of the ore upon iron, the sides of the amalgamator are often made of wood, so that only the readily interchangeable parts may be attacked.

Amalgamation being complete, a plug at the bottom of one side of the pan is opened, and, with the aid of a stream of water, the contents are run out into a somewhat similar but larger pan, known as a *settler*. The settlers are usually about 8 ft. in diameter ; they have no muller and no dies, but are provided with four radial arms carrying wooden shoes, which just touch the bottom and revolve slowly, at about 15 revolutions per minute. The thinning of the pulp by the water used in flushing out the amalgamator enables the amalgam and excess mercury to sink by reason of their high specific gravity, when the mixture is gently agitated to favour the free motion of the particles in the water. By adjusting the proportion of water to the rate of rotation adopted, the mercury may be allowed to sink, whilst even the coarsest particles of sand are kept in gentle motion. When the separation is complete, the contents of the settler are run off through a series of holes placed in vertical lines in the sides of the settler, the top aperture being opened first. In this way the lightest particles are removed first, and last of all the heaviest, the mercury with its dissolved silver being left on the bottom, to be drawn off through a plug-hole at the lowest level. Any particles of mercury or of heavy ore which have escaped separation in the settler, may be caught by passing the tailings from the latter through an *agitator*, which is a wooden vessel even larger than a settler, containing slowly revolving arms, so that only the heaviest particles are permitted to settle, and these are removed from time to time as they accumulate. The last traces of heavy stuff may be recovered by passing the material, suspended in water, over a series of blankets, which retain the heavier particles

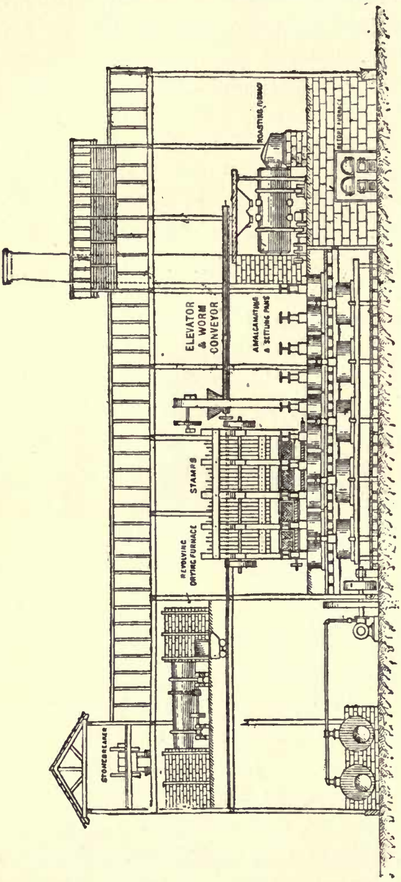


Fig. 99.—General View of a Silver-Mill.

only, or by some form of concentrating and dressing machinery. Fig. 99 illustrates the plan of a silver-mill, showing the crushing and roasting plant, with the amalgamator and settler.

The amalgam is separated from the excess of mercury by straining it through a long conical canvas bag, the residual solid amalgam being distilled or 'retorted,' and the silver fused. Occasionally the mercury from several amalgamators is collected in one settler, and is used a second time before recovering the silver. When the amalgam is very dirty and contains fragments of pyrites and the like, it is often crushed in a small amalgamator or *clean-up-pan*, and is then 'flooded' by throwing it into a large volume of mercury, so that the amalgam sinks, and the impurities float to the top, from which they are skimmed off, and re-amalgamated. The amalgam is then separated and retorted. The process is conducted rapidly in order to minimise the solution of amalgam in the large bulk of mercury used.

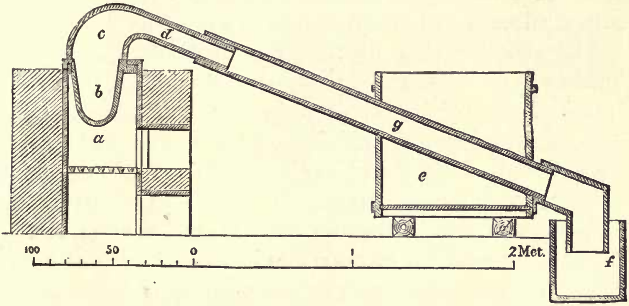


FIG. 100.—Apparatus for distillation of the Amalgam of Silver.

The distillation of the mercury from the amalgam is effected in a retort, shown in fig. 100. The same type of retort is also used for a similar purpose in gold-mills. It consists of an iron crucible (*b*, fig. 100), 22 in. wide and 11 in. deep, which is heated by a charcoal fire (*a*), the vapour of mercury being conducted by an iron hood (*c*) into an iron condensing tube (*g*) which traverses a cistern of water (*e*). The inside of the crucible is painted with lime, and an iron plate washed over with lime is fitted into the crucible, and withdrawn with the silver adhering to it at the close of the operation. 4 cwt. of amalgam are distilled in five hours. The latest form of retort is, however, bottle-shaped, and is placed horizontally in a furnace, the neck end protruding through one side wall, where it is connected with a condenser, whilst the other end, corresponding to the bottom of the bottle, is closed with a removable iron plate, through which the amalgam is introduced on iron trays, and the residual silver is withdrawn (see fig. 109, p. 498).

The alloy left after distilling the amalgam is melted in plumbago crucibles, and briskly stirred with an iron rod. Fumes of the oxides of bismuth, zinc, and antimony are given off, and a scum containing oxides of lead and copper forms upon the surface, and is skimmed off. When no more dross appears upon the surface, the metal is cast into ingots.

Amalgamation in Barrels for Extraction of Silver.— When refractory silver ores have to be treated, such as those which contain much arsenic or antimony, it is necessary to roast them with salt prior to amalgamation. This may be done in any of the furnaces described on pp. 133–144, but the Stetefeldt furnace is especially suitable for this work. The chloridised ore may then be treated by the barrel process or in pans. The former process, originally employed in Freiberg, is still in use in a few places, and is less wasteful of mercury than is the Patio process, because in it the mercury is used only as a dissolving agent, and not as a chemical precipitant. The Freiberg process resembles the Washoe process, in that the loss of mercury is purely mechanical, and not chemical.

In the Saxon process, as in the Mexican, the whole of the silver is converted into chloride of silver, from which the chlorine is removed by the action of metallic iron, and the silver, which has thus been reduced to the metallic state, is dissolved by mercury.

The ore treated at Freiberg contains the silver chiefly as a sulphide, but it also contains the sulphides of several other metals, particularly of antimony, bismuth, arsenic, iron, copper, lead, and zinc. The different kinds of ore are sorted and mixed, so that the mixture may contain less than one part of copper and five parts of lead per hundred, for both these substances are easily taken up by the mercury, causing undue consumption of that metal. The silver present in the mixed ores should amount to about 80 oz. in the ton. The presence of a large proportion of iron pyrites is necessary for the subsequent chemical changes, so that the mixture is made to contain about one-third of its weight of that mineral. The ore, crushed to a coarse powder, receives a chloridising roast (see p. 132) by heating it with one-tenth of its weight of common salt, whereby the silver, copper, and iron are converted into chlorides.

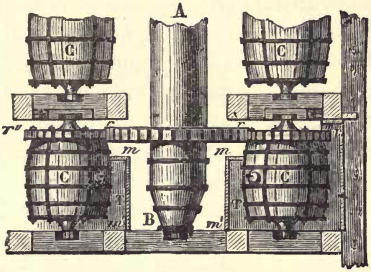


Fig. 101.—Amalgamation of Silver Ores at Freiberg. *r r''*, Gearing for transmitting motion from the shaft A B. *m m'*, Troughs for receiving the contents of the casks C.

The deep brown roasted ore, containing the sulphate of silver, is now sifted, and the lumps, mixed with more salt, are roasted again in order to complete the change.

The sifted powder is ground to a very fine meal, and introduced in charges of half a ton into twenty strong oaken casks (fig. 101), measuring about 3 ft. each way, and containing 3 cwt. of water. The casks are mounted on gudgeons, and can be rotated by means of toothed gearing. The charge is introduced through an opening, which is afterwards closed with a wooden plug having a small hole in it, through which the argentiferous mercury can be run off on the completion of the process, whilst at other times it is stopped by a peg. About 1 cwt. of wrought iron, in fragments, is put into each of the casks, which are then rotated at the rate of ten or twelve revolutions in a minute. The iron removes the chlorine from the chloride of silver, producing chloride of iron and metallic silver, which remains dispersed through the mixture in a finely divided condition. The iron also decomposes the chloride of copper in a similar manner, yielding finely divided metallic copper.

After having revolved for about two hours, the casks are opened for the purpose of introducing the mercury to dissolve the silver ; but before adding this, the contents must be brought to a proper consistence, as in the Washoe process, by adding either water or more of the prepared ore as required. 5 cwt. of mercury are then poured into each of the casks, and they are made to revolve, about twenty-five times in a minute, for sixteen or eighteen hours, during which time the mercury dissolves the metallic silver and copper. The casks are twice examined in order to see if the contents have a proper consistence. The chemical action which takes place in the casks raises the temperature, even in winter, to about 40° C.

In a more modern arrangement, the casks are fixed in a vertical position, the materials being mixed by a revolving agitator with iron arms, and steam is admitted into the casks through holes at the bottom, in order to facilitate the amalgamation by its heat.

At this stage the amalgam of silver and copper is found interspersed in minute globules throughout the mass ; in order to collect it, the casks are filled with water, and revolved eight times in a minute, during about two hours. The pegs stopping the small openings having been withdrawn, and a tube with a stopcock inserted, the barrels are turned with the plugs downwards, so that the amalgam may run out into a trough beneath. The mixture in the casks is subsequently emptied out through a grating which retains the pieces of iron, whilst the mud is collected in tubs, where it is stirred with water and allowed to deposit the small quantity of amalgam which it may contain. The mud is afterwards allowed to settle down, so that it may be again treated by the amalgamation process, when it yields a further quantity of about 4½ oz. of silver to the ton.

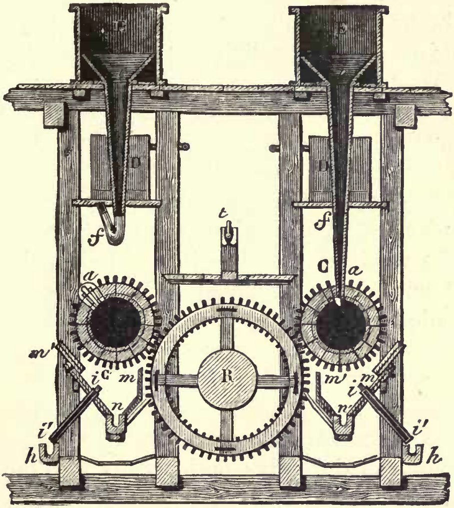


FIG. 102.—Amalgamation of Silver Ores at Freiberg. E, Reservoirs for the ground mineral. *f*, Leathern pipe for conveying it into the opening *a* of the cask C. D, Cisterns containing water. *m n m'*, Receptacles for the amalgam and spent charge. *i i'*, Pipe for conveying the amalgam into the gutter *h*.

The liquid amalgam of silver and copper is strained through canvas bags, as in the Mexican process, when a quantity of liquid mercury runs off (containing about 20 oz. of silver to the ton), leaving in the bags a pasty amalgam containing about 30 parts of mercury, 4 parts of silver, and 1 part of copper, with small quantities of other metals which existed in the ore, particularly lead, bismuth, zinc, antimony, and gold. The amalgam is sometimes allowed to settle in a narrow wooden cylinder, 8 ft. high, before being strained in the bags, when it separates into two layers, the lower consisting chiefly of mercury, which need not be strained.

The pressure is sometimes applied to the amalgam by a screw, and sometimes by a hydraulic press; in the latter case the amalgam is placed in an iron cylinder with a wooden bottom through which the liquid mercury is pressed out. The amalgam is finally retorted and the silver refined as in the Washoe process.

Wet Processes for Extracting Silver—Augustin Process. Several methods have been proposed from time to time to avoid the use of mercury in extracting silver from its ores. For example, after roasting the ores, first by themselves, and afterwards in admixture with common salt, to convert the whole of the silver into chloride, the latter is dissolved out with a saturated solution of common salt, and the chloride of silver in the solution is decomposed by leaving it in contact with scraps of copper, when the latter combines with the chlorine, forming chloride of copper, and the silver is separated in a finely divided metallic state, to be afterwards melted and cast into ingots. It has been recommended to mix chlorine-water with the solution of common salt employed in this process, in order to extract the gold at the same time.

This process has been employed with satisfactory results, at Freiberg, for the extraction of silver from the matte containing two-thirds of its weight of copper obtained in the copper-smelting process. The matte, having been roasted by itself, and afterwards with common salt, is stamped to powder, sifted, and placed, in quantities of about 6 cwt., in tubs with perforated false bottoms, over which a linen strainer is stretched. A hot strong solution of salt being let in from a reservoir, dissolves the chloride of silver and carries it through the strainer into tubs also provided with a strainer, and containing some spongy copper (cement copper, see p. 335), which is gradually dissolved, as chloride of copper, whilst metallic silver is deposited in its stead; this is removed from the tubs, washed first with hydrochloric acid to remove particles of copper and then with water, and moulded into small balls, which are dried and fused.

The liquid containing the chloride of copper and common salt is conveyed, usually by gravity, into another series of tubs containing copper, placed at a lower level, in order to ensure the complete removal of the silver, and afterwards into vessels placed below them, and containing iron, which causes the separation of the metallic copper, to be used over again for precipitating the silver.

The matte, having been treated with the solution of salt, until a copper plate dipped into the liquor is no longer whitened owing to the deposition of silver, is washed with water, and taken to the copper smelting-furnace.

Ziervogel Process.—A still simpler process consists in roasting the ore or matte containing the sulphides of copper, iron, and silver, so that they may be converted into sulphates, which are then heated sufficiently strongly to decompose the sulphate of iron and much of the sulphate of copper, leaving these metals as insoluble oxides, whilst the sulphate of silver is left undecomposed, and may be dissolved out by water and metallic copper, precipitated by sulphate of copper.

The Ziervogel process has been attended with very satisfactory results in its application to the extraction of silver from the copper mattes at Mansfeld, containing, in 100 parts, 80 parts of sulphide of copper, 11 parts of sulphide of iron, and $\frac{2}{5}$ part of sulphide of silver. The loss of silver experienced in treating this matte by the amalgamation process amounted to nearly $\frac{1}{10}$ of the metal present, by the Augustin process to nearly $\frac{1}{12}$, and by the Ziervogel process to only $\frac{1}{120}$. This process is not well suited to the treatment of ores containing arsenic, antimony, lead, or zinc.

The matte, having been granulated, ground, and sifted, is roasted with great care and judgment, in reverberatory furnaces, seven of which are connected with a single chimney 150 ft. high. The roasting occupies about ten hours, and is continued until a small sample taken out and mixed with water gives a liquor which produces a strong precipitate of chloride of silver on the addition of common salt (chloride of sodium), and has a light blue colour, from a little sulphate of copper having been left undecomposed.

The roasted matte is then introduced, in quantities of 5 cwt., into tubs similar to those used in the Augustin process (p. 450), and treated with hot water containing a little sulphuric acid, until the liquor which runs off becomes no longer milky when mixed with common salt, showing it to be free from silver. The solution of sulphate of silver, thus obtained, is run into tubs containing copper, where the silver is precipitated, and is afterwards washed with diluted sulphuric acid to remove adhering copper.

The sulphate of copper in solution is decomposed by metallic iron, and the copper is employed for precipitating the silver.

Von Patera Process.—This process, as carried out at Joachimstal, was applicable only to rich ores, and consisted in roasting them with common salt, as at Freiberg, in order to convert the silver into chloride of silver, which was then dissolved out by a cold dilute solution of *thiosulphate* (*hyposulphite*) *of soda*, which takes up chloride of silver much more readily than common salt does. The solution is then mixed with a solution of *sulphide of sodium*, which produces a black precipitate of sulphide of silver, and leaves the solution of thiosulphate ready to be employed for treating a fresh portion of ore. The sulphide of silver is collected on a canvas strainer, washed, dried, roasted to burn off part of the sulphur, and melted in plumbago crucibles with metallic iron, which takes up the rest of the sulphur, in the form of sulphide of iron, and leaves metallic silver. The sulphide of iron dissolves a part of the silver, and is worked up with a fresh charge of ore.

Russell Process.—In the Von Patera process, any lead sulphate that is present dissolves in the thiosulphate solution, and is precipitated with the silver in the form of sulphide. For this and other reasons this process was never largely used, but Russell's modification of it has made rapid headway, and is now extensively employed. The ore is treated with thiosulphate solution in the usual way, and crude sodium carbonate (soda ash) is subsequently added to the liquid portion : this has the effect of forming lead, iron, zinc, and manganese carbonates if those metals be present. These carbonates, being insoluble, settle to the bottom of the liquid, and may be separated from it, the copper and silver remaining dissolved. The precipitation of the latter with sulphide of sodium then proceeds in the usual way. Russell has also found that silver and its sulphide, sulpharsenide and sulphantimonide, are attacked and dissolved in a mixed solution of the thiosulphates of sodium and copper (cuprous thiosulphate), whereas sodium thiosulphate only dissolves chloride of silver. By leaching with this special solution, called the 'extra solution,' after the ordinary thiosulphate treatment, any residual silver is extracted. Even raw ore might be so treated in some instances, or ore which has only undergone an oxidising roasting. The precipitate produced by the sulphide of sodium may be collected in a filter press, and, after washing, may be treated with a mixture of sulphuric acid and sodium nitrate, which dissolves it, and the silver is recovered from the solution by the action of metallic copper, as in the Augustin process. Most of the sulphur from the sulphide is also separated, and may be used to prepare fresh sulphide of sodium.

The copper matte of Freiberg is sometimes roasted to convert the sulphide of copper into oxide, and is then boiled in lead-lined tubs with diluted sulphuric acid, which dissolves the oxide of copper in the form of sulphate of copper ; this salt is obtained in marketable crystals from the solution. The residue, which contains the silver and gold, is washed, mixed with half its weight of litharge, and made into balls, which are dried and smelted with more litharge and lead-slags. The lead obtained contains all the silver and gold, and may be cupelled.

Very poor ores have sometimes been treated by melting them, either in cupolas or reverberatory furnaces, with iron pyrites, which takes up the silver. By smelting the matte obtained with galena, the silver is obtained with the lead.

A considerable quantity of silver is now recovered by Claudet's process, from Spanish pyrites, after it has been calcined for its sulphur, in the manufacture of sulphuric acid. This process is described under COPPER.

Applications of Silver.—Pure silver is far too soft to resist the wear to which it is subjected in common use. It is therefore hardened by alloying it with copper, a considerable quantity of which may be added without materially altering the colour of the silver. The hardest alloy is that which contains 4 parts of silver and 1 part of copper. The standard silver used for coin and for silver articles in England contains, in 100 parts, 92½ parts of silver and 7½ parts of copper ; the continental silver coinage usually contains 90 parts of silver and 10 parts of copper.

In English commerce, the purity or fineness of silver is generally expressed as so many pennyweights (dwt.) better or worse than the standard silver, of which the troy pound contains 11 oz. 2 dwt. of pure silver and 18 dwt. of copper (commonly called *alloy*). Thus a French coin, which contains 24 dwt. of copper in the troy pound, would be described as worse 6 dwt., because it contains that quantity less silver per pound than the English coin. Mexican dollars contain 23½ dwt. of copper in the troy pound, being worse 5½ dwt.

The specific gravity of English silver coin is 10·3, and since all the alloys used to make counterfeits have tin for their chief constituent, they have usually a lower specific gravity, so that the best method by which to test whether a florin, for example, is good, without injuring it, is to ascertain its specific gravity, by weighing it first in the ordinary way, and afterwards when suspended in water, and dividing its weight in air by the loss of weight in water, when the quotient, for a genuine coin, would be 10·3. Of course, if the coin be new, it will be sufficient to ascertain that it weighs just as much as a good florin, and is of exactly the same diameter and thickness, which are readily measured by cutting in a piece of cardboard a slit through which a new florin will exactly pass.

Standard silver is whitened by being heated until the oxygen of the air has converted a little of the copper at the surface into oxide of copper, which is dissolved off by immersing the metal in weak vitriol (diluted sulphuric acid) or in ammonia, or by boiling it in a solution of cream of tartar and common salt. The film of nearly pure silver which then remains at the surface lacks lustre and is called *dead* or *frosted silver.* It is brightened by burnishing.

Oxidised silver, as it is erroneously called, is made by immersing articles of silver in a solution obtained by boiling sulphur with potash, when the metal becomes coated with a thin film of sulphide of silver.

The tarnish which is produced upon the surface of silver when exposed to air is also due to the formation of a coating of sulphide of silver by the action of sulphuretted hydrogen; the sulphide of silver is itself black, but a thin film of it upon the surface of the metal often exhibits the rainbow colours caused by the decomposition of the light reflected through it. Tarnished silver is most readily cleaned with a solution of cyanide of potassium, but this salt is so fatally poisonous that its general use should be discouraged.

Ammonia (hartshorn) will also remove the film of sulphide of silver if assisted by friction.

Plated articles were made of an alloy of copper and brass coated with silver. The brass having been melted with the requisite proportion of copper in a black-lead crucible, was cast into bars 3 in. broad, 1½ in. thick, and 18 or 20 in. long. The two faces of the bar were carefully smoothed with a file, and a plate of silver $\frac{1}{25}$ in. thick, and somewhat shorter than the bar, was laid upon each face and tied with iron wire. A little saturated solution of borax was allowed to run in round the edges, in order that this salt might melt and dissolve the oxide off the surface of the brass when heated in the furnace. The bar was then laid upon a coke fire and heated until the surfaces of brass and silver firmly adhered, when the compound bar was ready for the rolling-mill. This part of the process is known as *sweating*. After rolling, it was cleaned with diluted sulphuric acid. Sometimes the clean copper surface was washed over with solution of nitrate of silver before applying the plate of silver. A thin film of silver would then be chemically deposited upon the surface of the copper, and would both prevent oxidation and favour the adhesion of the silver plate.

The *plated wire* used for making toast-racks, &c., may be made of copper coated with silver. The strip of silver is bent round into the form of a hollow cylinder, its edges somewhat overlapping; a red-hot cylinder of copper is thrust into this, and the edges of the silver are joined together by rubbing with a steel burnisher. The copper core is then withdrawn, the tube of silver thoroughly cleaned inside, and slipped upon a bright copper rod so as to fit closely, leaving the ends of the copper somewhat projecting. Grooves are made in these ends, into which the silver is forced down, so as to exclude the air from the copper surface inside. The cylinder is made red hot and well rubbed with a steel burnisher, until the silver thoroughly adheres to the copper, and the compound bar is then drawn into wire.

Electro-plating is now very generally employed for coating articles of baser metal with silver. This art consists in decomposing a solution containing silver, with the aid of a galvanic battery, in such a manner that the metal may be deposited upon the surface of the article to be plated; German silver (p. 384) is generally employed as the material for the latter, the articles being then said to be *electro-plated on white metal.* They must be thoroughly cleansed by scouring with sand, if necessary, then by boiling them with soda to remove grease, washing with water, and dipping into very weak *aquafortis* (dilute nitric acid) to take off the film of oxide: they are finally rinsed in water.

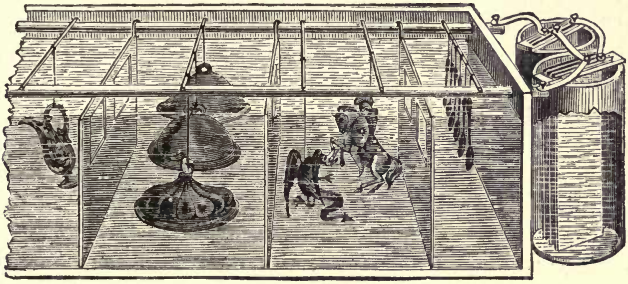


FIG. 103.—Process of Electro-plating.

The articles to be electro-plated are suspended by stout copper wires (fig. 103) in a vessel of wood or earthenware containing a solution of cyanide of silver in cyanide of potassium, of which every gallon contains an ounce of silver. The suspending wires are connected by stout copper wires with the negative pole of a dynamo-electric machine, or with the last zinc plate of a galvanic battery consisting of alternate plates of zinc and copper immersed in diluted sulphuric acid; the positive pole of the dynamo or the last copper plate of this battery is connected with a series of silver plates suspended in the silvering liquid opposite to the articles to be coated. The galvanic current transmitted from the battery causes the decomposition of the cyanide of silver in the solution, the silver being deposited upon the articles to be plated, and the cyanogen, which was combined with the silver in the liquid, unites with the silver upon the plates of that metal and forms a fresh quantity of the cyanide of silver equal to that which has been decomposed ; this dissolves in the liquid and should always maintain it at the same strength. The articles are weighed before and after plating, in order to ascertain the amount of silver which has been deposited upon them.

In order to secure the perfect adhesion of the film of silver, the objects to be plated are sometimes dipped into a solution of nitrate of mercury until they are covered with a thin coating of that metal, before they are immersed in the silvering bath. They are then *struck* by placing them in the silvering liquid and connecting them with the zinc of a strong battery for a short time, after which they are brushed with fine sand to show whether the coating is perfect, and the process of silvering is then proceeded with.

To preserve the silvering solution of uniform strength, the articles to be plated are generally kept in motion by attaching the connecting rods to a frame furnished with wheels which travel along a rail on the edge of a vat, the whole frame being moved by steam-power.

The deposit of silver is without lustre and requires burnishing. It is dried by immersing the article in boiling distilled water, and allowing it to dry by its own heat when removed. When a lustrous deposit is required, one gallon of the silvering liquid is mixed with 6 oz. of *bisulphide of carbon* (CS_2) and set aside for twenty-four hours. Two ounces of this solution are added to twenty gallons of the silvering liquid, and left for twelve hours before use. The action of the bisulphide of carbon in causing a lustrous deposit has not yet received a satisfactory explanation.

Silvering for Ornamental Purposes.—Where a very thin film of silver only is required, as for articles not subjected to much wear, advantage may be taken of the great malleability of this metal, in which it is surpassed only by gold, to beat it out into exceedingly thin leaves, which are applied to the surface to be silvered. The silver leaf is manufactured in the same manner as gold leaf, to which the reader may refer. It is applied to non-metallic objects with some adhesive liquid, such as gum or size. In covering metallic objects with silver leaf, they are heated to remove grease, and plunged into weak aquafortis to dissolve off the oxide. The surface is next scoured with wet pumice-stone, warmed, and again dipped in weak aquafortis, to roughen it, so that the silver leaf may more readily cling to it. If necessary, the surface is further roughened by hatching with a graving tool. The metal is next carefully heated till a thin film of oxide causes it to assume a bluish tint; the leaves of silver are then applied in successive layers, and well fixed by burnishing, the object being heated again before every application of the silver.

The process of *dry silvering* upon copper and brass, which is now seldom if ever practised, consisted in applying to the clean surface an amalgam of silver from which the mercury is afterwards expelled by heat. A pasty amalgam was made by dissolving silver in about six times its weight of mercury. The amalgam was applied with a brush made of brass wire dipped into a solution of nitrate of mercury, which, being decomposed by the copper and zinc of the brass, deposited a coating of mercury upon the brush, to which the silver-amalgam then readily adhered. The article was afterwards moderately heated to expel the mercury as vapour, when a dead film of silver was left upon the surface, which was afterwards burnished.

For silvering flat surfaces, such as the scales of barometers, chloride of silver has been employed. To prepare this, a piece of standard silver may be dissolved in *aquafortis* (diluted nitric acid) in a glass or earthen vessel, with the aid of heat. If any dark powder remain undissolved, it consists of finely divided gold, which is often found in old silver. The solution, which contains nitrate of silver and nitrate of copper, is mixed with hydrochloric acid, or with just sufficient common salt dissolved in water. The chloride of sodium decomposes the nitrate of silver, forming nitrate of sodium, and chloride of silver, which separates as a white curdy *precipitate*. The liquid is well stirred, the chloride of silver allowed to settle down, the liquid poured off and replaced by fresh water; after this has been repeated several times, the washed chloride of silver is dried in an oven, and finely powdered. 1 pt. of the powder is mixed with 3 pts. of pearlash, 1 pt. of chalk, and 1½ pt. of salt. The surface of the copper or brass to be silvered is rubbed with a wet cork or leather dipped in this mixture, when the metal decomposes the chloride of silver, forming chloride of copper (and, in the case of brass, chloride of zinc), and metallic silver is deposited.

A mixture of the chloride of silver with 10 pts. of cream of tartar is said to answer the same purpose.

Silvering on glass is effected by precipitating silver from a solution, in contact with the glass, by certain chemical agents, and, being a purely chemical process, will not be considered here. Looking-glasses are silvered with an amalgam of tin (see *Mercury*).

GOLD

Distribution in Nature.—There is no positive evidence that gold exists in Nature in any other than the metallic state, though it is believed by some to exist as a sulphide in some varieties of pyrites. Gold is always alloyed with small though very variable quantities of silver. Mercury, copper, bismuth, palladium, rhodium, and iron are also occasionally combined with it. In certain localities, notably in Transylvania, Colorado, and California, gold forms in some cases definite compounds with tellurium which are difficult to treat.

Gold not infrequently occurs in quartz veins as minute octahedra connected together into branch-like forms, and as filaments, thin plates, nuggets, grains, and dust. In alluvial formations, which are sometimes several hundred feet in depth, it is usually in the last two named conditions, whilst in pyritous deposits it is not uncommonly in a microscopically fine state of division. In many ores, gold, though present, is invisible to the eye. There are few regions in which this metal cannot be discovered, though in the great majority of cases its quantity is too small to pay for the labour of separating it from the other matters with which it is associated.

In England, small quantities of gold are found in the Cornish alluvial deposits which furnish the stream tin ore. In Wales, it has been found near Dolgelly. Ireland has furnished gold from Wicklow, where it is found scantily distributed through sands in the form of gold-dust, and very rarely in small rounded fragments or *nuggets*. In Scotland, the precious metal has been traced in Perthshire, and in Sutherlandshire.

On the continent of Europe, the gold mines of Hungary and Transylvania are the most important. At Königsberg, the metallic gold is disseminated through sulphide of silver.

In Sweden, gold is found associated with pyrites at Edelfors in Småland.

The sands of the Rhine contain minute quantities of gold, for which they are sometimes washed when work is scarce, although about eight million parts of sand must be washed for one part of gold.

In Spain, the province of Asturias formerly furnished a considerable quantity of gold, but the workings are now neglected.

Italy is by no means destitute of gold. Veins of pyrites containing gold are found in a granitic rock at the foot of Monte Rosa. The sands of some of the rivers on the southern slopes of the Alps also furnish gold.

Siberia yields gold distributed through *hornstone*, a variety of quartz. The sands of Siberian rivers are not considered to be worth washing if they contain less than one part of gold in a million.

The Ural mountains contain some rich gold districts, the metal being found in pyrites, in clay, and in the sands of rivers.

India, especially the Mysore district, Japan, Ceylon, Borneo, the Philippine Islands, and Thibet also contribute to the supply of gold.

Africa seems to have been the oldest and richest of the sources of gold. Sofala, on the coast of Caffraria, has sands abounding in gold-dust, and is reputed to have been the Ophir of the ancients. To the south of the great desert of Sahara, the negroes dig out earth rich in gold-dust, to a considerable depth.

In modern times, down to about the year 1850, Brazil, Chili, Peru, and Mexico supplied most of the gold employed throughout the world. Minas Geräes in Brazil was a celebrated auriferous district.

The following are the principal gold-producing States of the United States of America, in the order of their production: California, Colorado, Dakota, Montana, Idaho, Oregon, Arizona, Alaska, Nevada, New Mexico, Utah, and Washington,—the first-named leading by a long way. The discoveries in California and Australia, and latterly in the Transvaal, have greatly increased the supplies of gold in recent years.

The West Coast of Africa also yields gold, and the river sands are commonly washed by the natives of the country to recover the precious metal that they contain. But the Transvaal and the adjoining districts now form the chief centre of gold-mining, the out-turn having risen within a few years from practically nothing to one-quarter of the production of the whole world. In the Witwatersrand, which is one of the principal districts, the gold occurs in a quartzose conglomerate rock, termed *banket*, principally in the silicious cement which binds the pebbles together. The banket beds are very extensive and uniform in character ; but most of the mining is done at a considerable depth below the surface. At these lower levels the banket contains much pyrites, which necessitates the use of special gold-extraction methods ; but nearer the surface the pyrites is oxidised, and the ore is more friable.

Recently the gold-fields of West Australia have attracted much attention, and those of British Columbia, New Zealand, and British Guiana are becoming of greater importance.

Washing River-sands.—The simplest method by which gold is extracted is that of washing the alluvial deposits, the sands of rivers, &c. There are various modes of effecting this, according to the resources of the gold-washers, but in all cases the separation of the gold from the earthy matters depends upon the high specific gravity of the gold (19·3), the lighter earthy matters being carried off by the water.

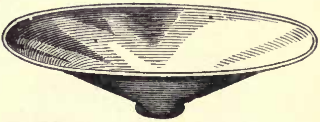


FIG. 104.—Gold-washing Pan.

In Africa, the deposits containing gold are washed by the negroes in the shells of gourds, being well stirred up with water, which is poured off with the earthy matter suspended in it, leaving the gold dust in minute flattened grains at the bottom. The gold is kept in tubes made from the quills of the ostrich or vulture.

In South America, the washing is conducted in shallow iron or zinc pans (fig. 104).

Sometimes the deposits are thrown upon the top of a sloping plank with shallow grooves cut across it, when the grains of gold settle down into the grooves, and the dirt is carried on by the stream.

Long shallow troughs of wood are employed by some gold-washers, lined at the bottom with coarse baize, or with tanned skins with the hair upwards. The grains of gold become entangled in these, and when the dirt has been washed away, the linings are well beaten over a tank of water to remove the gold.

At the Californian and Australian gold-diggings, a *cradle* (fig. 105) was formerly extensively employed. This is a wooden trough about 6 ft. long, resting upon rockers. At the head of it is a grating upon which the alluvial deposit to be washed is thrown. This end of the cradle is about 4 in. higher than the other, so that a stream of water entering it flows through and escapes at the lower end, left open for this purpose, carrying the dirt with it, and leaving the particles of gold, with a small quantity of dirt, in the trough. The contents of the trough are swept out into a pan, dried in the sun, and freed from the lighter matters by blowing upon them.

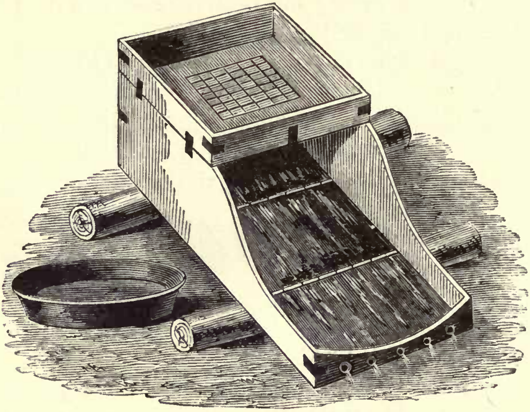


FIG. 105.—Cradle for Gold-washing.

In the gold washings of the Ural Mountains, the sands are thrown into boxes, the bottoms of which are made of perforated iron plates. These boxes are placed under a fall of water, in which the sands are stirred up with a shovel. The fine sand and gold dust are washed through on to sloping boards covered with baize, a workman being engaged in sweeping the deposit up the inclined plane with a heather broom. After a second washing on a smaller inclined plane the particles of magnetic iron ore are extracted by a magnet and the gold dust is melted in a plumbago crucible.

But these methods are primitive, and quite unsuited to the more extensive operations of the present day.

Extraction of Alluvial Gold.—In the alluvial *placer* deposits, which have been formed naturally by means of flowing water, nature has already concentrated the ore in part by a process of dressing. When the gold is more or less evenly distributed through the whole thickness of the deposit, which may form a cliff several hundred feet in height, the comparatively loose gravelly material of which it is composed is washed away by directing powerful jets of water upon it ; and the *paydirt*, carrying the gold, is allowed to flow through a gently sloping tunnel or channel, the bottom of which is irregular, so that the heavy particles of gold, which naturally gravitate downwards, may there be caught in the crevices of the stones or blocks forming the paving, while the lighter earth is swept away by the stream. Mercury to the amount of a few hundredweights is commonly introduced in the first part of the channel or tunnel ; and this, being heavy, is gradually distributed over the crevices of the bed. These globules of mercury, which are of sensible size, absorb readily all particles of gold coming into contact with them, and so retain many very fine particles of the precious metal, which otherwise might be washed away in spite of their high specific gravity. After a few days the washing operation is suspended, the tunnel or sluice is allowed to drain, and the amalgam is collected from the first part of the run, and is retorted in the same way as in the extraction of silver. Fresh mercury is introduced into the tunnel, and the washing of the gravel is continued. At longer intervals the whole sluice is 'cleaned up,' and the amalgam treated.

The jets of water used for breaking down the gravel are obtained by damming streams at the higher level, and leading the water from them through iron pipes to the nozzles, which are from 4 to 8 in. in diameter, and mounted on a swivel, so that the stream may be directed upon any part of the exposed bank. This system is known as *Hydraulicing.* When the precious metal is naturally concentrated, mainly at the bottom of the placer, a tunnel is cut into the bank at the richest level, and the material is extracted by the ordinary processes of mining. This is termed *Drift-mining.*

Extraction of Gold from Rock.—When the gold is disseminated through rock, this must be crushed in order to extract the gold. The crushing is usually effected by means of stamps, but occasionally by a dry-crushing process if water be scarce.

The ore is broken down in a stone-breaker to pieces of convenient size, and these are wet-crushed in stamps until the resulting powder can pass a sieve of about 30 meshes to the linear inch. The size of the particles and the volume of water to be used depend upon the grade of ore: when the gold is present in grains of appreciable size coarse crushing is preferable; and in the presence of pyrites, which is very easily ground to an impalpable powder, the fine material should be swept away from the stamps by the rush of water as soon as it is capable of passing through the mesh employed, otherwise a large proportion of *slimes* will be produced, and these may be accompanied by *float gold*—*i.e.* gold which is in such a fine state of division that it will remain suspended in water for hours, or even days.

The details of the processes subsequent to crushing are very diverse, depending upon the character of the ore and the bias of the manager. Commonly the ore and water flowing from the stamps are caused to pass over a wide copper plate—the width of the mortar-box—placed at a suitable angle and coated with mercury, which serves to retain the gold passing over it. This *apron* is about 10 to 12 ft. long, is made of the softest copper obtainable, in order that it may be easily amalgamated, is sometimes electro-plated with silver, and is fastened by copper screws to a wooden framework ; the angle must be so adjusted that the water flowing over it shall have sufficient force to carry away all the sand particles, whilst sufficient time must be given to enable all the gold to gravitate to the bottom and to come in contact with the amalgamated surface of the plate. With an increased volume of water or with a lighter or finer ore the apron must be placed at a reduced angle. The plates are first thoroughly cleansed by scrubbing with alkali and sand, and then with a weak solution of potassium cyanide ; when the surface is chemically clean it is amalgamated by scrubbing it with mercury until the copper cannot retain any more. Thus prepared, the whole of the copper is covered with a slightly soft amalgam, which is capable of arresting and dissolving any gold particles that come into contact with it. It is essential to success that the surfaces both of the amalgamated plates and of the gold particles shall be chemically clean, or perfect contact cannot be ensured, and no (or, at best, only imperfect) amalgamation of the gold will take place. Impure water, containing an excessive amount of sulphates or carbonic acid, will produce tarnish or stains upon the amalgam, and the apron must be frequently scoured with chloride of ammonium or cyanide of potassium in order to retain a perfectly bright surface. In some districts a little lime is introduced into the stamps with the object of lessening the trouble caused by these impurities. Greasy matter in the water is also very objectionable. At the same time the presence of impurities in the ore, such as sulphides of antimony or arsenic, compounds of tellurium, selenium, and bismuth, or even large proportions of ordinary pyrites, may cause the mercury to tarnish or *sicken*, or, under certain circumstances, to *flour* (that is, to become finely subdivided), sometimes to so great an extent that it is necessary to treat the ore by a different process. In other cases the particles of gold may be covered with a film of oxide of iron or of talcose matter, which hinders or prevents contact with the mercury. The simplest free-milling ore is one in which the gold is distributed in visible grains through a pure quartz gangue. As mercury takes up gold its capacity for dissolving a further quantity at first increases; and it is usual in amalgamating new copper plates to employ mercury which already contains a little silver or gold in order that they may have their full efficiency from the first. It is for this reason that the copper is sometimes electro-plated with silver initially. But as the amount of gold increases the amalgam thickens and becomes harder and less efficient; the plate must therefore be re-amalgamated from time to time. When a sufficient amount of amalgam has accumulated steam or hot water is applied to the plate; this softens the amalgam so that it may be readily scraped off, cleaned, and retorted. After the application of fresh mercury to the copper the process may be continued as before.

In most mills small amalgamated copper plates are placed within and along the sides of the mortar-box of the stamps, on the same level with the dies, but below that of the perforated screen. A considerable proportion of the gold may thus be arrested in the stamp-box, and this may in some instances be increased by introducing a little mercury with the ore.

The ore, after leaving the apron, is sometimes led over one or two similar amalgamated plates; but in any case it is usually submitted subsequently to some system of mechanical concentration, with the object of recovering particles of gold or amalgam that may have been carried away, and of separating the pyrites that may be present, in order that this material may be afterwards treated by a different process to recover from it the gold which it contains in a condition unfavourable to extraction by amalgamation. This concentration was formerly, and is still, largely effected by stretching blankets, canvas, or hairy skins on the bottom of the sluices leading from the amalgamated plates, so that the heavier particles may be entangled in the rough surfaces, from which they may be extracted afterwards by placing the material face-downwards in water and there beating it. When sufficient pyrites is present the pulp may with advantage be passed over a mechanical concentrator, such as the Frue vanner (p. 130). The water, sweeping the lighter particles forward, is finally passed to large settling tanks, made by damming the stream, in the first of which the coarser particles or *tailings* subside, whilst in the second the finer particles, which remain in suspension for a longer period, settle in the form of a fine mud, known as *battery slimes*. The pyritous concentrates may be sometimes amalgamated in pans in the manner described for the treatment of silver ores, or they may be roasted and submitted to the chlorination process shortly to be described. The tailings often contain sufficient gold to be worth extracting; and the cyanide process is especially adapted to treat this material.

The amount of gold extracted by amalgamation in the battery itself and on the copper plates varies with the ore and the method of treatment, but it should at least exceed 50 per cent.; from 60 to 70 per cent. is quite commonly extracted, or, with a good free-milling ore, from 70 to 80 per cent., a part of the residual 20 or 30 per cent. being recovered from the tailings. At the same time there is a loss of about $\frac{1}{2}$ oz. to 1 oz. of mercury per ton of ore treated, the more rebellious ores causing the highest loss.

To check the sickening of mercury a small quantity of a very chemically active metal, such as sodium, is occasionally dissolved in it. Sodium alone decomposes water with great violence, forming caustic soda and producing a rush of hydrogen ; but in sodium amalgam there is a large excess of mercury, which moderates this action, and the result is that only a very gentle evolution of hydrogen takes place over the whole surface of the amalgam when it is exposed to the influence of water. Either the sodium in the amalgam or the nascent hydrogen produced by it is found to prevent the formation of some forms of tarnish, and the mercury then remains bright so long as it still contains sodium. The sodium amalgam is mainly employed in amalgamating pans, but, in a few mills, is used even for the amalgamation of copper plates.

The Chlorination Process.—Advantage is taken of the readiness with which gold unites with chlorine to remove the precious metal from pyritous concentrates. Sulphides, however, but not oxides, are also attacked by this gas ; and as it is desirable that the smallest possible quantity of chlorine may be used, both on account of the expense and because the chlorides of the baser metals would ultimately pass into solution with the chloride of gold, the ore is roasted until it is practically free from sulphur. The resulting oxides, still containing the gold in the metallic state, are sifted into a wooden vat about 8 ft. in diameter and 3 ft. high. The vat is waterproofed inside with pitch, and has a perforated false bottom, covered with relays of quartz, gravel, and sand, to act as a filter. A pipe for the admission of chlorine leads into the space between the two bottoms, from which a cock serves to withdraw the solution ultimately on the side opposite to that at which the chlorine has entered. When about 6 tons of the fine ore have been moistened with from 5 to 10 per cent. of water, and charged into the vat, the top is completely closed in, and chlorine is admitted from below ; this gas gradually permeates the ore, combining with the gold to form auric chloride (Au Cl_3). The chlorine is passed until the absorption due to its combination with gold ceases, which is indicated by the escape of the gas if a vent be opened momentarily in the lid of the vat. This happens in from 12 to 24 hours after charging. The supply of chlorine is then stopped ; a manhole is uncovered, and water is introduced from above. The solution containing chloride of gold and any other soluble chlorides, is run through the cock into a second vat for the precipitation of the gold ; successive quantities of water are then passed through the ore and collected in the precipitation vat until all the chloride of gold has been washed out. When properly applied, this process should extract from 90 to 95 per cent. of the gold originally present ; and the residue left in the vat after washing may therefore be thrown away. The process is not well adapted to the treatment of ores containing comparatively coarse gold, because the grains tend to become covered with a film of chloride, which is but slowly removed as soon as the water in their immediate neighbourhood has become saturated, and this film checks the further attack of the chlorine upon the metal beneath. It is not desirable, however, to add more than enough water to moisten the ore, otherwise the mass will become less permeable to gas, and the action will be exceedingly slow. So also, if the gold be naturally alloyed with much silver, the rate of chlorination will be lessened owing to the formation of a crust of the very insoluble chloride of silver.

The chlorine is made in covered leaden vessels by the action of sulphuric acid upon manganese dioxide and common salt. The gas is passed through a wash bottle containing a small quantity of water, on its way to the chlorination vats, in order that any hydrochloric acid may be absorbed. This is very necessary, because the oxides of the base metals in the roasted pyrites which are not affected by chlorine would be attacked and partially dissolved by the hydrochloric acid, forming chlorides that would contaminate the solution of chloride of gold.

The precipitating vat is constructed of waterproofed wood, but has no false bottom; its diameter is about half that of the chlorination vat. When the solution derived from the chlorinated ore has been run into it, a solution of ferrous sulphate (protosulphate of iron) is introduced in sufficient quantity to precipitate the whole of the gold. The ferrous compound takes up chlorine from its combination with gold in order to form ferric salts; and the liberated gold settles to the bottom of the vat as a dirty brown or purplish black metallic powder. After the deposition of this powder a little of the solution is withdrawn from the vat and mixed with fresh ferrous sulphate in order to determine whether the whole of the gold has been separated. Should any further precipitate form, more of the iron salt must be added to the bulk of gold-liquor in the vat, and time must be given for this also to settle. Otherwise the clear solution is drawn off from above the gold deposit with the aid of a siphon, and is allowed to run to waste. Fresh quantities of gold solution are then introduced and treated in the same way until sufficient gold has accumulated upon the bottom of the vat, when it is filtered off, dried, and melted into bars; the gold produced is usually very pure, because other metals should not pass into the solution, or, if dissolved, should not be precipitated by the ferrous sulphate. Many substitutes for ferrous sulphate have been tried, such as wood-charcoal or cuprous or cupric sulphide, or sulphuretted hydrogen, which give either metallic gold or sulphide of gold, or mixtures of the two, as the case may be. But the original ferrous sulphate method still holds its own.

In some modifications of the chlorination process the chlorine is generated in the vat itself by mixing dilute solutions of bleaching powder and acid; in others the gas is introduced under pressure; and in others again rotating barrels are employed instead of vats, with the object of keeping the surface of the gold free from chloride by the friction of the particles of ore, and so reducing the time required to three or four hours.

The Cyanide Process for the Extraction of Gold.—The solvent action of dilute solutions of cyanide of potassium upon metallic gold in the presence of air forms the basis of a process which has been applied successfully to the treatment of ores and tailings, that would not yield their gold economically under any previously known treatment. In South Africa the cyanide process, introduced by McArthur and Forrest, has met with great success in extracting the fine gold from the tailings after the coarse gold has been removed from the ore by amalgamation in the ordinary way. As in the chlorination process, coarse gold would be acted on too slowly. This process has the great advantage over the chlorination process that it may be applied without previously roasting the ore or tailings, so that very large quantities may be rapidly and economically treated.

Ores containing arsenic and antimony have been successfully treated by cyanide in some cases without roasting.

The fact that cyanide of potassium is one of the most poisonous substances known has not practically interfered with its use for the extraction of gold.

Tailings containing pyrites, when exposed for any length of time to air, absorb oxygen, and become converted into sulphates which decompose the cyanide of potassium, and thus cause the loss of an expensive material. Ores which contain *cyanicides* (cyanide destroyers), as they are technically termed, are submitted to a preliminary treatment with a solution of alkali, or are sometimes mixed with a small proportion of lime prior to the cyanide treatment, as these substances break up the compounds which decompose the cyanides. It is further found to be economical to use very weak solutions of cyanide, as they dissolve the gold quite readily, whilst the loss due to decomposition of the solution is proportionately much less than with more concentrated liquors.

The ore from the batteries (or the tailings) is treated with the cyanide liquor in wooden vats, usually 20 to 40 ft. in diameter and 8 to 14 ft. high, each having a false bottom of cocoanut matting, twill, or canvas, supported on a wooden framework, to serve as a filter. The tanks are sometimes constructed of masonry or of iron, and occasionally they are rectangular, but the circular form is stronger, and is usually preferred. The ore must be comparatively free from slimes, which render the mass too compact, and hinder or prevent the percolation of liquid, by reason of their fine state of division. It is therefore either separated from slimes by dressing or is suspended in water and automatically distributed by rotating nozzles in a large vat, which, from the first, is kept filled with water ; the size of the vat is so regulated to the supply of air and water that the sand has time to settle, whilst the overflow carries away practically the whole of the slimes in suspension. When this vat is filled with the coarser particles the water is drained off and the contents are transferred to the cyanide vats.

The ore in these vats is allowed to drain for several hours, a very weak solution of caustic soda is next filtered through, and then the stronger of two stock solutions of cyanide is run in from the tank in which it is stored. This solution contains from 0·3 to 0·7 per cent. of potassium cyanide, or even less, according to the richness of the ore, and is used to the extent of about one third or one half of the weight of ore to be operated upon. This solution is either allowed to flow slowly but continuously through the ore ; or it is passed through more rapidly, and again pumped to the top and circulated a second time ; or the flow may be intermittent, the percolation being checked for two or three hours at a time. The first method is that most widely adopted. The gold is now present in the solution as a double cyanide of gold and potassium ($AuKCy_2$); this liquid is run off to the precipitating vessels, and the residue in the vat is treated, either directly, or, after draining for a few hours, with the weaker liquor, containing from 0·05 to 0·15 per cent. of cyanide. This washing is followed by a second treatment with water to remove the last traces of gold-solution.

From the different solutions thus obtained the gold is recovered separately, either by precipitation with metallic zinc or by electrolysis. When the former method is adopted, the liquid, after leaving the leaching vats, is passed to a long rectangular wooden box divided into ten or more separate compartments, so arranged that the solution enters beneath a false bottom in the first compartment, then overflows from the top through a narrow side channel to the bottom of the next, and so on, traversing all the compartments, and always entering at the bottom and leaving at the top of each. Each compartment is packed loosely with fresh turnings of metallic zinc, which should be as free as possible from lead, supported by a perforated tray, which forms the false bottom of the chamber. The solution has thus to pass through a length of 20 to 25 ft. of loosely packed zinc, and in doing so loses its gold by simple exchange, a double cyanide of zinc and potassium being formed, whilst metallic gold is substituted for some of the zinc which dissolves, and adheres as a brownish powder to the residual zinc, from which it presently becomes detached and collects in the spaces beneath the false bottoms. The liquor, almost freed from gold, and still containing cyanides, is pumped back to the storage tank for use again. Owing perhaps partly to the solvent action of cyanide, but mainly to the galvanic action set up between the zinc and the gold deposited upon it, zinc dissolves in quantities out of all proportion to the weight of gold separated, and an extraction of 4 or 5 dwt. of gold may be accompanied by a loss of 3 or 4 oz. of zinc. To clean up the zinc-extraction boxes, the solution is allowed to run off, the turnings are washed by passing water through them, and the zinc in each compartment in turn is rubbed between the fingers under water, in order to dislodge gold, the tray with the excess zinc is withdrawn, and the solution in the compartment is transferred to that next adjoining ; the gold slimes at the bottom are run out through a plug into a sieve, which retains the zinc fragments, whilst the slime passes through the meshes into a twill bag suspended beneath, in which most of the gold is caught. The liquid overflowing from this is carried to a settling tank, in which is deposited any finely divided gold that may be still floating in it. The zinc retained on the sieve is rubbed, and then returned to the precipitating boxes. A circular sieve with fine mesh revolving under water has been successfully employed to remove the gold from the surface of the zinc shavings. In this way cutting the hands with the zinc is avoided, and the gold is obtained much freer from zinc. Filter-presses have been used in a few places to obtain the gold slimes in the form of consolidated cakes. The separated gold is dried on a hot plate, and is ready for fusion. It may be roasted first, to oxidise any zinc, and some of the lead, that may be mechanically mixed with it ; but ordinarily it is fused direct. Plumbago crucibles are employed ; and the slimes are mixed with carbonate of soda and borax, together with sand or fluor spar if necessary. The proportion of fluxes depends upon the character of the slime, more carbonate of soda being used when there is much sand intermingled with it, and more borax being employed when there is much zinc. The bullion and slag are poured into conical iron moulds, and may be separated after cooling. The slag is then crushed under stamps, and washed in a pan for the extraction of entangled shots of metal, and the bullion is remelted into bars, in many instances after granulating it in water and roasting it to oxidise the base metals, thus producing a finer bar.

Siemens and Halske have introduced an electrolytic process for the treatment of the gold solution, which has been adopted at some mines. The double cyanide from the leaching vats is run into large tanks containing a number of parallel iron plates, suspended in canvas bags and connected with the positive pole of a dynamo; alternately with these, and only an inch or two away from them, are hung a like number of thin lead plates connected with the negative pole. The current flowing from the iron anodes to the lead cathodes causes the electrolytic decomposition of the liquid, and the gold is slowly deposited upon the lead in a coherent film. When this film is sufficiently thick the lead sheets are withdrawn, melted, and cupelled for the recovery of the gold. A very weak current is used at a pressure of about 7 volts.

Smelting of Complex Gold and Silver Ores.—Many ores containing copper, lead, or other base metals carry also a small percentage of gold and silver. The precious metals could not be extracted profitably from these by the processes which have just been described; but they may sometimes be recovered by smelting methods, when suitable ores for mixing are available. A lead or copper matte is first obtained, which will contain practically the whole of the precious metals; and these are afterwards extracted from it. The method by which the matte is obtained by the use of blast furnaces has been sufficiently described above. The process known as pyritic smelting has been applied to the treatment of suitable auriferous ores.

Pyritic smelting.—It has already been seen (p. 330) that pyritic smelting theoretically consists in the smelting of pyritous ores in blast furnaces by the heat derived from the partial oxidation of the ore itself, without the aid of carbonaceous fuel. At present a little added heat is introduced by the use of a hot blast, and by the addition of about two or three per cent. of wood or coke to the charge; the latter, however, acts quite as beneficially by serving to keep the charge open as by increasing the heat-production in the furnace. Only very rich pyritous ores can be treated by this process, since it depends for success upon the heat of combustion of the constituents of the ore; although in some instances half-measures have been adopted, and a considerable proportion of coke has been added to make good the heat deficiency of the ore.

The original intention of the inventor of the process was to use a water-jacketed furnace with somewhat narrow boshes, and to have a circular water-cooled curtain suspended inside from the top to within a couple of feet of the twyer-level. Into the annular space between the two water-jackets the slags, fluxes, and oxidised ores were to be charged, and from the top of this space the gases were to be withdrawn; whilst the pyrites was to be fed into the central space. A portion of the pyrites would burn at the twyer level, forming sulphurous acid gas, and iron oxide, which would at once unite with silica and other fluxes to form a slag, and the heat produced by these combinations would suffice to melt the unoxidised residue of the charge as well as the slag itself. The hot gases would pass through the chamber containing the oxides and fluxes, which would thus arrive preheated at the zone of combination, whilst the pyrites would remain cool owing to the absence of heated products of combustion from the central compartment of the furnace. This arrangement offers the further advantage that the gases leaving the furnace would not be compelled to force their way through pyritous material, which is apt both to be unduly crushed before charging, by reason of its brittleness, and to break down by decrepitation as it becomes hot. There should consequently be no risk of interference with the draught. Moreover, the whole of the combustible sulphur in the pyrites in this case would be brought to the zone of combustion, whereas ordinarily a portion of the sulphur in iron pyrites distils off unchanged by the heat in the upper regions of the furnace, and is practically lost. If copper were present in the ore the reactions of this process would resemble those of copper-smelting:—the copper in both the oxidised and sulphurised ore passing into the regulus as sulphide, and carrying with it practically the whole of the gold and silver, together with some of the lead, zinc, and iron ; whilst the slag should consist of silicates of iron with some lead and zinc and a negligible proportion of copper. The arrangements of the hearth and twyers resemble those of the ordinary blast-furnace. This type of furnace is not actually in use, but the pyrites is sometimes charged into the centre, and the fluxes and oxidised ores to the outside of the ordinary blast-furnace.

Usually the different constituents of the charge are mixed, as in common blast-furnace practice, and a blast of about 1½ lb. per square inch pressure preheated to from 300° to 600° C. is used, the furnace being water-jacketed and with little or no boshes. Large rectangular furnaces, averaging 12 to 14 ft. in length, and 3 ft. in width, with a height of 7 to 10 ft. from twyer-level to charging platform, have been found to be the most economical. A high stack is necessary to carry off the gases, and a chamber for the deposition of dust is interposed between the furnace and the stack.

The presence of zinc and lead in the ores leads to the formation of volatile substances, which carry a notable proportion of the precious metals with them. Zinc is especially objectionable in this respect. When any considerable proportion of lead is present some metallic lead is commonly reduced, and much of the silver and gold will be concentrated in this. But it is usually preferable to have only matte, which may consist mainly of sulphide of iron, but which should contain at least 1 or 2 per cent. of copper, as it is found that the presence of this element greatly favours the concentration of the gold and silver in the matte.

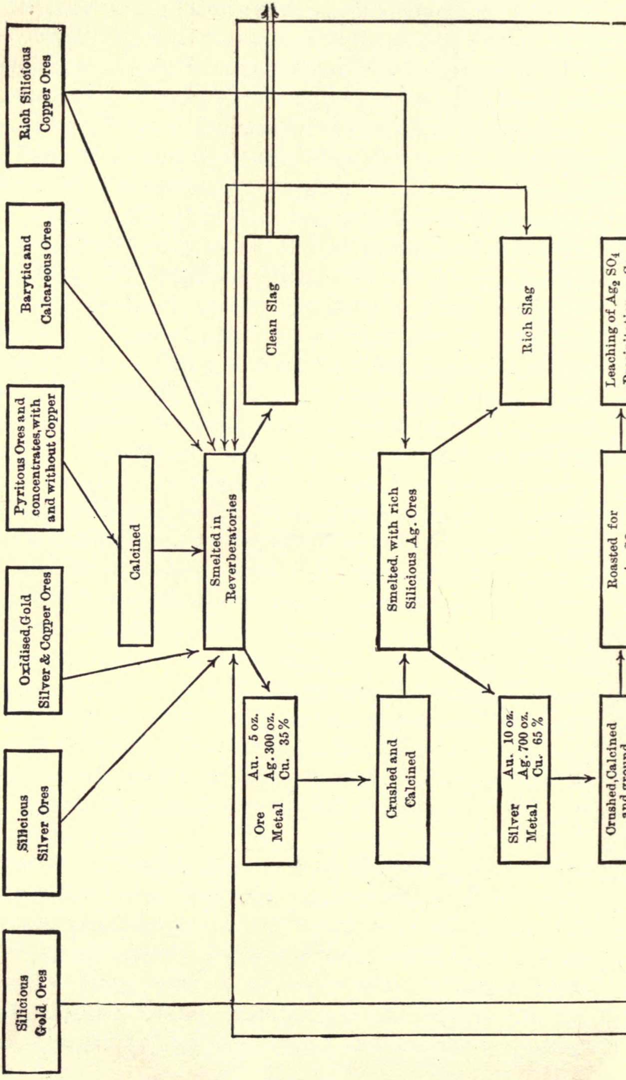
The complex matte produced in this manner is treated by one of the many wet or dry methods for the extraction of the precious metals, and for the recovery of the other valuable constituents. The following scheme (see folding table, p. 480), taken from Ulke's article in 'The Mineral Industry,' shows the practice of the Boston and Colorado Smelting Company, and affords a typical illustration both of the way in which complex ores may be treated and of the manner in which such treatment may be graphically represented to those who have a knowledge of the general principles of metallurgy.

When it is required to separate a little gold from a large proportion of alloyed silver the alloy is heated with sulphuric acid, which converts the silver into sulphate of silver, capable of being dissolved by water, and leaves the gold untouched.

Parting by Sulphuric Acid.—The alloy of silver and gold, in which, of course, the former metal must predominate, is melted either in wrought-iron or plumbago crucibles, and poured into water in order to *granulate* it or divide it into a flaky condition, thus exposing a large surface to the action of the acid. The granulated metal is dried, weighed, and boiled with concentrated sulphuric acid. When the alloy is rich in gold the operation is performed in platinum stills, but in the more common case, where the silver contains only a few grains of gold in the pound, cast-iron pans are employed; each pan (about 2 ft. wide) has an iron lid, from which a bent pipe passes down into an air-tight leaden tank, where the vapour of sulphuric acid which escapes during the boiling may be condensed. A large quantity of sulphurous acid gas passes off during the operation, and this is conducted from the leaden tank by a pipe of the same metal into a large leaden chamber, 30 ft. long by 10 ft. wide and 6 ft. high, in which it is reconverted, by a chemical process, into sulphuric acid, which is used over again.

One fire is made to heat two of the iron pots, in which the granulated silver is placed, together with twice its weight of concentrated sulphuric acid, which is gently boiled until the silver is entirely converted into sulphate of silver, forming a pasty mass of minute crystals. This is taken out by cast-iron ladles, and thrown into leaden cisterns, where it is stirred up with water, and boiled by passing

To face p. 480.


Rich Silicious Copper Ores
Barytic and Calcareous Ores
Pyritous Ores and concentrates, with and without Copper
Oxidised, Gold Silver & Copper Ores
Silicious Silver Ores
Silicious Gold Ores
Calcined
Smelted in Reverberatories
Clean Slag
Ore Metal
Au. 5 oz.
Ag. 300 oz.
Cu. 35 %
Smelted, with rich Silicious Ag. Ores
Crushed and Calcined
Rich Slag
Silver Metal
Au. 10 oz.
Ag. 700 oz.
Cu. 65 %
Leaching of $Ag_2 SO_4$
Roasted for
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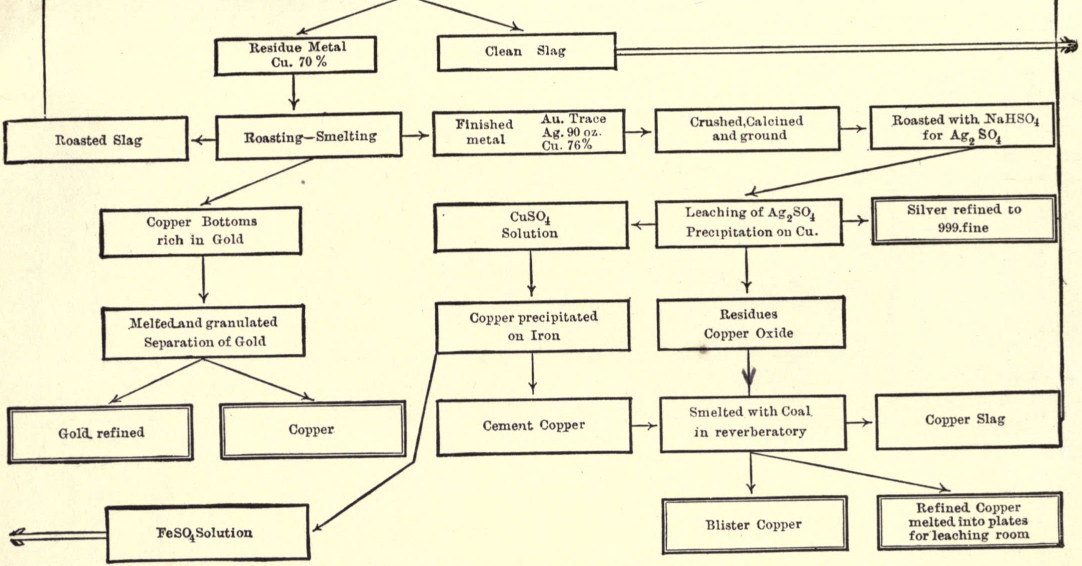

Note: Marketable products are enclosed within a double line.

Waste products are connected with the margin by a double arrow.

Precious metals are quoted in ounces per ton.

steam into it through perforated leaden pipes connected with a boiler. The boiling water dissolves the sulphate of silver, and the finely divided gold is left as a black powder, which, when accumulated in sufficient quantity, is well washed and dried. It still retains a small proportion, varying from $\frac{1}{30}$ to $\frac{1}{50}$ of its weight of silver.

The solution of sulphate of silver is drawn off, by leaden siphons, into leaden troughs, where it is left in contact with shavings of copper. The copper enters into solution, forming sulphate of copper, and separates the silver, in a finely divided state, as a grey powder, which is allowed to settle down ; the solution of sulphate of copper is run off into another cistern, and the silver washed with fresh water, drained, and compressed by hydraulic pressure into cakes of 60 lb. each in a square cast-iron box. The cakes are dried, melted in plumbago crucibles, and cast into ingots. Cast-iron crucibles strengthened by shrinking hot iron hoops upon the cold crucibles are sometimes employed, but, since they become impregnated with silver, the latter must be extracted by melting some lead in them when they are worn out.

The solution of sulphate of copper formed in displacing the silver by copper is evaporated to a proper strength in shallow leaden pans, and the sulphate of copper is allowed to crystallise out on cooling. The liquid remaining after the last crystals have separated contains the excess of sulphuric acid which has been employed in the process, very little sulphate of copper being left in it, because this salt is almost insoluble in moderately strong sulphuric acid. This liquor is boiled down in a platinum still until the water has boiled away, and the concentrated sulphuric acid is left in the still ready to be employed for the treatment of a fresh quantity of silver.

The sulphate of copper (blue vitriol) obtained in this process is a salt for which there is a considerable demand ; it is largely used for dressing grain intended for seed, to prevent smut, and more particularly for the treatment of potato crops. It is also employed in electrotyping, dyeing and calico-printing, and in many other branches of industry, as well as in several forms of galvanic battery.

When there is no market for the sulphate of copper the solution of the salt is decomposed by scrap iron (p. 333) to recover the metallic copper.

In such works for the refining of gold and silver the processes can be conducted economically only when great care is taken to avoid the loss of any particles of the precious metals. Thus all the old crucibles are ground and treated with mercury in the amalgamation mill, and after as much gold and silver as possible have been thus extracted the residues are sold to the *sweep-washers*, who extract a little more by melting them with lead. The very dust off the floors is collected and treated in a similar manner. One part of gold can be profitably extracted from 2,000 parts of alloy by this process of parting by sulphuric acid. Its introduction has affected the metallurgy of gold in the same way as Pattinson's process did that of silver, much old silver plate having been treated by it for the sake of the gold which had not been found worth extracting by the older and more expensive method of parting by nitric acid.

When the alloy contains copper as well as silver and gold it may also be treated in the same way, the copper being removed, with the silver, as a soluble sulphate; but the process does not succeed well with an alloy containing more than 75 parts of copper in 1,000, so that, if it be richer, it is either melted with more silver or is cupelled with lead (p. 425), in order to reduce the copper to the right proportion.

Nor should the alloy contain more than one-fifth of its weight of gold, or the sulphuric acid will not extract the silver. When platinum stills are employed for parting by sulphuric acid it is necessary that the alloy should be free from lead and tin, which are apt to melt upon the bottom of the still and seriously to corrode the platinum.

Parting of Gold and Silver by Nitric Acid.—Silver is easily dissolved by nitric acid and converted into nitrate of silver, but this acid, if pure, does not attack gold. If the nitric acid contain chlorine, however, it will dissolve some of the gold, so that it is always necessary to test it by adding a little solution of nitrate of silver, which will render it milky from the separation of the insoluble chloride of silver, if any chlorine be present. An alloy containing two parts of gold to five parts of silver is the most suitable for this process. If it contain a larger proportion of gold than this the acid will be unable to penetrate to the centre of the mass, whilst, if it contain more than three parts of silver to one of gold, the latter will break down to a fine powder after the silver has been removed by the action of the acid. With the proportion first named the silver may be completely dissolved, but the skeleton of gold may be still sufficiently coherent to hold together unless it be violently boiled or roughly handled. Originally the proportion of three to one was employed, and the term *quartation*, or *inquartation*, applied to the process, was derived from this fact. Alloys containing a larger percentage of silver than this will yield all their silver to the acid, but the gold will be left in the form of a dark brown or black powder.

The alloy, in a granulated state, is heated with twice its weight of moderately strong nitric acid (sp. gr. 1·32) in a still made of platinum, glass, or earthenware, connected with an apparatus for condensing the vapours of nitric acid which pass off. Whilst the silver is being dissolved a large quantity of the red gaseous oxides of nitrogen are evolved, resulting from the action of the silver upon the nitric acid, and when these are no longer perceived the silver is known to be dissolved. The still is then cooled, the solution of nitrate of silver drawn off, and the undissolved gold boiled with a little more nitric acid to extract any remaining silver. It is then washed with water, dried, melted, and cast into an ingot. The use of the nitric acid method of parting gold is practically confined to assay laboratories, where it is universally employed.

In order to recover the silver from the nitrate, hydrochloric acid is cautiously added, so as to separate the bulk of the silver as the insoluble chloride, leaving the nitric acid in the solution, which may be used again, if care be taken to leave a little nitrate of silver undecomposed in the solution, so as to ensure the absence of chlorine. The separated chloride of silver is washed with water, moistened with sulphuric acid, and some bars of zinc or iron placed in it, when chloride of zinc or iron is formed and dissolved, the silver being left in the finely divided metallic state. The rest of the zinc is taken out, the silver allowed to remain in contact with dilute sulphuric acid to dissolve any particles of zinc, then thoroughly washed with water, dried, melted, and cast into ingots.

Refining of Gold.—The gold obtained by parting with sulphuric acid may be refined by mixing it with one-fourth of its weight of dried sulphate of soda, and treating it, in an iron pan, with oil of vitriol, to the amount of three parts for every five parts of sulphate of soda. Heat is applied as long as any vapours of sulphuric acid escape. This is repeated a second time, but without driving off the whole of the sulphuric acid. The mass is then boiled with sulphuric acid, when the gold alone is left, and is melted with a little saltpetre, which extracts a little platinum, before casting it into an ingot. At the Russian mint the re-melting is effected in a small reverberatory furnace with a cavity in which the gold collects. The explanation of this process is simply that the sulphuric acid combines with the sulphate of soda, forming the bisulphate, and may then be raised to a higher temperature without vaporising than is possible with uncombined sulphuric acid. The higher temperature employed enables the sulphuric acid to attack the remainder of the silver.

Gold dust and nuggets of gold never consist of the pure metal, but always contain silver, and sometimes copper and small quantities of other metals, such as antimony and bismuth. Grains of platinum and its allied metals are also very commonly found in alluvial gold. The purest native gold has been found at Giron, in New Grenada, containing only $\frac{1}{100}$ part of silver. Some Californian gold contains as much as nine parts of silver and one part of copper in a hundred parts. Californian gold also sometimes contains small grains of an extremely hard alloy of osmium and iridium, which occasion great injury to the die in coining, since they remain unchanged when the gold is cast into ingots.

At the American mint the Californian gold, which contains about $\frac{1}{1000}$ of its weight of the osmiridium alloy, is melted with thrice its weight of silver, which lowers its specific gravity, and allows the very heavy osmiridium to settle to the bottom. The greater part of the melted metal is ladled out, leaving the rest very rich in osmiridium at the bottom. This is repeatedly melted with silver, by which the proportion of gold is still further diminished, and ultimately the mixture of osmiridium with silver and a little gold is boiled with sulphuric acid, which extracts the silver, leaving the osmiridium mixed with some powdered gold, which may be removed by washing.

When gold contains platinum or palladium it is very much lighter in colour. These metals cannot be separated by the ordinary refining processes. Platinum, which by itself is insoluble in nitric acid, dissolves readily in it when alloyed with an excess of silver; this metal may therefore be removed from gold by fusing the metal with sufficient silver and parting with nitric acid. The presence of platinum or of palladium (which also dissolves in the nitric acid) is indicated by the yellow colour that they impart to the acid used.

The presence of lead or antimony, even in very minute proportion, is found to render gold extremely brittle. Such is sometimes the case with Australian gold. It may be refined by stirring a little corrosive sublimate (chloride of mercury) into the melted gold, when the chlorine combines with the base metals, forming chlorides, which are expelled in the form of vapour together with the liberated mercury. F. B. Miller's process for refining such gold by forcing into the melted metal a current of chlorine gas through a fire-clay tube (on a small scale the stem of a tobacco pipe might be used) is now almost universally employed. The chlorine converts the silver present in the gold into chloride of silver, which collects, in a melted state, upon the surface of the gold, whilst any arsenic, antimony, bismuth, lead, or zinc is also converted into chloride, and driven off in the form of vapour. The gold is practically unaffected by the chlorine. The operation is stopped when red-brown fumes, which give a deposit upon pipe-clay, are observed. The metal is then poured into an iron mould, and on cooling is separated from the slag, which usually retains a small proportion of gold. The silver is afterwards easily extracted from its chloride.

Properties and Uses of Gold.—Perfectly pure or *fine gold* is nearly as soft as lead—far too soft, therefore, to resist the wear to which it would be subjected in coinage and gold plate. The standard alloy used for coin, in England, consists of 11 pts. of gold and 1 pt. of copper, which is harder and more fusible than pure gold. Formerly the gold was alloyed with silver, or with silver and copper, and this latter alloy is still employed by goldsmiths. The guinea was composed of 11 pts. of gold, $\frac{1}{2}$ pt. of silver, and $\frac{1}{2}$ pt. of copper. The specific gravity of sovereign gold is 17·157 (that of pure gold being 19·3). The safest method of ascertaining whether a sovereign is genuine consists, as in the case of silver coin (p. 455), in showing that it has the same size and weight as a sovereign known to be genuine. A new sovereign weighs

123¼ gr., but it is a legal tender as long as it is not less than 122½ gr. in weight. So hard is the alloy that, with proper wear, a sovereign will circulate for eighteen years without falling below the legal standard.

The gold coin of the United States and of France contains only 9 pts. of gold to 1 pt. of copper.

The fineness or purity of gold is commonly expressed by stating how many carats of gold are present in 24 carats of the alloy. Thus pure gold would be 24 carats fine ; sovereign gold, 22 carats fine.

Fractions of a carat are expressed in grains (4 grains are equal to 1 carat) and eighths of a grain ; thus, French gold coin would be styled of 21 carats 2⅜ gr. fine, or *worse* 0 *carat* 1⅝ *gr.*, implying that it contained so much less gold than the English standard.

The Testing of Gold.—The fineness may of course be judged of, as in the case of sovereign gold, from the specific gravity, since the specific gravities of silver and copper (respectively, 10·5 and 8·8) are so much lower than that of gold (19·3). But this test has been found fallacious in a case where bars of platinum (sp. gr. 21·5) were coated with gold and sold as solid ingots of that metal, which was formerly more than twice the price of platinum. Gold of 18 carats fine has the specific gravity 16·8.

The goldsmith or pawnbroker generally tests the gold by touching its surface with a stopper wetted with *aquafortis* (nitric acid), which produces a green stain upon the metal when a very large proportion of copper is present, nitrate of copper being then produced. This is, at best, a rough test and would of course fail altogether if the surface only of the base alloy were coated with fine gold.

The use of the *touchstone* admits, in practised hands, of a far more exact determination of the value of the alloy, and unless it be pretty thickly coated with richer metal, deception is more easily detected. The touchstone is a piece of black basalt, or even of black slate, over which the gold to be tested is drawn so as to leave a streak of fine particles of the metal upon the surface; this streak of course remains untouched when moistened with nitric acid, but if a streak of any base alloy (of copper and zinc for example), made to imitate gold, be made upon the surface of the touchstone, the nitric acid will immediately dissolve it.

The acid employed in this test is generally mixed with a minute proportion of hydrochloric acid (98 pts. by weight of nitric acid, of sp. gr. 1·34, 2 pts. of hydrochloric acid, of sp. gr. 1·173, and 25 pts. of water). The streak is not apparently affected by the acid if the gold be not below 18 carats fine; by making several streaks in succession, or by grinding off a part of the surface upon the touchstone, any error arising from a thin external coating of fine gold may be avoided; a glass rod, or the feather of a pen, serves for moistening the streaks with the acid.

In order to determine by the touchstone the proportion of gold which is present in the alloy, the streak is compared with that made by a series of *touchneedles* composed of alloys containing gradually diminishing quantities of gold. In experienced hands, the quantity of gold may thus be ascertained with an error of not more than one per cent.

The exact assay of the alloys of gold is an imitation, on the small scale, of the metallurgic processes of inquartation, cupellation, and parting. A weighed quantity of the alloy, say 10 gr., together with $2\frac{1}{2}$ times its weight of pure silver, is wrapped in about 60 gr. of pure lead foil and melted in a bone-ash cupel (fig. 106), heated in a muffle (fig. 107), which is raised to a suitable temperature by means of coke or gas. The lead and copper are both converted into oxides, the oxide of copper dissolving in the oxide of lead, and both being absorbed by the bone ash. After the *brightening* (p. 428) the alloy of silver and gold

FIG. 106.—Cupel.

which is left on the cupel is hammered flat, annealed by heating to redness, rolled out thin, coiled up into the form of a tube, and boiled, first with weak nitric acid (sp. gr. 1·18), and then with a stronger acid (sp. gr. 1·28), in order to extract the silver; the gold is left in the form of a little tube (*cornette*) having much the appearance of red earthenware. It is well washed with water, carefully transferred to a small crucible without breaking it, dried, and heated to redness in the muffle, when it shrinks, and assumes the ordinary appearance of pure gold. Its weight is ascertained by a very accurate balance, and multiplied by $2\frac{4}{10}$ (10 gr. having been assayed) to express the fineness of the gold. To avoid errors, the exact assayer commonly passes a *proof* or weighed quantity of pure gold through the same process, at the same time, with the addition of a proportion of copper about equal to that in the alloy, and corrects his assays by altering the recorded weight of the assay by the amount of the difference observed in the weight of the pure gold. Silver assays are made in the same manner in the muffle, but of course without 'parting.'

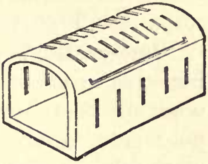

FIG. 107.—Muffle.

The alloy of copper and gold is much redder than pure gold; the addition of silver whitens it, and its surface may be brought to any shade of gold colour by heating it until a portion of the copper is oxidised, and dissolving off this oxide with an acid. Goldsmiths commonly *colour* their gold by boiling it for twenty minutes with a mixture of 1 pt. of common salt, 2 pts. of saltpetre, 1 pt. of alum, and 4 pts. of water, the mutual action of which would result in the production of a little hydrochloric acid (from the chloride of sodium), and a little nitric acid (from the saltpetre, nitrate of potash); this *pickle* dissolves not only the copper, but some of the gold, which is recovered by precipitating it with solution of ferrous sulphate (p. 472).

The great value of gold, and its perfect freedom from alteration by exposure to the atmosphere, have led to many devices for making the smallest quantity of the precious metal cover the greatest extent of surface, by taking advantage of its extreme malleability and ductility, in which it far surpasses all other metals.

Gold-beating.—Pure gold may be extended by hammering so as to present a surface 650,000 times as large as it originally possessed, but for this purpose it should be nearly pure gold, a very small quantity of some other metals materially injuring its malleability. Gold alloyed with copper or silver is, however, often beaten into moderately thin leaves, when a colour different from that of fine gold is required, but it is of course much more liable to tarnish. It has been shown that the presence of less than $\frac{2}{10}$ of one part of bismuth in 100 of gold suffices to lower the tensile strength of the metal from 7 tons to $\frac{1}{2}$ ton per square inch; and its extensibility under the load becomes so small as to be imperceptible. One quarter of one per cent. of lead reduces the tensile strength of the gold by nearly one half, and the elongation under load falls from 30 per cent. to 5 per cent. of the length of the bar.

Standard gold (alloyed with copper) has a tensile strength of 18 tons per square inch and a maximum elongation under load of 34 per cent.; but the addition of 3 gr. of lead to 1 lb. of the alloy may bring the tenacity down to 5 tons, and the extension to almost nil. Dentists' leaf gold for filling teeth is generally beaten from fine gold, because it is more easily pressed into a compact form.

The gold is melted in a crucible with a little borax, which prevents it from sticking to the crucible, and poured into a small cast-iron mould, warmed and slightly oiled, in which it forms an ingot of $\frac{3}{4}$ in. in width, and 2 oz. in weight. This ingot is annealed by burying it in hot ashes, and hammered upon a steel anvil until its thickness is reduced to $\frac{1}{8}$ in., the metal being once or twice re-heated or annealed during the process. The gold is then passed between perfectly cylindrical steel rollers, which are turned at exactly the same rate in opposite directions, until it is reduced to a riband so thin that a square inch of it weighs 6½ gr. It is of course necessary to anneal the gold several times during the rollings.

The riband is now exactly divided, with the help of a pair of compasses, and cut up into pieces of one inch square. One hundred and fifty of these pieces are piled up alternately with pieces of tough paper or vellum (prepared calf-skin) 4 in. square, rubbed over with a little fine plaster of Paris, to prevent the gold from sticking. Twenty vellums are placed above, and twenty below the pile, which is then firmly secured by passing two strong belts of parchment across it.

The beating is performed with a hammer weighing about 16 lb., having a circular face 4 in. in diameter and somewhat convex. The pile is placed upon a heavy block of marble, 9 in. square, sunk into a very strong wooden bench. The workman uses the hammer with one hand, directing the blows well in the middle of the pile, and turning it occasionally. After a time, the packet is opened, the middle leaves are shifted to the outside, and the beating is continued until the leaves have been extended to nearly the same size as the vellums. They are then taken out of the pile, and each leaf is cut with a sharp knife into four equal squares, which will measure about an inch each way. These are made into packets, as before, with *gold-beaters' skin*, a membrane which is separated from the outer surface of the intestines of the ox, and is prepared for use by hammering it between folds of paper in order to extract the grease, and steeping it in an infusion of nutmeg and cinnamon, in order to preserve it; it is then dried and rubbed over with plaster of Paris. The packets made up of gold-beaters' skin, with alternate layers of gold, are beaten as before, but with a ten-pound hammer, for about two hours, the packet being skilfully rolled and bent now and then, in order to loosen the leaves. When these are again extended to about 4 in. square, they are spread out upon a leathern cushion, and cut into four equal squares by applying a cross of cane cut to sharp edges, and fixed upon a board. These squares are again made up into packets with gold-beaters' skin, and hammered out a third time, with a seven-pound hammer, to about 3½ in. square. They are then dexterously lifted off the skin, with a delicate pair of wooden pincers, spread out upon a leathern cushion by blowing them flat down, and cut down to one size by a square of sharp-edged cane fixed to a board, and pressed upon the leaf of gold extended on the cushion. The gold leaves are then packed between the leaves of books made of printed paper, rubbed over with red chalk to prevent adhesion; there are usually twenty-five leaves in each book, their average thickness being $\frac{1}{282000}$ of an inch. Mechanical power has been lately substituted for manual labour in gold-beating.

When one of these leaves is held up to the light, it exhibits a beautiful green colour, and if it be rendered still thinner, either by beating, or by floating it upon a very weak solution of cyanide of potassium, which slowly dissolves it, it transmits, when taken upon a glass plate and held up to the light, a blue, violet, or red light, in proportion as its thickness diminishes. Even when it is so transparent that one may read through it, the yellow colour and lustre of the gold are still visible by reflected light. These varying colours of finely divided gold are turned to account in the colouring of glass and in painting on porcelain.

Gold thread is made by covering a cylinder of silver with gold leaf, and drawing it through a wire-drawing plate until it is reduced to the thinness of a hair. In this manner, one grain of gold may be made to cover 364 ft. of wire. For making gold lace, this wire is flattened by passing it between rollers, and is twisted by machinery round a thread of yellow silk, which is then made up into lace or braid.

Gilding.—The most obvious method of gilding consists in applying gold leaf to the object required to be covered, an art requiring great delicacy and skill.

Wash-Gilding was formerly effected by painting gold amalgam on the thoroughly cleansed surface to be coated, with the aid of a brass wire brush dipped in nitrate of mercury. The object so prepared was then heated over a charcoal fire, at the lowest possible temperature, until the mercury was volatilised. The gold was thus left on the surface, and was brightened by rubbing with a burnisher of polished hæmatite, wetted with water. Several curious processes, very difficult of explanation, were employed by persons experienced in the art of gilding, for giving the required shades of colour and degrees of lustre to the film of gold left by the mercury. One of these, intended to produce red gold, consists in coating it with *gilder's wax*, containing wax, red ochre, verdigris (acetate of copper), and alum. The object, having been coated with this composition, is strongly heated in the flame of a wood fire, quenched in water, and scrubbed with vinegar. This process probably reddens the gold by alloying it with a little copper from the verdigris.

Buttons, trinkets, &c., made of brass or copper, have been coated with gold by immersing them in a boiling alkaline solution containing that metal; 2,400 gr. of fine gold are dissolved in a mixture of 21 (avoirdupois) oz. of nitric acid (sp. gr. 1·45), 17 oz. of hydrochloric acid (sp. gr. 1·15), and 14 oz. of distilled water. This solution of (chloride of) gold is mixed with 4 gallons of distilled water, and 20 lb. of bicarbonate of potash, and boiled for two hours. The articles, having been thoroughly cleansed from oxide, are suspended from a hoop of brass or copper wire, and moved about in the boiling liquid until they are judged to have acquired a sufficient coating of gold, which is the case after less than a minute with small articles. The gold is deposited, in this process, in consequence of the copper taking its place in chemical combination in the liquid ; the film is bright and not dead as in the amalgamation process, but it could be deadened, if required, by dipping the articles in solution of nitrate of mercury before exposure to the gilding solution, when they would become coated with mercury, which would form an amalgam with the gold deposited from the solution, and this would be left as a dead film on expelling the mercury by heat.

Electro-gilding has now practically taken the place of all other methods for gilding metallic surfaces. It is effected, like the corresponding process of silvering (p. 457), by immersing the thoroughly cleansed articles to be gilded in an appropriate solution of gold, and connecting them by metallic wires with the zinc end of a galvanic battery of which the copper end is in metallic connection with a plate of gold, which is gradually dissolved, replacing the gold which has been deposited. The gilding bath is heated by steam to about 95° C., which facilitates the deposition of the metal. A solution for electro-gilding may be prepared by dissolving 1,550 gr. of gold in a mixture of 14 (avoirdupois) oz. of nitric acid (sp. gr. 1·45), 11 oz. of hydrochloric acid (sp. gr. 1·15), and 10 oz. of water. To this liquid, containing the chloride of gold, a solution of cyanide of potassium is added carefully, as long as any cyanide of gold is separated. This precipitate is allowed to settle, the clear liquid drawn off, and the precipitate redissolved in some more solution of cyanide of potassium. Enough water is then added to bring the solution up to five gallons.

In gilding polished iron and steel, they may be heated until they assume a blue tint, and successive coatings of gold leaf may be applied with a burnisher, a gentle heat being employed after every coating except the last, which is burnished cold.

MERCURY

THIS metal, also called *quicksilver*, is of very rare occurrence in Great Britain, the whole of the mercury employed in the arts being imported from Spain, California, Austria, Russia, Italy, and latterly also from Mexico and China, the largest quantity of the metal being now furnished by Spain. A considerable quantity is found in the metallic state, either collected in cavities, or disseminated in globules throughout its ore, *cinnabar*,[1] which has the same composition as *vermilion*,[2] being a compound of mercury with sulphur (HgS), containing, when pure, 86 parts of mercury in the hundred. Native mercury sometimes contains silver. Cinnabar is usually met with in moderately hard dark brown masses which are very heavy (sp. gr. 8·2), and exhibit a red colour when scraped with a knife. Some specimens have a red colour without scraping, and all yield a powder of a more or less bright red colour.

Native *calomel*, a combination of mercury with chlorine, is sometimes found in very small quantity associated with cinnabar.

The extraction of mercury from its ore is effected, like that of zinc, by distillation, but since this metal is converted into vapour at a much lower temperature than zinc (mercury boils at 357° C.), it requires much more elaborate arrangements for the condensation of its vapour into the liquid form, and

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[1] Derived immediately from the Latin *cinnabaris*, applied not only to this ore, but apparently also to red-lead, and to the red gum resin known as *dragon's blood*, from the Indian name of which, *cinoper*, the word appears to have originated.

[2] Probably from *vermeil*, French for red coral.

in many works a considerable quantity of the metal is wasted, on account of the imperfect character of the condensers, the escaping vapour proving most injurious to the health of the persons employed. Indeed, the metallurgy of mercury, in all its branches, is lamentably injurious to health, the miners as well as the smelters being liable to salivation, and seldom living to an old age.

In some of the earlier smelting processes, more than half the mercury contained in the ore was lost, partly owing to incomplete extraction, and partly through direct loss of reduced mercury, which either escaped as a vapour uncondensed, or found its way in the vaporous or the liquid form into the masonry of the furnace. Many tons of mercury have been recovered by breaking up and re-distilling the foundations of old furnaces. The uncondensed vapour discharged into the air has been so injurious in many districts that work had to be suspended for several months in the year. These older processes are here described at some length, on account of their historic interest, and because they illustrate the principles upon which the newer processes depend. In the modern plant described later on, nearly the whole of the mercury is recovered, so that poorer ores may be worked, greater economy is assured, and the works may be carried on throughout the year.

Extraction at Almaden.—The mines at Almaden, a town of La Mancha, in Spain, have been the most productive, the cinnabar being found in large veins surrounded by sandstone and clay slate. The mercury is extracted by simply roasting the ore, when the oxygen of the air converts the sulphur into sulphurous acid gas, and the mercury passes off in vapour.

The roasting-furnace formerly consisted of a fire-place in which a wood fire was maintained, the flame of which kindled the ore stacked upon an arch of fire-brick (c, fig. 108), provided with openings for the passage of the flame. Upon this arch some large blocks of sandstone, very

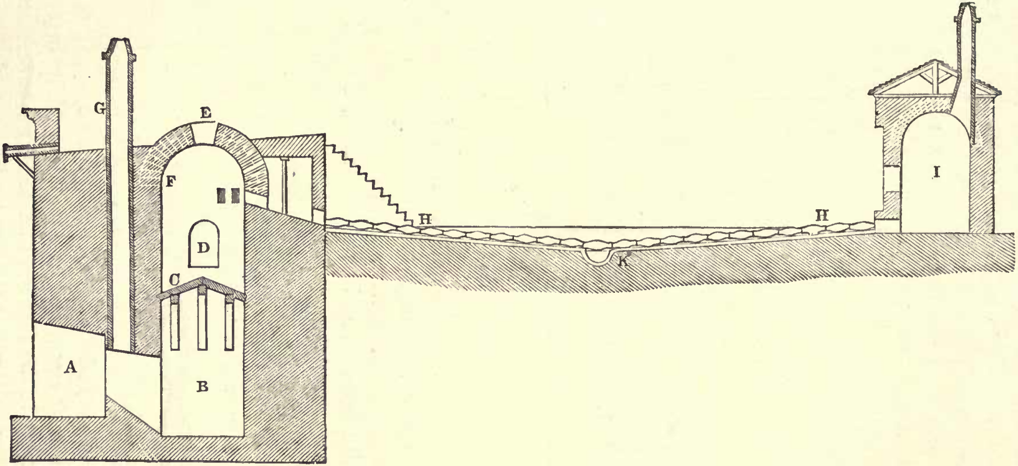

FIG. 108.—Aludel Furnace for the extraction of Mercury. A, Opening for charging the fuel. B, Fire-space. C, Arch for sustaining the ore. D, E, Openings for charging the ore. F, Chamber for receiving the ore. G, Chimney. H, H, Rows of aludels. . I, Condensing chamber. K, Gutter for mercury.

poor in cinnabar, were piled ; above these, small fragments of richer ores, over which again were placed the cakes made up by kneading with clay the finely divided mercury which has condensed from the fumes without running together into liquid metal, as well as any cinnabar that had escaped in vapour unchanged during a previous roasting, and had been condensed again as a black powder. The air, which entered through the openings in the brick arch, furnished oxygen to the sulphur of the sulphide of mercury, and converted it into sulphurous acid gas, whilst the mercury, which resembles gold and silver in being unable to combine with oxygen at high temperatures, was reduced to the metallic state, and converted into vapour, partly by the heat of the fire beneath, and partly by that produced in the combustion of the sulphur. The sulphurous acid gas and the vapour of mercury passed out through flues in the side of the furnace, into the condensing apparatus, which consisted of 300 pear-shaped stoneware pipes, called *aludels* (fig. 110), open at both ends, and fitted into each other, the joints being cemented together with clay. These were arranged so as to form twelve separate and parallel flues each composed of 25 aludels. The first 12 of each set nearest to the furnace, inclined downwards, towards a central gutter (K), whilst the last twelve ascended a corre-

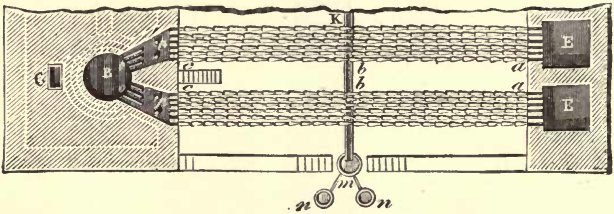

FIG. 109.—Plan of Aludel Furnace for extraction of Mercury.

FIG. 110.—Aludels.

sponding inclined plane, the centre aludel of the series being perforated in the lower side, so that the condensed mercury might run out into a gutter which conducted it into receiving basins underneath the furnace. The vapour of mercury that escaped condensation in the aludels passed, together with the sulphurous acid gas, into a chamber (I, fig. 108) in which a further considerable quantity of the mercury was condensed to the liquid state. The sulphurous acid gas eventually escaped through the chimney.

The imperfect character of this condensing apparatus is evident ; the loss of mercury vapour through the leakage of the numerous joints, and through the openings in the lowest aludels, was very great. Each roasting lasted about twelve hours, and the furnace required three or four days to cool before receiving a fresh charge, affording a striking contrast to the system of nearly continuous working adopted in the metallurgic processes of this country. The system has now been superseded, excepting in a few places where the old furnaces have been retained for the treatment of special material, such as mercury soot, made up into briquettes with clay.

Idrian Method of Extraction.—The mercury mines at Idria, in Austria, were formerly worked by State prisoners and criminals. In these mines the ore is found both in limestone and in a bituminous slate, and contains a considerable proportion of bituminous matter. Previously to the year 1794, the aludel furnace just described was also employed at Idria, but it was then superseded by a very large brick structure containing a series of condensing chambers. The roasting furnace (fig. 111) consisted of a grate upon which wood was burnt, surmounted by three perforated arches (B) of fire-brick, for receiving the ore, the large fragments being placed upon the lowest arch, the smaller pieces on the next, whilst the uppermost supported a number of shallow earthen dishes containing the dust of the ore and the mercurial soot from former operations. Air was admitted to the heated ore through small passages in the walls, and the sulphurous acid and vapour of mercury were drawn by the two chimneys through six condensing chambers (C, D, fig. 111) on each side of the furnace, so connected by narrow openings that the vapours were forced to pervade one chamber before entering another. In the final chamber (D) of each series, which was surmounted by the chimney, the last portions of mercury were condensed by a cascade of water. The greater portion of the mercury was condensed into the liquid form in the first three chambers of each series, and was collected in an underground gutter that conveyed it into a tank, from which it was ladled out to be filtered through cloth, and put into the wrought-iron bottles, containing about 76½ lb. each, in which it is imported to this country. The last three of each series of condensing chambers received the remainder of the mercury chiefly in the form of dust or soot, consisting of finely divided mercury, with some sulphide of mercury which had escaped in vapour, and some carbon from the bituminous matter in the ore. About a week was required to complete the distillation, including the time required for cooling the furnace. Only about 8½ pts. of mercury were obtained from 100 pts. of ore. In 1803, a fire broke out

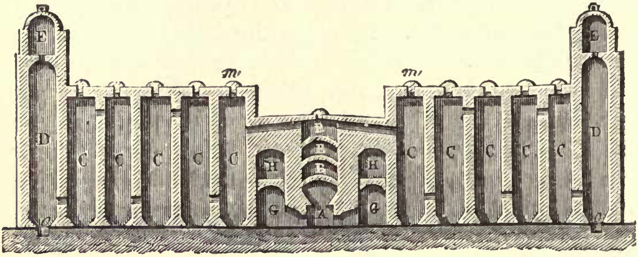

FIG. 111.—Section of Idrian Furnace and Condensing Chambers. A, Fireplace. B, Arches upon which the ore is placed. C, D, E, Condensing chambers. G, H, Air channels.

in the mines at Idria, and the combustion being maintained by the bituminous matter in the ore, it became necessary to flood the workings with water. The vapours of mercury evolved proved very injurious to the health of the neighbourhood.

A great advance was made by Alberti, who introduced at Idria a process for the treatment of ores containing $\frac{1}{100}$ or less of mercury, in which the ore was heated on the hearth of a reverberatory furnace (*a*, fig. 112), the mercurial vapour being passed — 1, through a condensing chamber (*d*); 2, through a wide sloping iron pipe (*f*) kept cool by the constant trickling of water over it, from the perforated gutter (*e*); 3, into a second condensing chamber (*g*); 4, through a second iron pipe (*h*), similar to the first, into a chimney (*k*). The hearth of the reverberatory furnace was divided into three compartments, the ore being first thrown, through a hopper (*b*), into that farthest from the grate, and being afterwards raked out into each of the other compartments in succession, so as to be exposed to a gradually increas-

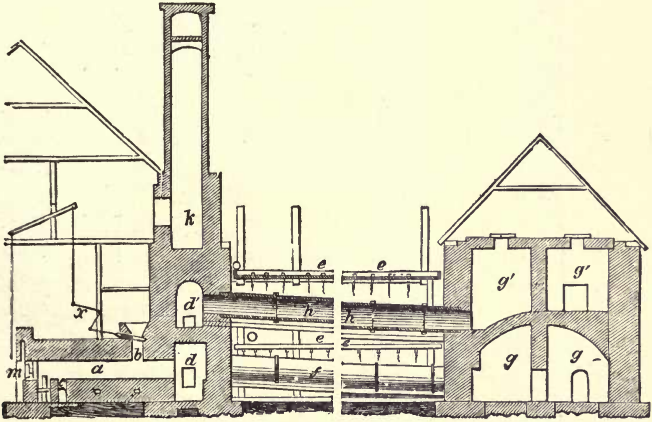

FIG. 112.—Alberti Mercury-furnace.

ing temperature until it was drawn out in a spent condition through a channel near the fire-bridge, whilst fresh ore was charged at the other end of the hearth. Wood was the fuel employed. Besides the liquid mercury which was run out into proper receptacles, a large proportion of mercurial soot, containing finely divided mercury, was collected in the condensing pipes and chambers. This was dried, raked over on an inclined plane as long as any mercury ran out, and afterwards distilled to obtain the last portions of the metal. This furnace was continuous instead of intermittent.

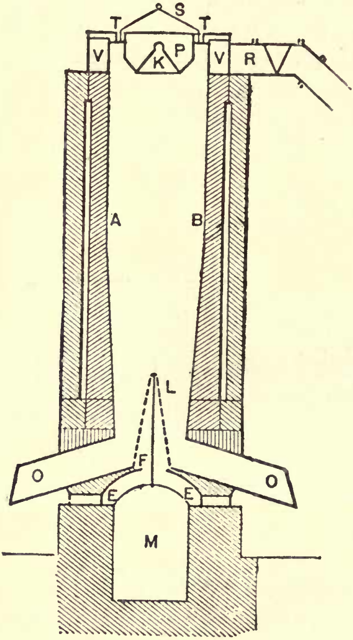

Fig. 113.—The Novak Furnace.

Modern Idrian Processes.—At the present time the rough lumps of ore, except those of the highest grade, are usually treated in small shaft-furnaces, resembling kilns, with a condensing plant attached; whilst the finer ore, which would choke the draught in a kiln, is treated in a reverberatory furnace. Of the former the *Novak* Furnace (fig. 113) is the latest type. It is a double-walled furnace of which the lining is of fire-brick. The outer shell is built of ordinary brick and is surrounded by a sheet- or cast-iron jacket, which serves to prevent the escape of vapour, whilst the whole shaft of the furnace rests upon a stout iron plate

F supported on the legs E, to check the escape of liquid (condensed) mercury into the foundations. The ore and fuel are charged intermittently through the bell mouth, which is covered with the bell K and a water-sealed lid S, when not in use. The air required for the combustion of the fuel is supplied through the perforations in L. The spent ore, which should contain less than 0·05 per cent. of mercury, is raked out in lump form through the side tubes O. The mercury vapour, ascending, passes into the annular cast-iron chamber V, and thence through two flues (R) side by side to the condensing plant.

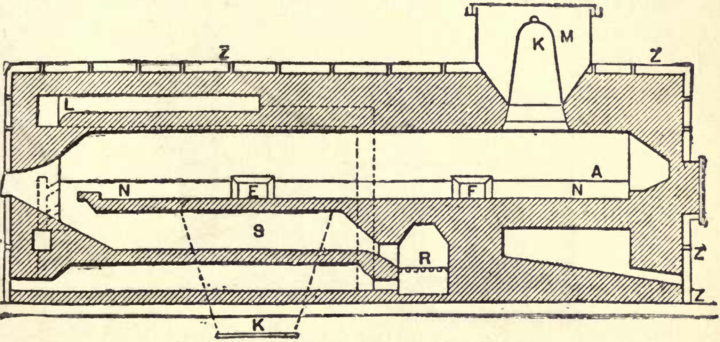

FIG. 114.—The Czermak Furnace.

The loss of mercury is said to amount to only 9 per cent. of the gross weight of mercury in the charge; and the operation of the furnace is so satisfactory that some thousands of tons of ore which had already been treated by old processes, have recently been re-worked with profit.

The *Czermak* reverberatory furnace (fig. 114), like the last described, is covered with and built upon iron plates (Z) to prevent loss of mercury. A fire of wood or brown coal is made upon the grate R, and the ore is charged through the hopper M, upon the hearth N, where it is gradually worked forward with the aid of tools introduced through the working doors E F, and is finally discharged through E into a receptacle K in front. The vaporised mercury, with the flue gases, passes through apertures into the flue L, and thence to the condensers. Czermak employs, in place of the ordinary brick condensing chambers, a series of vertical glazed earthenware pipes, connected alternately above and below, so that the gases pass through them upwards and downwards by turns. These pipes are cooled by a water spray, and at each lower joint have a tube prolongation dipping into a trough of water ; the tubes are open at the bottom, so that the condensed mercury may trickle down and collect in the troughs. Such a furnace is capable of treating about 32 tons of ore per diem, with a consumption of about 1,000 cb. ft. or $\frac{3}{4}$ ton of brown coal per ton of ore.

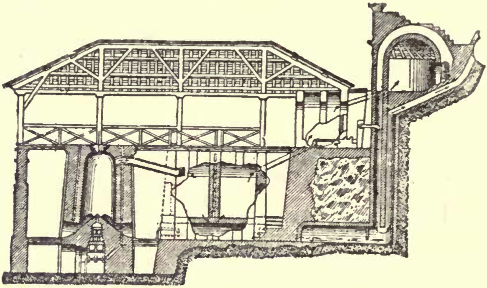

FIG. 115.—The Gascue-Rodriguez Furnace

Extraction of Mercury in Spain.—The older furnaces are now almost superseded by more economical arrangements. In one of these (the Livermore) the ore is heated to the roasting temperature as it passes over an inclined plane in a thin layer, where it is exposed to the products of combustion from a grate mixed with an excess of preheated air. The vapour is condensed in a series of masonry chambers. Another furnace in use is the *Gascue-Rodriguez* (fig. 115) : it is of the continuous type, like nearly all the modern forms of mercury plant. The ore is charged in lump form, mixed with about 0·5 per cent. of coke, into a conical shaft about 9 ft. high and 6 ft. 6 in. in diameter at the bottom, and 6 ft. at the top (internal measurement), the top of the shaft being closed as usual with a bell when not required to be open for the introduction of ore. Beneath the shaft is a grate, separated from it by a perforated dome, which allows the heated gaseous products to pass through the shaft; thence accompanied by the vapour of the reduced mercury they pass by an iron pipe to a series of four large brick condensing chambers, after which they are led to four smaller chambers of similar construction, placed at a higher level, and are then finally discharged into a lofty stack. In practice the grate is only used at the beginning of an operation. When the furnace is hot, the combustion of the coke in the charge and of the sulphur present in the ore renders the use of extra fuel unnecessary. The ores treated rarely contain on the average more than 0·75 per cent. of mercury; a considerable proportion of arsenic is also present, and this is for the most part recovered as arsenious acid in the condensing chambers. The furnace treats about 8½ tons of ore per diem with an average loss of about 3 per cent. of the mercury contained, and at an expenditure of about 11 lb. of coke per ton of ore. As in all shaft-furnaces, the bulk of the ore charged into the Gascue-Rodriguez furnace must be in the form of lumps.

Extraction in the Palatinate.—On the west bank of the Rhine there have been several small mercury mines which yielded sulphide of mercury associated with sandstone. These ores were made to yield their mercury by distilling them with lime, a process generally resorted to in the smaller mercury works. The distillation was effected in cast-iron pear-shaped vessels (A, fig. 116), thirty of which were heated by the same fire, in a *gallery furnace* (M), the grate of which ran through its entire length, and was fed with coal, which did not come into contact with the iron vessels, these being arranged in the upper part of the furnace, on each side of the grate, in two rows, one above the other, so that the flame might circulate around them before escaping through the openings into the chimney. The ground ore was mixed with about $\frac{1}{4}$ of its weight of quick-lime, and about 70 lb. of the mixture were introduced into each of the cast-iron bottles, which were then about $\frac{2}{3}$ full. The neck of each vessel fitted into a stone bottle (B) half full of water, placed outside the furnace, to receive the mercury. The water above the metal became filled with *black mercury* containing undecomposed sulphide and finely divided mercury; this was dried and distilled again with more lime.

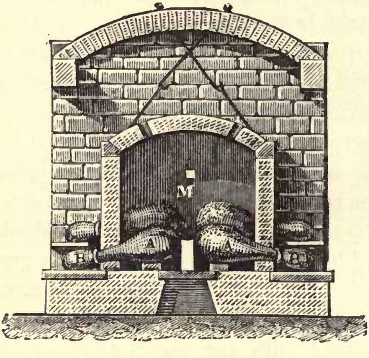

FIG. 116.—Extraction of Mercury in the Palatinate.

Extraction in Mexico.—In Mexico a gallery furnace was at one time very largely employed, and is still used at some of the mines; the furnaces are very crude erections, the retorts are made locally of fire-clay, about $2\frac{1}{2}$ ft. long by 9 in. in diameter, and tapering towards the neck; twelve are placed back to back in each furnace, with fire-clay condensers of similar shape but shorter. The charge amounts to about 12 to 25 lb. per retort, according to the grade of the ore, and is sometimes mixed with $\frac{1}{10}$ to $\frac{1}{5}$ of its weight of lime. The poorer ore is used in heavier charges. The time required for the distillation ranges from $\frac{1}{2}$ to 12 hours according to the nature of the ore. The mercury in the condenser is mixed with a black mud consisting mainly of finely divided mercury. This is separated from the fluid parts by filtration through cloth, and the mud is re-distilled, While the condenser is being cleansed, the residue is scraped out from the retort, which is then ready for charging again. The loss of mercury amounts usually to 50 to 60 per cent. of that originally present in the ore.

The Scott and Huttner furnace has also been employed in Mexico. It consists of a tall shaft, with zigzag shelves, so arranged that the ore passes from side to side on its path from the top to the bottom, and meets with hot gases from furnaces on either side. The Mactear muffle furnace has more recently been introduced for comparatively rich ore with excellent results. The ore is spread to an average depth of nearly 3 in. over the bed of a muffle about 20 ft. long by 9 to 12 ft. wide, heated by two fire-places, from which the flame plays over the top of the muffle, and thence the hot products of combustion are led to six flues running beneath the muffles. The ore is introduced, if necessary, mixed with lime, and worked through doors opening into the ends of the muffle; and the gases and vapour from within the muffle (which are of course unmixed with ordinary furnace gases) are led to a series of vertical condensers of the Czermak type. With such a furnace, about twelve tons of ore can be treated in a day with a loss of about 7 to 10 lb. of mercury per ton of ore treated.

In these processes, the lime, when used, reacts with the sulphide of mercury, yielding sulphide of calcium, which remains in the iron bottle, mercury which passes over in vapour, and oxygen which converts a part of the sulphide of calcium into sulphate of lime.

Ure's Retort Furnace.—The operation in the gallery furnace is obviously attended with waste and inconvenience. The trouble of charging and discharging so many small bottles and of cementing the joints is very considerable, and led to the introduction, in some places, of cast-iron retorts (*a*, fig. 117) resembling those used in distilling coal for gas. They were about 7 ft. long and 1 ft. square in sectional area, so that they might be charged with 700 lb. (instead of 70 lb.) of the mixture of the ground cinnabar with lime, introduced at the back of the retort, which was then closed with an iron plate. The front end was also closed with an iron plate, which was provided with a sloping cast-iron pipe (*b*), 4 in. in diameter, having a door through which it could be cleared with a wire. This pipe dipped into water contained in a condenser (*c*) resembling the *hydraulic main* of the gas works, being an iron pipe, 18 in. wide, and 20 ft. long, which ran along the front of the range of retorts, and received the mercury condensed from them, being itself kept cool by a stream of water running through a wooden trough around it.

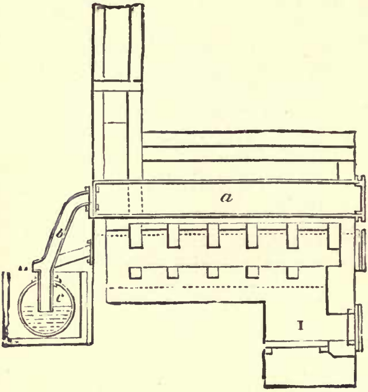

FIG. 117.—Ure's Retort for extraction of Mercury from Cinnabar.

Extraction in Hungary.—In Hungary, a considerable quantity of mercury is extracted from the grey copper ore (*Fahl-erz*) during the process of roasting preliminary to the smelting for copper. The roasting is effected by burning the ore in mounds about 40 by 20 ft., and 4½ ft. high, in which channels are constructed for the admission of a moderate supply of air. A layer of small ore having been spread upon the ground, and covered with some larger pieces of ore already once roasted, some wood and coal are spread over them, then a layer of ore, the outside being covered with powdered ore so as to prevent a too free passage of air, and to retain the vapour of mercury. The heap is kindled through shafts left for the purpose, when the heat evolved by the combustion of the wood and coal ignites the sulphur of the ore, which burns away as sulphurous acid, whilst the mercury is converted into vapour and condensed among the cooler portions of the fine ore on the outside of the heap. After about three weeks, the upper layers are thrown upon a sieve and washed with water, the fine ore which passes through the sieve being separated from the mercury by washing.

The Purification of Mercury.—The mercury imported into this country generally contains lead, bismuth, and zinc as impurities, which cause globules of it to *tail* or leave a metallic streak behind them when rolled over a glass plate, whilst pure mercury runs off in globules, leaving the glass clean.

It may be purified by pouring it into a wide dish (such as a photographic tray), where it may form a thin layer, and covering its surface with diluted nitric acid (sp. gr. 1·15). The acid is allowed to remain in contact with it for a day or two, being frequently stirred, until the mercury no longer tails upon glass. The lead, bismuth, and zinc are dissolved by the acid, in the form of nitrates, together with a portion of the mercury, so that the acid should be preserved in order to assist in the purification of another portion of the metal. Proto-nitrate of mercury may be substituted for nitric acid in this process, the baser metals contained in the quicksilver exchanging places with the mercury in the solution ; so that ultimately a solution of the metallic impurities results, and an equivalent quantity of mercury becomes added to the metal undergoing purification. The mercury may be separated from the acid or nitrate solution by pouring them both into a funnel stopped with the finger, on removing which the mercury runs off, the finger being replaced to retain the acid ; the mercury is then well washed with water in a dish, and dried, first with blotting-paper, and afterwards at a gentle heat. Any dust or other mechanical impurities may be easily removed by filtering the mercury through a cone of writing-paper, in the apex of which a few pin-holes have been made.

An old and simple process for the purification of a small quantity of mercury consists in shaking it in a bottle with air and a little powdered sugar, which helps to divide the mercury and expose the lead, &c., to the action of the air, which converts them into a grey powder. By repeating the agitation with fresh portions of air, nearly all the foreign metals may be removed, and the sugar with the adhering oxides may be separated by filtering through pricked paper. The same result may be attained by blowing a current of air through the impure mercury for a lengthened period.

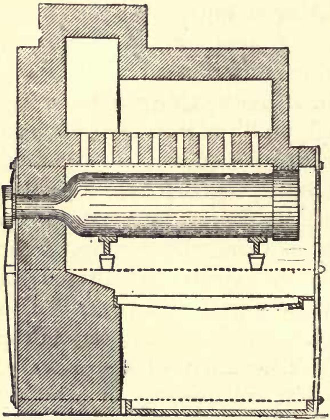
FIG. 118.—Amalgam Retort.

But these methods can only effect the removal of metals which are more oxidisable than mercury. Squeezing the amalgam through wash-leather or canvas may remove the greater portion of the gold or silver. But the only way to obtain perfectly pure mercury is to distil it. Even distillation, however, may fail, if conducted in ordinary retorts, because the metal is liable to boil with sudden more or less violent concussions (*bumping*), that may cause some of the impure mercury to be carried over mechanically with the vapour, whilst traces of volatile metals like cadmium or zinc distil with the mercury. But by hermetically closing all apertures in the retort and receiver excepting one, which is connected with a mercurial air-pump, the distillation may be conducted *in vacuo*, when it will proceed quite quietly, and at a temperature so greatly reduced that only the merest traces of the other volatile metals accompany the mercury vapour, and these can afterwards be removed from the condensed mercury, if necessary, by treatment with acid.

It has already been explained that in the amalgamation process mercury is separated from gold and silver by distillation. Fig. 118 shows the retort referred to on p. 446 as being in common use in silver mills. It is also employed in many of the larger gold mills. The figure shows the manner of supporting the cast-iron retort above the grate. The products of combustion pass around the retort and then through channels in the roof to the flue above. The amalgam is placed on trays introduced through the wide end of the retort, which is then closed by a tight-fitting lid; and the condenser for the mercury vapour is attached to the narrow end.

Uses of Mercury.—Many of the useful applications of mercury depend upon its being the heaviest substance that is liquid at the ordinary temperature. Its specific gravity being 13·54, a column of mercury 30 in. high serves, in the barometer, to measure the pressure of the atmosphere, whilst 33 ft. (396 in.) of water are required for the same purpose.

The great interval between the temperature at which mercury congeals to the solid state (39° below the freezing-point of water) and that at which it boils (257° above the boiling-point of water) renders it especially suitable for filling thermometers, an application for which it is also recommended by the circumstance that it has a very low *specific heat*, or requires much less heat to raise it to a given temperature than most other liquids which could be employed for thermometric purposes: thus, a spirit thermometer, in which alcohol is used to show the expansion, rises and falls much more slowly than the mercurial thermometer, because the specific heat of alcohol is 15 times as great as that of mercury; in other words, fifteen seconds would be required by a spirit-thermometer to measure a temperature which would be indicated in one second by a mercurial thermometer of the same weight. A further advantage on the side of mercury is derived from its not adhering to the glass. Moreover, in a spirit-thermometer, the indications are affected by the presence of the vapour of alcohol in the space above the column, which should be perfectly vacuous, and is nearly so in the case of the mercurial thermometer, for the metal does not evolve an appreciable amount of vapour at temperatures below the boiling-point of water.

That mercury does give off a little vapour, even at the ordinary temperature, is shown by the appearance of minute globules of metal condensed, in cold weather, upon the glass in the upper part of a barometer, and by the experiment of suspending a gold leaf at the height of an inch or two above the surface of mercury in a bottle, when it is found, after some time, to be whitened by the combination of mercury vapour with the gold.

Mercury is remarkable for its property of uniting with other metals at the ordinary temperature, to form combinations which are termed *amalgams.* Iron and platinum are the only metals in ordinary use which are not attacked by mercury ; and even these may be made to yield amalgams by suitable treatment. It adheres to platinum and wets its surface, but does not unite chemically with it. Gold is soon penetrated by mercury, and becomes very brittle. The surface of a gold ring, for instance, is instantly whitened by mercury, and if allowed to remain in contact with it for a short time, the gold is rendered so brittle as to be useless ; a mere external coating of amalgam may be removed, and the colour of the gold restored, by warming it with a little nitric acid, the surface of the gold being afterwards burnished.

Silvering Looking-glasses.—An amalgam of tin is still often employed for silvering the backs of looking-glasses, which is performed in the following manner. A sheet of tin-foil (generally hardened by a minute proportion of copper), somewhat larger than the plate to be silvered, is laid upon a stone or marble table, which is swung upon an axis, so that it may be gradually sloped by a screw when required. The upper surface of this table is perfectly smooth and level, and has a gutter running round it, with a spout for collecting the superfluous mercury. The tin-foil is applied to the table with a brush, so that it may be free from wrinkles, and the surface having been laid truly horizontal, a little mercury is spread over it with a roll of flannel, so that every part of the tin-foil may be amalgamated. A very thin layer of mercury is then poured over the surface, and the edge of the clean dry plate to be silvered is very carefully pushed forward over the table, so as to carry the superfluous mercury before it, and to prevent any air from entering between the amalgam and the glass. Some flannel is placed on the glass, with a weight upon it, and the table is very slightly inclined to drain off the excess of mercury. After about five minutes, the plate is loaded with several heavy weights, and allowed to remain for twenty-four hours, in order that the amalgam may be made to adhere firmly to the glass ; the inclination of the table is somewhat increased from time to time, to promote the draining away of the excess of mercury. When the weights are removed, the plate is laid upon a sloping wooden table, the upper edge of which is raised gradually by a pulley until the plate is perpendicular. After three or four weeks, when the excess of mercury has drained off, the looking-glass is ready for framing. The amalgam adhering to the glass contains one part of mercury and four parts of tin.

Amalgams.—The amalgam which is employed to promote the action of glass-frictional electrical machines is composed of two parts of zinc and five parts of mercury.

Magnetic amalgam is the fanciful name at one time bestowed upon the amalgam of one part of metallic sodium with thirty parts of mercury, which is liquid at a very moderate heat, but solidifies on cooling to a hard crystalline mass. It is cast into ingots which are kept in air-tight iron vessels with lime, to absorb any moisture, which would act upon the sodium in the amalgam and convert it into soda. This amalgam is sometimes used in the amalgamating mills for gold and silver ores, to facilitate the amalgamation and prevent *flouring* (p. 443).

Amalgams, generally, may be made either by dissolving the metal directly in mercury, or by chemical means. This latter may be effected by the action of a baser metal upon a solution of mercury; zinc, for example, placed in a solution of proto-nitrate of mercury, forms nitrate of zinc, and displaces an equivalent proportion of mercury, which then amalgamates with the residual zinc, forming zinc amalgam. Or metallic mercury may be placed in a solution of a metal less chemically active than itself; thus, mercury, placed in a solution of silver or gold, exchanges places with the precious metals, some of the mercury dissolving in the liquid, whilst the separated silver or gold dissolves in the remaining mercury. Another method, equally applicable to all metals, is to place metallic mercury in a solution of the other metal, and to pass a sufficiently strong galvanic current through the solution to decompose it by electrolysis, taking care that the mercury itself is connected to the negative pole of the battery or dynamo, and that the other plate or anode, by which the current enters the solution, is made either of the metal of which the latter is composed, or of a substance which will not dissolve in it at all. The metal is thus deposited by the action of the current in intimate contact with the surface of the mercury, by which it is at once absorbed. Even sodium amalgam may thus be made from a solution of sodium carbonate. The metals are, however, most usually amalgamated by the direct method.

One of the principal uses of amalgams is the preparation of fillings for teeth. These usually contain silver and tin, often with gold, platinum, or copper in addition.

PLATINUM

THIS valuable metal has been brought into use in quite modern times. Its existence was known early in the sixteenth century; and it was re-discovered by an assayer in New Granada in 1735, and was introduced into Europe in 1748. Its name, derived from the Spanish, signifies *little silver*, since it somewhat resembles that metal in colour; it has also been called *white gold*, and it is said that when first discovered, much of it was thrown away, lest, from its durability and high specific gravity, it should be employed for debasing gold.

Platinum always occurs, like gold, in the metallic state, and most commonly in alluvial deposits in which gold is also present. Nuggets of platinum have rarely been found, the largest on record being one of 21 lb. weight. The metal is commonly met with in flattened grains of a light steel-grey colour. The Ural mountains have furnished the largest quantity of platinum, but it has also been obtained from Brazil, Borneo, and Australia, and in small quantities from the United States. A mineral containing over 50 per cent. of platinum, combined with about 40 per cent. of arsenic, as an arsenide, was found in small quantity in 1888, with a nickel deposit, near Sudbury in Canada. It has received the name *Sperrylite.*

The (native) *Platinum ore*, as it is called, is separated from the earthy matters by washing the latter away, when the grains of platinum remain behind with grains of gold, magnetic iron ore, corundum, and a very heavy alloy of osmium and iridium. The platinum itself is far from pure, containing only from 75 to 85 per cent. of that metal, the remainder consisting of iron, sometimes found to the amount of 13 per cent., iridium, rhodium, palladium, osmium, and copper. When any considerable quantity of gold dust is present, it is separated from the platinum by the process of amalgamation. The magnetic iron ore is extracted by a magnet.

Wollaston's Extraction Process. — The grains of platinum ore are heated with nitric acid which dissolves any silver, copper, iron, and lead, in the form of nitrates; after these have been extracted, the residue is washed with water, and heated with hydrochloric acid, which dissolves the magnetic oxide of iron; it is then again washed with water, and gently heated for several hours with hydrochloric acid to which a little nitric acid is added from time to time. The platinum is thus dissolved, together with palladium, rhodium, and some iridium, whilst the osmium and the rest of the iridium are left undissolved. The acid solution containing the chlorides of platinum, &c., is poured off, and the residue heated with fresh portions of acid as long as anything is dissolved, when any quartz and corundum are left, together with the grains of the alloy of osmium and iridium. These grains are employed, on account of their surpassing all other metallic substances in hardness, in making the nibs of gold pens upon the points of which they are soldered.

The liquid containing the chloride of platinum is mixed with a solution of sal-ammoniac (chloride of ammonium) containing $\frac{1}{6}$ of its weight of the salt, of which about 4 pts. are employed for every 10 pts. of the ore. A yellow precipitate is then deposited, which contains the greater part of the platinum, in the form of *ammonio-chloride of platinum*, a combination of the chlorides of ammonium and platinum.

This yellow precipitate is washed with cold water, dried, and strongly heated in a plumbago crucible, when the sal-ammoniac and the chlorine are driven off, and *spongy platinum* is left as a grey porous mass. This is finely powdered in a wooden mortar, or, better, between the hands, rubbed to a paste with water, passed through a sieve in order to render it perfectly uniform, and poured into a slightly conical brass mould closed below with blotting-paper wrapped round a steel stopper. When the water has drained off, a plunger is forced in by a coining press, so as to condense the mass, which has at first the specific gravity 4·3, until its specific gravity is 10, when it will have been reduced to about $\frac{2}{5}$ of its former bulk, and have acquired a metallic appearance. The disk is now sufficiently coherent to be removed from the mould and is intensely heated for about 36 hours in a porcelain kiln, when it contracts to about $\frac{4}{5}$ of its former volume. It is taken out of the furnace at a white heat, and hammered upon its ends, not upon the sides, lest it should crack. After being heated and hammered in this way several times, the particles become thoroughly welded together into a compact malleable mass of metal, of specific gravity 21·5.

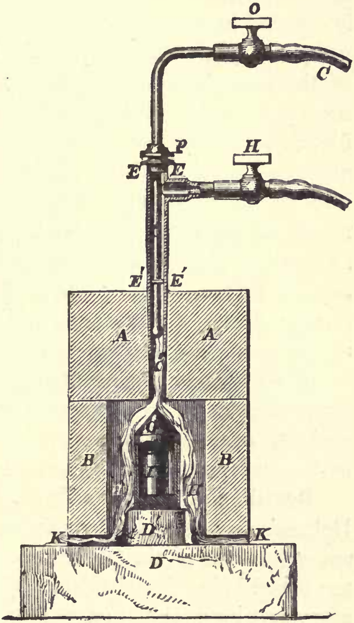

FIG. 119.—Platinum melted in Crucible by the Oxy-hydrogen Blowpipe.

Instead of welding the platinum into a compact mass, it may be melted in a crucible by the intense heat of the oxygen-coal-gas or oxy-hydrogen blowpipe-flame, a temperature of 1775° C. being necessary for the purpose. The crucible is made of gas-carbon, and is enclosed in another crucible (I, fig. 119) made of lime, and provided with a conical cover (G) of the same material. The furnace is made of three blocks of lime strengthened by iron wire, one (D) serving for the hearth, upon which is placed a hollow cylinder (B) of lime, which has been bored in the lathe until it is wide enough to leave a clear space (H) of about $\frac{1}{6}$ in. round the lime crucible. At the lower part of this cylinder are four openings (K) for the escape of the steam produced in the combustion of the hydrogen and oxygen. The furnace is covered in with a block of lime (A) about 2½ in. thick, in which a slightly conical passage is bored for the reception of the blowpipe-jet which passes down to within an inch of the apex of the conical cover of the lime crucible. The blowpipe (E) consists of two concentric copper tubes, the outer one through which the hydrogen is passed being about ½ in. in diameter, and terminating in a somewhat tapering nozzle of platinum (C) about 1½ in. long, which fits into the conical passage through the upper block of lime. The oxygen is conveyed through the inner copper tube, also furnished with a platinum nozzle, the opening of which is about $\frac{1}{10}$ in. in diameter.

The hydrogen and oxygen are supplied from their respective gas-holders, their passage being regulated by the stopcocks H, O, under a pressure of about 16 in. of water, the hydrogen being lighted before the oxygen is turned on.

Deville and Debray's Extraction Process.—Deville and Debray's process for extracting platinum from its ores resembles one of the methods of extracting gold and silver, the metal being dissolved out by melted lead and afterwards recovered by cupellation.

2 cwt. of the platinum ore mixed with an equal weight of galena (sulphide of lead) is thrown, in small portions, into the concave hearth of a small reverberatory furnace built of fire-brick. The materials are stirred with an iron rod until the platinum has entirely dissolved in the fused galena. A little glass is then introduced, to melt over the surface, and a quantity of litharge (oxide of lead) equal in weight

to the galena is gradually added. The sulphur in the sulphide combines with the oxygen of the oxide, and passes off as sulphurous acid gas, leaving the metallic lead in combination with the platinum, whilst the alloy of osmium and iridium, being unaffected by the lead, sinks, in separate grains, to the bottom (its specific gravity varying, according to its composition, from 19·4 to 21·1). After remaining at rest for some time, the upper portions are ladled out and cast into ingots, and the remainder is added to the next charge.

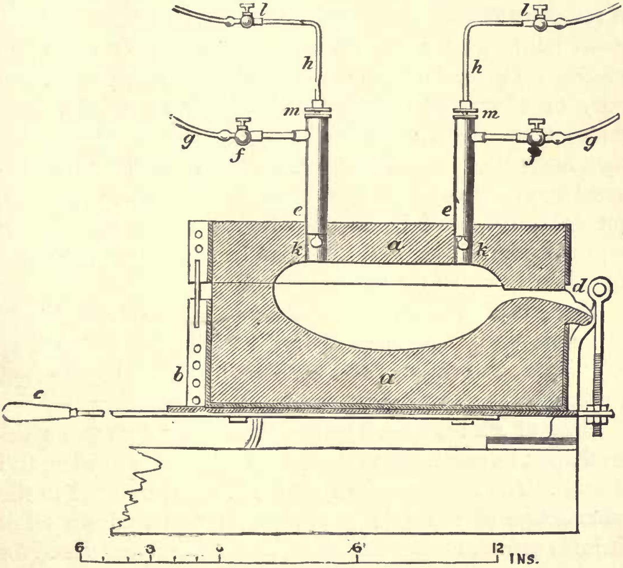

FIG. 120.—Lime Furnace for melting Platinum with the Oxy-hydrogen Blowpipe. *a a*, Blocks of lime hollowed out to form the furnace. *k k*, Openings for the oxy-hydrogen blowpipes. *e e*, Outer tubes conveying the hydrogen or coal-gas. *h h*, Inner tubes conveying the oxygen. *d*, Spout for pouring the melted platinum.

The lead containing platinum is treated in a cupellation furnace (p. 426), when the lead is removed as an oxide, leaving the platinum in a spongy state upon the cupel, whence it is transferred to a small furnace made of lime (fig. 120) and melted by the flame of the oxy-hydrogen blowpipe (coal-gas may be substituted for hydrogen), the intense heat of which volatilises any silver, gold, lead, palladium, and osmium. When the metal is sufficiently refined, it is poured through an opening in the side of the furnace into an ingot mould made of gas-carbon or of wrought iron lined with platinum. In this manner, 25 lb. of platinum have been melted and refined in three-quarters of an hour, with a consumption of about 43 cb. ft. of oxygen. The melted platinum resembles silver in its property of absorbing oxygen mechanically at a high temperature and evolving it again as it cools, exhibiting the phenomenon of *sprouting* (p. 429). The platinum so prepared may contain traces of iridium, rhodium, and palladium, but is usually sufficiently pure for general purposes. If required perfectly pure, it is re-dissolved in fused lead, and the alloy is treated by a chemical process.

Since platinum is one of the most malleable and ductile of the metals, being surpassed, in the former quality, only by gold, silver, and copper, and in the latter by gold and silver, it is easily rolled into sheets or drawn into wire.

Uses of Platinum.—The principal uses of platinum depend upon its resistance to the action of heat, of oxygen, and of acids. The largest quantity of the metal is devoted to the manufacture of the stills employed for boiling down oil of vitriol in order to expel the water, and of the siphons used for drawing the hot acid out of the stills. Similar stills are often employed in the operation of parting gold and silver with sulphuric acid (p. 480). The joints of these stills are soldered with fine gold, and they are usually gilded inside, for otherwise they are liable to become porous under the influence of the boiling acid, allowing it to exude. They are protected from external injury and from the direct action of the fuel by an iron casing. Some platinum stills have been made weighing upwards of 60 lb. and costing above 2,000*l.* They are slowly corroded by the action of the acid, and require occasional repair by soldering them with gold.

Platinum is also much employed for evaporating basins and crucibles for chemical purposes, and thin foil and wire of this metal are indispensable in operations with the blowpipe. When the particles of the metal have been imperfectly consolidated by hammering, it is found to blister under the influence of a very high temperature. The permanence of platinum under the action of heat has led some persons to adopt an erroneous estimate of its durability under other conditions, so that it is often forgotten that platinum is a soft metal and therefore ill-adapted to resist ordinary wear. It is easily corroded and rendered brittle by carbon and silicon, for which reason platinum crucibles are never allowed to come into direct contact with solid fuel, but are heated either in the flame of a gas or spirit lamp, or in a muffle (p. 489), or enclosed in a clay crucible lined with magnesia to prevent the platinum from sticking to the heated clay.

Metals must never be melted in platinum crucibles, since most of the metals are capable of forming alloys with it ; and for the same reasons, easily reducible metallic oxides, or compounds containing arsenic or phosphoric acids, should not be melted in contact with platinum. Caustic alkalies and saltpetre in a melted state also act upon the metal, and phosphorus and arsenic combine with and corrode it very rapidly at moderately high temperatures.

Neither sulphuric, hydrochloric, nitric, or hydrofluoric acid separately has any action upon platinum, but a mixture of hydrochloric with nitric acid dissolves it, though more slowly than it dissolves gold.

An alloy of platinum, iridium, and rhodium is sometimes employed for crucibles, which are harder and less easily corroded than those made of pure platinum. To obtain the alloy, an ore of platinum containing the other two metals is mixed with a quantity of lime equal to that of the iron contained in the ore, and fused by the oxy-hydrogen blowpipe in a furnace made of lime (p. 519). The iron and copper are converted into oxides which form a fusible slag with the lime, whilst the gold, palladium, and osmium are expelled in the form of vapour, and the alloy of platinum, iridium, and rhodium remains.

Small tubes, &c., may be easily extemporised with platinum wire and foil, by taking advantage of the readiness with which surfaces of this metal unite when hammered at a high temperature.

Platinum vessels are cleaned by smearing them with a paste containing equal bulks of borax and cream of tartar with a little water, drying and heating them till the mixture melts, and immersing them for several hours in diluted sulphuric acid. Heating in contact with fused bisulphate of potash, or with powdered sal-ammoniac, is also employed for the same purpose. The platinum vessels are finally well washed with water and burnished with agate.

The circumstance that platinum expands less than any other metal when heated, enables it to be cemented into some kinds of glass, by fusing the latter, whilst other metals which differ much from glass in their rate of expansion by heat, would crack it as they cool. This renders platinum of great importance in the fabrication of various philosophical instruments.

Though pure platinum is unaffected by nitric acid, it may be rendered soluble in that acid by previously alloying it with ten or twelve times its weight of silver; this method is used when it is required to separate platinum from gold in the process of assaying the latter metal, with which platinum is frequently associated. If the platinum be present in small proportion (not exceeding 3 or 4 per cent.) in the alloy of gold and silver obtained by cupellation (p. 425), the whole of it will be dissolved together with the silver, in parting by nitric acid; but when the quantity of platinum is larger, which is indicated by the difficult fusibility of the button on the cupel, and by the blanched appearance of the gold eventually obtained, the latter must be again fused with at least three times its weight of pure silver, the alloy rolled very thin, and boiled for half an hour, and a quarter of an hour, respectively, with the two strengths of nitric acid mentioned at page 489, in order to remove the whole of the silver and platinum. An alloy of silver with one-third of its weight of platinum is employed by dentists on account of its great elasticity. Platinum surfaces are united either by welding or soldering. For the latter purpose gold is generally used; but the arsenide of platinum is sometimes substituted for it. This compound fuses at a sufficiently low temperature to enable it to be melted with the aid of a good blowpipe. The arsenic may afterwards be expelled by prolonged heating at a high temperature.

The remarkable property of platinum, especially in the finely divided states of spongy platinum and platinum black, of condensing gases into its pores and thus promoting their chemical action upon each other, has been utilised in the manufacture of anhydrous sulphuric acid.

IRIDIUM

Iridium is a metal resembling platinum in most of its properties, but it has a somewhat higher specific gravity (22·4) and fusing-point (2500 C.). It occurs in nature associated with platinum, and commonly as a finely divided, granular, and intensely hard alloy with osmium, that is generally known as *osmiridium* or *iridosmine.* The granules of this alloy are so hard that they cannot be crushed, and they are insoluble even in aqua regia. In order to extract the iridium from the alloy, the latter is fused with about five times its weight of zinc, which is then volatilised at a high temperature, leaving the osmiridium in the form of a thin skeleton, which may be crushed and sifted through fine lawn. The powder is mixed with barium peroxide in the proportion of 1 to 5, and heated to a full red heat for an hour.

On boiling the mass with aqua regia (3 parts of hydrochloric to 1 of nitric acid), the osmium is converted into osmium peroxide (OsO_4), which is very volatile, and passes off as a pungent and poisonous vapour at 100° C., the iridium remaining in the solution, from which it may be separated as an insoluble double chloride on the addition of chloride of potassium, the barium having been removed previously by the addition of exactly the right quantity of sulphuric acid. The iridium extracted from the chloride may still contain a little ruthenium and platinum.

The principal use for osmiridium grains is in the formation of the points of gold pens, for which its extreme hardness and durability render it especially suitable. Its very great hardness, coupled with its infusibility, render it exceedingly difficult to work, and only grains which are naturally of the right size can be used. A compound of iridium with about 7 per cent. of phosphorus, and known as phospho-iridium, is now largely used in its stead. The compound may be obtained by heating osmiridium with an excess of phosphorus, and as it fuses at a white heat, it may readily be prepared in grains of the desired size, which, in respect of hardness, are scarcely inferior to those of osmiridium itself.

Platin-iridium, containing from 10 to 20 per cent. of iridium, is employed in making standard weights.

PALLADIUM

Palladium is generally found in small quantity, not exceeding 1 per cent., associated with the ore of platinum, from which it is extracted by a process which is purely chemical. Formerly there existed a pretty abundant source of this metal in the form of an alloy with gold found in the mines of Brazil, but of late years this has failed, and palladium has risen to an extremely high price. In appearance it resembles platinum, but it is much harder, though it possesses considerable malleability and ductility. It is quite unchanged by air at the ordinary temperature, but assumes a bluish colour, from the formation of a thin film of oxide, at a moderately high temperature, becoming bright again at a higher temperature, the oxide being decomposed. It dissolves in nitric acid, giving a yellowish solution. Palladium fuses at a somewhat lower temperature than platinum, but cannot be fused in an ordinary furnace. It is only half as heavy as platinum, its specific gravity being 11·5, so that it would be much better adapted for making very accurate balances and other philosophical apparatus.

ANTIMONY

THOUGH antimony is far too brittle to be employed in its pure state for any useful purpose, it is of great service in hardening the softer metals, lead and tin.

Ores of Antimony.—Antimony is occasionally found in Nature in the metallic state, as at Andreasberg in the Hartz, where it is alloyed with small quantities of silver, iron, and arsenic. The only ore from which it is largely extracted is *Antimony glance*, *grey antimony ore*, or *stibnite* (Sb_2S_3), a sulphide of antimony, containing, when pure, 71¾ per cent. of antimony and 28¼ per cent. of sulphur. It is found chiefly in France, Australia, Japan, Italy, Austria-Hungary, the United States, and Borneo, often associated with galena and iron pyrites, and with quartz and heavy spar, in veins traversing rocks of granite or slate. The appearance of grey antimony ore is very characteristic; it commonly resembles a compact bundle of dark grey metallic needles converging towards one point, and often exhibiting a blue iridescence due to a thin film of oxide. It is very heavy (sp. gr. 4·63), and melts easily even in the flame of a candle. The fusibility of sulphide of antimony is taken advantage of in order to separate it from the gangue. The ore is heated on the concave hearth of a reverberatory furnace, the hearth being lined with charcoal to prevent oxidation of the sulphide, which melts and is run out into moulds, where it is cast into the form of the cakes sent into commerce as *crude antimony*, which contains, in addition to the sulphide of antimony, sulphides of arsenic, iron, and lead.

The *oxide of antimony*, senarmontite (Sb_2O_3), occurs in Algiers, and is smelted in France.

Red antimony, a compound of oxide and sulphide of antimony, is found in Tuscany, and smelted at Marseilles.

English Process of Smelting.—In England, the *regulus of antimony*, or metallic antimony, is extracted from the sulphides by melting the ore in crucibles with metallic iron, which takes the sulphur from the antimony, forming sulphide of iron, and leaving an impure metallic antimony which is afterwards refined.

The crucibles are charged with a mixture of about 42 lb. of liquated ore, crushed to a powder, with 3 lb. of wrought-iron turnings, 4 lb. of common salt, and about 1 lb. of skimmings from a subsequent operation. A ball of loose tin-plate scrap is placed in the upper part of each crucible above the charge; and the pot is heated to a dull red heat for about half an hour, when the reaction should be complete. The contents of the crucible are poured into a conical mould, which is then covered with a lid. In this process, which is known as *singling*, the crucibles are heated in the bed of a reverberatory furnace about 50 ft. long and 7 ft. wide, with a grate at one end, and a flue leading to the chimney at the other. The hearth is level, and the roof is in the shape of a low arch, the bricks being covered with a cast-iron plate. There are 21 openings 14 in. sq. in the roof on each side through which the crucibles may be lowered on to the hearth of the furnace, where they are heated by the flame circulating around them. In order to ensure the reduction of all the antimony, and to leave a slag which may be rejected, an excess of iron must be used, which remains alloyed with the antimony. The singles of antimony are therefore impure, and must be refined by the process of *doubling*, which consists in re-melting the antimony (after separating it from the sulphide of iron) in charges of 84 lb., mixed with 7 or 8 lb. of liquated stibnite, and 4 lb. of common salt. In this case an excess of sulphide of antimony is used, with the result that the whole of the iron is removed from the metal by exchange. The residual sulphide contains a notable amount of antimony, but it is produced in small bulk, as will be seen by reference to the weights used ; and the more valuable metal is recovered by introducing 1 lb. of the residue with each charge of raw material operated upon in singling. The doubles of antimony will contain a small percentage of sulphur, owing to the partial solubility of the sulphide in the metal, and this must be removed. The antimony is sent into the market with its whole surface covered with the large fern-like crystals, which have given to the product the name *Star-antimony*.

In melting for star-metal, the antimony from the doubling process is carefully picked free from all traces of slag, and melted with a small proportion of *antimony flux*, stirred with an iron rod, and poured at once into iron ingot moulds. The flux is made by melting 3 parts of potassium carbonate with 2 parts of sulphide of antimony until the fusion is tranquil. It not only removes any traces of sulphur, but is essential to the production of the crystalline surface. The production of the star is not a sure evidence of purity, but as it is the indication usually accepted in commerce, every care is taken in pouring the metal. The presence of any of the slag from the doubling process prevents starring ; and, in pouring, the metal must not be allowed to run into the ingot mould until the latter has been completely covered with the slag produced from the antimony flux. The pot is therefore tilted very slowly, so that the slag is poured first, for wherever the antimony comes into direct contact with the wall of the mould, the surface is not starred. So much depends upon the right composition of the flux, that this is tested on a small scale before use, and is only accepted when the stars upon the trial ingot are perfect. The ingots are scoured with sand and warm water, and find their way into the market under the name *French-metal.*

During the course of the smelting operations about $\frac{1}{10}$ of the antimony present in the ore is volatilised; but it condenses, for the most part as oxide, in the flues, from which it may be collected, and the antimony recovered by heating it with carbonaceous matter.

German Smelting-Process.—In Germany, the ore is melted on a granite hearth in a small reverberatory furnace, with scrap-iron or with carbonate of soda and carbonaceous material; in the latter case the stibnite is sometimes partially roasted to oxide first. The carbon is necessary for reduction, because sulphide and oxide of antimony heated together do not yield the metal as do the corresponding compounds of copper, but form *glass of antimony,* which is an oxysulphide, a combination of the two. The crude metal produced is refined by re-melting with soda on a hearth similar to that first employed, and then, after withdrawing the slag, adding glass of antimony and a small proportion of fresh carbonate of soda. The sulphur and iron are thus removed by oxidation, and the metal is ladled into ingot moulds, with the same precautions that are taken to produce a good star-metal by the English method.

Properties of Antimony.—Antimony can be easily distinguished from most other metals by its hardness, brittleness, and crystalline structure; a slight tap with a hammer suffices to break an ingot of antimony, and the broken surface exhibits large shining plates;[1] it is so brittle that it may be easily reduced to a fine powder in a mortar. In these respects it resembles bismuth; but the latter metal has a pinkish

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[1] The addition of a minute proportion of tin to antimony causes it to crystallise more readily and in larger crystals.

hue, by which it may be distinguished from antimony at a glance. It is comparatively a light metal, its specific gravity being only 6·7. It melts at 425° C., and at a higher temperature it gives off much vapour, which produces a thick white smoke of oxide of antimony. Its applications have been noticed in the preceding pages.

BISMUTH

BISMUTH is a comparatively rare metal which is found associated with the ores of nickel, cobalt, copper, and silver, chiefly in Saxony, Austria, Peru, Australia, and Bolivia. The two last-named furnish the bulk of the supply. Bismuth is commonly found *native* (*i.e.* in the metallic state), and is then usually extracted from the ores which contain it in that condition, by taking advantage of the readiness with which it fuses (266° C.) and drains away from the other constituents of the ore. At Schneeberg, in Saxony, it is extracted from an ore containing from seven to twelve per cent. of bismuth, associated with a compound of arsenic and cobalt. This is broken into pieces about the size of a nut, and introduced, in charges of about 50 lb., into sloping cast-iron cylinders (fig. 121) heated by a wood fire. The lower opening (*b*) of each cylinder is closed with a fire-clay stopper having an aperture through which the melted bismuth may run out. The upper openings are closed by an iron door (*d*); in about ten minutes after charging, the metal begins to run into an iron pot (*a*), kept hot by a separate fire in the channel (K), and containing a little coal-dust to prevent the oxidation of the bismuth. The ore is turned over occasionally, to promote the separation of the metal, which liquates out in the course of half an hour, when the residue is raked out from the upper end of the cylinder, where it falls, down an incline, into a trough of water, and a fresh charge is introduced. With five cylinders over a single furnace, one ton of ore is smelted in eight hours. The iron pans are emptied into moulds in which the bismuth is cast into bars weighing from 25 to 50 lb. each.

The rich ores from Australia containing about 60 per cent. of bismuth are smelted by fusion in black lead pots with carbonate of soda, borax, and tartar.

But bismuth occurs sometimes as *bismuthine* or *bismuth glance* (Bi_2S_3), as *bismuth ochre* (Bi_2O_3), and *bismutite* or *bismuth spar* $[2\ (4\ Bi_2O_3.3CO_2)+9H_2O]$, as well as in other less common combinations; and from these the metal cannot be extracted by mere liquation. Such ores are commonly smelted in Saxony by roasting them, and then heating them in crucibles with a sufficient quantity of iron and carbon to reduce the bismuth, and of slag to flux the impurities in the ore. The arsenic present, combining with the cobalt and a part of the iron, forms a speise which floats on the bismuth, and, having a higher melting-point, solidifies before it, so that the still fluid bismuth may be poured from beneath, and thus be separated perfectly. The crude bismuth, like tin, is purified by liquating it at the lowest possible temperature, on a slanting iron plate.

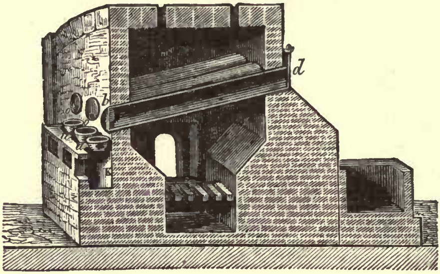

FIG. 121.—Liquation-Furnace for Bismuth.

As it comes into the market, bismuth contains considerable quantities of arsenic, iron, and silver, which do not, however, seriously interfere with its limited applications.

The arsenic may be expelled by heating the metal in crucibles, exposed freely to the air at a temperature of 400° C., when the arsenic passes off in vapour.

When a sufficient quantity of silver is present, it is extracted from the bismuth by the process of cupellation (p. 425), the bismuth becoming converted into an oxide, which is removed, like the litharge formed when lead is cupelled, leaving the silver upon the cupel. The bismuth may of course be recovered from the oxide which is produced and absorbed by the cupel. When lead containing bismuth is cupelled, the lead is first converted into oxide, so that towards the end of the process, nearly pure bismuth is left on the cupel, which will oxidise in its turn if the process be continued.

This affords a means of separating bismuth and lead, the oxide formed in the later stages of cupellation being kept separate from those obtained at first. Bismuth may also be desilverised by the Parkes process, with the aid of metallic zinc (p. 415). Antimony, being a more oxidisable metal than bismuth, may be removed by melting the metal in an oxidising atmosphere, stirring well and skimming off the oxide of antimony which forms. The latter, however, may contain a considerable proportion of bismuth.

Properties and Uses of Bismuth.—Bismuth is known by its peculiar reddish colour and its highly crystalline appearance. A blow with the hammer breaks it easily, though it is not quite so brittle as antimony. It may be obtained in very beautiful crystals with iridescent surfaces by melting a considerable quantity in a crucible and cooling it very gradually by covering the crucible over and surrounding it with hot sand. After the lapse of a certain time a crust of bismuth will have formed on the sides of the crucible, and if the still liquid central portion of the bismuth be then poured out, the crust will be found to consist of well-defined crystals, apparently cubes, but really rhombohedra.

Its brittleness renders bismuth unfit for use in the metallic state, by itself, except for the construction of *thermo-electric piles*, which are made of alternate bars of bismuth and antimony, and may be employed as very delicate thermometers, in order to measure slight differences of temperature by the electric currents which they produce.

The use of bismuth in alloys depends upon its low melting-point (266° C), and its property of expanding very considerably during solidification, the solid metal occupying $\frac{1}{32}$ more space than the liquid metal. Another remarkable physical peculiarity of bismuth is the circumstance that the specific gravity of the metal is diminished instead of being increased by strong pressure. Thus, a cylinder of bismuth of specific gravity 9·783 was placed in a steel cylinder fitted with a plunger, and subjected to a pressure of 200,000 lb., when its specific gravity was found to have diminished to 9·556, having been reduced by about $\frac{1}{43}$ part. The compressed bismuth exhibited scarcely any crystalline structure.

Newton's fusible alloy is composed of two parts of bismuth, one of lead, and one of tin, and melts at 94° C., so that it liquefies readily in boiling water, although the most easily fusible of its constituents, the tin, has a melting-point of 232° C. Such an alloy is used as a soft solder by pewterers. An alloy, similar to this, but having half the tin replaced by an equal weight of cadmium, melts at a temperature of 61° C.

Some kinds of type-metal and stereotype-metal contain bismuth in order that they may expand into the finest lines of the mould during solidification. For a similar reason, an alloy of tin, lead, and bismuth is employed for testing the finish of a die.

Bismuth is more easily converted into vapour than are many other metals, and it may be boiled at a moderate white heat.

ALUMINIUM

THIS metal, although discovered by Wöhler in 1828, has only within the last few years been usefully applied, the cost having previously been too high. Though never found as a metal in nature, it is probably the most abundant of all metals in a state of combination, since it exists in every variety of clay (silicate of alumina), in quantities varying from twelve to twenty per cent. Another mineral containing aluminium is *cryolite*[1] ($Al_2F_6.6NaF$), in which the metal is combined with sodium and fluorine, and forms thirteen per cent. of the mineral, which is found in abundance in Greenland.

A particular variety of clay known as *bauxite*, which is found at Baux, near Arles, in the south of France, and in Ireland, and in many parts of the United States of America, is the principal source of the alumina from which aluminium is at present obtained; this mineral contains about one-third of its weight of aluminium, combined with oxygen (forming *alumina*), together with silica, oxide of iron, and water.

Deville's Extraction Process.—Even at the highest temperature attainable in any ordinary furnace, deriving its heat from the combustion of fuel, aluminium cannot be extracted from alumina by the action of carbon or any similar reducing agent; and the combination of aluminium with oxygen is so powerful that no ordinary metal (not even sodium or potassium) is able to break it up and so to reduce the aluminium. The earlier process for the production of aluminium on a manufacturing scale consisted in obtaining pure alumina by chemical means from any of its compounds, and then heating this in intimate admixture with carbon in a current of chlorine gas. The tendency

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[1] So called from the Greek for *frost*, on account of its resemblance to ice.

of carbon to combine with oxygen forming carbonic oxide, coupled with that of chlorine to unite with aluminium forming aluminium chloride, enabled the smelter to produce from the refractory alumina a compound (aluminium chloride) which could be attacked by sodium, with the production of metallic aluminium and common salt. In working the process, the ground bauxite was mixed with *soda-ash* (containing carbonate of soda and caustic soda) and heated in a reverberatory furnace, when the soda combined with the silica and alumina, forming *silicate of soda* and *aluminate of soda*, whilst the carbonic acid was expelled in the form of gas. The mass, after cooling, was treated with water, which dissolved the aluminate of soda. This solution was mixed with enough hydrochloric acid to remove the soda, when the alumina was separated as a gelatinous precipitate, composed of *aluminium hydroxide*, a compound of alumina with water. This was mixed with common salt and charcoal powder, to a stiff paste, which was made up into balls as large as an orange, very thoroughly dried, and strongly heated in earthen cylinders through which perfectly dry chlorine gas was passed. The salt was added in order that it might combine with the chloride of aluminium to form a double chloride ($Al_2Cl_6.2NaCl$), which is more easily condensed to the solid form, and is less easily acted upon by moist air than is the single chloride. The double chloride distilled over and was condensed. 10 pts. of this salt were mixed with 2 pts. of sodium in small pieces, and with 5 pts. of cryolite or of fluor-spar, to form a liquid slag which should suffice to cover the surface of the metal. This mixture was thrown upon the red-hot hearth of a reverberatory furnace, which was then immediately closed to exclude air. The sodium acted violently upon the chloride of aluminium, abstracting its chlorine and liberating the aluminium, which collected, in the melted state, beneath a layer of slag containing the chloride of sodium and the cryolite. The metal thus obtained always contained silicon and iron in considerable quantity.

Modern Electro-Smelting Process.—At the best, Deville's process was exceedingly costly, and it is now entirely superseded by the electrical method, which has greatly reduced the cost. In carrying out this process, small lumps of cryolite, or of cryolite and fluor-spar, are placed around 3-in. carbon rods in a large box or furnace, lined to a thickness of several inches with carbon. The carbon-lining is connected to the negative pole of a powerful dynamo, and the carbon rods are attached to a copper frame which is joined up to the positive pole. The carbon anodes are at first placed in contact with the lining, so that a current flows ; the rods are then withdrawn a little way from the lining, and the electric arc which plays between the separated surfaces raises the temperature locally to such an extent that the surrounding pieces of cryolite fuse and the rods may be still further separated from the lining. In time the whole bath is fluid, and the anode rod dips into the liquid, causing the electrolysis of the oxide. No electric arc is then allowed to form, but the temperature of the bath is maintained by the conversion of electricity into heat as it overcomes the electrical resistance of the bath. The temperature required to carry on the operation is only a dull red heat, which is obtained and regulated by the distance apart of the poles (the lining and the rods) in the bath. Pure alumina obtained by passing CO_2 through a solution of aluminate of soda, obtained as above, is thrown into the furnace, and may dissolve to the extent of 25 per cent. ; the alumina alone becomes reduced, and the aluminium sinking through the fluid bath, accumulates at the bottom of the cavity, from which it may be tapped or ladled at intervals, whilst fresh quantities of alumina are introduced as required in place of that which has been decomposed. When the whole of the alumina has been reduced, the electrical pressure suddenly rises ; on adding a further quantity the voltage again falls. The process may, therefore, be continuous, but it is slow, and is comparatively costly by reason of the low chemical equivalent of aluminium. The current employed commonly has a pressure of about 7 volts, and the amount of metal extracted depends upon the volume (ampères) of current passed. In round numbers, it may be considered that each electrical horse-power available should produce about 1 oz. of aluminium per hour. About 1 lb. of carbon is consumed for each pound of aluminium produced.

There are several modifications of this method, but the principle is practically the same in all.

The Cowles Process.—Prior to the introduction of the electro-smelting process just described considerable quantities of aluminium-copper alloys were produced in the Cowles electric furnace. This consisted of a rectangular vessel, lined with carbon dust rammed into position, and provided at each end with an opening through which bundles of stout carbon rods could be introduced. These rods were connected, at one end with the positive, and at the other with the negative, pole of a powerful dynamo. The opposite carbon rods were at first allowed to meet in the centre, and the space around them was filled with the charge of alumina and charcoal together with granulated copper, or with copper oxide and charcoal, mixed in suitable proportions. As soon as the current was switched on to the apparatus the rods were withdrawn slightly from one another, an electric arc passed between them, and the surrounding mass melted; little by little they were then still further withdrawn, until, at length, the whole of the charge in the furnace was fused. In this furnace the alumina was reduced by the carbon of the charge, at the high temperature of the electric arc, and in the presence of the copper; for this metal at once united with the reduced aluminium to form a fusible alloy, which could be tapped out of the furnace as soon as the smelting of the charge was complete. It is possible to reduce alumina alone in such a furnace, but in the absence of copper, the product contains so much carbon that its metallic properties are destroyed. The temperature obtainable by means of the electric arc exceeds any that has at present been reached by the combustion of fuel, and thus affords the means of reducing the most refractory oxides and melting the most infusible metals. A miniature electric furnace, in which a carbon tube containing the substance to be treated is placed in the path of a powerful electric arc, has been employed by Moissan to produce such metals as molybdenum and chromium in sufficiently large quantities to permit of the investigation of their properties.

Properties and Uses of Aluminium.—Aluminium is a white malleable metal about as hard as zinc, and fusing at 625° C. It is remarkably light, having a specific gravity of only 2·6, and is unaffected by air; unlike silver, it is not even tarnished by air containing sulphuretted hydrogen. A bar of aluminium suspended from a string sounds like a bell when lightly struck.

An infallible method for soldering aluminium is a desideratum. The difficulty lies rather in finding a flux which will dissolve alumina, and thus afford clean surfaces to be united, than in securing a suitable mixture of metals.

Of the alloys of aluminium in common use, those with copper are best known. The so-called aluminium gold is an alloy containing from 95 to 90 per cent. of copper, with from 5 to 10 per cent. of aluminium. Within this range the colour varies from that of almost pure gold (the 5 per cent. alloy) to that of a pale gold, containing silver. These mixtures are much harder and lighter than gold, and they are liable to tarnish; but they may have a tensile strength of from 18 to 40 tons per sq. in., those with the larger proportion of aluminium being stronger, but also more brittle. With more than 11 per cent. of aluminium the bronze is so hard and non-ductile that it is practically useless for general purposes.

The strong electro-positive character of aluminium has been utilised for the production of special alloys by heating the finely divided metallic aluminium with an oxide of the metal to be alloyed with it, using a crucible in an ordinary fire. A part of the aluminium is used up in reducing the oxide, whilst the remainder alloys with the separated metal. But this tendency to reduce other oxides renders it very difficult to obtain perfectly pure aluminium. The mere heating of the metal in contact with iron or any of its compounds leads to the absorption of iron; and contact with silica or even with clay at furnace temperatures causes the introduction of silicon; and as iron and silica are so universally distributed, few, if any, samples of commercial aluminium contain less than 1 per cent. of these two elements conjointly.

The lightness of aluminium indicates it as specially suitable for marine or balloon fittings; and now that the cost of production is so much reduced, the metal is taking its place in these fields. It must never, however, be exposed in direct contact with another metal, to the action of salt-water, or of any aqueous solution, as under these conditions a powerful galvanic action will be set up, and the aluminium will become corroded, locally, with great rapidity. Brass, gun-metal, and copper fittings are especially to be avoided; and wherever these metals must be used they should be electrically insulated from the aluminium. The metal, alone, is a little too soft for the sheathing of ships, and experiments have been tried with alloys of 94 pts. of aluminium with 6 pts. of either nickel or copper, which have the extra strength and hardness required, without suffering much in respect of lightness. It is yet to be seen whether they will resist the action of salt-water as well as the pure metal has done in its preliminary trials.

The use of small quantities of aluminium, as a deoxidiser, in steel and iron, and in ordinary brass and bronze alloys has been tried, frequently with good effect. The former application has already been referred to.

An alloy of silver with two-thirds of its weight of aluminium has been used in France, under the name of *tiers-argent*, as a substitute for silver, being much harder than that metal and less than half the price.

Aluminium is sometimes employed for making small weights, for which it is well adapted by its lightness and resistance to the action of air. The beams of small balances have also been made of aluminium. The readiness with which it may be rolled into sheet and stamped has led to the proposal to use it for the fittings of railway saloons and of ships' cabins.

MAGNESIUM

LIKE aluminium, this metal has only been extracted in considerable quantity during the last few years, a demand for it having arisen in consequence of its property of burning with a very brilliant white light, which is found useful for producing specially brilliant illuminations as well as for taking photographs at night or in places where sufficient daylight does not penetrate.

Magnesium occurs abundantly, in combination with oxygen and carbonic acid, in *magnesite* (carbonate of magnesia) and *dolomite* or magnesium limestone (carbonate of lime and magnesia). Another source of the metal is *carnallite*, which is found in large quantity above the rock-salt in the salt mines of Stassfurth, in Saxony. This mineral is composed of magnesium, potassium, chlorine, and water, and contains about one-twelfth of its weight of magnesium. The water may be expelled by heat, leaving the *double chloride of magnesium and potassium.*

Magnesium may be extracted from the dried carnallite by mixing it with $\frac{1}{10}$ of fluor-spar, to act as a flux, and $\frac{1}{10}$ of sodium in small pieces. By fusing this at a moderate heat, the chloride of magnesium is made to give up its chlorine to the sodium, and the magnesium collects in the melted state beneath a liquid slag composed of chloride of sodium, chloride of potassium, and fluoride of calcium. The magnesium may be purified by distilling it. It may also be prepared by an electrolytic process : a mixture of the chlorides of magnesium and potassium is melted in a porcelain or iron vessel, fitted with a cover, and with tubes for conveying away the chlorine produced. The current enters the fused mass through a carbon anode-rod, and leaves either through the iron crucible, or through an iron rod suspended in the porcelain vessel. The chloride is broken up by the action of the current, chlorine is evolved on the carbon rod, and escapes through the tube, to be recovered and utilised outside, whilst the metallic magnesium deposits in the fused condition upon the iron, and then falls, and collects, upon the bottom of the vessel. Magnesium bears considerable resemblance to aluminium, but is a whiter metal, and even lighter than aluminium, its specific gravity being only 1·74. It melts at 750° C., and boils at about 1100° C. It is a little more easily tarnished than zinc when exposed to air. Like zinc, it may be worked at a somewhat elevated temperature, 450° C. being that most suitable. Magnesium wire is made by forcing the heated metal through holes in a steel plate, and magnesium riband by passing the wire between heated rollers. When the end of a piece of wire or riband is held in a flame, it catches fire and burns with a dazzling light.

The highly actinic light produced by burning magnesium renders it especially serviceable in photography ; and it is mainly in this field that magnesium is used commercially. In a few instances it may be employed in the refining of metals, owing to its great affinity for oxygen and other non-metals ; and it is sometimes used in making alloys.

SODIUM

Metallic sodium was, until quite recently, extracted from carbonate of soda, which is made from chloride of sodium.

The well-dried carbonate of soda is mixed with powdered charcoal, some chalk being added to prevent the fusion of the mixture, which is strongly heated in wrought-iron cylinders protected from the fire by a coating of clay. The carbonate of soda contains sodium, oxygen, and carbonic acid; the carbon of the charcoal combines with the oxygen, and the sodium is converted into vapour and condensed in vessels containing petroleum; for sodium cannot be exposed to the air, even for a few minutes, without combining extensively with oxygen, and it even takes up that element, with great violence, from water. Castner, in 1886, greatly reduced the cost of sodium by using fused caustic soda and bringing the carbon into intimate contact with it by weighting the carbon with iron. For this purpose he coked a mixture of finely divided iron (or its oxide) and gas-tar. The 'coke' contained about 70 pts. of iron and 30 pts. of carbon, and was ground before being used. By this process a much greater yield of sodium was obtained than by the older method, and as the temperature required is lower, there is a considerable saving in respect both of fuel and of wear and tear of plant.

Sodium may be produced electrolytically from fused sodium chloride or other compounds; and Castner has been successful in obtaining the metal on a large scale by electrolysing fused caustic soda at a temperature of 313° C., in iron vessels heated by a gas flame. The success of the process depends largely upon the maintenance of the right temperature during the electrolysis. The greater proportion of the world's consumption of this metal is now produced by the electrolytic process. Sodium would scarcely be taken for a metal by an ordinary observer, in the state in which it is found in commerce, where it occurs in greyish earthy-looking light masses; but when these are cut with a knife, the fresh surfaces exhibit a brilliant lustre.

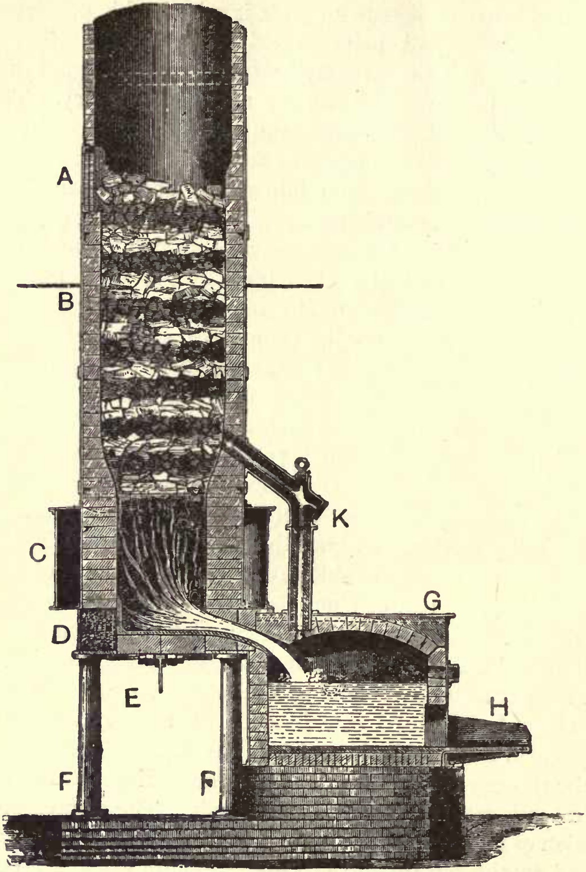

FIG. 122. Stewart's 'Rapid' Cupola.—This cupola represents a type which has of late years been somewhat widely introduced into iron foundries (see p. 211).—A is the charging-door. B, the charging-platform. C, the air-chamber, with a series of twyers at different levels passing through the refractory lining into the contracted melting-chamber within. D is a fettling door for repairs, &c. E, a hinged drop bottom which may be opened after a day's work is over to facilitate the cleaning up of the cupola. F F are columns which support the cupola and give free access to the bottom; G is the fore-hearth in which the metal collects. H, the tap-hole; and K, the hot-air pipe lined with ganister, connecting the fore-hearth and the body of the cupola. Such a cupola, with a charging-door 19 ft. 6 in. from the ground, with an external diameter of shell of 4 ft., and an internal diameter of 1 ft. 10 in. in the melting-chamber, should be capable of melting about 5 tons of pig-iron per hour.

TABLES

TABLE I., *showing the Names and some of the Properties of the more important Metals.*

Name of Metal	Symbol	Atomic Weight	Specific Gravity (Water = 1)	Approx. Fusing-Point in degr. Cent. (Vide Table VIII.)	Length at 100° C. of a bar which measures 1 at 0° C.[1]	Weight of one cub. ft. in lb.	Approx. Tensile Strength per sq. in. in tons
Aluminium	Al	27·0	2·6	625	1·0023	163	12·0
Antimony	Sb	120·0	6·7	425	1·0011	419	0·5
Bismuth	Bi	207·5	9·8	266	1·0013	613	1·5
Cadmium	Cd	111·7	8·6	321	1·0033	542	—
Chromium	Cr	52·4	6·8	2000 [2]	—	424	—
Cobalt	Co	59·4	8·5	1500	1·0012	530	= Iron
Copper	Cu	63·2	8·8	1050	1·00167	549	8·5 to 15·0 [4]
Gold	Au	196·6	19·3	1045	1·00147	1208	7
Iridium	Ir	192·5	22·4	2500	1·0007	1400	—
Iron	Fe	55·9	7·8	1600	1·00123	490	23 [5]
Lead	Pb	206·4	11·4	327	1·0028	709	0·8 to 1·5 [4]
Magnesium	Mg	23·9	1·7	750	1·0027	108	—
Manganese	Mn	54·8	8·0	1900	—	499	—
Mercury	Hg	199·8	13·59	− 39	1·0181 [3]	847	—
Nickel	Ni	58·7	8·9	1450	1·0013	549	= Iron
Palladium	Pd	106·3	11·4	1500	1·0012	717	22 [4]
Platinum	Pt	194·3	21·5	1775	1·0009	1344	24 [4]
Silver	Ag	107·7	10·5	950	1·0019	657	17 to 18
Sodium	Na	23·0	0·98	96	1·0071	60	--
Tin	Sn	118·8	7·3	232	1·0023	455	2 to 3·5 [4]
Tungsten	W	3·6	19·1	2000 [2]	—	1190	—
Zinc	Zn	65·3	7·1	417	1·0030	445	1·3 to 14 [4]

NOTE.—The figures in the tables must be looked upon only as approximately true: no two pieces of metal would give precisely the same result.

---

[1] For the same kind of metal, the greater its density, the greater its expansion for a given increase in temperature.

[2] Not lower than 2000°.

[3] Total expansion.

[4] Signifies that the figures refer to wrought metal.

[5] For the strength of iron and steel, see Tables II. and III.

TABLE II., *showing usual Tensile Strength and Extensibility of Various Grades of Iron and Steel.*

Percentage of Carbon in Specimen	Common Range of Tensile Strength in tons per sq. in.	Common Range of Maximum Extensibility on 10″ bar, per cent.
0·03 to 0·07	20 to 30	20 to 35
·07 ,, ·15	22 ,, 32	
·15 ,, ·25	25 ,, 35	15 ,, 25
·25 ,, ·35	28 ,, 40	12 ,, 24
·35 ,, ·45	32 ,, 45	10 ,, 21
·45 ,, ·55	33 ,, 50	7 ,, 15
·55 ,, ·7	35 ,, 53	5 ,, 10
·7 ,, ·9	38 ,, 65	2 ,, 7
·9 ,, 1·1	40 ,, 75	1 ,, 5
1·2 ,, 1·3	43 ,, 52	0·5 ,, 2

NOTE.—The wide variations in the above numbers allow for the differences in composition and treatment of commercial samples of steel which so greatly affect the mechanical properties of the metal.

TABLE III., *showing Standard Strengths for Puddled Iron.* (Morris.)

Description of Iron	Best Iron		Best Best Iron	
	Tensile Strength in Tons per sq. in.	Percentage Contraction of Area	Tensile Strength in Tons per sq. in.	Percentage Contraction of Area
Rounds and Squares	22·5	20	23·5	30
Flats . . .	22	15	23	20
Angles and Tees .	21·5	12·5	22	17·5
Plates, with Fibre .	21	8	22	10
,, across ,, .	17	4	18	5

NOTE.—An especially good soft sample of iron might have a lower tensile strength than shown in this table, but it would exhibit a proportionately greater contraction of area; a specimen may therefore be classed as 'up to standard' if it show a combination of slightly diminished strength with a decidedly superior ductility as compared with the figures quoted.

TABLE IV., *showing the Specific Gravity, &c., of some of the Non-metallic Materials employed in works.*

Name of Substance	Sp. Gr.	Weight of one cub. ft. in lb.	No. of cub. ft. in one ton	Crushing strain in lb. per sq. in.
Brickwork, common .	1·6 to 2·0	100 to 125	22·4 to 17·9	—
,, London Stock .	1·84	115	19·4	—
,, red . . .	2·16	134	16·7	808
,, Stourbridge fire	2·2	137	16·3	1,717
,, Welsh fire .	2·4	150	14·9	—
Cement	1·7	106	21·1	5,000
Chalk, in lumps . .	2·0	125	17·9	—
,, powder . .	2·64	165	13·6	—
Clay	1·9	119	18·8	—
,, fire- (Newcastle) . .	2·52	157	14·2	—
Concrete	1·9	119	18·8	—
Granite, Aberdeen . .	2·62	163	13·7	10,900
,, Cornish . .	2·66	166	13·5	6,300
Limestone, blue Lias . .	2·47	154	14·5	—
,, compact . .	2·58	161	13·8	8,000
Masonry (mean) . . .	2·1	131	17·1	—
Mortar	1·38 to 1·9	86 to 119	26 to 18·8	—
Quartz	2·55 to 2·77	159 to 173	14·1 to 12·9	—
Sand, coarse . . .	1·61	100	22·4	—
,, fine	1·52	95	23·6	—
Sandstone, Arbroath pavement . . .	2·47	155	14·4	7,884
Sandstone, Bramley Fall .	2·5	156	14·3	6,050
,, Caithness . .	2·64	165	13·6	6,490
,, Craigleith . .	2·45	153	14·6	5,287
,, Derby grit .	2·4	150	14·9	3,100
,, red (Cheshire) .	2·15	133	16·9	2,185
,, Yorkshire paving	2·51	157	14·2	5,714
Slate, Cornish . . .	2·51	157	14·2	10,000
,, Welsh . . .	2·88	180	12·4	to 21,000

TABLE V., *Results of Experiments on some of the Principal Varieties of Building Stones by the late Professors Daniell and Wheatstone, of King's College, London.*

	Percentage Composition															
Nature of Stone:	SANDSTONES					MAGNESIAN LIMESTONES				OOLITES				LIMESTONES		
Name of Locality:	Craigleith	Darley Dale	Heddon	Kenton	Mansfield	Bolsover	Huddlestone	Roach Abbey	Park Nook	Ancaster	Bath Box	Portland	Ketton	Barnack	Chilmark	Ham Hill
Silica	98·3	96·40	95·1	93·1	49·4	3·6	2·53	0·8	—	—	—	1·20	—	—	10·4	4·7
Carbonate of lime	1·1	0·36	0·8	2·0	26·5	51·1	54·19	57·5	55·7	93·59	94·52	95·16	92·17	93·4	79·0	79·3
Carbonate of magnesia	—	—	—	—	16·1	40·2	41·37	39·4	41·6	2·90	2·50	1·20	4·10	3·8	3·7	5·2
Iron and alumina	·6	1·30	2·3	4·4	3·2	1·8	0·30	0·7	0·4	0·80	1·20	0·50	0·90	1·3	2·0	8·3
Water and loss	—	1·94	1·8	0·5	4·8	3·3	1·61	1·6	2·3	2·71	1·78	1·94	2·83	1·5	4·2	2·5
Bitumen	—	—	—	—	—	—	—	—	—	traces	traces	traces	traces	traces	traces	traces
	Approximate Crushing Strain in Pounds on the Square Inch															
First fracture	4263	6253	1847	3411	1989	4974	2016	1705	1847	1705	1279	2132	1563	1137	2984	1563
Crushing weight	7887	7106	3979	4974	5116	8314	4334	3908	4334	2345	1492	3908	2558	1776	7177	4050
	Specific Gravities															
Of dry masses	2·232	2·628	2·229	2·247	2·338	2·316	2·147	2·134	2·138	2·182	1·839	2·045	2·145	2·090	2·481	2·260
Of particles	2·646	2·993	2·643	2·625	2·756	2·833	2·867	2·840	2·847	2·687	2·675	2·706	2·706	2·627	2·621	2·695
	Absorbent Powers when Saturated under the Exhausted Receiver of an Air-Pump															
Weight of water, in grains, absorbed by pieces, two ins. cube	0·143	—	0·156	0·143	0·151	0·182	0·239	0·248	0·249	0·180	0·312	0·206	0·244	0·204	0·053	0·147

TABLE VI., *showing the Specific Gravity, &c., of certain Gases.*

Name of Gas	Sp. Gr. Water = 1	Weight of one cub. ft. in lb.	Volume of one lb. in cub. ft.
Air	·001293	·08072	12·387
Carbonic acid	·00197	·1234	8·101
Carbonic oxide	·00125	·0784	12·753
Chlorine	·00318	·1968	5·081
Hydrogen	·0000895	·00559	178·83
Nitrogen	·00125	·0784	12·753
Oxygen	·00143	·0892	11·204
Steam	·000805	·0502	19·913

TABLE VII., *showing Typical Percentage Compositions of certain Representative Alloys.*

Name of Alloy	Aluminium	Antimony	Bismuth	Cadmium	Copper	Gold	Iron	Lead	Nickel	Silver	Tin	Zinc
Aich's metal	—	—	—	—	60	—	1·8	—	—	—	—	38·2
Aluminium bronze	5 to 10	—	—	—	95 to 90	—	—	—	—	—	—	—
Anti-friction metal	—	12	—	—	—	—	—	88	—	—	—	—
Arguzoid	—	—	—	—	56	—	—	3·5	13·5	—	4	23
Bell-metal	—	—	—	—	78	—	—	—	—	—	22	—
Brass—best	—	—	—	—	71·4	—	—	—	—	—	—	28·6
,, common	—	—	—	—	66·6	—	—	—	—	—	—	33·3
,, gilding metal	—	—	—	—	90 to 80	—	—	—	—	—	—	20 to 10
,, yellow	—	—	—	—	60	—	—	—	—	—	—	40
,, pin-wire	—	—	—	—	63	—	—	—	—	—	—	37
,, white (Dewrance's Loco-metal)	—	44·4	—	—	22·2	—	—	—	—	—	33·3	—
Britannia metal	—	6·2	—	—	1·8	—	—	—	—	—	92	—
Bronze coinage	—	—	—	—	95	—	—	—	—	—	4	1

TABLE VII.—*continued.*

Name ot Alloy	Aluminium	Antimony	Bismuth	Cadmium	Copper	Gold	Iron	Lead	Nickel	Silver	Tin	Zinc
Bronze for bearings (light) . . .	—	—	—	—	84	—	—	—	—	—	13	3
Bronze for bearings (heavy) . . .	—	—	—	—	77	—	—	—	—	—	9	14
Bronze for bearings (anti-friction) .	—	—	—	—	6	—	—	—	—	—	14	80
Bronze for wheel boxes	—	—	—	—	80	—	—	—	—	—	18	2
Dutch-metal . .	—	—	—	—	84·6	—	—	—	—	—	—	15·4
Electrum . . .	—	—	—	—	51·6	—	—	—	25·8	—	—	22·6
Fusible metal—Lichtenberg's . . .	—	—	20	—	—	—	—	50	—	—	30	—
Fusible metal—Rose's	—	—	50	—	—	—	—	25	—	—	25	—
,, ,, Wood's	—	—	50	12·5	—	—	—	25	—	—	12·5	—
German silver . .	—	—	—	—	50to 60	—	—	—	25to 15	—	—	25to 15
Gold coinage (standard) . . .	—	—	—	—	8·33	91·66	—	—	—	—	—	—
Gun-metal . . .	—	—	—	—	90	—	—	—	—	—	10	—
Muntz's metal . .	—	—	—	—	60to 64	—	—	—	—	—	—	40to 36
Pewter, plate . .	—	7	2	—	2	—	—	—	—	—	89	—
,, triple . .	—	15	—	—	—	—	—	6	—	—	79	—
,, ley . .	—	—	—	—	—	—	—	20	—	—	80	—
Silver coinage (British)	—	—	—	—	7·5	—	—	—	—	92·5	—	—
Solder, soft—fine .	—	—	—	—	—	—	—	33·3	—	—	66·6	—
,, ,, common	—	—	—	—	—	—	—	50	—	—	50	—
,, ,, coarse .	—	—	—	—	—	—	—	66·6	—	—	33·3	—
,, brazing ('Hard') .	—	—	—	—	50	—	—	—	—	—	—	50
,, glaziers' . .	—	—	—	—	—	—	—	25	—	—	75	—
,, gold . .	—	—	—	—	22·2	66·6	—	—	—	11·1	—	—
,, pewterers' .	—	—	11·8	—	—	—	—	29·4	—	—	58·8	—
,, silver . .	—	—	—	—	32 3	—	—	—	—	38·5	—	29·2
Speculum-metal . .	—	—	—	—	66·6	—	—	—	—	—	33·3	—
Sterro-metal . .	—	—	—	—	55to 70	—	1to2	—	—	—	1to2	34to 44
Tutenag . . .	—	—	—	—	45·7	—	—	—	17·4	—	—	36·9
Type-metal . .	—	25	—	—	—	—	—	75	—	—	—	—
,, . .	—	25	—	—	—	—	—	50	—	—	25	—

TABLE VIII., *showing relation of Centigrade and Fahrenheit Thermometer Scales.*

Equivalent Degrees		Equivalent Degrees		Equivalent Degrees	
C	F	C	F	C	F
0°	32°	500	932	1050	1922
100	212	538	1000	1093	2000
121	250	593	1100	1149	2100
150	302	625	1159	1200	2192
204	400	649	1200	1260	2300
232	450	700	1292	1300	2372
250	482	750	1382	1400	2552
260	500	760	1400	1450	2642
266	511	800	1472	1500	2732
300	572	816	1500	1600	2912
316	600	871	1600	1649	3000
327	621	900	1652	1775	3227
371	700	927	1700	1800	3272
400	752	950	1742	1900	3452
417	783	982	1800	2000	3632
427	800	1000	1832	2204	4000
482	900	1038	1900	2500	4532

NOTE.—1° C. = $\frac{9}{5}$ × 1° F., and 1° F. = $\frac{5}{9}$ × 1° C.
Freezing-point of water = 0° C. or 32° F.

Hence are derived the following Formulæ for the Conversion of Centigrade into Fahrenheit Readings and *vice versâ.*

$$n^\circ \text{ C.} = (\tfrac{9}{5}n^\circ + 32^\circ) \text{ F.}$$
$$n^\circ \text{ F.} = \tfrac{5}{9}(n^\circ - 32^\circ) \text{ C.}$$

In the above table are transcribed some of the principal temperatures quoted in this book, together with certain even numbers on each of the thermometric scales, and the corresponding readings on the other scale.

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PRINTED BY
SPOTTISWOODE AND CO. LTD., NEW-STREET SQUARE
LONDON

192697