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OF
COPPER

M. EISSLER, M.E.

THE HYDRO-METALLURGY OF COPPER

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THE HYDRO-METALLURGY

OF

COPPER

BEING

AN ACCOUNT OF PROCESSES ADOPTED IN THE HYDRO-METALLURGICAL TREATMENT OF CUPRIFEROUS ORES, INCLUDING THE MANUFACTURE OF COPPER VITRIOL . . .

WITH

CHAPTERS ON THE SOURCES OF SUPPLY OF COPPER AND THE ROASTING OF COPPER ORES

BY
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"THE METALLURGY OF ARGENTIFEROUS LEAD"
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PREFACE.

A LONG period has elapsed—to be measured by centuries—since the Hydro-Metallurgical Treatment of Copper Ores was originated at the Rio Tinto Mines. Several processes have since been evolved, as the result, in large measure, of the investigations of manufacturers of sulphuric acid, who employ iron sulphides containing a low percentage of copper for the production of the acid, and who made it a special study to extract the residual copper from the burnt pyrites and cinders. The successful solution of that problem led to the adaptation of various leaching processes at a few low-grade copper mines, where smelting operations would have been too costly for the profitable treatment of the ores.

The application of the various lixiviation processes has had only a limited scope up till now; but it is more than likely that in future more attention will be given to them, owing to the necessity which (it may be expected) will arise for an economical exploitation of the low-grade copper deposits occurring in various parts of the globe. These can be made to pay by leaching—which, when judiciously applied, is cheaper than smelting—and in view of the increasing consumption of copper many of these hitherto undeveloped sources of supply will no doubt be opened up and utilised.

In the present volume, no claim is made to originality, the descriptions given of various processes now in operation having been collated from various sources. It will be readily understood that, for commercial reasons, access for purposes of investigation to the various establishments where such processes are carried on is denied—a fact which accounts in great measure for the lack of detailed information on the subject.

In compiling the volume, I have consulted Dr. George Lunge's "Handbuch der Soda Industrie" (Braunschneig, 1879), which gives a description of various kilns and furnaces in use at the date of publication by various sulphuric acid manufacturers, and still employed with certain improvements at the present time. M. de Launey, in "Annales des Mines, 1889," contributed an excellent article entitled "Memoire sur d' Industrie du Cuivre dans la Region de Huelva," containing notes on the treatment of the Rio Tinto Ores; Dr. Schnabel's "Metallhüttenkunde" (Berlin, 1894) and Balling's "Die Metallurgie" (Berlin, 1885) contained illustrations of furnaces and descriptions of some of the methods employed in various parts of the globe; while in some of the volumes of "Mineral Industry" (published by the Scientific Publishing Company of New York) references to methods employed in the United States are to be found: and to these several sources of information I have likewise to acknowledge indebtedness.

Closely connected with the study of the Hydro-metallurgy of Copper is the Manufacture of Blue Vitriol, a substance which is not merely won as a by-product but is manufactured as a staple article, and for whose production extensive establishments are erected, requiring skill and knowledge for their conduct and management.

PARIS,
February, 1902

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THE
HYDRO-METALLURGY OF COPPER.

INTRODUCTION.

THE Hydro-metallurgical Treatment of Copper is adopted for cupriferous ores which are too poor in copper contents to stand the high smelting charges that prevail in nearly every copper-producing district, owing to the high price of fuel; and the wet methods have consequently solved many low-grade problems which would otherwise have remained dormant. Similar methods are applied also to the treatment of alloys of copper with silver and gold, for the purpose of separating the precious metals and other ingredients, such as nickel, cobalt, bismuth, etc.

The immense deposits of cupriferous iron pyrites in the district of Huelva, in Spain, of which the Rio Tinto is the principal mine, would never have become available had it not been for the application of these methods, which are specially suited to the local conditions prevailing in those regions.

But before applying the wet methods it is essential to study the character of the ores, and to see if they are fitted for such treatment.

Sulphuric acid is the agent which plays a great *rôle* in dissolving the copper, but its production by natural agencies is very slow, as the sulphur in the ore heaps requires twenty years before its transformation into sulphuric acid and the complete sulphatisation of the iron and copper. To assist nature the ore heaps are roasted, and even then it takes about two-and-a-half years to obtain 80 per cent. of the copper contents at Rio Tinto. Any enterprise of this character, therefore, must be prepared for a great lock-up of capital, represented by the large ore heaps constantly undergoing the preparatory roasting.

Beside sulphuric acid, hydrochloric acid and chlorine play an important *rôle* in the methods to be described.

Owing to the large percentage of sulphur which the low-grade copper pyrites contain, they are utilised for the manufacture of sulphuric acid, and at several points in Europe and in the United States important centres of this industry have gradually been developed. The ordinary pyrite burners—used for driving off the sulphur fumes, to be utilised in condensing chambers—have gradually given way to mechanical roasting furnaces, especially for the treatment of the fines; and the kilns or burners which are in practical use for the purpose will be found described in this volume.

PART I.

THE PRODUCTION OF COPPER AND ITS SOURCES OF SUPPLY.

CHAPTER I.

THE CHEMICAL PROPERTIES OF COPPER.

IN a dry atmosphere, at the ordinary temperature, copper remains unaltered. In a damp atmosphere, in the presence of carbonic acid, it becomes covered with a thin coating of copper carbonate—verdigris. If heated to redness in a current of air, it becomes coated with a grey-black layer of cupreous and cupric oxide, which will scale off if suddenly cooled in water.

Copper is easily soluble in nitric acid, in aqua regia, and in strong boiling sulphuric acid. In dilute sulphuric and muriatic acids, with admission of air, it dissolves slowly.

If an impure plate of copper be used as an anode in an acid solution of sulphate of copper, and another plate be taken as a cathode, a properly regulated electric current will precipitate chemically pure copper upon the cathode, the anode dissolving in the same ratio, while the impurities contained in the latter, including often gold and silver, remain as a residual mud. This is the basis of modern electrolytic refining of copper. Copper has two oxides.

The **Cupreous Oxide** (Cu_2O) melts at a red heat without decomposition. It is freely dissolved in molten metallic copper. In a pulverised condition it can be changed into the higher oxide by gently heating it in air. It is easily reduced to metallic copper, and forms a fusible slag with silica. Melted with sub-sulphide of copper in proper proportions, the copper in both substances is reduced entirely to the metallic state, while the sulphur of the sulphide combines with the oxygen of the cupreous oxide, and forms sulphurous acid gas. This reaction, and a few analogous ones, are the main basis of the treatment of most ores of copper. If cupreous oxide is melted with sulphide of iron (FeS) in proper proportions, the copper combines with sulphur to form subsulphide, which, together with a portion of the undecomposed sulphide of iron, forms matte, while the iron that has been changed to a protoxide by the oxygen of the cupreous oxide, combines with silica, should that be present, to form slag. The matte being heavier sinks to the bottom and can easily be separated from the supernatant slag, and the first step in the fusion of copper ores has been accomplished.

Nitric acid converts cupreous oxide into cupric oxide, which is then dissolved. Sulphuric acid decomposes it into cupric oxide and copper; the cupric oxide is dissolved. Muriatic acid dissolves cupreous oxide into cupric chloride, which by the addition of water is precipitated as a white powder. Ammonium dissolves the cupreous oxide to a colourless solution, which when exposed to the air changes to a blue colour on the formation of ammonium cupric oxide.

The **Cupric Oxide** (CuO) is not fusible, but is easily reduced through carbon, carbonic oxide, and hydrogen to metallic copper. It will not combine with silica to form a slag at ordinary metallurgical temperatures unless there be such conditions present as will reduce it first into a cupreous oxide. If cupric oxide is melted with subsulphide of copper (Cu_2S) in proper proportions, sulphurous acid and metallic copper are formed. If cupric oxide is melted with sulphide of iron in proper proportions, copper is separated in metallic form, the iron is converted into ferrous oxide, and sulphur volatilises as sulphurous acid. If they are not in proper proportions, matte is obtained containing the copper as a subsulphide, together with intermediate sulphides of iron and a silicate of the ferrous oxide that has been formed. It is soluble in ammonia. Ferrous chloride converts cupric oxide into cupreous and cupric chlorides, with formation of ferric oxide. Ferric chloride converts cupric oxide into cupric chloride.

Silicate of Copper in the presence of a strong base, such as ferrous oxide or lime, is reduced by carbon to the metallic state. When heated with sulphide of iron, sulphide of copper and silicate of iron are obtained. When heated with metallic iron, silicate of iron and metallic copper are obtained.

Sulphides of Copper. There are two sulphides, of which only the subsulphide Cu_2S is of importance, as the CuS loses one half its sulphur at a comparatively low temperature. The subsulphide is fusible at a lower temperature. Metallic lead has no decomposing effect on the sulphide of copper.

Copper Sulphate ($CuSO_4 + 5H_2O$). The crystallised copper sulphate dissolves in 4 parts of cold water. At 100° it loses 4 molecules of water; at 200° it loses all its water. At a bright red heat it decomposes into copper oxide and sulphuric acid. When heated with carbon at a dark red heat the copper is separated, with formation of carbonic acid and sulphurous acid; but at a bright heat carbonic acid and copper sulphide is formed. When heated with subsulphide of copper, the reactions are similar to those of cupreous and cupric oxide. From solutions of the copper sulphates, the copper is precipitated by means of iron and zinc as metallic copper; by means of hydrogen sulphide and the sulphides of the alkaline metals it is precipitated as a sulphide. By the electric current, copper separates from the copper sulphate on the cathode, whereas the acid goes to the anode. If on the anode ferrous sulphate is present in solution, it is converted into ferric sulphate.

Cupreous Chloride (Cu_2Cl_2) is only slightly soluble in water. It is easily dissolved in hydrochloric acid, sodium chloride, potassium chloride, calcium chloride, magnesium chloride, ferrous chloride, zinc chloride, manganous chloride. From solutions of the cupreous chloride metallic copper is precipitated by iron and zinc; by means of hydrogen sulphide and the sulphides of the alkaline metals of earth, as copper sulphide; by means of calcium hydroxide, as cupreous oxide. By the electric current copper separates from the cupreous chloride solutions on the cathode, whereas the chlorine goes to the anode. If cupreous chloride solutions are present at the anode, they are converted into cupric chloride by the chlorine.

Cupric Chloride ($CuCl_2$) is easily soluble in water. With copper oxides it combines in various proportions, forming oxychlorides. From solutions of the cupric chlorides metallic copper is precipitated by means of iron and zinc; sulphuretted hydrogen and the sulphides of alkaline metals and earths precipitate sulphides; by calcium hydroxide copper hydroxide is precipitated. By pressing sulphurous acid into cupric chloride solutions, cupreous chloride is precipitated. By the electric current copper separates at the cathode and chlorine on the anode. The knowledge of these reactions is essential in the carrying out of the hydro-metallurgical operations of copper ores.

CHAPTER II.

*THE PRODUCTION OF COPPER FROM THE ORE.**

THE advances made in the metallurgical treatment of copper ores are in proportion to the great strides which have been made in other departments of the industrial arts and sciences during the past century, but the limit of improvements has not yet been reached, as the continued efforts to ameliorate the plants at numerous mines tend to lower the cost of production. The tendency of the metallurgist is to work in the direction of rapid treatment of the ores, and to invent methods whereby he can obtain the metallic copper with the least amount of tedious and costly manipulations. The marvellous success that has already been accomplished is shown by the results attained at Lake Superior, where ores containing ½ per cent. of copper can be treated at a profit. Of course, in this case, the simplicity of the metallurgical operations required to make the copper-contents of the ores marketable has wonderfully assisted the metallurgist in his operations.

There is a striking difference in a modern copper-smelting plant, when compared with those which were in operation 20 or 30 years ago. A 30 to 50 tons cupola was then considered a large furnace, whereas, if the notable copper mines of to-day are passed in review, it will be found that the up-to-date water-jackets are smelting, year-in and year-out, from 200 to 250 tons and even 300 tons, daily. The same comparison applies to

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* This chapter comprises the substance (with some additions and revision to date) of a Paper read by the Author before the Institution of Mining Engineers, at their General Meeting in London on May 23rd, 1901; the Paper being reproduced here by arrangement with the Council.

reverberatory smelting furnaces, whose ancestors can be seen in Swansea, where tradition and custom have adhered to the original size of 9 feet by 15 feet internal dimensions, whereas a modern reverberatory furnace has a laboratory of 16 feet by 35 feet, smelting 50 tons of ore daily; and even these are small when compared with those lately erected at the Boston and Montana Company's works, where regenerating reverberatory furnaces are smelting from 125 to 150 tons of roasted ore into matte daily.

It is not only in the direction of capacity and size that advances have been made, but also in the simplification of the processes of extraction. Let any student on the subject take up old text-books and compare the many and varied manipulations through which the ores, matte, and the great nomenclature of intermediate products had to pass before fine copper was obtained, with the simplicity of manipulation of the modern metallurgist, obtaining the same results in two or three operations. These resolve themselves, practically, into (i) converting the raw or the roasted ores into a liquid condition—by smelting; and (ii) the conversion of the resulting matte, by bessemerising, into metallic copper.

The most notable advance in smelting has been the utilisation of the sulphur, iron, and other oxidisable substances in the ores as generators of heat, so that they practically smelt themselves without the aid of extraneous heat; the application of this principle being known as "pyritic smelting."

The principal supply of copper is derived from the United States, which country furnishes over 55 per cent. of the world's production. In that country the methods of treatment have made the most marked advance, and it is matter for reflection that in the United States, where the ruling wages are higher, supplies dearer than elsewhere, and distances to markets are enormous, the producers of copper have been able to control the markets of the world and to compete with mines more favourably located.

All copper is not produced by smelting; in some isolated cases, as at Rio Tinto, in Spain, the copper-contents are extracted by wet methods, or leaching; and in Arizona, U.S.A., sulphuric acid is used as a solvent for the extraction of copper. The brilliant results achieved at the Rio Tinto mines by the natural decomposition of the ores, which after being exposed in immense heaps to atmospheric agencies are then lixiviated, goes to prove that, where local conditions favour the introduction of wet methods, copper can be won at a very low cost by these means; and although no exact data are at hand, it is well known that the Rio Tinto mines produce copper at about £20 per ton, or (in U.S.A. currency) five cents per pound, and no doubt there are many low-grade deposits which can be made remunerative by the application of hydro-metallurgical processes.

Where copper ores are mixed with a large proportion of earthy ingredients, these are removed by mechanical means—namely, concentration—and the enriched products or "concentrates" are turned over to the smelter. This method is pursued at Lake Superior, Butte (Montana), and at some mines in Arizona, U.S.A.

There is a wide field open for investigation in devising a profitable method of treatment of zinciferous copper ores, by which the zinc may be extracted and the residues then treated for copper. Large quantities of copper ores are neglected, because they carry from 25 per cent. and upwards of zinc, and the smelters charge a heavy penalty for ores carrying over 8 or 10 per cent. of zinc, the charge being 2*s.* (50 cents) per unit of zinc, above this legal minimum.

Owing to the increased demand for fine copper, the large producers refine their product electrolytically; and when the ores carry gold and silver, the separation of these precious metals is effected during this process, in course of which they are collected in the separating-vats and made marketable by well-known methods.

Many copper mines prove profitable owing to the precious metals in their ores, and in some instances it is doubtful whether the mines could have been made to pay in the absence of their gold and silver contents. Such mines as the Le Roi and its neighbours, in the Rossland district of British Columbia, might be called gold mines, as the output at the Le Roi, for 1898, was about 825 tons of copper, 68,000 oz. of silver, and 52,850 oz. of gold. The Anaconda Mine, Montana, U.S.A., produced in the same year over 5,000,000 oz. of silver and 16,610 oz. of gold. Such mines as the United Verde in Arizona, U.S.A., the Mount Lyell in Tasmania, the Great Corbar in New South Wales, and many others, carry gold and silver, which add largely to the profits made.

If an ore be taken which carries 6 per cent. of copper and 6 oz. of silver, and something more than traces of gold, the converter bars will average 100 oz. of silver and 6 to 7 dwts. of gold, or a value of £13 15*s.* (66 dollars) per short ton of fine copper; and allowing £3 (15 dollars) for electrolytic refining charges, this will leave a profit of £10 15*s.* (53 dollars), or 1¼*d.* (2½ cents) per lb. of fine copper produced.

The cost of electrolytic refining ranges from £2 10*s.* to £4 (12 to 20 dollars) per ton, according to localities.

It is a difficult matter to establish the average price at which a pound of copper is being produced, as local conditions vary in each district, and so many factors play an important rôle in raising or lowering its cost of production. The most astonishing feature in the American production is the fact that, in Michigan, metallurgical skill has enabled producers to treat at a profit ores which carry only 0·65 per cent. of metallic copper, equal to 13 lb. of copper to the ton. This at 7½*d.* (15 cents) per pound is equal to 8*s.* 1½*d.* (1·95 dollars) per ton: the mining, concentrating, and smelting costs are 4*s.* 11½*d.* (1·19 dollars), leaving a profit of 3*s.* 2*d.* (0·76 dollars) per ton of ore, and the copper costs 4·575*d.* (9·15 cents) per lb.

In large ore bodies having a width of 20 to 100 feet, the cost of breaking the ore should be low, but there is a set-off in the expense of timbering, and therefore 12*s.* 6*d.* to 16*s.* 8*d.* (3 to 4 dollars) per ton for mining costs (including developments) ought to be well within the limits.

At the United Verde mine in Arizona, U.S.A., where the claim is made that copper is being produced under the most favoured conditions in that territory, mining costs per lb. of copper should be 1½*d.* (3 cents) on ores averaging 7 per cent. As the ores are heap-roasted, smelted for matte, and bessemerised on the spot, with coke costing £2 10*s.* (12 dollars) per ton, these operations involve an outlay of about 2·25*d.* (4½ cents) per lb., and the shipment to the eastern electrolytic refinery 0·50*d.* (1 cent): making the cost, with the refining charges, about 4·75*d.* (9½ cents) per lb.; in which figures no account is taken of the gold and silver. With some exceptions, the copper produced in the Lake Superior regions also averages about

4·50*d.* (9 cents) per lb., and the above figures can be taken as the basis of the cost of copper at the principal centres of production in the United States.

Copper mining, at the prices which rule at present, say $7\frac{1}{2}$*d.* to 8*d.* (15 to 16 cents), is very profitable; but the margin of profit in mines which carry no precious metals must have been very narrow when copper was selling at 5·25*d.* to 5·50*d.* ($10\frac{1}{2}$ to 11 cents) per lb., especially at low-grade mines.

The fact that in most copper mines surface and shallow workings have yielded high-grade oxidised ores has enabled many mines to give profitable results under the most adverse working conditions; it is the rich surface ores which have furnished the capital to build railways and construct improved smelters; and when the poorer sulphide-ore zone was reached, the road was paved for their commercial working. A rich surface showing on any copper property may prove, however, most deceptive, as the true value of the mine can only be determined when the sulphide-ore zone is reached. In some instances extensive oxidised ore bodies occur, which may furnish such ores for years—the Copper Queen mine in Arizona, U.S.A., may be mentioned as an example.

Copper, from a metallurgical point of view, is produced by four different methods, namely: (1) From metallic or native ores, such as are found in the Lake Superior mines, where they are of great purity, and require no other treatment than the ordinary refining and casting for commercial purposes; (2) copper produced from sulphide ores by smelting in reverberatory and blast furnaces, with the attendant preliminary preparation of the ores, and the subsequent converting and refining operations; (3) the production of the metal from oxidised ores by a reducing smelting in blast furnaces, with subsequent refining; and (4) the metal is produced from sulphide and oxidised ores by various leaching processes and subsequent precipitation.

The bulk of the metallic copper is produced from low-grade ores, of which some examples are given in Table I. (page 14).

In Table II. (page 15), the production of copper is given arranged according to the various countries whence it is derived.

The quantity of 468,463 tons (Table II.), at an average price of £60 per ton, represents a value of £28,107,780. It would be interesting to ascertain the quantity of silver and gold contained in the copper produced, but as many mine owners refuse to give the necessary data, it is impossible to make such a computation. The eleven electrolytic copper refineries in the United States

TABLE I.

Name of Mine or Company.	Locality.	Copper-content.	Silver.	Gold.
		per cent.	Oz. per ton.	Oz. per ton.
Copper Queen	U.S.A., Arizona	8·000	—	—
United Verde	,, ,,	7·000	?	?
Mountain Copper Company	,, California	8·000	—	—
Anaconda	,, Montana	4·260	4·16	0·014
Atlantic Mining Company	Lake Superior	0·648	—	—
Calumet and Hecla	,,	3·000	—	—
Kearsarge	,,	1·990	—	—
Osceola Consolidated	,,	1·070	—	—
Quincy Mining Company	,,	1·560	—	—
Tamarack	,,	1·330	—	—
Wolverine	,,	1.150	—	—
Great Hall	Canada, British Columbia	3·470	—	—
Le Roi	,,	2·350	1·53	0·780
Tilt Cove	Newfoundland	3·500	—	—
Cape Copper	Cape Colony	10·000	—	—
Great Cobar Copper	New South Wales	4·220	0·50	0·194
Mount Lyell	Tasmania	3·520	2·38	0·090
Atacama District	Chile	5·000	—	—
Boleo	Mexico	6·000	—	—
Mansfeld	Germany	2·500	5·00	—
Rio Tinto	Spain	3·000	1·50	traces.

have an estimated annual yield of 198,600 tons of copper, 170,273 oz. of gold, and 21,199,200 oz. of silver. Taking the gold at £4 per oz. and the silver at 60 cents per oz., this represents £3,225,000, or an average of £16 5*s*. of gold and silver per ton of copper treated, although, no doubt, these values fluctuate very largely according to localities.

Table II.—The World's Production of Copper for the Years 1898, 1899, and 1900.*

No.	Countries.	1898. Tons.†	1899. Tons.†	1900. Tons.‡	Per cent. of total Production 1900.
1	United States of America	239,241	259,517	268,229	55·35
2	Spain and Portugal	53,225	54,220	52,872	11·00
3	Japan	25,175	27,560	27,840	5·60
4	Chile	24,850	25 000	25,700	5·20
5	Germany	20,085	23,460	20,310	4·10
6	Australasia	18,000	20,750	23,000	4·70
7	Mexico	15,668	19.121	22,050	4·60
8	Canada	8,040	6,730	8,446	1·70
9	South Africa	7,060	6,490	6,720	1·45
10	Russia	6,000	6,000	8,000	1·65
11	Bolivia	2,050	2,500	2,100	0·40
12	Italy	3,039	3,000	3,000	0·75
13	Norway	3,615	3,610	3,935	0·83
14	Peru	3,040	5.165	8,220	1·70
15	Newfoundland	2,100	2,700	1,900	0·40
16	Austria-Hungary	1,540	1,505	1,355	0·30
17	United Kingdom	640	550	650	0·16
18	Sweden	480	520	450	0·11
19	Argentina	125	65	75	
20	Algeria	50	0	0	
	Totals	434,023	468,463	484,852	—

* Compiled from *The Mineral Industry*.

† Tons of 2,240 lb.

‡ The production of copper for 1901 in the European countries amounted to 100,241 tons consequently there was an increase over and above the production for 1900.

The first ten mines in Table III. produce 48 per cent. of the world's output, and the other thirty 30 per cent., leaving 22 per cent. to the mines not enumerated.

TABLE III.—LIST OF THE PRINCIPAL MINES AND THEIR PRODUCTION FOR 1899.

No.	Name of Mine.	Country.	Tons.*
1	Anaconda	Montana, U.S.A.	48,176
2	Calumet and Hecla	Lake Superior, U.S.A.	43,750
3	Rio Tinto	Spain	33,882
4	Boston and Montana	Montana, U.S.A.	30,000
5	Mansfeld	Germany	20,785
6	United Verde	Arizona, U.S.A.	19,641
7	Copper Queen	,, ,,	16,473
8	Tharsis	Spain	12,000
9	Boleo	Mexico	10,335
10	Iron Mountain	California, U.S.A.	10,000
11	Arizona Copper Company	Arizona, U.S.A.	8,514
12	Besshi	Japan	8,000
13	Tamarack	Lake Superior, U.S.A.	7,924
14	Mount Lyell	Tasmania	7,600
15	Montana Ore Purchasing Company	Montana, U.S.A.	6,857
16	Ashio	Japan	6,500
17	Quincy Mining Company	Lake Superior, U.S.A.	6,384
18	Butte and Boston	Montana, U.S.A.	5,267
19	Detroit Company	Arizona, U.S.A.	6,208
20	Wallaroo and Moonta	South Australia	5,073
21	Osceola Consolidated	Lake Superior, U.S.A.	4,888
22	Parrot Mining Company	Montana, U.S.A.	4,743
23	Butte Reduction Works	,, ,,	4,486
24	Colorado Smelting and Refining Company	,, ,,	4,273
25	Cape Copper Company	Cape Colony	4,140
26	Mason & Barry, Limited	Portugal	4,000
27	Great Cobar	New South Wales	3,520
28	Utah Consolidated	Utah, U.S.A.	3,487
29	Old Dominion	Arizona, U.S.A.	2,811
30	Sudbury	Canada	2,738
31	Namaqua Copper Company	Cape Colony	2,350
32	Rossland	British Columbia, Canada	2,336
33	Wolverine	Lake Superior	2,137
34	Atlantic	,, ,,	2,087
35	North Mount Lyell	Tasmania	2,000
36	United Globe	Arizona, U.S.A.	1,987
37	Nelson	British Columbia, Canada	1,873
38	Tilt Cove	Newfoundland	1,800
39	Kiadebek	Russia	1,800
40	Franklin	Lake Superior, U.S.A.	1,600
		Total	372,425

* Tons of 2,240 lb.

TABLE IV.—THE WORLD'S PRODUCTION OF COPPER SINCE 1879.

Year.	Tons.*	Year.	Tons.*	Year.	Tons.*
1880	153,959	1887	223,798	1894	324,764
1881	163,369	1888	258,026	1895	334,554
1882	181,622	1889	261,205	1896	378,440
1883	199,406	1890	269,615	1897	405,350
1884	220,249	1891	275,589	1898	434,023
1885	225,592	1892	291,474	1899	468,463
1886	217,086	1893	302,021	1900	486,084

* Ton of 2,240 lb.

TABLE V.—CONSUMPTION OF COPPER IN DIFFERENT COUNTRIES IN 1899.*

Countries.	Tons.
United States of America (outside of existing stocks)	190,887
Germany	97,656
Great Britain	82,404
France	47,633
Austria-Hungary	16,921
Russia	12,509
Italy	8,520
Belgium	5,500
Netherlands	2,400
Denmark, Sweden, Norway, Spain, and Balkans	2,600
Exportation to Asia and other Countries	1,250
Japan, Australia, and Eastern Asia	9,000
Total Consumption	477,271

* *Recueils Statistiques*, by the Metallgesellschaft Frankfurt-am-Main, 1900.

TABLE VI.—STOCKS OF COPPER ON HAND IN FRANCE AND GREAT BRITAIN, EXCLUDING COPPER IN TRANSIT FROM CHILE AND AUSTRALIA, ACCORDING TO REPORTS BY MESSRS. H. R. MERTON AND COMPANY, LONDON.

Year.	Stocks on Jan. 1st. Tons.	Year.	Stocks on Jan. 1st. Tons.
1888	35,001	1895	51,575
1889	96,194	1896	43,604
1890	94,942	1897	31,776
1891	62,449	1898	27,895
1892	53,486	1899	22,702
1893	51,556	1900	17,797
1894	43,428	1901	12,600

Most mines are being pressed into greater activity to increase the output, with the result that the copper production during the last two or three years of the last century was the largest in the history of this metal; and, in spite of the discovery and development of new copper-ore bodies and the activity of existing producers, they are barely keeping pace with the increasing demand for this metal. The best authorities on the subject seem to agree that the price of copper will be maintained at a higher level than heretofore, notwithstanding the recent drop in the metal, which evidently seems to be the result of market manipulation; the principal argument brought forward in support of this view being that many of the great copper mines cannot maintain indefinitely their present ratio of production, and that there are at present very few new large ore bodies being developed which promise to become large sources of supply in coming years. The general opinion is that eventually any reduced output from the large mines will be equalised by the production of numerous smaller properties now in course of development.

The following figures prove that the increase in the world's production was not large: in 1899 the production was 468,463 tons, whereas in 1898 it amounted to 434,023 tons, showing an increase of only 34,440 tons, or 7½ per cent.; further, in 1900 the production was 486,084 tons, whereas in 1899 the production was 468,463 tons, an increase of 17,621 tons, or barely 4 per cent. From these figures it may be inferred that an over-production of the metal is not likely to take place, in view of the increasing demand for it which exists for electrical, naval, and railway purposes.

Taking the price of copper, on an average, as at £60 per ton, there is a handsome margin of profit in mines which can produce the metal at £40 per ton; so that a mine which can turn out 1,000 tons of copper a year at that price would show a yearly profit of £20,000, amply sufficient to justify the investment of a substantial amount of capital.

TABLE VII.—AVERAGE PRICE OF COPPER.

Year.	Chile Bars, G.M.B., per ton * in London.			Lake Copper in New York.			
				Per lb.	Per ton.		
	£	s.	d.	Cents.	£	s.	d.
1888	81	11	3	16⅔	77	0	0
1889	49	14	8	13¾	63	10	0
1890	54	5	3	15¾	72	15	0
1891	51	9	4	12⅞	59	10	0
1892	45	13	2	11½	53	0	0
1893	43	15	6	10¾	49	10	0
1894	40	7	4	9½	43	15	0
1895	42	19	7	10¾	49	10	0
1896	46	18	1	10⅞	50	17	6
1897	49	2	7	11⅓	52	5	0
1898	57	16	7	12	55	15	0
1899	73	13	9	17⅝	81	7	6
1900	highest, £80; lowest, £50.						

* Tons of 2,240 lb.

In studying the question of supply and demand, it would be interesting to present such facts as would embody the future possibilities of all the prominent mines, with regard to their ability to maintain or increase their present output of copper; but only a few general remarks on the subject can be offered here, and they embrace only the districts where notable copper mines are located.

Although copper ores are found distributed over the whole world, the chief centres of production are not very numerous, if it be considered that Montana, Michigan, and Arizona, in the United States of America, and Spain and Portugal, account for 285,939 tons, or over 61 per cent. of the total production. The United States is the largest copper-producing country; next in importance are Spain and Portugal; then comes Chile, whose productions tands about equal with Japan's; and next in importance is Germany, followed by Australasia and Mexico.

There is very little doubt that the ore bodies of Butte, Montana, U.S.A., will extend to great depth; it is questionable whether they will maintain their present copper values, but with improved methods they will be able to maintain their present production for many years.

The deposits of Lake Superior, U.S.A., are of great extent, and are known to exist at great depths. The conclusion can be drawn that the supply from that region will be maintained, and possibly, owing to the increase in the price of the metal, as new and old mines are being opened, the present ratio of production in that region may increase.

The Rio Tinto mines are of such known extent that the present production will be maintained for some generations to come.

Judging from indications as they present themselves to the observant copper prospector, it is more than likely that a few years hence, Arizona, U.S.A., will greatly increase its present production. Mexico will, given the necessary railway facilities, more than double its present production.

Although Colorado, U.S.A., figures as a copper producer, the metal is won mostly as a by-product in the treatment of its silver-lead and other ores, and from the copper ores sent to the custom smelters from various quarters of the western states.

Besides Shasta county, other counties in California, U.S.A., promise to become producers of copper; and in Idaho, U.S.A., when railway communication shall have been established with the Seven Devils country, some valuable copper deposits will become available.

In the Seven Devils district, and in the adjacent Snake River cañon, copper deposits are very abundant. There is, in that vicinity, an extensive series of Triassic basic lavas, with intercolated layers of slates and limestone. There are also diorites, intrusive in these beds. All of these igneous rocks apparently contain copper, which was easily concentrated into deposits of various kinds; some, fissure veins; others, zones of impregnation; others, contact deposits. In the locality of the original discovery in the Seven Devils, the copper occurs in typical contact-deposits. Small masses of limestones are embedded in a later, intrusive diorite; at the contact, and usually in the limestone, are found irregular bodies and bunches of bornite, chalcocite, and a little chalcopyrite, containing some 10 oz. of silver and a little gold per ton. The limestone at the contact is very crystalline, and contains, associated with the ores, abundant garnet, epidote, quartz, calcite, and specularite. The copper sulphides, as shown by their intergrowth, were certainly formed at the same time as the gangue minerals.

Wyoming, as well as Nevada, U.S.A., will also be added to the list of copper producers. Utah, U.S.A., too, has some valuable copper mines.

Late discoveries of alluvial gold in Alaska, U.S.A., have given an impetus to prospecting in that Arctic region, and the reports of copper discoveries there are too numerous to be ignored; but, so far, attention can only be given to the properties which are located near the sea coast. When a railway line connects Walfisch Bay with the Cape Town to Buluwayo line, something will be heard of the now dormant deposits of copper in German South-west Africa. New Caledonia is at present shipping its ores to various ports of Australia, but no doubt, in course of time, it will have its own smelting establishments. In Brazil, a French company is inaugurating work on some promising mines, which are favourably located for economical exploitation. There is no telling where new discoveries may be made, and consequently such a contingency as an exhaustion of the copper supply in a generation or two is not likely to take place, for many localities which are copper-bearing will become productive when provided with railway and transport facilities. On the other hand, there is so far no indication that over-production can take place.

The development of the copper-mining industry in the Western states of America and in Mexico is greatly assisted by custom smelters, who have a very uniform rate of charges, according to location; and it will be interesting to examine Table VIII., containing a schedule of the smelting charges by one of the Arizona smelters, located at the Needles.

TABLE VIII.

Copper ores containing Lead. Percentages.	Smelting charge per Ton.				Copper ores containing Lead. Percentages.	Smelting charge per Ton.			
	£	s.	d.	Dollars.		£	s.	d.	Dollars.
0 to 5	2	12	1	12·50	30 to 35	1	7	1	6·50
5 „ 10	2	7	11	11·50	35 „ 40	1	2	11	5·50
10 „ 15	2	3	9	10·50	40 „ 45	0	18	9	4·50
15 „ 20	1	19	7	9·50	45 „ 50	0	14	7	3·50
20 „ 25	1	15	5	8·50	50 „ 60	0	10	5	2·50
25 „ 30	1	11	3	7·50	60 and over		—		free.

The zinc limit in lead ores is 5 per cent., and in copper ores 10 per cent., and for each unit over and above 10 per cent., 2*s.* 1*d.* (50 cents) per unit is the penalty.

The payment for lead above 5 per cent. per unit on a 16*s.* 8*d.* (4 dollars) basis, New York price, is shown in Table IX., and for each advance or decline of 2½*d.* (5 cents) in the New York price, a corresponding variation of ½*d.* (1 cent) is made in the price per unit.

TABLE IX.

Copper-ores containing Lead. Percentages.	Payment per Lead Unit.				Copper ores containing Lead. Percentages.	Payment per Lead Unit.			
	£	s.	d.	Cents.		£	s.	d.	Cents.
0 to 5		*nil*		*nil*	30 to 35	0	2	1½	51
5 „ 10	0	1	8	40	35 „ 40	0	2	2½	53
10 „ 15	0	1	8	40	40 „ 45	0	2	2½	53
15 „ 20	0	1	8	40	45 „ 50	0	2	3	54
20 „ 25	0	1	8½	41	50 „ 60	0	2	3½	55
25 „ 30	0	2	1	50	60 and over	0	2	3½	55

Sulphur, up to 5 per cent., is allowed free in copper ores, but 1*s.* 0½*d.* (25 cents) per unit is charged for excess above it.

The smelting rates on copper ores are shown in Table X.

TABLE X.

Percentages of Copper.	Smelting charge per Ton.				Percentages of Copper.	Smelting charge per Ton			
	£	s.	d.	Dollars.		£	s.	d.	Dollars.
0 to 5	1	13	4	8·00	15 to 20	1	2	11	5·50
5 ,, 10	1	9	2	7·00	20 ,, 25	1	0	10	5·00
10 ,, 15	1	5	0	6·00	25 ,, 30	0	18	9	4·50

Neutral bases, such as silica and iron, are charged 7½*d.* (15 cents) per unit up or down to a maximum charge of £2 12*s.* 1*d.* (12·50 dollars) per ton.

The payments for copper ores are shown in Table XI.

TABLE XI.

Percentages of Copper.	Rate per Unit.				Percentages of Copper.	Rate per Unit.			
	£	s.	d.	Dollars.		£	s.	d.	Dollars.
0 to 5	0	6	3	1·50	15 to 20	0	8	9	2·10
5 ,, 10	0	5	3½	1·75	20 ,, 25	0	8	11½	2·15
10 ,, 15	0	8	4	2·00	25 ,, 30	0	9	2	2·20

Gold is being paid for at the rate of £4 3*s.* 4*d.* (20 dollars) an oz.; and silver at 2*s.* 6*d.* (60 cents) an oz.

The western smelters greatly prize lead ores of a high percentage, and make no smelting charge for ores containing over 60 per cent. of lead, as this metal is mainly utilised as a collector for the gold and silver contained in the dry ores.

The railway companies charge their freights in accordance with the value of the ores, the low grade paying lower rates than the high-grade ores.

CHAPTER III.

THE OCCURRENCE AND DISTRIBUTION OF COPPER ORES.

(1) **Arizona, U.S.A.**

Copper ores are extensively distributed throughout this territory, which, in course of time, is destined to become the second in the rank of producers in the United States. At present, the chief centres of production are: Bisbee, in the southern portion of Chochise county; Jerome, in Yavapai county; Morenci and Clifton, in Graham county; and Globe, in Pinal county. Large quantities have also been produced in Pima county, near Tucson, and in the Santa Rita Mountains, near Rosemont. With the advent of improved railway communication, many localities will become producing centres, as many promising prospects are idle for lack of capital and transport facilities. Those which deserve to be mentioned are: The Azurite copper mines, in the Surritas mountains; Olive Camp, in the Pima mining district; the San Xavier mine, near Tucson; the Hillside copper mines, in the Eureka district; the Ray copper mines of Pinal county; the Kennedy-Bryan group, in Pinal county; the Helvetia copper mines, situated 31 miles south of Tucson; the Dos Cabezas mines; the Grand Reefs, in Graham county; the Piety group, in Pinal county; the Castle Creek district, in Yavapai county; and many others.

The production of copper in this territory for 1899 amounted to over 55,000 long tons.

United Verde Mines.—These mines, situated at Jerome, 28 miles from Prescott, in Yavapai county, are owned by Senator Clark, of Montana, who built his own railway to connect the mine with the Prescott and Phœnix line. He produces from 1,500 to 1,800 tons of copper monthly, containing considerable quantities of gold and silver. The ore bodies are of great extent and value, and cannot be exhausted in a lifetime. From different levels adits have been driven, which have opened the mine to a depth of 600 feet. By one of those strange incongruities peculiar to mine administration, the splendid smelting works are located on the top of a mountain, and the ore has to be hauled up steep inclines by electric traction, instead of taking advantage of the natural declivity, which would allow the automatic handling of the ore, if the smelter had been located at the foot of the mountain, and would have made it also possible to utilise the ample water supply of the Verde river, not so very far distant from the base of the mountain range on which this mine is located.

The mines, smelting plant, and town of Jerome are situated on the eastern slope of the Black Hill range, nearly upon the crest, at an altitude of about 5,600 feet above sea level, and at least 1,800 feet above the Rio Verde valley, which spreads out in a grand panorama to the east and south.

The ore bodies are found in slates, and to a limited depth the ores were carbonates and oxides. Below the surface ores is found a partially oxidised, rich black sulphide of copper, and below this are found the unaltered sulphide ores. Most of the ores from this mine are now heap-roasted before going to the smelter. In 1899, the mine produced about 20,000 tons of copper.

Geologically considered, the United Verde is in a zone of slates and intruded dioritic rocks, the neighbouring limestones being of later age, uncomformably superposed, and apparently having no connection with the deposits.

The other three great copper producing districts of Arizona, namely, Bisbee, Globe, and Clifton, resemble each other, in that the deposits occur in a region of limestones and intrusive eruptive-rocks and under climatic conditions of extreme aridity.

Bisbee.—The camp is situated near the head of a cañon, on almost the extreme southern edge of Cochise county, about 6 miles from the Mexican boundary line. The Bisbee mine is owned by the Copper Queen Company. It is reached by its own railway, which connects with the Southern Pacific Railway at Benson, about 35 or 40 miles north-west. The town is scattered up and down the cañon for at least a mile; but the business portion is centred immediately east and south of the smelting plant.

At Bisbee the Copper Queen deposits are in flat-lying limestones, which are underlaid by quartzites, and have not been developed to any great vertical depth.

The appearance of the oxidised ore is very peculiar, and to the inexperienced eye would appear like so much clay enclosing nodules of cupriferous limonite. Disseminated through these clayey ore bodies is found an appreciable quantity of finely divided metallic copper. To a depth of 400 feet, the copper is mainly in the form of carbonates, with hydrated oxides of iron and alumina, carrying about 8 per cent. of copper; but below this depth, sulphide ores are encountered.

At this mine copper bars were produced by a single fusion from the oxidised ores. In 1894, matte smelting was adopted, but there is still enough oxidised ore in the mine to enrich the matte, which averages 45 per cent. The production of copper from this mine in 1899 was 16,473 tons.

All the copper at the Arizona carbonate mines is produced by a single fusion in water-jacket furnaces, and, in case any excess of sulphide ores are present, a matte is produced simultaneously, which is roasted in kilns and added to the ore charges. The copper is produced as black copper, containing from 95 to 97 per cent. of copper, and the matte carries 50 to 60 per cent. of copper.

Clifton-Morenci Copper District.—In this district, situate near the borders of New Mexico, the area of mineralisation is much larger, and the geological conditions more complicated. A series of quartzites and limestones resting on granite have been extensively cut through by igneous intrusions of both basic and acid eruptives, and subsequently broken by a complicated system of faults. The ore is found both in the eruptive-rocks and in a certain horizon of limestone.

The principal mining companies are the Arizona Copper Company of Clifton, and the Detroit Copper-Mining Company of Morenci. The former draws its ore supplies from various groups of mines, situated from 5,000 to 7,000 feet above sea level. The most important of them, the Longfellow group, is situated in the heart of the Morenci field, side by side with the mines of the Detroit Copper-Mining Company, has been a producer since 1872. Up till a few years ago, practically all the ores were taken from the contacts of magnesian limestone and porphyry. These ores were oxidised and self-fluxing, and a single smelting was all that was necessary to produce copper bullion, 98 per cent. fine. The mineralised limestone belt extended fully 1 mile in length. The ore bodies, however, were largely superficial in their occurrence, and were never found in quantity at a greater depth than 300 feet below the surface, the average depth of pay ore being 150 feet. The ores, generally, have been formed by the replacement of limestone by solutions of copper. As early as 1891, the mines situated in the magnesian-limestone field began to give evidence of exhaustion. Extensive exploration by the diamond drill was only successful in exposing and throwing more light on the mineral formation. Exploration for new ore bodies in this direction being unsuccessful, attention was turned to the extensive porphyry belt, against which the limestone and calcareous shales abut.

On the surface of the porphyry belt there were practically no indications of copper. There was, therefore, nothing definite to follow from the surface. Under the circumstances, it was deemed advisable to pierce the Humboldt mountain by a tunnel, which would cut under the apex of the mountain, at a depth of fully 400 feet. This work, conducted with judgment, was successful in exposing enormous bodies of low-grade sulphide ores, which, however, were so low in grade that for a time it was doubtful whether they could be treated with profit. An enormous amount of capital had been sunk in the development of the ore bodies, and further large outlays were made on concentrating plants and on other plants necessary for the treatment of these ores. The problem was successfully solved and the ore bodies exposed proved much more extensive than the original magnesian limestone belt.

In addition to the Longfellow group, the company has also groups of mines known as the Queen, Coronado, and Metcalf. Of these, the last-named, so far, has been the most important. It has produced largely a low-grade oxidised ore, found on the surface of the Metcalf hill. This ore, while extremely low in grade, occurs in great quantity. For its treatment concentration and leaching have both been found necessary.

Both at Clifton and Morenci, concentration of the carbonate ores has been carried on; this gave rich concentrates, but the losses in the tailings being heavy, leaching works have been erected for their treatment by means of sulphuric acid, using metallic iron to precipitate the copper. The acid is made on the spot from the sulphide copper ores.

The metallurgical plant is one of the largest in the territory, and consists of smelting furnaces with a capacity of 500 tons per day, concentrating plant with a capacity of 750 tons per day, a leaching plant with a capacity of 150 tons per day, a two-converter Bessemer plant, operated entirely by gas engines; a sulphuric-acid plant, and a bluestone plant. In addition to the Bessemer plant, three of the concentrating plants are operated by gas engines. The gas engines employed have a rated capacity of 750 horsepower, and have been found to be extremely economical in fuel. The company is now producing copper at the rate of about 9,000 tons per annum. It employs about 1,500 men on its mines, railways, and works.

The Detroit Copper-Mining Company of Morenci, the property of Messrs. Phelps, Dodge & Company, produces about 6,000 tons of copper per annum, and employs 1,000 men. This company is about to build a narrow gauge (3 feet) railroad from Morenci to Guthrie, a distance of 18 miles. The Company is also erecting a 100-ton concentrating plant, and is making many improvements of a substantial order.

Globe Copper District.—The Globe district is situated on the north-western slope of the Pinal mountains, about twenty-eight miles from the old and once famous Silver King mine. In the period from 1876 to 1883, this district attracted much attention by reason of the many discoveries of rich silver mines. At present mining activity is confined chiefly to copper. The completion of the Gila Valley, Globe, and Northern railway, a branch of the Southern Pacific railway, now gives access to the region, and has greatly stimulated its development. The first location on what is now considered the main copper-bearing belt was made in 1875 by the locators of the Silver King mine, and it was named the "Globe." This location is now held and worked by the Old Dominion Copper Company which also has two other locations on the same vein—the South-west Globe and the Globe Ledge. The vein is described as following a contact, having a diorite footwall and a limestone hanging-wall containing fossils of the Carboniferous period. On the west side of the outcrop, there is a capping of trachyte, which conceals outcrops in that direction. Good ore was proved by Dr. Trippel in a drift west from the shaft, and openings were afterwards made through the bed of trachyte; these have been extended downward on ore for over 300 feet. This deposit was regarded by Dr. Wendt as a fissure vein, and he notes that in approaching the ore body through the long adit tunnel running lengthwise of the claims the conditions are similar to those observed in the Longfellow mines at Clifton and the Queen and Prince mines at Bisbee, especially as regards the decomposition and kaolinisation of the rock.

The main ore bodies are in limestone, and the ores are mostly oxidised, but large bodies of sulphide ores have been found on the second and third levels, with oxidised ores below them. The ores carry a large amount of silica, and frequently require heavy additions of lime and iron to the smelting charges.

TABLE XII.—COPPER-PRODUCTION IN ARIZONA, U.S.A. FOR 1898, 1899, AND 1900.*

Name of Mine.	1898.	1899.	1900.
	Tons.†	Tons.†	Tons.†
Arizona Copper . .	8,111	8,514	8,793
Copper Queen . .	15,066	16,473	15,349
Detroit . . .	5,102	6,208	4,799
Old Dominion . .	800	2,811	3,194
United Verde . .	18,896	19,671	17,844
United Globe . .	1,271	1,987	
Other Mines . .	223	334	1,584
Totals . .	49,469	55,998	51,563

* Compiled from *The Mining Industry*. † Tons of 2,240 lb.

(2) Montana.

The principal copper camp in Montana is Butte, well known through the famous Anaconda mine. Like a promontory, a butte rises boldly above the surrounding country as a landmark to prospectors, giving this locality in Silver Bow county the name of Butte, which, prior to the development of its copper resources, was known as a prominent silver-producing camp.

The mining district around Butte City forms a rectangle seven miles long by four miles wide. The country rock is mainly granite, traversed by dykes of volcanic rocks, which seem to be in close association with the eruptive rocks of the Butte. The copper belt occupies a large portion of this area, and the ore deposits occur in very irregular masses. They do not seem to have in many places defined walls, and the ore occurs mostly in shoots, which pinch out along the strike, but are very persistent in depth. The ore formation is a succession of lenses, and this lenticular form is very characteristic of the smaller ore deposits. The width of the ore shoots varies, from a few feet up to 100 feet, as in the Anaconda mine.

In these large ore bodies occur horses and large bunches of country rock, which, together with the very poor ore, are left behind to fill in the stopes. Like those of most large copper ore bodies, the outcrop ores are of brown quartz, heavily charged with iron. After breaking through this quartz capping, quartz, associated with soft red and yellow iron oxides, rich in gold and silver, occurs, but showing very little copper. On deeper sinking the copper zone is gradually approached, and at water level the unaltered region is finally reached.

As the ore bodies do not present very sharply defined walls, Mr. S. F. Emmons has suggested that they have formed along a series of small fissures marking some line of disturbance, and not from a general faulting, and have enlarged the original channels by replacement of the walls.

The mineral characteristics are varying proportions of sulphide of copper, chalcopyrite, and pyrite, and occasional bornite. The gangue is mainly granitic with some quartz.

The prominent characteristics of the Butte copper lodes are, first, an upper oxidised zone extending down from 200 to 400 feet from the surface, which contains less than 1 per cent. of copper on the average, the value being principally in silver. Below this is a rather ill-defined zone characterised by great values in the rich copper sulphides, associated with pyrite and chalcopyrite. The proportion of these rich sulphides gradually decreases with depths, until in some mines the ores consist only of pyrite with a slight admixture of chalcopyrite.

Mr. Hiram W. Hixon, in his "Notes on Lead and Copper-Smelting," gives the cost of making 1 lb. of copper at the Anaconda mine as shown in Table XIII. This cost does not include freight at New York City. In each lb. of copper there is recovered an average value of about *2d.* (4 cents) in precious metals.

The Butte sulphide ores are concentrated at the Anaconda works in plants similar to those of Lake Superior. In some of the works jigs and Frue-vanners are used. The concentrates, which contain about 40 per cent. of sulphur, are roasted in mechanical furnaces down to about 6 per cent. Ores containing 10 to 12 per cent. of sulphur are not roasted. The coarse ore is smelted in cupola-furnaces, and the fine ores in reverberatory furnaces.

TABLE XIII.

Pound of Copper Sold.	Pence.	Cents.
Mining	1·556	3.112
Concentrating	0·307	0·614
Smelting	1·076	2·153
Converting	0 353	0·705
	3·292	6·584
Casting	0·178	0·356
Refining	0·500	1·000
Melting	0·200	0·400
Total cost . . .	4·170	8·340

TABLE XIV.—COPPER-PRODUCTION IN MONTANA, U.S.A., FOR 1898, 1899, AND 1900.*

Names of Mines and Works.	1898.	1899.	1900.
	Tons.†	Tons.†	Tons.†
Anaconda	47,863	48,176	‡ —
Boston and Montana	27,678	35,267	29,553
Butte and Boston	3,125		7,567
Butte Reduction-works	4,323	4,486	5,566
Colorado Smelting and Refining Company	3,418	4,273	5,113
Hecla Consolidated Mining Company	53	69	59
Parrot Company	5,555	4,743	‡ —
Montana Ore Purchasing Company	5,841	6,857	9,936
Other Mines and Works	—	2,578	55,809
Totals	97,856	106,449	113,603

* Compiled from *The Mining Industry*. † Tons of 2,240 lb.
‡ Included under other mines.

(3) Michigan, U.S.A.

Lake Superior District.—In this region copper is found in the metallic state in the upturned rocks of Algonkian age (see Fig. 1), known as the Keweenawan series, in both the sedimentary and the interstratified igneous rocks, which were deposited unconformably on the iron-bearing Huronian series, and they in turn are overlapped by nearly horizontal Cambrian sandstones.

The Keweenawan series consist of eruptive layers, and of sandstones and conglomerates largely made up of a detrital eruptive material, the latter predominating. These rocks have experienced intense and long-continued metamorphic action, which has produced amygdaloidal structure. The metal occurs as a cement, binding together and replacing the pebbles of a porphyry-conglomerate; or filling the amygdules in the upper portions of the interbedded sheets of massive rocks; or as irregular masses, sometimes of great size, in veins, or in irregular masses along the contacts between the sedimentary and the igneous rocks. When in small veins, they traverse the beds at right angles to strike and dip. Minute specks of copper-minerals are found in the succeeding sandstones, but not in sufficient quantity to be of any commercial importance. No other metallic minerals are found in association with the copper, except silver, which also mostly occurs in the metallic state. The rocks of the Keweenawan system are most strongly

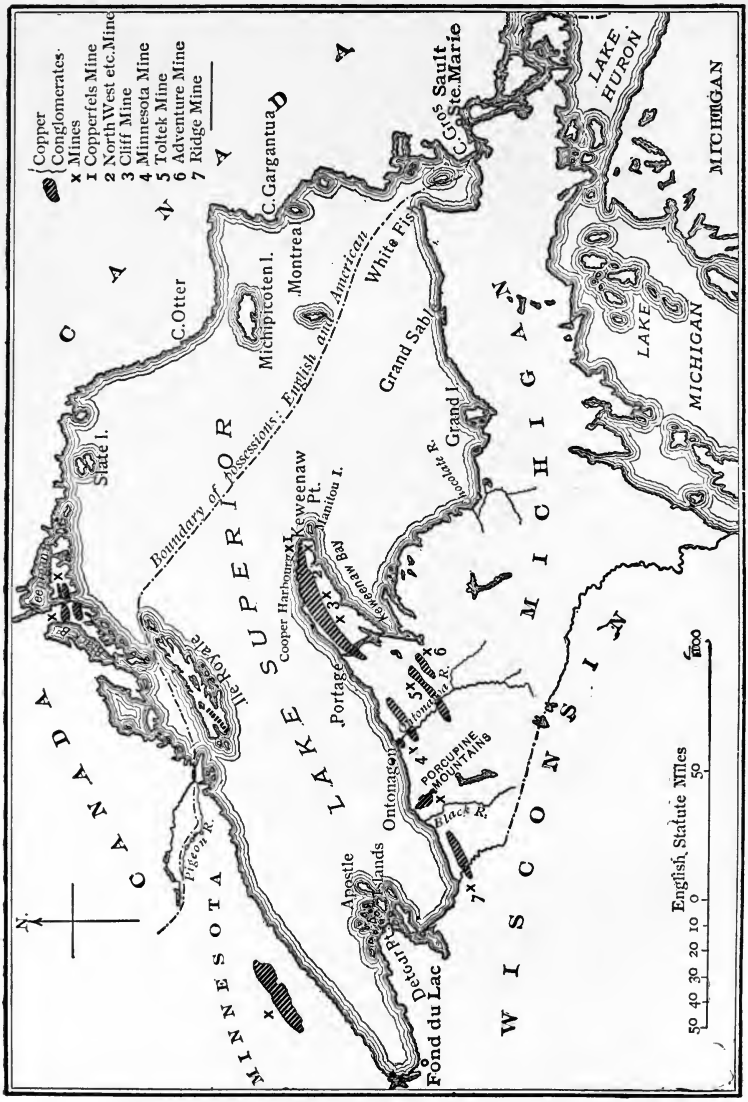

FIG. 1.—MAP SHOWING COPPER DEPOSITS AROUND LAKE SUPERIOR.

developed on the southern shore of Lake Superior at Keweenaw Point, where they dip north-eastward under Lake Superior, and reappear with a south-easterly dip on Isle Royale and the Canadian shore. Western Lake Superior occupies this synclinal trough.

There are three districts in this locality: (1) Keweenaw Point on the easternmost end; (2) Portage Lake in the middle; and (3) Ontonagon, at the western end.

The Portage Lake district is the most important, and here are located the Calumet and Hecla, Tamarack, Peninsula, etc., mines. The miners distinguish the occurrence of ore in the different workings as either amygdaloid or conglomerate ores. At one time this section was the leading copper-producer in the United States, but of late years, Butte, Montana, has taken the lead. The locality was evidently known to some prehistoric races who mined for the metal, ample evidence of which was found by the early explorers. In the workings large masses of native copper, weighing many tons, have been encountered, and the amygdules are often entirely filled with native copper; but when their filling is not exclusively metallic, the copper is accompanied by native silver, calcite, quartz, chlorite, etc. When, as sometimes occurs, a mass of copper is met with, extending some 20 or 30 feet along the course of a vein, and weighing considerably above 100 tons, its removal is attended by a certain amount of difficulty. In order to extract such a mass of copper the rock is first stoped from one side of it, and the metal subsequently divided (by means of cross-cut chisels) into fragments of such dimensions as to admit of their being taken upon rollers to the shaft and thence raised to the surface.

The permanency of the ore deposits in these regions require no further evidence than the depth of some of the shafts whence the ores are raised. These, in several instances, exceed 4,000 feet, and shafts are being continued to a depth of 5,000 feet. When it is considered that the productive Lake Superior mines extend along a narrow belt, nearly 100 miles in length, it is evident that they will constitute, for a long time to come, important factors in the world's copper supply.

Lake Superior copper has always been sold on the market as refined copper, but as the largest portion of the copper from other districts is now electrolytically refined, Lake Superior brands no longer enjoy the same exclusive reputation as heretofore.

In the Lake Superior district, the ores are, on an average, of a low grade, the copper being disseminated through the rock in small metallic particles. This necessitates a preliminary stamping of the rock and the subsequent concentration of the mineral, which is sent to the smelter. There are employed at the reduction works large ball stamps, capable of crushing 300 to 400 tons per stamp per day, and the stamp product is concentrated on jigs and slime tables. Owing to the low grade of the rock, every possible economy has to be used in mining, with great capacity for the crushing plants and all the accessory operations, so as to reduce costs to a minimum. The ores of this region do not carry any gold.

The stamp discharges the ore through screens, with perforations $\frac{3}{16}$ inch in diameter, to hydraulic separators, and thence to jigs and rotary slime tables. The only middlings produced are in re-jigging the overflow from the coarse jigs, which make the richest concentrates. The middling heads that are thus separated by re-jigging from the waste tailings are sent back to the stamps for re-crushing. At the mills, two grades of concentrated products are made, carrying about 25 per cent. and 85 per cent. of metallic copper respectively.

To give an idea how close the margin is, at which some of these mines had to work, it is only necessary to adduce the example of the Atlantic Mine. That mine in 1894 crushed 330,000 tons of ore, producing 3,120 tons of mineral or concentrate, less than 1 per cent. of the quantity of rock stamped, yielding 2,416 tons of copper, or 77½ per cent. of copper in the concentrates, and the copper was sold at 5·25*d.* (10½ cents) per lb.

Table XV.—Copper-Production in Michigan, U.S.A. for 1898, 1899, and 1900.

Name of Mine.	1898.	1899.	1900.
	Tons.*	Tons.*	
Arcadian	—	890	357
Atlantic	1,950	2,087	2,209
Baltic	18	269	774
Calumet and Hecla	42,010	43,750	36,340
Central	130	—	—
Franklin	1,593	504	1,635
Mass	—	27	—
Osceola	5,269	4,888	5,000
Quincy Mining Company	7,309	6,384	6,302
Tamarack	10,044	7,924	8,214
Wolverine	2,159	2,137	2,133
All other Mines	11	662	1,429
Totals	70,493	69,522	64,393

* Tons of 2,240 lb.

Table XVI.—Production of Copper in the United States from 1897 to 1900 Inclusive.*

States and Territories.	1897.	1898.	1899.	1900.
	Tons.†	Tons.†	Tons.†	Tons.†
Arizona	36,170	49,475	55,972	51,520
California	6,308	9,618	10,677	13,232
Colorado	4,213	4,853	4,739	3,493
Michigan	65,107	69,951	69,574	64,387
Montana	105,874	96,866	106,229	113,599
Utah	1,721	2,404	4,156	8,261
Eastern and Southern States	1,664	1,999	1,698	3,088
All others	901	953	2,227	5,597
Copper in sulphate of copper	1,867	3,132	4,245	5,051
Totals	223,825	239,251	259,517	268,229

* In 1901 the production of copper in the United States amounted to 263,346 tons, and consequently was below the production of the previous year.

† Tons of 2,240 lb.

The consumption of copper in the United States for 1899 amounted to 174,822 tons. About two-thirds of the copper produced in the United States is electrolytically refined.

TABLE XVII.—PRODUCTION AND CONSUMPTION, AND IMPORTS AND EXPORTS OF COPPER IN THE UNITED STATES SINCE 1882.

Year.	Imports.	Exports.	Stock on hand on January 1st.	Production.	Consumption.
	Tons.*	Tons.*	Tons.*	Tons.*	Tons.*
1882	237	2,788	?	41,191	?
1883	282	22,630	?	52,101	16,359
1884	86	47,245	13,394	66,138	18,979
1885	256	50,966	13,394	75,934	22,993
1886	238	29,605	15.625	72,428	40,918
1887	94	19,196	17,857	82,700	63,598
1888	48	35,714	17,857	104,338	53,047
1889	55	32,589	33,482	109,253	81,184
1890	296	17,857	29,018	119,609	85,977
1891	1,408	51,394	45,089	133,511	94,685
1892	693	40,198	33,929	148,774	118,201
1893	2,472	80,387	25,000	149,544	70,629
1894	5,235	75,737	26,073	163.394	84,267
1895	7,194	54,332	34,698	177.881	120,619
1896	12,234	125,851	38,822	214,149	102,083
1897	12,026	128,851	21,821	227,763	126,438
1898	19,410	133,824	24,269	239,241	122,382
1899	42,218	111,573	39,608	259,517	174,822
1900	46,342	157,469	39,608	268,229	155,169

* Tons of 2,240 lb.

TABLE XVIII.—PRODUCTION OF COPPER IN THE UNITED STATES.*

Year.	Arizona.	California.	Colorado.	Michigan.	Montana.	New Mexico.	Utah.	Eastern & Southern States.	Allothers not enumerated.
	Tons.†	Tons.†	Tons.†	Tons.†	Tons.†	Tons.†	Tons.†	Tons.†	Tons.†
1880	616	?	?	?	?	?	?	?	?
1881	1,726	?	?	?	?	?	?	?	?
1882	8,028	369	667	25,505	4,043	388	270	873	388
1883	10,659	715	515	26,454	11,010	368	153	449	1,053
1884	11,934	391	899	20,950	19,238	27	118	545	594
1885	10,137	209	512	32,482	30,266	36	57	113	513
1886	7,141	192	182	35,830	25,718	248	223	154	594
1887	7,941	714	898	33,836	35,134	126	1,116	90	1,086
1888	14.821	700	724	38,617	43,977	728	952	45	1,445
1889	14,702	759	1,384	39,024	46,691	1,645	1,072	40	1,618
1890	16,508	714	2,678	44,953	49,553	388	273	1,875	?
1891	18,700	1,673	3,125	51,071	50,536	714	759	580	1,540
1892	17,135	1,430	3,236	47,960	73.348	223	893	580	536
1893	19,550	1,261	3,179	50,653	69,066	123	585	185	1,502
1894	19,880	54	2,914	51,128	81,793	?	528	1,088	483
1895	21,575	101	2,734	57,920	86,950	?	1,190	1,453	601
1896	32,922	880	4,259	64,312	102,213	?	1,585	1,674	915
1897	36,170	6,308	4,213	65,107	105,874	?	1,721	1,664	901
1898	49,475	9,618	4,853	69,951	96,866	?	2,404	1,994	953
1899	55,972	10,677	4,739	69,574	106,229	?	4,156	1,698	2,227
1900	51,520	13,232	3,497	64,387	113,599	?	8,261	3,088	5,597

* Compiled from *The Mining Industry*. † Tons of 2,240 lb.

(4) Mexico.

Boleo Mine, in Lower California.—At Boleo, opposite Guaymas, on the peninsula of Lower California, is located this now well-known copper mine, which is exploited by a French Company, and Mr. E. Fuchs has given the following description in his "Notes sur les Gisements of Cuivre de Boleo,"* of this remarkable deposit of copper ore, which occurs in Tertiary sandstones, conglomerates, and tufas. The eastern slope of the (mostly eruptive) mountain range extending through the peninsula is a plateau, gently descending towards the Gulf of California, and cut by precipitous cañons. It is formed of strata containing characteristic Miocene fossils. Tufas decidedly predominate, and the series contains three or four copper-bearing beds, covering a large area, and cropping out at many places in the cañons. These lie immediately upon conglomerates formed of pebbles of eruptive rock (different and characteristic for each horizon), and are overlain by clayey tufas. The whole is traversed by several fissures, of which the largest and most important is a fault fissure, occurring at the western border of the district, and striking about parallel with the sea shore.

In the ore beds above the ground water level, disseminated oxidised ores prevail, such as black oxide of copper, and the protoxide, with atacamite ($CuCl_2 + 3CuO + 3H_2O$), azurite. malachite, and chrysocolla, with crednerite ($2Mn_2O_3$, $3CuO$) In the second ore bed (counting downwards) there are peculiar globular concretions, like oolites, of copper oxide and carbonate, sometimes several centimetres in diameter, which are locally called *boleos*, whence the name of the district. The third ore bed lies in part below the ground water level, and contains, in addition to the foregoing minerals, the copper sulphides chalcosite (Cu_2S) and covellite (CuS). The ore beds are composed of tufa, in which ores, in disseminated spots and veinlets, as well as globular concretions, are irregularly distributed, with a visible tendency to concentrate towards the bottom of the bed, where they form a compact ore layer, 6 to 10 inches thick.

The Boleo mine produces about 10,000 tons of copper per annum. The black copper resulting from smelting is shipped to the United States.

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[*] Association Française pour l'Avancement des Sciences, 1885.

Michoacan.—At Inguaran, in the Ario district in the State of Michoacan, are large bodies of low-grade concentrating ores, and these mines have passed into the hands of Messrs. de Rothschild, who will build a line of railway from the mines to Zihuatanejo on the Pacific. In ore samples which the writer has seen, the copper sulphides seem to be pretty evenly disseminated in a granitic rock, and should form a splendid concentrating material.

Sonora.—During a recent journey into some portions of the State of Sonora, the writer had occasion to inspect some promising copper deposits, and there is very little doubt that Mexico will, in course of time, become an important producer of copper.

The copper-mining industry in Mexico is greatly benefited by Messrs. Guggenheim Brothers, who own large smelting works at Aguas Calientes, and ores from smaller properties are sent to these works for treatment.

(5) Canada and British Columbia.

British Columbia.—The principal ore deposits are located near Rossland, and Mr. R. G. McConnel, of the Geological Survey of Canada, after a short visit in 1894, reported* the country about Rossland to be "an area of eruptive rock, mostly diorite and uralite-porphyrite, cut by many dykes," but as no complete geological survey had been made, nor any lithological study, only a very general description has been given. The main mass of all the country is evidently diorite, although it presents many different gradations in composition and structure, varying from a fine-grained aphanitic rock, with very little hornblende, at one extreme, to nearly massive hornblende at the other, often showing mica and pyroxene. Much of it looks like a basic syenite, and the ore bodies traverse the diorite. In going over this region, the variations are seen to be very marked, in some places the rock being stratified, as if of sedimentary origin, but in all probability it is a more or less altered eruptive. Porphyry dykes, from 1 foot up to 60 and 80 feet wide, traverse the country, many with a north-and-south strike, but with no apparent dislocation of the veins through which they cut; indeed, at six such points of intersection the

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* "Summary Reports of the Geological Survey of Canada," 1894–5.

ore seemed to be concentrated, and even to follow along the dyke for some distance, but this must be made clear by further underground work.

In the Rossland district, the prospecting work has shown clearly that there is a large system of lines of fracture with an east to west and north-east to south-west trend, and a persistent northerly dip, along which more or less ore has concentrated, either as bodies of solid sulphides or sulphides scattered through the country rock. Some of these fissures can apparently be traced through several 1,500 feet claims, and along them are the large ore shoots now being mined or developed, the maximum width of pay ore, so far, being about 35 feet. Many of these fissures have been, or are now being, prospected, and in many instances, with surface indications of the most unfavourable character, the improvement has been very marked in the increase of the amount of ore and its value. The great probability that more rich ore shoots will be found by following these fissures has made all such property valuable, and is deciding the commencement of extensive exploratory work. Again, large shoots of low-grade ore, mostly the coarse-grained magnetic-iron pyrites or pyrrhotite, assaying from traces to £1 5*s.* to £1 10*s.* (6 to 8 dollars) in gold, have been found, and are being explored for better-grade ore, and so far with some success.

The surface of these ore shoots is covered with the typical iron capping, or reddish brown sintery mass, and experience enables the prospector to distinguish between disintegrating sulphides and barren diorite, heavily iron-stained by the oxidising of the bisilicates, or the iron pyrites nearly always present in this rock. Although it is difficult to prospect such rock, which may be much iron-stained, but indicates no vein whatever in the vicinity, nearly all work is done along one wall, and the ore appears to follow along one wall, where the rock is not too full of fissures that disguise true conditions. It is doubtful, however, if more than one wall really exists, although a parallelism of lines of fracture may for a short distance seem to prove the contrary. Wherever the ore is found to consist almost of pure sulphides, it will be found lying along and parallel to such a wall, after which ore is disseminated more or less through the enclosing rock, often following along small fissures, which in some cases form small veins of good ore that run for a considerable distance away from the main deposit. In all the mines, the ground is faulted, thus dislocating the ore deposits and stringers, and complicating the search.

Copper ores also occur at Nelson, in the Boundary District, around the Kootenay Lake, on Coal Hill, in Copper Creek, near Pitt Lake, on Vancouver Island, and elsewhere.

The ores nearly all carry gold and silver, but the average copper contents are low, and in the Le Roi mine do not exceed 2½ per cent., but the gold value is about £2 to £2 10s. (10 to 12 dollars) and silver 1½ oz. per ton. Other mines are the War Eagle, Centre Star, Iron Mask, Josie; and in the Nelson District, the Silver King is the leading producer.

Canada.—The chief centre of production is Sudbury, where the ores also carry nickel, and are worked for both copper and nickel. They contain about 3 per cent. of copper and 2½ per cent. of nickel. The ore bodies occur in igneous rocks as iregular masses, and consist of an aggregate of pyrrhotite and chalcopyrite with various nickel minerals.

(6) Chili.

Chili was at one time the greatest copper-producer in the world, whereas now it takes the fourth place on the list. Its total production for 1899 amounted to 25,000 tons from the working of a great number of small mines, no less than 3,500 sending their ores to Valparaiso, Lota, Coronel, Coquimbo, Chañaral, Guyacan, Tocopilla, and other works, where they are smelted and whence the product is shipped to Europe.

The principal copper mines are situated in the provinces of Atacama, Antofagasta, Coquimbo, and Aconcagua, and the most important mines are those of San Juan and Carrizal near Copiapo, la Higuera near Coquimbo, and Tamayo about 65 miles from Coquimbo, situated in a mountain district.

It is almost impossible to give a general idea of the geological conditions under which the various ore bodies occur, but in Chili, as in most copper-producing countries, the ores are carbonates to a depth of about 150 feet, followed by 60 feet or more of oxides, and eventually by copper and iron pyrites.

In the Cordillera district, operations are being facilitated by the construction of railways, and, owing to improved prices for copper, no doubt Chili will be able to maintain for many years to come its present ratio of production, but it is doubtful whether it will ever reach the old figures, as its exportation in 1882 amounted to about 43,000 tons.

Some of the mines have reached depths of 1,700 to 1,800 feet, which proves that the ores bodies in that country are of a permanent character. The largest proportion of the ore is smelted in reverberatory furnaces. No doubt Chili has felt the exhaustion of the rich surface ores, and whatever copper is now produced in those regions comes from the poorer sulphide zones.

(7) Germany.

Mansfeld.—At Mansfeld, in the Southern Harz Mountains, copper ores occur, disseminated through sedimentary beds, in which they have been chemically deposited, locally termed *kupferschiefer*, or copper-bearing shale, and in these shales mining has been extensively carried on for centuries. The metalliferous bed occurs in the Zechstein, a member of the Permian formation, which is regarded as the equivalent of the magnesian limestone of England. At Mansfeld, the highest horizon of the series consists largely of unstratified gypsum, in which are numerous cavities, locally called *gypsschlotten*, caused by the solvent action of water upon sulphate of lime. With the gypsum is associated a soft bituminous dolomitic limestone, locally known as *asche*, and beneath this follows a stratified fetid limestone, below which is the true Zechstein, giving name to the formation. In depth, this passes into a bituminous marly shale, the lowest portion of which, seldom above 18 inches in thickness, constitutes the chief copper-bearing stratum, and extends with wonderful regularity for many miles. Of this, sometimes only from 4 to 5 inches is sufficiently rich to pay the cost of smelting, the proportion of copper in the ores treated varying from 2 to 5 per cent. Under the cupriferous shale, is a calcareous sandstone, varying in colour from white to grey which is in part a conglomerate. This, in accordance with its colour, is called either the white layer, *weissliegendes*, or grey layer, *grauliegendes* and sometimes contains copper ores. The area over which these copper-bearing shales are found has an extent of about 190 square miles.

In the slates the ores are sulphides, but in the underlying sandstones carbonates predominate, evidently due to the decomposition of the *kupferschiefer* ores, and their infiltration into the sandstone. Formerly only the shaly ores were treated, but now the underlying siliceous sandstone deposits are utilised, not only for copper, but for their cobalt and nickel contents. In some localities the ore is for the most part an argentiferous *fahlerz*, and a considerable quantity of silver is obtained in these districts.

The production of copper in 1898 of the Mansfeld mines amounted to about 18,000 tons.

Rammelsberg.—After Mansfeld, the most important copper mine in Germany is the Rammelsberg deposit, which occurs as a big lenticular mass in Devonian slates.

(8) **Spain and Portugal.**

In the south-western portion of the Sierra Morena is a zone of clay slate some 120 miles in length, which courses in a north-westerly direction through the province of Huelva, from Aznulcollar and Castillo de las Guardas, in Spain, to San Domingos in Portugal.

The age of the enclosing rocks remains doubtful, as some geologists believe them Silurian, some Devonian. As a rule they are vertical, or nearly so. They enclose enormous deposits of cupriferous iron pyrites, and their occurrence throughout this whole belt is so very uniform that the description of one mine is the history of all of them. Near the ore deposits, and parallel to them are dykes of porphyry, syenite, and diabase. The deposits of cupriferous pyrites consist of a series of more or less continuous lenticular masses, which occur generally at the junction of rocks of dissimilar character, and consequently form contact deposits. They extend for a great length and range from all sizes up to about three-quarters of a mile in length, and reach a width of 500 feet. The ore is an intimate mixture of iron pyrites with a little copper pyrites.

At Rio Tinto, there are four lodes, the north, middle, south, and valley. The slate, which stands nearly vertical, is altered in the immediate vicinity of the deposits, by the action of the iron salts resulting from the decomposition of pyrites, and not only becomes softer, but also assumes a yellowish-white or reddish-grey tint. Although some rich ore is met with in patches, the deposit is of low grade averaging between 3 and 4 per cent. The length of this deposit is over 2,000 feet, and a depth of over 1,000 feet has been reached in the workings. It was wrought by the Romans, and some of their old workings reached a depth of 300 feet. The Tharsis workings are west of Rio Tinto, and the deposits resemble those of the last-named locality as to their mode of occurrence.

In addition to copper, the Rio Tinto and Tharsis pyrites contains about 1½ oz. of silver per ton, together with traces of gold, which for many years were not recovered; but, after the introduction of the Claudet process, the precious metals were also obtained.

The Rio Tinto mines produced, in 1898, 1,465,380 tons of ore, of which 820,862 were reserved for local treatment, the remainder being ore for shipment.* The amount of copper produced at the mines was 20,426 tons; the copper in the pyrites shipped was 13,456 tons, making a total of 33,882 tons.

The average copper-content of the ore was 2·85 per cent. The reserve heaps, from which the copper is extracted at a very low cost, are estimated to contain 114,700 tons of fine copper. The shipping ores are an important source of revenue, as besides the copper, the sulphur is made available in the production of sulphuric acid, and is being paid for at the rate of about 5*d.* a unit, which, on 48 per cent. of sulphur, amounts to £1 per ton. By the aid of the diamond drill, the ore reserves have been estimated at over 130,000,000 tons, and with the present annual output of 1,400,000 tons there are still 70 years of production in sight at this mine.

The Tharsis mines comprise six lodes or deposits of the same general character as the Rio Tinto, and the workings are of great antiquity. The ore is piled in heaps, where it undergoes natural oxidation, expedited by intermittent washings with water. The copper is precipitated from the leach water on iron in creosoted timber sluices. A large quantity of the pyrites is exported. The Mason & Barry Company has mines in Portugal, and the character of the ore and the percentage of copper are about the same as at Rio Tinto. The copper-bearing formation of Spain extends into Portugal, and the three

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* *The Mineral Industry*, vol. vii., page 217.

most important deposits are those of San Domingos, Aljustrel, and Grandola.

[For further particulars concerning the ore deposits of the Rio Tinto and adjoining districts, and the working thereof, the reader may be referred to the next chapter—on the Copper Region of Huelva.]

TABLE XIX.—PYRITES AND COPPER STATISTICS FROM THE REPORTS OF THE RIO TINTO COMPANY.

Year.	Pyrites Extracted.				Pyrites Consumed.		Copper produced at Mines.
	For Shipment.	For Local Treatment.	Totals.	Average Copper-contents.	Weight.	Average Copper-contents.	
	Tons.	Tons.	Tons.	Per cent.	Tons.	Per cent.	Tons.
1876	189,962	159,196	349,158	1·500	158,597	1·500	946
1877	251,360	520,391	771,751	2·375	211,487	2·000	2,495
1878	218,818	652,289	871,107	2·780	211,403	2·180	4,184
1879	243,241	663,359	906,600	2·780	236,849	2·450	7,179
1880	277,590	637,567	915,157	2·865	274,210	2·481	8,559
1881	249,098	743,949	993,047	2·750	256,827	2·347	9,466
1882	259,924	688,307	948,231	2·805	272,826	2·401	9,740
1883	313,201	786,682	1,099,883	2·956	288,104	2·387	12,295
1884	312,028	1,057,890	1,369,918	3·234	314,751	2·241	12,668
1885	406,772	944,694	1,351,466	3·102	354,501	2·270	14,593
1886	336,548	1,041,833	1,378,381	3·046	347,024	2·306	15,863
1887	362,796	819,642	1,182,438	3·047	385,842	2·283	17,813
1888	434,316	969,317	1,403,633	2·949	393,149	2·208	18,522
1889	389,943	824,380	1,214,323	2·854	395,081	2·595	18,708
1890	396,349	865,405	1,261,754	2·883	397,875	2·595	19,183
1891	464,027	972,060	1,436,087	2·649	434,532	2·651 1·309	21,227
1892	406,912	995,151	1,402,063	2·819	435,758	2·569 1·465	20,017
1893	477,656	854,346	1,332,002	2·996	469,339	2·659 1·544	20,887
1894	498,540	888,555	1,387,095	3·027	485,441	2·594 0·988	20,606
1895	525,195	847,181	1,372,376	2·821	518,560	2·595 0·986	20,762
1896	591,752	845,580	1,437,332	2·931	549,585	2·529 1·068	20,817
1897	575,733	812,293	1,388,026	2·810	582,540	2·595 0·967	20,826
1898	644,518	820,862	1,465,380	2·852	618,110	2·600 1·023	20,426
1899	644,271	1,005,573	1,649,844	2·719	636,323	2·511 1·120	23,230
1900	704,803	1,189,701	1,894,504	2·744	665,967	2·553 1·187	21,120

(9) Australia.

South Australia.—Copper is known to exist throughout the Commonwealth, and at one time was extensively mined in South Australia, which still glories in the wonderful tales of its past copper production. The Kapunda mine, opened up in 1842, and the oldest copper mine in South Australia, was closed in 1879. In 1845, the Burra Burra mine was discovered, but it is exhausted.

The Wallaroo and Moonta mines were discovered in 1860 and 1861, and are at present the chief copper producers in South Australia. The Wallaroo mine is situated on Yorke Peninsula, 10 miles north of the Moonta mines. The country rock is schistose. The average grade of the ore in 1897 was 15·9 per cent., and the quantity of copper produced was 5,073 tons. The Moonta mine is also situated on the Yorke Peninsula. The deepest shaft is down 2,400 feet. The cost of producing copper is £48 per ton.

New South Wales.—This colony is spoken of as a great copper producer, although there is only one large ore deposit, which furnishes the bulk of the supply, and this is the Great Cobar mine. From the date of the commencement of operations in 1876 to 1892, there were treated from this mine 213,182 tons of ore, giving a return of 23,611 tons of refined metal—an average production of 11·07 per cent. of copper per ton of ore. After lying idle for some time, the mine was let on a 10 years' lease to tributers on a 10 per cent. royalty, with the result that there are now five water-jacket cupola furnaces in operation, smelting 500 to 600 tons of ore daily, the tributers having wisely discarded the old reverberatory-smelting methods.

Queensland.—Cupriferous deposits abound in Queensland; Peak Downs and Mount Perry acquired great celebrity, but were ultimately abandoned. In northern Queensland, copper is found throughout the Cloncurry district, in the upper basin of the Star River and the Herberton district. The returns from the copper fields in this colony are, at present, small, owing to the lack of suitable fuel for smelting purposes, which renders the economic treatment of the ore difficult; and the development of the mines is greatly retarded by the want of easy and cheaper communication with the coast; but it is expected that these disabilitics will be overcome at no distant date, and a revival of the industry is hoped for. In this connection should be mentioned the Chillagoe copper mines; and a railway, to connect the mines with the sea coast, will start from Bedford. The ore deposits occur in limestone, and are said to bear some resemblance to those of Arizona.

Western Australia.—Copper deposits have been worked for some years, rich lodes of the metal having been found in the Northampton, Murchison, and Champion Bay districts, and also in the country to the south of these districts, on the Irwin river.

Victoria.—Copper-mining has not attained any great proportions in Victoria, although deposits have been found in several parts of the State, particularly in the Beechworth district, where they have been traced over an area of some fifty square miles.

Copper is sometimes found in the Australasian mines in a virgin state, and beautiful specimens of the pure metal have been exhibited at different times, but it occurs generally in the form of oxidised copper ores, carbonates, sulphates, phosphates, and silicates of copper. Copper sulphides and arsenides of copper are generally found in deep sinking. The metal has also been found associated with tin, in the form of stannine.

Tasmania.—The Mount Lyell mine and adjacent mines in Tasmania have been recently described (as follows) by Mr. Herbert I. Daily, in a paper read (December 19th, 1900) before the Institution of Mining and Metallurgy.

The location of the deposit is on the eastern slope of the southernmost spur which proceeds from the peaks of Mount Lyell on the west coast of Tasmania. Although the mountain ranges and valleys of the west coast area are heavily timbered and clothed with dense undergrowth, yet little or no soil covers the surface. The Silurian bed rock is overlaid by about 12 ot 18 inches of white quartz "wash," on the top of which lies a covering of boggy peat of a corresponding thickness. The annual rainfall averages 100 inches a year which will give an idea of the inclemency of the weather.

The belt of the country in which the chief copper deposits have been located lies at the contact of a series of schist rocks and conglomerates with alternating quartzites. The whole region belongs to the Silurian period. The contact of the rocks mentioned is somewhat faulted in places; and at the line of division an outcropping band of hematite is noticeable. The Silicious schist rocks of blue, grey, and green coloration which occupy the western side of the belt are micaceous and chloritic. Bands of hydromica schists are also common. The stratification of these schists has a general strike of N.W. and S.E.; with a south-westerly underlie of 75° on the western side of the copper belt; but at its northern end the schists are twisted almost at right angles to this strike, their lines of cleavage having a cardinal bearing of N. 67 E., and a general north-westerly dip of 60°. These schists are highly mineralised, and numerous impregnations of copper pyrites have been located, but principally confined to the grey schists; whereas the blue and green bands, although highly mineralised and cupriferous, are not productive of pay ore.

The conglomerate rocks which occupy the eastern side of the copper belt are non-metalliferous. The sedimentary rock consists of massive concreted pebbles of quartzite, with occasional particles of schist—veritable pudding stone. In the beds of the creeks which trend from the eastern slope of the copper belt, native copper and alluvial gold are found, both in the recent alluvial gravels and the clay pug deposits. The matrix of these metals in the alluvial gravel and pugs is evidently the known and now uncovered copper deposits.

The three important ore bodies of the field are those of the Mount Lyell, and North Mount Lyell, and the Lyell Tharsis mines. These principal copper deposits occupy the zone of contact between the conglomerates and the highly tilted schists. They are all lenticular, and although the major axis of the deposits is parallel to the strike of the line of contact, yet no lengthy contiguity of pay ore can be traced, and great stretches on the contact remain uproductive.

A remarkable feature about the principal ore bodies of the belt is their total dissimilarity in character, both as regards the value of the ore and classification of the deposit.

The Mount Lyell deposit is a massive body of iron pyrites singularly free from gangue; and carrying copper, gold, and silver. The Lyell Tharsis deposit, which is situated about one mile north of the Mount Lyell mine, is an impregnation. Here the country rock, which is micaceous and chloritic schist, contains the ore in two distinct bands, the copper being in the form of bornite and chalcopyrite.

In the North Mount Lyell mine several ore bodies have been located, the chief of which is a bonanza deposit of bornite ore.

Several other copper deposits have been discovered at Mount Lyell, the principal being in the areas of the Mount Lyell blocks.

The total quantity of ore treated to March 31st, 1900, was at the Mount Lyell 610,659 tons:—

Average assay value of copper 3·52 per cent.
" " " " silver 3·47 ounces.
" " " " gold 0·127 "

The working cost of producing blister copper from the ore is as follows; per ton of ore:—

	£	s.	d.
Mining	0	2	11.76
Removal of overburden . .	0	2	0·00
Smelting	0	15	10·70
Converting	0	2	2·30
	£1	3	0·76

	tons.
The total quantity of copper matte produced at the works to March 30th, 1900, was	40,625
The quantity of blister copper produced	29,597

Of an average assay value of 98·81 per cent. copper.
" " " " 95·58 oz. silver.
" " " " 3·88 oz. gold.

(10) Cape Colony.

The only productive mines are located in Namaqualand, where operations commenced in 1852, the Cape Copper and Namaqua Copper companies having been successful in opening payable ore bodies. A narrow-gauge railway, 91 miles long, connects the mines with Port Nolloth, on the sea coast, 300 miles north of Cape Town.

Copper is made at the works of the Cape Copper Company by the direct method of Messrs. James and Nicholls.*

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* "The Direct Method Considered as the Future Metallurgical Treatment of Copper Ores, Argentiferous or otherwise," by Christopher James. *Transactions of the Institution of Mining and Metallurgy*, 1896, vol. v. p. 2.

There are good copper prospects in the Transvaal, in the north-eastern portion of the Murchison range in the vicinity of Palabara, but owing to the lack of railway facilities they are not exploited.

(11) Russia.

Copper* is found in the Ural and the Altai Mountains, also in the Caucasus, Finland, and in the Kirghese steppes.

In the district of Nijne-Tagilsk is a copper-bearing metamorphic schist, enclosed in limestone belonging to the Upper Silurian formation, and in these schists occurs the celebrated cupriferous mass of Miednoroudiansk. In 1836 a block of malachite was found in this locality, weighing 330 tons.

The bedded deposits of the western slope of the Ural belong to two different formations, the Permian and the Triassic. The principal centres of production are Bogolovsky and Polfsk, and the Kiadebek mine is the largest producer.

(12) Miscellaneous Deposits.

No details have been published relating to the copper deposits in Japan.

In Sweden and Norway, the production of copper arises from the operations of the Röros, Sulitelma, and Falun mines.

Italian ores are derived from three sources: Monte Catini, Mossetana, and Baccheggiano.

The opening up of ore deposits in the Cerro de Pasco district has placed Peru again on the list of copper-producing countries. Among small producers are Bolivia, Austria-Hungary, Newfoundland, and the United Kingdom.

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* "A Treatise on Ore Deposits," by Mr. J. Arthur Phillips, 1884.

CHAPTER IV.

THE COPPER REGION OF HUELVA.

Description of the Mineral Deposits.* The mineral deposits of the province of Huelva are comprised in the East and West zone, which extends from San Domingos to Seville, and is about 20 kilometres wide, and in which is also the porphyry belt. They are indicated in the plan given in fig. 2.

In the *Northern Zone* are the following deposits:—

San Domingos.
El Carpto.
La Zaza.
San Miguel.
Chaparrito.
El Castillo de las Guardias.
Huerta de la Romanero.
San Telmo.
Cueva de la Mara.
La Concepcion.
La Penna.
Sotiel.
Gloriosa.
Poyatos.
Aguas Tenidas.
La Poderosa.
Rio Tinto.
La Joya.

It the *Southern Zone* are the following deposits:—

Lagunazo.
La Coronada.
Buitron.
Tharsis.
Azarosa.
Las Herrerias
El Gutto.
Menacillo.

In the *Western Zone* the formation extends into Portugal through the hills of Caveira, about 9 kilometres from the village of Grandola, near the bay of Setubal.

In the *Eastern Zone* are found the workings of Cerro Muriano and of Barrancanès near Sevilla.

All these deposits present the same characteristics, namely,

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* For this description and the accompanying illustrations (in which the French terminology is preserved), I am indebted to M. de Launey's "Memoire sur l'Industrie du Cuivre dans la Région d'Huelva" (*Annales des Mines*, tome xvi: Vve. Ch. Dunod, Paris, 1889.)—M. E.

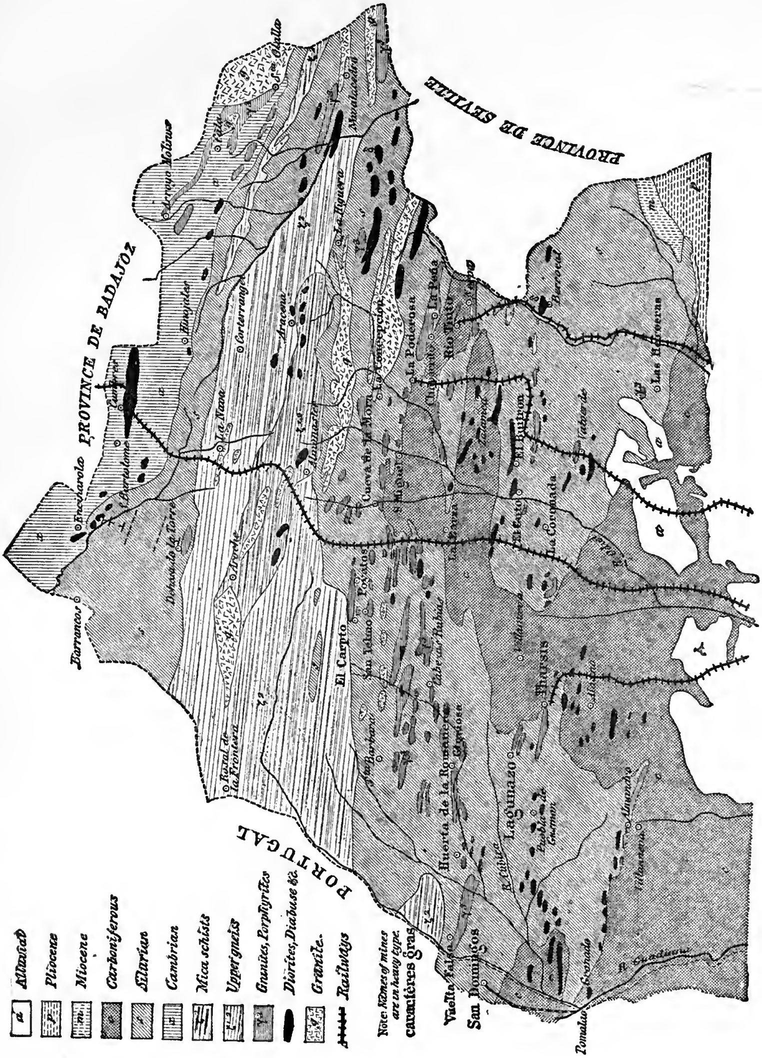

Fig. 2.—Geological Map of the Copper Region of Huelva

lenticular masses parallel with the layers of slate, which is also the strike of the veins in the porphyry. It is probable that the three phenomena—

1. The folding of the slates ;
2. The eruption of the porphyry ;
3. The metalliferous formation—

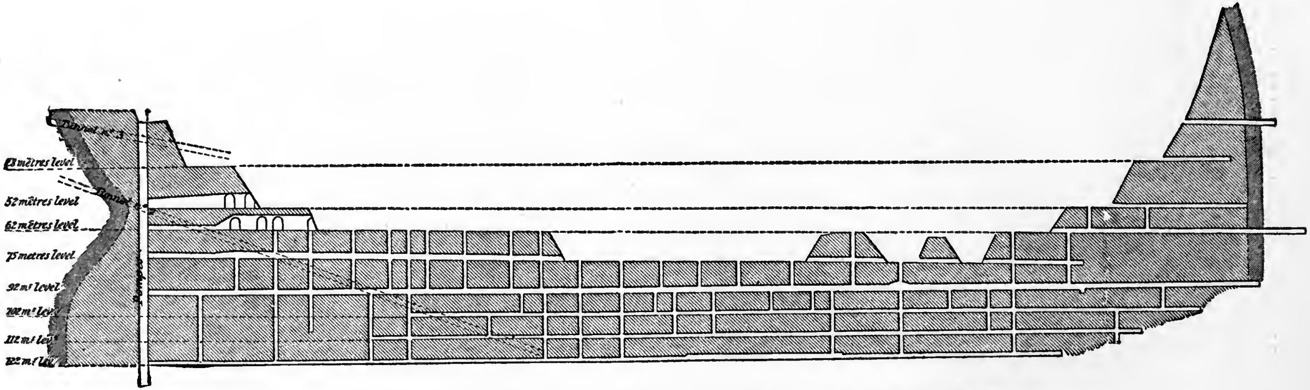

FIG. 3.—LONGITUDINAL SECTION OF THE WORKINGS OF THE SAN DOMINGOS MINE.

are in close relation with one another, and represent the three successive phases of one action. Only a few of the deposits will be described.

The **San Domingos Deposit** is located in Portugal, close to the Spanish frontier, and is exploited for a length of 500 metres, and for a width of 60 metres; its strike is parallel with the slates, and the ore body is perfectly vertical, see Fig. 3.

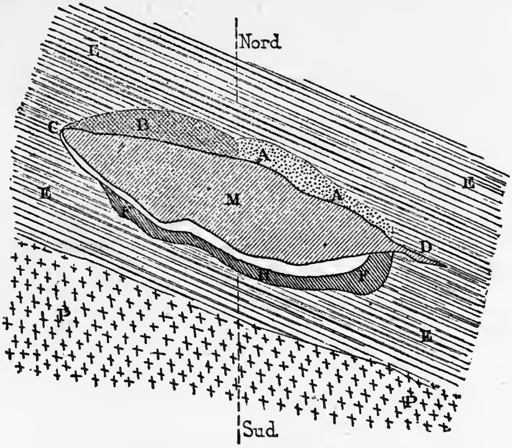

FIG. 4.—PLAN OF THE SAN DOMINGOS DEPOSIT.

The plan, Fig. 4, shows the rocks which are in contact with the deposit.

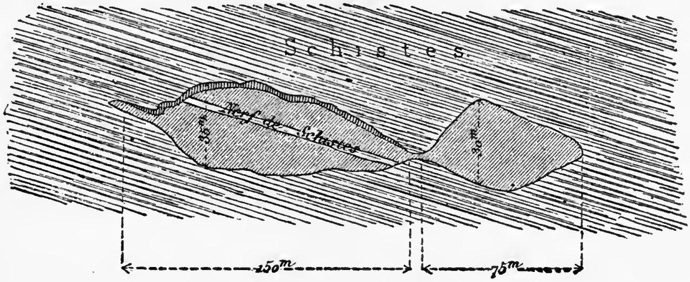

FIG. 5.—PLAN OF THE LAGUNAZO DEPOSIT.

To the north the very regular Silurian schists extend for several kilometres in length, to the south in immediate contact with the deposit is the Diabase, F, then come the schists, E, and several hundred metres beyond are the granitic rocks, P.

The deposit is composed principally of iron pyrites, containing in small proportions copper, lead, and zinc sulphides. Here and there are horses of schist, which have conserved their structure, but contain numerous veins of quartz. The enormous mass of ore is very homogeneous, and does not show any local enrichment or impoverishment. The ore body, principally composed of iron pyrites, contains 1 to 4 per cent. of copper, disseminated throughout the whole mass.

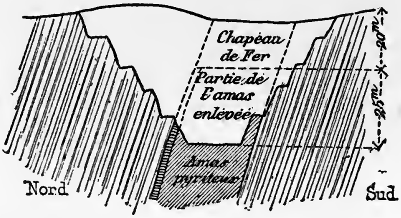

FIG. 6.—TRANSVERSE SECTION OF THE OPEN-CAST WORKINGS OF THE LAGUNAZO DEPOSIT.

2. The **Lagunazo Deposit,** see Figs. 5 and 6, is composed of two lenses, following one another along the strike of the schists. The one to the west is from 35 to 150 metres wide, and is exploited by open-cast workings, and the other to the east is prospected by means of underground drifts. The inclination of the ore bodies is to the north, which is also the inclination of the schist rocks in this whole region.

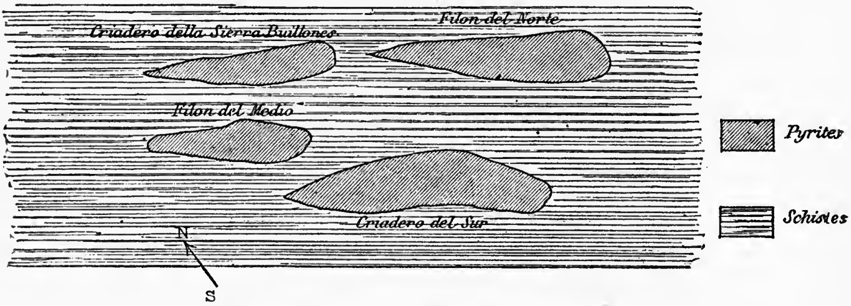

FIG. 7.—PLAN OF THE THARSIS DEPOSIT.

The whole surrounding country is traversed by numerous cupriferous veins 8 to 10 centimetres in thickness, which show themselves on the surface by some oxidised copper ores enclosed in quartz. As far as Tharsis, which is only 5 kilometres distant, these traces of mineral veins are nearly continuous.

By examining the workings, it will be seen that the hanging wall on the north is composed of white decomposed schists, but to the south the schists are intact. The deposit, like all the others, is covered with an iron hat 20 to 30 metres thick. The mineral, like that at San Domingos, contains 3 per cent. copper, Small veinlets of rich black copper occur in the mass, and this ore was followed by small drives in the ancient Roman workings.

The **Tharsis Deposits** are composed of four lenses in two series (Fig. 7). The northern one embraces the Criadero de la Sierra Buillones mine, and the Filon del Norte. To the south is the Filon del Medio, and Le Criadero del Sur.

The Filon del Norte is exploited for a length of 600 metres, and the greatest width was 140 metres. The Criadero de la Sierra is over 500 metres long, and has a maximum width of over 100 metres. The Filon del Medio is about 400 metres long.

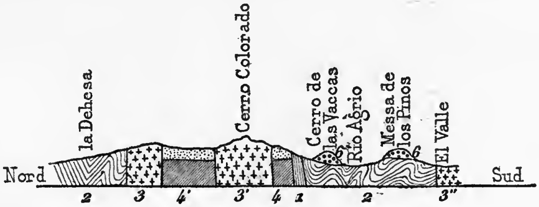

FIG. 8.—NORTH AND SOUTH SECTION OF THE RIO TINTO MINES.

The **Rio Tinto Deposit.** The transverse section, Fig. 8, represents the formation of the whole region. To the north are the clay slates (2) of la Dehesa; then going south is the porphyry formation (3); then the pyrite ore formation (4′), called Filon Norte; another mass of porphyry (3′); and then another pyrite ore formation called Filon de San Dionisio (4); then the carboniferous schists (2); and then another mass of porphyry (3″). A ferruginous deposit is indicated above the Cerro de las Vaccas, and de la Mesa de los Pinos; which is in the form of a horizontal layer 3 to 4 metres thick, and composed of a rich hematite ore which is exploited as an iron mine.

In regard to the ore deposits, 4 and 4′, designated as the

San Dionisio and del Norte mines, the former is shown in transverse section in Fig. 9.

Fig. 10 gives the plan of the open-cast workings, showing the different levels.

The inclination of the ore body is to the south, and the open-cast workings have reached a depth of about 150 metres, and bore-holes have followed ore to a depth of 80 metres. The dimensions of the ore body show a length of 550 metres by a width of 100 to 120 metres.

The north wall of the deposit is difficult to classify, owing to the metamorphism of the rocks, and the iron capping which covers the same. In immediate contact with the ore is usually a quartzose and pyritous rock, which is often kaolinised. This is an excellent flux in the smelting operation, owing to its silica contents, and the small quantity of metal it carries. This rock is traversed by veinlets of quartz which must have originated during the formation of the ore body.

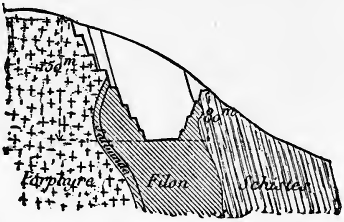

Fig. 9.—Section of the Open-Cast Workings of the South Reef, Rio Tinto Mines.

The south wall is formed of schists, which have only been slightly altered by the sulphurous waters.

The ore body presents itself in the shape of an irregular mass, composed exclusively of pyrites without any quartz or schist rocks, showing no regular direction of crystallisation, or signs of concretion on the wall rocks. The same is composed of iron pyrites with some copper, zinc, and lead sulphides, traversed by small veins 10 to 20 centimetres wide of black copper and chalcopyrite, and covered like all the ore bodies in this country by an iron capping twenty metres thick. The San Dionisio ore body is cut off to the east abruptly, but to the west the same extends as a narrow vein for a considerable distance.

The Filon del Norte is exploited in certain points for a width of 400 metres, on an average 150 metres, and for a length of over 2,000 metres. The country between the two ore bodies has been prospected by means of a cross cut, and the country rocks are impregnated for the whole distance by pyrites.

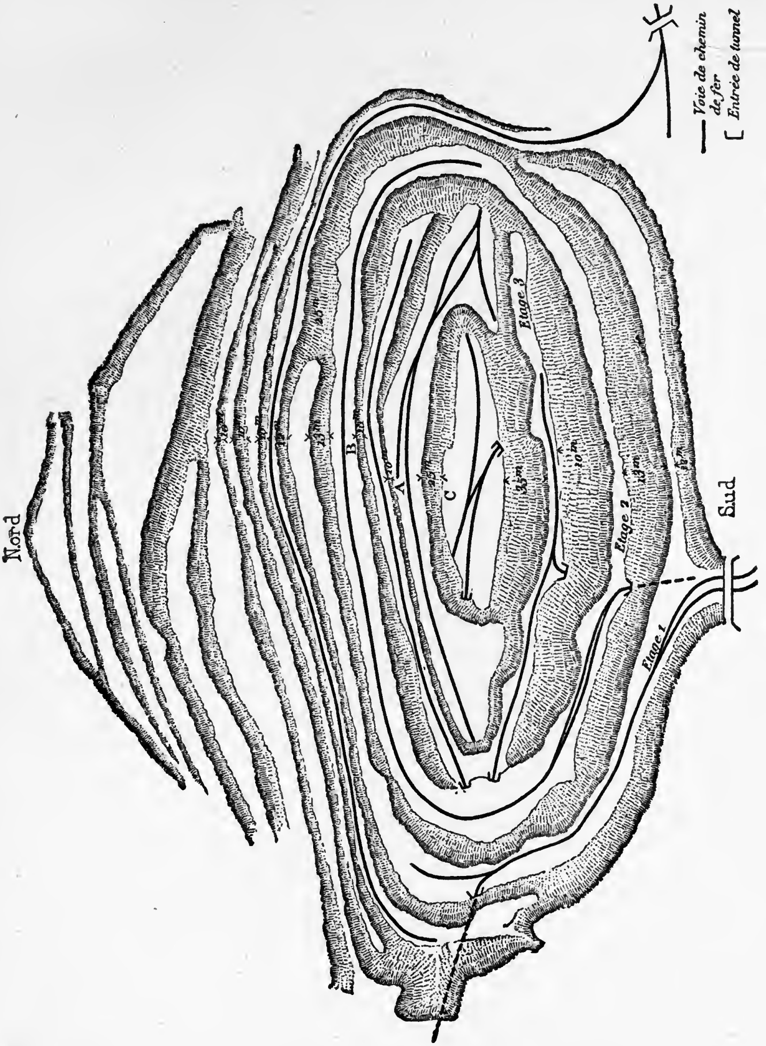

Fig. 10.—Plan of Open-Cast Workings of South Reef, Rio Tinto Mines.

General Characteristics of the Huelva Deposits.—"The great pyrite deposits of Rio Tinto, Tharsis, etc., in the Huelva provinces of Southern Spain," recent reports say, "are enormous bodies covered with a gossan which extends down to a depth of 130 to 150 feet, and consist mainly of iron oxide, with 50 to 55 per cent. iron, a little sulphur and arsenic, and only a trace of copper. Between this and the solid pyrite below is a very regularly distributed zone of earthy, porous material, from a few inches to a foot in thickness, carrying an average value of £7 in gold and silver. These values have evidently been brought down in solution by ferric sulphate, which, in contact with the underlying pyrite, has been reduced to ferrous sulphate, with precipitation of the gold and silver. It is in the pyrite mass below the 'iron hat' that the copper values are found, and these gradually decrease with depth, from 4 to 5 per cent. in the upper 100 to 200 feet, to 1¼ per cent. at the depth of 900 feet, varying somewhat with local conditions. The present iron gossan at a remote geological period was also a massive copper and iron sulphide-ore body, and during its oxidation the original copper contents were leached down and reprecipitated in the more recent fractures and clefts in the pyrite mass, thus enriching the upper part; and this accounts for the presence in veinlets and streaks of such minerals as copper glance, bornite, chalcopyrite, accompanied occasionally with galena, zinc blende, grey copper in quartz, and these minerals are without doubt of a secondary formation.

"At times these clefts are so large that they can be separately mined; thus, the old Roman mining was done chiefly on these richer clefts within the poorer mass of pyrite. Most commonly, however, they are quite small, and constitute a strongly branching network in the normal pyrite mass; and that the copper content of these secondary minerals is derived from the weathered, superficial mass is shown quite simply in the fact that these veins are most common in the zone immediately under the 'iron hat.' They extend downward something like a hundred metres or more, and then commences the solid pyrite mass, little fissured and comparatively barren in copper."

PART II.

METHODS OF HYDRO-METALLURGICAL TREATMENT OF COPPER.

CHAPTER V.

APPLICABILITY OF THE HYDRO-METALLURGICAL TREATMENT OF COPPER.

THE smelting process, or "dry" method, is employed for the treatment of ores when they carry a high percentage of copper; the lower grades are smelted to advantage after a preliminary concentration, and if the gangue is of such a character that it will form easily fusible slags in the furnace. This is the case with quartzose ores, carrying a large amount of iron pyrites, which after roasting furnish the necessary iron oxides for fluxing purposes. The rapid progress in analytic chemistry has been the means of devising proper methods for the "wet" treatment of poorer ores and by-products, by means of solutions which extract the copper. Under favourable conditions, ores which contain only from ½ to 1 per cent. of copper are treated by these methods, especially when their treatment is in connection with some other industries, such as the manufacture of sulphuric acid; or if the by-product (in the shape of residues) can be utilised in iron smelting works; and especially if the ores are rich enough in sulphur, in which case every unit is being paid for outside of their copper values.

Not every low-grade copper ore is found adapted to hydro-metallurgical treatment, owing to impurities which interfere with the chemical reactions. Such would be the case with the ores containing considerable quantities of lime, magnesia, ferrous oxide, manganese. Their preparation to make them adaptable to the lixiviation process would require the addition of considerable quantities of chemical ingredients, rendering its carrying out too costly; and even if lixiviation was successful, the subsequent precipitation would become difficult, owing to the impure cement copper which would result, causing additional work and expense during the refining operations.

The ores which are adapted for this treatment are poor oxides and sulphides in a quartz gangue; whereas ores having a gangue containing ingredients soluble in acids or other solvents, are not adaptable to this method. Often rich by-products, matte, black copper, are treated by the wet process, as well as ore heaps which have undergone decomposition by atmospheric agencies, and the mine waters which flow from copper mines.

To make the copper soluble, certain preparatory operations have to be first carried out before the same can be dissolved in water, acid, or other solvents.

First of all, the operations will be considered which are carried out in the wet extraction of copper, and the chemical principles will be examined which produce the reactions in the various processes which have evolved in the course of time. Then will be passed in review the practical operations as they are carried out at various works, the cost of producing copper by these methods being given where attainable; and it is noteworthy that at the Rio Tinto mines, one of the world's great copper producers, the metal is being produced at a lower cost than elsewhere.

The granules of copper matte, black copper, and metallic copper are also treated by wet methods, which usually have for an object the production of blue vitriol and the separation of the precious metals.

The wet processes for the treatment of ores are employed for

1. Ores which contain the copper as oxides or carbonates.
2. Ores which contain the copper as a sulphate.
3. Ores which contain the copper as a sulphide.

1. The copper oxides do not occur in nature in sufficient quantities to form by themselves a special subject of treatment, but are usually found in association with carbonates.

2. Soluble sulphates do not occur in large quantities in the ores, but ore heaps when exposed to atmospheric agencies decompose, and sulphates are formed which can be leached out. Cupriferous iron pyrites become converted, on exposure to air, into soluble sulphates; the iron pyrites are converted into ferrous sulphates, which on further oxidation produce free sulphuric acid and basic iron salts. By the action of free sulphuric acid on subsulphide of copper, copper vitriol is formed.

3. When sulphides are present and they are roasted in furnaces, the copper is rapidly converted into a soluble condition. This roasting is either oxidising or chloridising. Sulphide ores are converted into sulphates, oxides, or chlorides. The sulphate is soluble in water, the oxide in hydrochloric acid, sulphuric acid, and chlorine compounds; the cupric chloride in water, the cupreous chloride in hydrochloric acid and solutions of chlorine compounds.

A. **Conversion of the Sulphides into Sulphates.** This operation is effected as follows:—

a. The natural decomposition of the ores by exposing them to atmospheric agencies. This is employed when the ores are easily decomposed into cupreous and ferrous sulphates. By repeatedly leaching the ores and saturating them with a brine containing ferrous sulphates (which is obtained after the precipitation of the copper), their decomposition is facilitated, as the same exerts a decomposing influence on the copper sulphides. It takes a number of years to convert all the copper contents into sulphates, and even then the extraction is not perfect.

b. The slow roasting of the ores. The conversion of sulphides into sulphates by slow roasting is employed with ores which contain a very large per centage of iron pyrites, and a small quantity of copper sulphides. The roasting is carried out in heaps, when a portion of the copper sulphides will remain in an undecomposed condition and a portion will be converted into copper oxides.

c. The roasting of the ores with ferrous sulphate or other easily decomposing sulphates is generally carried out by mixing pulverised copper-bearing pyrites with ferrous sulphate, and roasting the mixture; which converts the largest proportion of the copper into sulphates. This roasting is generally carried out in heaps, seldom in furnaces.

B. **Conversion of the Sulphides into Cupreous and Cupric Chlorides.** This can be effected by either the wet or the dry process.

a. When the wet method is employed, they are treated with ferric chlorides, or with ferrous chlorides and hydrochloric acid. By saturating the ores with sodium chloride or calcium chloride the decomposition is facilitated.

b. By roasting the ores with sodium chloride. The wet method requires plenty of time; whereas the dry chlorination by roasting is quickly effected, and gives a higher extraction. The wet process is only employed, when the expense of roasting is too high owing to cost of fuel, and when the roast gases are noxious to the surroundings and cannot be discharged into the atmosphere.

It also happens that ores contain impurities, which are soluble in the solvents—such, for instance, would be the case with calcareous ores—when it will be necessary to burn them in a kiln, so as to produce caustic lime, which can be washed away without causing a great loss of metal.

The solution of the ores takes place:

1. By means of water.
2. By dilute sulphuric or hydrochloric acid.
3. By brines containing iron sulphate.
4. By brines containing ferrous and ferric chlorides.
5. By leaching oxides or roasted ores with a solution of ferrous chloride and sodium chloride.

1. *The solution with water* can only be seldom applied, as the copper cannot all be converted into a soluble condition, and consequently heavy losses of copper take place. Very often copper is contained as a sulphate in mine waters, from which it is precipitated, on being pumped from the mine in long sluices, by means of scrap iron.

2. *Sulphuric and hydrochloric acids* act with great energy, but resort to their use depends on their cost. Sulphuric acid has the advantage that it dissolves the copper oxides produced during roasting with great facility; whereas the iron oxides are more easily attacked by hydrochloric acid. By using sulphuric acid as a solvent, iron vitriol is obtained as a by-product, and this acid is naturally employed when the copper has to be converted into soluble copper sulphate. Cupric oxide, carbonate, and also arsenate of copper are easily dissolved in this acid. The lixiviation of the ores should be continuous, and the plants should be so arranged that the solutions flow from one vat to another, which enriches them, and the wash waters should be employed for leaching fresh quantities of ore.

Hydrochloric acid does not form basic salts in such quantities as sulphuric acid. The iron sulphates in solution decompose in the presence of air into basic iron sulphate and free sulphuric acid; consequently when hydrochloric acid is employed, a brine is produced which does not contain free acid, and therefore the precipitation of the copper does not require so much metallic iron as do the sulphate solutions.

3. *Brines containing iron sulphates* are employed in lieu of sulphuric acid, and they act through the free acid which they contain. The iron sulphate, by being converted into basic ferrous sulphate, gradually changes metallic copper, its oxides, and also its sulphides, into cupreous sulphates. Ferrous sulphate also dissolves cupric oxide with separation of basic ferric oxide.

4. *Ferric chloride, or solutions containing ferrous chloride,* are produced by the precipitation of copper dissolved in hydrochloric acid by means of iron, or similar salts contained in solutions. Cupreous oxide, cupric oxide, copper carbonate, and metallic copper are easily dissolved in ferric chloride, the first three with separation of iron oxide, the last with reduction of ferrous chloride. The ferrous chloride becomes oxidised to ferric chloride with separation of iron oxide:—

$$\overset{3}{\cancel{6}}FeCl_2 + \overset{1\frac{1}{2}}{3}O = 2Fe_2Cl_3 + Fe_2O_3 \cdot \tfrac{1}{2}$$

5. *The leaching of oxide or roasted ores with a solution of ferrous chloride and sodium chloride* was introduced for the first time by G. Ferentschik, at Stefanshütte in Hungary, in 1869, and has been improved by Sterry Hunt and Douglas, in the United States. The process is based on the following reaction:—Neutral ferrous chloride converts copper oxide, with separation of iron oxide, into cupreous and cupric chlorides, the cupreous chloride being easily soluble in hot solutions of sodium chloride. The copper can be completely dissolved in this manner, with separation of iron oxide, and can also be completely precipitated.

The reaction of ferrous chloride on cupreous and cupric oxide is as follows:—

$$3CuO + 2FeCl = Cu_2Cl + CuCl + Fe_2O_3.$$
$$3Cu_2O + 2FeCl = 2Cu_2Cl + 2Cu + Fe_2O_3.$$

The second reaction shows that in the presence of cupreous oxide a part of the copper is separated in a metallic condition, which is dissolved in the cupric chloride, reducing the same to cupreous chloride.

CHAPTER VI.

THE PRODUCTION OF COPPER FROM SULPHATES

IT was in the year 1752 that the first cement copper was produced in the Rio Tinto Mines, in Spain,* from ore heaps which had undergone a natural decomposition by atmospheric influences' and which had been leached out by water and the copper precipitated on iron. The process met with a strong opposition from the then General Superintendent of the "Hacienda Real," Don Pedro de Lerina, who stated that the cement copper obtained was nothing more or less than iron coated with copper, and that this falsification would do a great deal of harm to the Spanish copper trade. After a long series of experiments by some celebrated chemists at Madrid, it was shown that the Don had made a mistake, but it took a long time before the lixiviation process was looked upon with favour.

Theoretically it appears as if this process is a very simple one, but in practice it is found that the problem is not easily carried out; and it was only after a long series of experiments that the system was perfected. The first method which was used was that of natural cementation of the ores, by exposing them to atmospheric influences and washing out the soluble salts. Then came the artificial cementation, by which the ores were heap roasted and then lixiviated. In the third period of the history of these famous mines, the rich ores were smelted and the poor ones were lixiviated. These processes are still carried out, to this date, with the exception that heap roasting is abandoned.

The **Natural Cementation** consists simply in watering the heaps of ore, so as to dissolve the copper and silver which are

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* "Annales des Mines: Memoire sur l'Industrie du Cuivre dans la Région d' Huelva," M. L. de Launay. Paris, Vve. Ch. Dunod, Éditeur, 1889.

present as sulphates, and then precipitating the copper by means of iron.

The mineral is broken to the size of a fist, and then piled up in a large open space, where it is left for about ten years. These piles, according to the slope of the ground, have a depth of from 5 to 12 metres, and at regular intervals there are channels left to permit the draining of the water. Vertical chimneys are built with bricks, which communicate with the longitudinal channels, and in these the temperature is frequently taken by means of thermometers tied to strings.

These ore heaps contain several million tons of ore, and on their surface are laid a series of pipes with spigots, by means of which they are wetted down at regular intervals during a number of years. The water circulating in the heaps becomes gradually charged with the soluble sulphates, and collects in sluices which surround the heaps. They contain on an average 2·8 per cent. copper, and when their contents are reduced to about $\frac{1}{4}$ per cent. the residues are shipped to England, France, Germany, or the United States, where the sulphur in them is employed for the manufacture of sulphuric acid, and the resulting residues, known as purple ore or blue billy, go to iron smelteries. In this operation, which is very simple, the temperature of the ore heaps has to be carefully regulated. If the same is too low, the copper does not dissolve; if too high, steam is generated in the heap and access of air prevented, and the oxidation of the copper is retarded. The heaps ought to be maintained at an average temperature of 100° Fahr.

The lixiviation should be carried out in such a manner, as to dissolve the maximum quantity of copper with the minimum quantity of water; and to effect this it is necessary that the water should remain in contact with the ore for a certain length of time, so as to allow the oxygen of the air to penetrate the wet pyrites and accomplish their sulphatisation. For this purpose the brine which flows from the heaps is frequently analysed, and if the same is found not to be rich enough in copper, fresh water is not added on the heaps till after the lapse of a month or two.

The amount of water consumed by these operations being very large, special reservoirs have had to be constructed.

Precipitation by Means of Iron. The brines or cement waters are conducted by means of sluices to the precipitating basins, which at San Domingos consist of ten rows, each row consists of 24 basins, which have a square section of 4 metres by 4 metres. These basins are coated with asphalt, so that the bricks shall not be attacked, and in these are piled up regularly the pigs of iron. The copper which precipitates on the iron is called "cascara." After a month, the flow is stopped in one of these basins and the cascara is scraped off from the pigs, and if necessary the iron consumed is replaced by fresh pigs.

To obtain good results in this operation it is necessary to regulate the flow in these basins to a nicety, so that the cascara be obtained as pure as possible, and also that as small a quantity of iron as possible should be consumed.

The cascara which is obtained contains 65 per cent. of copper, and the *consumption of iron is said to be over two tons to one ton of copper*, whereas theoretically the consumption should be 0·86 of a ton. The loss of iron is caused by the presence of a certain quantity of ferrous sulphate in the liquors, which the pig iron reduces to ferric sulphate, and also by the precipitation of a certain quantity of iron oxide with the cascara.

The cascara is dried, sometimes in reverberatory furnaces, and packed in sacks holding 45 kilograms each.

When the solutions contain a considerable quantity of iron oxide salts, the consumption of iron increases in precipitation as $Fe_2O_3 + Fe = 3FeO$, and also when solutions of neutral ferric salts remain for a considerable time in contact with the atmosphere, basic salts separate and acid is set free, which requires a certain quantity of iron for its saturation :—

$$4FeSO_4 + 2O = Fe_4 3SO_8 + 3SO_3.$$

and with chlorides :—

$$6FeCl_2 + 3O = 2Fe_2Cl_6 + Fe_2O_3.$$

The **Artificial Cementation** formerly carried out at Rio Tinto consisted in the roasting of the ore heaps (called teleras); their lixiviation in vats; the precipitation by iron; the collecting of the precipitate; and the treatment of the residues in terreros

The teleras contain from 200 to 1500 tons, and average from 1½ to 2 per cent. copper. The small heaps burn two months, the large ones six months. The small heaps require for 100 tons of ore 0·76 cubic metre of wood, and the larger ones consume 0·26 cubic metre per 100 tons. The extraction from small heaps is better than from the large ones.

The leaching is carried out in vats which are constructed of cement; they are 100 feet long, 34 feet wide, and 5 feet deep. The false bottoms are made of square timber, and the solutions are drained into large settling tanks or masonry reservoirs. The leaching is commenced by covering the ore with water and letting it remain in contact from two to six hours; after draining off the solution, fresh water is pumped on the ore, which remains in contact from eight to ten hours. The number of washings which are applied in this manner vary from five to six, and together they remain in contact with the ore for about fifty hours; in the solutions the copper is present as a sulphate, each cubic metre of solution contains from 5 to 6 kilograms of copper.

The leached-out residues still assay 0·4 to 0·5 per cent. of copper, and to regain this copper, which is mostly present as a sulphide, they are submitted to a further decomposition, by building up large heaps at the lower works called "Terreros," which are traversed by a system of canals built of dry masonry, and these are connected with a system of vertical chimneys about 8 inches in diameter, also built of dry masonry, which establish a free circulation of air. As soon as these damp residue heaps have reached a certain height, the decomposition of the sulphides begins, causing an elevation of temperature. Care is taken to prevent the firing of the heap, by properly regulating the admission of air into the canals.

From time to time these heaps are leached out in place and the solutions treated after the manner described above under Natural Cementation. At the present time upwards of 7,000,000 tons are under treatment in terreros. The cement copper obtained is washed and concentrated in buddles and classified according to the percentage of copper and arsenic; the higher grades being shipped to England and run down with mattes, while the low grades are smelted at the mines with the first-class ores.

Costs at Rio Tinto. The cost of producing copper by sulphatisation is as follows:—

			francs	francs.
Cost of Mining:—	Labour	per ton	1·3600	
	Explosives	„	0·2750	
	Tools of all kinds	„	0·2900	
	Animal traction	„	0·2820	
	General expenses	„	0·9350	
	Removal of waste rock	„	0·8750	
	Total	„		4·0170
Cost of Roasting:—	Combustibles	„	0·2500	
	Building up of ore heaps	„	0·4250	
	Transport of mineral calcines	„	0·1250	
	Maintenance of tools	„	0·0125	
	Salaries of officials	„	0·0750	
	Stores	„	0·0150	
	Total	„		0·9025
Cost of Cementation:—	Iron consumed	„	1·8700	
	Charging and discharging the cement copper	„	0·5100	
	Sundries	„	0·4500	
	Total	„		2·8300
	Total cost per ton of ore treated			7·7495

Mr. Cumenge, in his Notes on Rio Tinto, gives the following details as to the cost of producing copper at these mines:—

			francs.	francs.
Cost of Roasting:—	Discharging and spalling ore.	per ton	0·1475	
	Building up the Teleras	„	0·4450	
	Fuel for roasting	„	0·1500	
	Supervision	„	0·0150	
	Tools of all kinds	„	0·0250	
	Maintenance of tools and shops	„	0·1000	
	Total	„		0·8825
Cost of Cementation:—	Cost of lixiviation	„	0·5300	
	Pumping of water 35 m. high	„	0·0900	
	Discharging the basins	„	0·2525	
	Cleaning the pigs of iron	„	0.2125	
	Salaries of officials	„	0·2050	
	Total	„		1·2900
	Mining cost per ton he takes only at			1·9230
	Total cost per ton of ore treated			4·0955

As it takes 66 tons of ore to make one ton of copper, at the end of the year the above amount of 4·0975 must be multiplied by 66, which would bring the price per ton of copper as follows:—

	francs.
66 tons of mineral per ton of copper at frs. 4·0975	270·435
Drying of the cascara and sacking same	9·670
Supervision of the basins	4·945
General expenses in all the departments	30·180
Pig-iron for precipitation	397·675
Sundries	12·097
Total	725 per ton.

By the processes now in vogue at these mines, it takes from two to two and a half years to extract about 80 per cent. of the copper value from ores containing 2·70 per cent. During the first four months about 50 per cent. of the value is extracted.

Ores yielding only 1½ per cent have been treated at a profit in Rio Tinto, and may be considered of even great value at the present price of copper, which, if taken only at £50, or 1250 francs, per ton, would be equal to 1·25 franc the kilogram; and consequently 1½ per cent. ore yields 15 kilograms per ton, having a value of 18·75 francs, which leaves the very handsome margin of profit as follows:—

	francs.
By taking the value of the copper in a 1½ per cent. ore as above at	18·75
And the cost of treating and obtaining the copper in this ton as above at	7·74
It leaves a margin of profit per ton of ore of	11·01

As it requires 66 tons of ore to make 1 ton of copper, the profit per ton of copper would be 66 × 11·01 = 666·66 francs, or about £26.

Copper Extraction at Agordo.* At these mines, in Italy, ores containing 1 to 2 per cent. of copper, are finely pulverised and mixed with a solution containing ferrous sulphate, till a thick paste is formed, which is moulded into small cones, and these, when dried in the open air for three weeks, are piled into regular heaps. After being covered with fines they are set on

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* *Oesterreichische Zeitschriften für Berg und Hüttenmänische*, 1861 und 1862; und Carl A. M. Balling, *Die Metallhüttenkunde*, Berlin, 1885.

fire. The small heaps burn from four to five months, the larger ones from ten to twelve months, whereby the largest portion of the copper is converted into a sulphate; the ferrous sulphate being decomposed into sulphuric acid and ferric oxide.

The roasted ores are leached in wooden square vats having 40 to 50 cubic metres capacity; they are perfectly water-tight, provided with false bottoms made of boards or acid-proof stoneware, leaving at regular intervals openings between them, and on top of them are placed filters of straw, coke, or any other suitable material. The percolating solutions flow from the vats through wooden troughs or lead pipes into the collecting tanks, from whence they are pumped back again on to the lixiviation vats and made to circulate through fresh ore charges.

Fresh water is pumped on to the ores which are nearly exhausted, to act as a last wash to press out the last of the solutions. The solutions which circulate are continually enriched and they remain in contact with each charge for twenty-four hours. The rich solutions have a density of 31° to 34° B., and the weak ones 15° B. After leaching the ores three times, the residues are used for covering the ore heaps, and when separated from the roast heaps they are leached again, and the residues from these second leachings still contain from 0·25 to 0·50 per cent. of copper; they are sifted, the finer part is rejected as worthless, and the coarser part is used again as a covering of the ore heaps, and then again manipulated as described. The consumption of iron at Agordo was very high owing to the presence of ferric sulphate in the solutions, and the formation of large quantities of basic iron salts (brumini), which rendered the cement copper impure. The arsenic in the ore was present in the solution as a ferric arsenate and increased the quantity of brumini.

Copper Extraction at Stadtberge.* The ores contain carbonates, metallic copper, red oxide, and copper glance. They are treated by solutions of sulphuric acid as follows:—After crushing they are dumped into masonry vats to a height of three feet, and are there exposed to the action of sulphurous acid vapours. For the production of these vapours, two conical shaft furnaces are employed in which pyritic ores are roasted, and the

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* *Oesterreichische Zeitschriften*, 1871, page 109.

sulphurous acid mixed with a current of air passes into a canal, where they mingle with the gases generated from saltpetre, thereby producing sulphuric acid which passes upwards through the ore. It takes eight to nine days to decompose sixty-five tons of ore.

For the extraction of the soluble copper sulphates, the weak solutions from previous leachings are employed, which are collected in reservoirs and are pumped on to the ores. After the first leaching, the ore is again exposed for several days to the action of the acid vapours, when a second lixiviation with weak solution is effected, and then the ore is washed with clean water to remove the last of the acid solution.

From the solutions which mark 20° B., the copper is precipitated by means of scrap iron, which is then washed on sieves and the collected copper is melted in reverberatories. The slimes which remain from the washing of the cement copper are smelted to black copper in small shaft furnaces. After the copper is precipitated, the solutions are used for the production of iron vitriol or for the further extraction of copper from the ores. This process extracts from ores containing 2·21 per cent. of copper only 1·33 per cent., leaving 0·88 per cent. in the residues. The result of seven years' practice has proved that to produce 100 lb. copper, 3¾ tons of ore were required. For the production of the necessary sulphurous acid 681 lb. pyrites and 744 lb. of zinc blende were required, and 127·2 lb. of iron were used up in precipitation. It was found more advantageous to burn the ores, so as to render the iron oxides and alumina insoluble, and to employ the sulphuric acid direct for dissolving the copper.

Neill Leaching Process. This is a method now being made the subject of experiment in the United States, according to the Patent Specifications No. 650784. The process depends on the solvent action of sulphurous acid upon the oxides or carbonates of copper, in the presence of water and an excess of the sulphurous acid. Under these conditions the oxidised compounds of copper are quickly attacked by the solvent, the copper goes into solution as cuprous sulphite ($Cu_2SO_3 + H_2O$), which salt, though insoluble in water, is soluble in an excess of the sulphurous acid solution.

If, therefore, the excess of sulphurous acid is driven out by heat, the cuprous sulphite will be precipitated from the solution as a cupro-cupric sulphite, which is a finely crystalline dark red salt, carrying 49·1 per cent. copper, and being very heavy, readily settles from the solution. After filtration or decantation from the solution, this cupro-cupric sulphite may at once be melted in any well-known and usual furnace or crucible, practically without fluxes and without the formation of slag, to a button of pure copper.

The SO_2 gas is produced by burning pyrites or native sulphur. Theoretically, in proportion to the pounds of sulphur consumed, this solvent will dissolve *twice* as much copper as sulphuric acid, as is shown by the following formulæ:—

$Cu_2SO_3 + H_2O$ contains two units of copper and one of sulphur.
$CuSO_4 + H_2O$ contains one unit of copper to one of sulphur.

The sulphurous acid, being a weaker acid, does not dissolve so many other metals, which foul the solution and absorb sulphur. The precipitation of the cupro-cupric salt is effected by heating the solution in a wooden tank, by means of waste steam, to the point of boiling, when the cuprous sulphite falls to the bottom of the tank. This precipitate is easily handled and melted. In practice some of the sulphurous acid becomes oxidised to sulphuric acid, and therefore a part of the copper contents of the solution is usually present in the form of copper sulphate; but this portion is small, in some cases amounting only to 15 per cent. of the copper in the ore. Even allowing that the copper contained in the solution as sulphate will amount to 25 per cent. of the ore contents, we then have only to reduce with iron one-fourth as much copper as would be the case if other solvents had been employed; and, furthermore, this copper is more readily reduced, and with almost the theoretical consumption of iron, as the iron in the solution is in the ferrous not the ferric condition, having been reduced by the sulphurous acid gas, and thus it does not form the basic salts, which consume so much metallic iron in the precipitation.

In practice, the process is operated as follows:—If the ores are carbonates and oxides, they are crushed in rock-breakers and rollers fine enough to pass a screen of 20 mesh to the linear inch, and charged into a covered tank made of wood, or iron lined with wood, or other non-corroding material. This tank has previously been charged with water containing some sulphurous acid—two tons of water being used to one ton of the ore. This water is obtained from the last washing of the previous charges, and from the tower which is placed at the end of the system to absorb the last traces of the sulphurous acid gases. During the charging of the ore this water is continuously agitated, and the charge is kept in agitation during the period of leaching. The sulphurous acid gas, obtained either from burning pyrites or native sulphur, is first passed through a washing apparatus to free it from impurities (SO_3), and is then forced by means of an air-compressor through the charge in the leaching tank, entering it from the bottom. The amount of gas to be passed through the charge is large, as these gases usually only carry 3 to 5 per cent. sulphurous acid gas; and this large volume of gases serves to keep the pulp in the leaching tank in a constant state of ebullition, which is most favourable to the solution of the copper. The dissolving of the copper can be completed in the one tank, but it is preferable to have several tanks located one above the other, so that the gases from the lowest one pass through the others in rotation thus absorbing the sulphurous acid gas more completely; and in this case, when the solid material in the lowest tank is shown by a test sample to be barren of copper, this tank is emptied into receivers below it, and then each of the upper leaching tanks in turn is emptied into the next below, and a fresh charge is placed in the highest tank.

The pulp drawn from the last leaching tank is received in another tank in which it is still kept in agitation, and at once placed under a pressure of air which forces the entire contents of the tank, pulp and all, into the filter press. This apparatus retains the sand and slimes of the ore, while the solution containing the copper is forced out, and is conveyed by suitable pipes to the tanks where it is to be steamed to precipitate the copper. The pulp in the filter is at once washed by pressing successive small quantities of water through it, and these wash waters are forced either to the steaming tank or to the wash water tank to be used in the next fresh charge of ore, according to the contents of the water in copper. The sands are then discharged from the filter presses into suitable cars or conveyors, and taken to the waste dumps.

The solution containing the copper is heated by the exhaust steam from compressors to the boiling point, and maintained at that till the free sulphurous acid has been expelled, then the solution is allowed to settle for a period; after settling, the same is drawn off into other tanks in which the balance of the copper is reduced by scrap iron. As this solution is hot when drawn from the steaming tank it gives up its copper very quickly, and the tank room required is therefore small. The final waste water carries only traces of copper.

The **cuprous sulphite precipitate** from the steam tank is dried, placed in a reverberatory furnace, and melted. It does not require any material manipulation, but melts readily to metallic copper, which can be ladled into bars, or can be refined on the same hearth. This copper will not carry any silver or gold, therefore will not require any separation.

If the ore to be treated is a *sulphide ore*, it must first be crushed as before, but must then be roasted to drive off the sulphur, and reduce the copper to the oxidised state; this roasted pulp must then be cooled, otherwise the operations are the same as already described, and the apparatus the same. It is possible also that the sulphur driven out in the roasting of such an ore may be used to dissolve the copper out of the roasted pulp.

From the foregoing description, it is obvious that the Neill process will not extract the silver and gold from the ores; and also that it is not applicable to ores containing too many ingredients soluble in the sulphurous acid solution, such as ores containing lime, alumina, iron, or other soluble compounds. The passing of the whole bulk of the ore through filter presses seems to be a very objectionable feature of the process.

Leaching Copper Ores at Kedabeg, Russia.* Ores containing 3 per cent. of copper, are treated by a leaching process. The ore is cheaply roasted in kilns or Gerstenhöfer furnaces without fuel, the copper being thus brought into a suitable form for leaching. This presents no great difficulty, as the copper,

* "Mineral Industry," vol. vi. p. 249.

originally existing as a sulphide, is oxidised partially to sulphate in the furnace, the sulphatisation being completed to a certain extent later during the leaching by the ferric sulphate formed in the roasting, and also present in the residual solutions from the electrolytic precipitation, the latter being run into the leaching ponds. A comparatively long time is required to obtain a practically complete change of the copper to sulphate, several years' leaching being necessary to reduce the copper contents to 0·5 to 0·7 per cent. Cu. However, from 50 to 70 per cent. are obtained at a very small cost in the first year. The copper is precipitated in wooden vats by means of scrap iron, a rapid circulation being kept up all the time. In this way 409½ metric tons of cement copper, with 65 to 75 per cent. Cu, are produced per annum.

At **Majdanpec, in Servia,**[*] are large refuse ore heaps which contain on an average 2 per cent. of copper, which is present as an oxide and sulphide. The ores are moist enough to permit of their being moulded and pressed into bricks, which weigh five kilograms each. They are stacked up into regular brick kilns of 300 tons capacity, and remain for about a month exposed to atmospheric influences, which dries them, and they are then set on fire and roasted. Each kiln requires about seven tons of cordwood, and when the kiln is well on fire the draught is regulated by covering the outside with fines. The oxides are sulphatised by the sulphuric acid disengaged from the sulphides, and the roasting is finished in about three months. The inner red portion of the kiln has undergone the best roasting, and can be extracted to within ¼ to ⅛ per cent. of its copper contents, whereas the outer portions of the kiln are not so well roasted, and their copper contents can only be extracted to within ½ to ¾ per cent.

The lixiviation is carried out in four sets of vats; each set is composed of four vats; the vats are 4 metres long, 2 metres wide, and 1·6 metre deep. They are provided with false filter bottoms. The first two sets are used for lixiviation, the third set for precipitation, and the fourth set for the crystallisation of the ferrous sulphate which accumulates in the solutions. The solutions remain in contact with the ore for seven hours, and

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[*] *Berg & Huttenmännische Zeitung*, 1885, p. 58.

after filtering, are pumped back on to the ore contained in another vat, and are made to circulate through fresh ore charges till they are saturated with copper, and then are led into their respective precipitation vats. The same process is repeated with the weaker solutions, which are enriched by circulating them through fresh ore charges, and they remain in contact with them for four hours, and a wash is given with the warm acid solutions which result from the precipitation vats, as these still retain some traces of copper oxide. The ores receive a final water wash, whereby the last traces of the solutions are pressed out.

Gradually the solutions become enriched with iron salts and are withdrawn into the fourth set of vats. Steam is injected, and after settling this becomes free of iron oxides changing the brown colour of the liquid into a greenish tint. The waste solutions are acid and are used as final washes, and when they become charged with magnesian and aluminous salts, these are allowed to crystallise out, and the solutions are returned again to the manipulation.

The cement copper obtained on precipitation with iron is very clean, as it contains 92 per cent. copper. It is cast into ingots and brought on to the market as black copper.

CHAPTER VII.

THE PRODUCTION OF COPPER CHLORIDES BY WET PROCESS.

THE reactions which take place in this process are founded on the principle that, if copper sulphides are brought into contact with ferric chloride, they are converted into cupreous and cupric chlorides, and the ferric chloride is converted into ferrous chloride, as follows:—

$$CuS + Fe_2Cl_3 = 2FeCl + CuCl + S.$$
$$Cu_2S + Fe_2Cl_3 = 2FeCl + Cu_2Cl + S.$$

Doetsch Process. These reactions were formerly employed at Rio Tinto in the carrying out of what is called the Doetsch process.* The mineral is not roasted, and averages 2·68 per cent. copper, present as CuS and Cu_2S; and after the extraction of the copper it is found that the iron pyrites remain unaltered. The process demonstrates that ferric chloride dissolves only the copper from the ore, but leaves the iron pyrites intact, which is of great importance. Consequently by the Doetsch process a solution is obtained, which contains cupreous and cupric chlorides and ferrous chloride.

The solution of ferric chloride is obtained by dissolving sodium chloride in green vitriol or iron sulphate.

There is produced an alkaline sodium sulphate and ferric chloride.

In carrying out the process, the ore is broken in rock

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* "Notes sur le Rio Tinto," by M. E. Cumenge; "Mémoire sur l'Industrie du Cuivre dans la région d'Huelva," par M. L. de Launay; "Annales des Mines," tome xvi.

breakers to the size of about half-an-inch, and built up into heaps 4 to 5 metres high, 16 metres long, and 16 metres wide. These heaps are traversed in their longitudinal and vertical directions by a regular system of canals and chimneys built in dry masonry. While the heaps are being built up, they are mixed with the ferrous sulphate and salt in the solid state, in the proportion of about ½ per cent. of the weight of the ore, and after the heap is built up the same is well wetted down. It takes about four months to extract 1·34 per cent. or 50 per cent. of the copper, and after two years a total of 2·20 per cent. is extracted, so that the final loss is 0·48 per cent.

The solutions which run from these heaps are precipitated by iron (according to the formula)

$$CuCl + Fe = Cu + FeCl.$$
$$Cu_2Cl + Fe = 2Cu + FeCl.$$

in vats, and as the copper is mostly present as cupreous chloride, one equivalent of iron is required to precipitate two equivalents of copper ; consequently a great reduction has been made in the cost of precipitation.

The ferric chloride after action on the ore is reduced to ferrous chloride, and to make the process continuous, the ferrous chloride is regenerated into ferric chloride, which is accomplished by injecting chlorine gas into the waste liquors by passing them through coke towers.

The solutions which run from the ore heaps contain 5 to 7 kilograms of copper per 1000 kilograms or one cubic metre.

The regeneration of the waste solution takes place according to the reaction

$$2FeCl + Cl = Fe_2Cl_3.$$

The chlorine gas is produced by heating salt with ferrous sulphate in a reverberatory furnace, holding a charge of 200 kilograms, plenty of air being admitted through the working doors and canals practised in the fire bridge. The reaction in the furnace is shown by the following formulæ :—

$$2SO_4, Fe + 2ClNa + 3O = Fe_2O_3 + 2SO_4Na + 2Cl.$$
$$3SO_4, Fe + 3ClNa + 3O = Fe_2O_3 + 3SO_4Na + 3Cl.$$

resulting in the production of ferric oxide and sulphate of soda.

The ferrous sulphate is found in large quantities on the shores of the Rio Tinto river, where the same is formed by the evaporation of solutions holding iron, which come from the ancient workings of the Romans, Carthaginians, Arabs, and Spanish, and from the drainage of the waste heaps which are full of iron pyrites. The large Terreros also furnish crystals of ferrous sulphate and salts of the ferric sulphate.

During the reaction in the reverberatory furnace, a certain quantity of hydrochloric acid is produced, which is again reconverted into chlorine gas, by introducing a certain quantity of dioxide of manganese near the flue. This mineral is found in considerable quantities on the Rio Tinto concession. The gases from the furnace pass into a tower and are absorbed by ferruginous waters, which fall in a shower from above, and in this manner they become charged with ferric chloride, according to the above-mentioned formulæ. As this regeneration takes place continuously, it is only necessary to replace the solutions absorbed by the ore by freshly prepared brine.

By this process the sulphur in the pyrites is not destroyed, and consequently the leached-out ores are still fit for the manufacture of sulphuric acid; there is also a large saving in time as compared with the atmospheric production of sulphates and leaching, and the consumption of iron by precipitation is also considerably reduced.

The cost of producing copper by the Doetsch process has been established by Mr. Cumenge, according to the results which he accomplished after a campaign of four months, during which he obtained 224 tons of cement copper.

	francs.
The cost of lixiviation	83·81
Precipitation	181·16
General expenses	28·04
Total per ton of cement copper	293·01

Or per ton of pure copper 345 francs.

The details of these expenses are:—

		francs.	francs.
Lixiviation . .	250 kilos salt for chlorine and mixture, 68 frs. per ton	17·06	
"	Sulphate of iron, 0·20 ton at 12 frs. per ton	3·00	
"	Fuel, pumping, labour	63·75	
			83·81
Precipitation . .	Iron consumed, 1·12 ton at 92·85 francs	104·00	
"	Labour	77·00	
			181·16
General Expenses .	Material	5·25	
" "	Repairs on the basins	11·87	
" "	Transport on materials, machinery .	4·00	
" "	Maintenance of roads	1·29	
" "	Salary of employés	5·72	
			28·04
	Total treatment expenses		293·01

The extraction after four months amounted to 1·34 per cent. of the copper contents and there were 75 tons of mineral employed to produce a ton of pure copper; therefore the cost price of a ton of copper will be as follows:—

	francs.
Value of 75 tons of mineral at 4 francs	300
Treatment charges per ton of pure copper as above . .	345
Transport to Huelva and England and other expenses .	30
Total	675

The 75 tons of ore will furnish at the expiration of two years a total of 1·650 tons of copper: therefore for the supplementary 0·650 tons of copper only the treatment charges must be brought into calculation, namely:—

	francs.
345 francs × 0·650 = ...	222·50
Plus the transport, 30 francs × 0·650 .	19·50

Consequently at the end of two years 1·65 tons of copper would have been produced from the 75 tons of ore, costing 918·75 francs, making the cost per ton of copper 556 francs, or £22 per ton, which at the selling price of £50 would leave a profit of £28, equal to 700 francs.

When these figures are compared with those given under the heading of the sulphatising process, it will be seen that the Doetsch process gives a benefit of 950—825 = 125 francs, over and above the one realised by the old process.

From the above calculation it will be seen that 1·12 ton of iron was employed to precipitate 1 ton of cement copper which would equal 1·3 tons iron to 1 ton of pure copper.

Treatment by Means of Ferrous Chloride and Hydrochloric Acid.—When ferrous chloride and hydrochloric acid are exposed for a considerable period to atmospheric agencies, they are converted into ferric chloride and ferric hydroxide, which, last in its turn, is attacked by the hydrochloric acid and converted into ferric oxide. Through these reactions a process has been at work at Stadtberge, in Westphalia,* to convert copper sulphides into copper chlorides by the action of the ferric chloride, which is converted into ferrous chloride.

The copper chlorides are leached out by means of solutions acidulated with hydrochloric acid. The cupreous ferrous chloride solutions are collected in vats and the copper precipitated by iron. The resulting mother liquors are acidulated with hydrochloric acid, and are then employed, either for the chlorination or for the leaching of the ores after conversion into copper chlorides.

The chlorination of the ores, therefore, is effected by wetting down the ore heaps with the solutions containing ferrous chloride, which are acidulated with hydrochloric acid. The Stadtberge ores contain 2 to 2½ per cent. copper, present as copper glance, sulphate, and a small quantity of oxides. After crushing in rock breakers to 1½ to 2 centimetres, they are placed in wooden receptacles lined with clay, provided with false bottoms, holding about one hundred tons each. The solution by means of pumps is circulated through the ore, remaining in contact for several hours before being drawn off; and the extraction is considered completed after three days, when the same is drawn into the precipitation vats. The solution coming from the precipitation vats contains per litre:

	grams.
Ferrous chloride	177·97
Ferric chloride	2·64
Cupric chloride	1·12
Sodium chloride	1·33
Aluminium chloride	9·77
Calcium sulphate	7·88

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* Schnabel, "Handbuch der Metallhüttenkunde," Berlin, 1894, page 221.

For each 50 kilograms of ore there is added to this solution 2 kilograms of hydrochloric acid of 20° B. To convert the silver in the ore into a chloride there are added to each litre of solution 200 grams of common salt. The brine dissolves cupreous sulphate, oxides, and carbonates, which renders the ores porous and fits them for the natural atmospheric decomposition which follows this impregnation. After three days the copper contents of the ore have been lowered to about $1\frac{3}{10}$ per cent. The solution which has been drawn off is utilised to dissolve the copper chlorides after the ore has undergone atmospheric decomposition.

After the impregnation, the ores are shovelled out and built up into heaps three metres high, which remain exposed to atmospheric agencies for three months, so as to dry out all the moisture. At the expiration of this period the greatest portion of the copper, down to 0·4 per cent., is converted into cupreous and cupric chloride, cupric oxichloride, and cupric sulphate. The silver is converted into a chloride. The ores are now submitted in vats to a series of lixiviations by the mother liquors and freshly prepared solutions, till they contain 0·4 per cent., and the residues exposed again to further atmospheric decomposition, when they are leached again.

This process gives very good results, and the consumption of iron in the precipitation amounts to 105 kilograms iron for 100 kilograms copper. After the chlorination of the copper in the heaps the ore is allowed to remain in contact with the brine for twenty-four hours before being drawn from the vats, and the same ore is treated with from 12 to 16 solutions. The first leaching on fresh ores is effected by means of the first brine which has run off from a preceding charge, as the same contains sufficient acid to dissolve the oxichloride of copper in the ore. When the solution is drawn off, the subsequent brine is the second weaker leach from a previous charge, and this is continued till four leachings have been effected, and the resulting brine collected together for precipitation. The copper contents per litre from the first solution are 30 to 40 grams, the second brine contains 20 to 25 grams, the third brine 15 to 20 grams, and the fourth brine 10 to 15 grams. The subsequent brines, which receive an addition of hydrochloric acid, are circulated so as to enrich them before being precipitated.

Claudet Process.—This method has been pursued in Great Britain for the treatment of Spanish ores which contain silver, and consists in chloridising the copper and silver by roasting with common salt, dissolving the chlorides out with hot water, precipitating the silver as iodide, and then the copper with metallic iron. There are five different stages in the process, namely:—

1. Crushing the ore and mixing with salt.
2. Calcining, or roasting, the same.
3. Leaching the roasted ore.
4. Precipitating the silver from the argentiferous copper liquors.
5. Precipitating copper from the desilverised liquors.

The roasted ore is mixed with 13 per cent. to 20 per cent. of salt, and the mixture calcined in muffle furnaces. The muffle is connected with a condensing tower, built of fire-brick, and packed with bricks and coke, over which a stream of water is kept running to condense the acid gases evolved from the furnace mixture. The acid solution, running off at the bottom of the tower, is used to dissolve the oxide of copper out of roasted ore, as will be described.

The object in the calcination is to oxidise sulphur and chloridise the silver and copper (or rather to render all the copper soluble with the least possible expenditure of acid in leaching). About 77 per cent. of the calcined ore is soluble in water (*i.e.*, the copper being present as protochloride and subchloride), 20 per cent. in dilute acid (the copper present as oxide), and the remainder, 3 per cent., is unchanged copper sulphide. The heat of the furnace is not allowed to exceed a dull red, or else the protochloride is decomposed.

The calcined ore, while still hot, is taken to the leaching tanks. These are built of wood, and about 10 feet square and 5½ feet deep. Each tank holds 20 tons of calcined ore, which rests on a false bottom, on which a rough sort of filter is formed of screened furnace ashes. The ore is first washed with weak liquors from a previous operation, then with the acid solution from the condensing tower, and finally with hot water.

Only the first strong liquors are run to the Claudet tanks, the weak liquors being used as first washings for another tank of ore. The residual ore is thrown out of the leaching tanks and after draining is ready for shipping as purple iron ore, which is used in the puddling furnaces.

The Claudet process of precipitating silver consists in first ascertaining the amount contained in the copper liquor (it averages 3 to 6 grains of silver per gallon, and from 0·2 to 0·7 lb. of copper) and passing it, together with a slight excess of an iodide of zinc solution, into the Claudet tanks, which are usually circular and of about 3,500 gallons capacity. The zinc iodide is of such strength that one gallon precipitates 500 grains silver. The reaction is

$$2AgCl + ZnI_2 = 2AgI + ZnCl_2.$$

The liquor is allowed to settle for 48 hours, and being desilverised, is run off into the copper precipitating tank.

The precipitated iodide of silver accumulates in the Claudet tank for about a month, at the end of which time it is swept into another vat, and, after washing with dilute acid and water, is digested with scrap zinc, when the following reaction occurs:—

$$2AgI + Zn = ZnI_2 + 2Ag.$$

The iodide of zinc thus regenerated is dissolved out and used again for precipitating silver from fresh liquors. The silver residue, consisting of metallic silver mixed with a little gold and considerable sulphate of lead, etc., is sold to silver refiners.

The desilverised copper liquors are precipitated with scrap iron, in wooden vats, the solution being kept at a temperature of from 150° to 170° Fahr. by the use of steam. The copper in the first liquor admitted is precipitated in three or four hours, each subsequent liquor taking a longer time. When the iron is so enveloped in copper that about twenty-four hours are required to throw down the copper from a fresh liquor, the tank is cleaned out. When dried, the precipitate contains 75 per cent. or more of metallic copper. The iron required for precipitating is about 110 per cent. of the copper.

CHAPTER VIII.

THE PRODUCTION OF COPPER CHLORIDES BY DRY PROCESS.

Henderson's Process.—In 1860 Henderson patented a method for extracting copper from the residues or cinders resulting from the manufacture of sulphuric acid—a method largely employed in Europe.

The pyrites which are imported from Spain and from Norway contain from 3 to 8 per cent. of copper, and are burnt by the acid manufacturers in pyrites burners, which will be presently described. The burnt ores from this first operation are then submitted to a second chloridising roasting in reverberatory muffle and mechanical furnaces (which also are fully described in Chapter XIV.), with the addition of sodium chloride, which converts the largest portion of the copper into a cupric chloride, and a small portion into cupreous chloride. After roasting, the ore is lixiviated, and from the solution the copper is precipitated by iron. The quantity of sulphur which remains in the cinders from the sulphuric acid works varies, amounting from 3 to 7 per cent. After the copper is extracted the lixiviation works sell their residues to the iron works, these residues being known as "Blue Billy."

The chemical reactions which take place in this process are as follows:—

The sulphur in the roast product from the pyrite burners is generally present as a sulphide of iron, and when roasted with sodium chloride, cupric sulphate is produced, and the evolved chlorine acting on it, converts it into cupric and cupreous chloride with formation of sodium sulphate.

The intermediary reactions which take place in the roasting furnace are expressed as follows:—

The cupric sulphate is principally produced by the action of the sulphuric acid contained in the iron sulphates of the kiln residues; or the same is produced through the sulphuric acid produced from the undecomposed iron pyrites, which latter when acted upon by sodium chloride are converted into iron sulphate and ferrous and ferric chlorides. These chlorides exert a strong chloridising action on the copper. The sulphuric acid acting on the sodium chloride disengages chlorine, and if any sulphuric acid is present as a hydrate, hydrochloric acid is also generated. Chlorine gas exerts a chloridising effect on the copper sulphides, and hydrochloric acid acts on the copper oxides.

The roast products from the chloridising roasting are a mixture of cupric chloride, cupric oxide, cupric sulphate, cupreous chloride, sodium sulphate, ferric chloride, ferric oxide; also sulphates and chlorine combinations of the other metals contained in the ores. The roasting should be conducted in such a manner, that as large a proportion as possible of the copper combinations should be soluble in water, as otherwise a large quantity of acid solutions will be required to dissolve out the copper. The production of ferrous sulphates in the furnace should be avoided, as the same goes into solution and consumes a large quantity of iron during precipitation.

To carry the process out successfully, it is necessary that the copper and sulphur contents should not be too high, and also that the temperature during roasting be moderate.

If the copper contents are too high, the decomposition of the copper sulphides during the first roasting or burning for the manufacture of sulphuric acid is not complete; and the result is, that during the second chloridising roasting, which is not carried out at a temperature high enough to decompose copper sulphides, the copper will not become completely chloridised, and therefore the extraction during the subsequent lixiviation is not complete or perfect. Practice has demonstrated, that at Oker the limit of the copper contents should not exceed 8 per cent. At various works in England the limit is placed at 6 per cent. The sulphur contents should not exceed one and a half the equivalent of copper, as otherwise the consumption of sodium chloride would be too great, and the time of the roasting operation would be unnecessarily prolonged. If the sulphur contents are too low, raw pyrites have to be added to the roasting charge in the furnace, and the temperature must not exceed a cherry red heat, as otherwise too great a quantity of cupric chloride becomes volatilised.

The roast gases from the chloridising roasting contain sulphurous acid, hydrochloric acid, and chlorine; and to prevent these gases from becoming noxious, and also to utilise them, they are passed through coke towers, shown in Fig. 11. The gases enter by the pipe, *m*, into the first tower, and then pass down the second tower, and from it rise into the third tower, and then pass down again the fourth one, and through the tube, *z*, into the flue leading to the main chimney. The towers are filled with coke, and water passes through the pipe, R, in a shower through the towers, which absorbs the gases and the resulting acid solution collects in a tank over which the towers are erected.

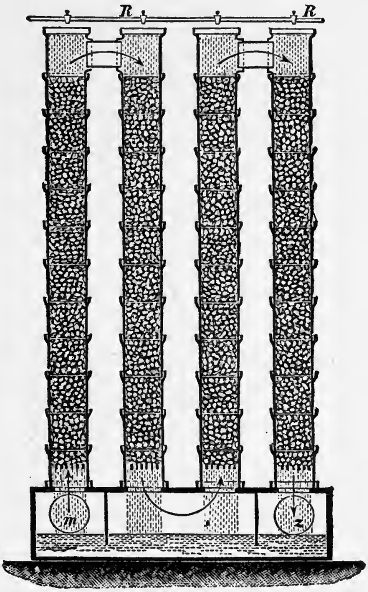


FIG. 11.—COKE TOWER.

The chloridising roasting takes place in reverberatories, muffle or shaft furnaces. The reverberatories require less fuel than the shaft or muffle furnaces, but their roast gases are in a diluted and contaminated form, and are not suitable for condensing in towers. They have either stationary or movable hearths and are occasionally heated by gas generators, which are subsequently described.

At Oker, the ores* which are treated by this method have the following composition:—

Pyrites	60 per cent.
Copper sulphides	23 ,,
Zinc blende	6 ,,
Galena	2 ,,
Gangue	9 ,,

---

* Schnabel, "Handbuch der Metallhüttenkunde." Berlin, 1894.

These ores are roasted in the pyrites burners, from which the escaping sulphurous acid was conducted to the sulphuric acid factory. The roasted ores contain 6 to 9 per cent. of copper, and 5 to 8 per cent. sulphur. The chemical composition of the residues from the pyrites burners was as follows:—

Copper, mostly as oxides	7·83	per cent.
Iron „ „ „	40·53	„
Lead „ „ „	2·09	„
Silver	0·008	„
Zinc, mostly as oxides	1·95	„
Manganese, mostly as oxides	0·40	„
Sulphur	3·80	„
Sulphuric acid	9·51	„
Clay	4·43	„
Other gangue	11·65	„

The roasted residues are mixed with 15 per cent sodium chloride and crushed in Chilian mills, to the size of 10 mesh to the linear inch. About 15 tons of ore are crushed daily and roasted in reverberatory furnaces, holding 2½ tons to a charge, and kept at a dark red heat for 4 hours. The heat is then lowered, and the stirring continued for 5 hours, plenty of air being admitted into the furnace. The charge is then withdrawn and the furnace charged afresh, about 5 tons are roasted in 24 hours, consuming from 1200 to 1400 lb. of coal. The composition of the roasted ores is as follows:—

$CuCl_2$	8·17 per cent.	Soluble in water.	CuO.	3.18 per cent.	Insoluble in water.
AgCl	0·006 „		Cu_2S	0·03 „	
$FeCl_2$	1·38 „		$PbSO_4$	1·26 „	
$ZnCl_2$	3·42 „		Fe_2O_3	47·91 „	
$MnCl_2$	1·71 „		Fe_2SO_6	1·02 „	
$NiCl_2$	0·15 „		FeS_2	1·18 „	
$CaCl_2$	3·17 „		Al_2O_3	0·44 „	
$Al_2(SO_4)_3$	0·56 „		ZnO	0·46 „	
MgSO CuSO Na_2SO	20·50 „		$CaSO_4$	1·19 „	
			Insoluble in acids	3·19 „	

The average results show, that the copper after a chloridising roasting will give 75 per cent. of cupric chloride and neutral sulphates, which are soluble in water, 20 per cent. of the copper is soluble in dilute acids, as cupreous chloride, cupric oxichloride, cupric oxide and basic cupreous sulphate; whereas 5 per cent. is present as copper sulphide soluble in aqua regia.

The solution takes place in square lead-lined vats, having a capacity of 5 to 10 tons. The ore is dumped on to a false bottom, provided with a filter made of coke, straw, or any other suitable material; the charging of the vats takes place, while the ore is still hot, and the solutions are made to flow into the vats by means of earthenware or india rubber tubing. The first washes are given with the waste liquors coming from the precipitation vats, which is followed by a hot water wash, and about 75 per cent. of the copper is extracted by this first leaching. To dissolve the cupreous chlorides and oxides, the leaching is continued with the acid liquors coming from the condensing towers, or with water acidulated with hydrochloric or sulphuric acid marking 8° B., which are heated by means of steam. In this manner every five tons of ore required 125 kilograms of 50° B. chamber acids, which were diluted to 8° B. This acid was allowed to remain in contact with the ore for two days, at the expiration of which time the same became neutralised and contained in 100 parts:—

Copper	0·58	per cent.
Aluminous earth and iron oxide	2·13	"
Zinc oxide	0·06	"
Manganous oxide	0·12	"
Cobalt and nickel	0·02	"
Lime	0·07	"
Magnesia	0·04	"
Alkalies	0·62	"
Chlorine	0·13	"
Sulphuric acid	2·39	"

There are generally given three washes with the precipitation liquors, and six water washes. They should be made to circulate as long as copper is being dissolved, and each wash should remain in contact with the ore for only a few hours.

The waste liquors which are employed for the first washes contain a considerable quantity of ferrous chloride and alkaline chlorides, and have a density of 18° B. The leaching with this solution is continued, as long as the filtrate shows a blue coloration, and they contain in 100 parts:—

Copper	3·71	per cent.
Lead	0·01	"
Silver	0·005	"
Iron oxide Aluminous earth	0·29	"

Zinc oxide	4·97	per cent.
Manganese oxide	0·58	„
Cobalt and nickel oxide	0·04	„
Magnesia	0·27	„
Alkalies	10·60	„
Sulphuric acid	8·95	„
Arsenic Antimony	Traces.	

The solutions are drawn off into the precipitation vats, which are also lead lined, and to facilitate the precipitation, they are heated by steam. The waste liquors from the precipitation vats flow into sumps and are pumped back again when required for the fresh ore charges. The liquors which are obtained from the condensing towers, are collected in separate receptacles and are utilised for the dissolving of the cupreous chlorides and oxides as mentioned above.

The residues were utilised in the lead smelting works, where they are used as a flux owing to their high iron contents.

Dry Chloruration Process.—This method, as formerly practised at Rio Tinto on ores carrying about $2\frac{3}{4}$ per cent. copper, consisted in roasting them with salt in teleras, in pyramidal, shaped heaps about 3 metres high, 8 metres long, and 6 metres wide, which contain about 800 tons. They are constructed with channels and chimneys for regulating the draught after they are set on fire. While building up the heaps, the salt is mixed in with the ore, about 14 tons of salt to 800 tons of ore.

The roasted ore is put into basins and leached with water, and by this operation about $\frac{1}{5}$th of the copper contents are extracted. The ore is then taken and built up in "terreros," which are quite a distance from the mine, at a locality called Naya, to which place there is railway transport. Here the ores are submitted, first, to the action of sulphurous acid while roasting, so as to shorten the period of sulphatisation; second, to the action of sodium chloride and peroxide of maganese, for the purpose of producing copper chlorides.

The first of the two reactions is explained by the fact that, if a heap of roasted or raw ore is subjected to the action of sulphurous acid in the presence of steam, which is developed through the heating of the moist ore heap, sulphuric acid is produced, which in its turn acts on the oxides in the ore and produces sulphates.

When sodium chloride and manganese dioxide is mixed with the ore, the following reaction will take place:—In the presence of steam charged with sulphuric acid, whose formation has just been explained, the sodium chloride will produce hydrochloric acid, which reacting on the dioxide of manganese evolves chlorine which forms ferric chloride, and this when in solution, acts on the copper and argentic sulphides. It is also possible that the manganese dioxide in presence of sulphuric acid and under the influence of heat produces free oxygen, which exerts an oxidising action on the undecomposed pyrites.

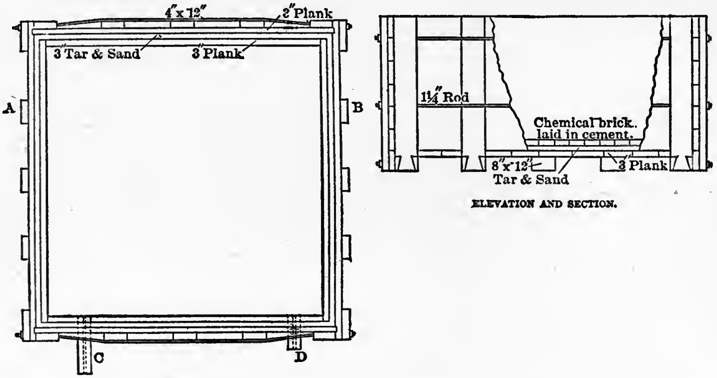
In practice, these principles are carried out as follows:—the "teleras" are set on fire, and while they are burning a discharge of sulphurous acid takes place, and on top of the burning teleras are dumped crude and also roasted ores mixed with from two to three per cent. of salt, and two to three per cent. of manganese dioxide. This mineral is found in great quantity in the province of Huelva, in the vicinity of the Rio Tinto mines. The heaps are built up to a height of eight metres, and around them are narrow ditches which carry away the cementation waters to the reservoirs.

The balance of the operation is carried as follows:—by watering down the teleras for months and years and gathering the solutions by means of the small ditches mentioned. Occasionally the surface of the teleras is stirred up with picks, so as to prevent the same from getting cemented and impervious to the percolation of water.

The solutions which result from the leaching of the teleras is called "brown liquor," and after the copper has been separated from it by iron, the waste liquors are used to dissolve copper from the "fine ores," which operation is carried out in large leaching tanks; as these liquors contain ferric chloride and give the reaction explained on page 65. The copper in the solutions is precipitated with iron. The residues after lixiviation, as they still contain about ½ per cent. of copper, are taken to the lower works and built up into "terreros" after being mixed with other poor ores.

At Natrona, Alleghany County, Pennsylvania, the Pennsylvania Salt Manufacturing Company uses Spanish pyrites containing 2 per cent. of copper, and the burnt cinder is roasted with salt to produce copper chlorides which are leached in tanks, whose construction is described by Mr. B. G. Clemmer.*

Every supporting timber, plank, and pin should be painted on all sides with hot, soft tar before being put in place. This is absorbed by the wood and protects it against the destructive action of the acid liquors. The tanks should be constructed of 3-inch planks, with an inside shell of the same thickness, and a space of 3 inches between the tank and the shell. All should be put together with wooden pins, and bound together as shown in the illustrations (Figs. 12, 13). The space between the tanks and the shells should be filled with a mixture of hard tar and sand. The bottoms should be covered, to the depth of 3 inches, with the same mixture fused to that between the shell and the tank. This bottom covering should then be protected against wear of the shovels by a layer of chemical brick laid in cement (Fig. 13).



ELEVATION AND SECTION.

PLAN.

FIGS. 12 AND 13.—LIXIVIATION TANKS.

The holes for drawing off the liquor are bored through wooden blocks 6 inches square, set inside of the tank near the bottom, and are provided with wooden spigots or plugs extending to the weak and strong liquor launders. All the launders are made preferably of very sappy yellow pine, dug out; with the ends, or joints halved together and calked with oakum or red lead.

* See "Mineral Industry," vol. viii. p. 197.

The proper dimensions of the lixiviating tanks are 12 × 12 × 4 feet, for the settling tanks 12 × 12 × 6 feet, and for the precipitating tanks 12 × 12 × 6 feet.

In preparing the mixture of hard tar and sand, composed of about equal parts, care must be exercised, not only to produce a homogeneous mass, but also that all the moisture and air be expelled. The usual method of procedure is to heat the hard tar in a large kettle, and stir it until all the moisture and air be expelled, then adding the sand hot, and stirring the mixture until the desired result is obtained. The sand must of course be first screened, and have all combustible matter burned out before mixing with the tar.

Cost at Natrona, Pennsylvania, for treating a ton of 2,000 lb. of Spanish pyrites cinders. The works have a capacity of dealing with 200 tons of mixture (cinder and salt) daily.*

2 samplers	@ $2·50	$ 5·00
6 mill men	,, 1·75	10·50
1 mechanic	,, 2·00	2·00
2 engineers	,, 2·00	4·00
3 firemen	,, 1·75	5·25
4 weighmen and furnace chargers	,, 1·75	7·00
28 furnace men	,, 1·75	49·00
1 hoistman	,, 2·00	2·00
27 furnace material handlers, coal and cinder wheelers	,, 1·50	40·50
2 leachers	,, 1·75	3·00
4 copper precipitators	,, 1·50	6·00
Unloading cinders and salt		20·00
Loading purple ore for shipment		15·00
21 tons of salt	,, 3·00	63·00
Pyrites fines		7·00
20 tons of coal	,, 1·00	20·00
5½ tons of sheet iron scrap	,, 7·00	38·50
Repairs, depreciation, management, etc.		40·00
		$338·25

or $ 1·87 per 2000 lb. of pyrite cinders, or $ 1·69 per 2,000 lb. of mixture.

At Ore Knob, North Carolina, ores are finely pulverised and roasted in reverberatories. The roasted ores contained 7·75 per cent. of copper oxide and 4·15 per cent. of copper

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* "Mineral Industry," vol. viii. p. 202.

sulphate. They were transferred into agitating vats 6 feet in diameter and 5 feet deep, with a conical bottom, holding 1,500 lb. of ore and 1,500 gallons of ferrous chloride solution of 22° B. The solution is heated by steam to 70° C. and is agitated by means of mechanical stirrers for 8 hours, and after remaining quiescent for 4 hours, the now clear solution is drawn off. The residues are utilised in the iron smelting works.

The solutions are transferred to the precipitating tanks, which are 13½ feet in diameter and 5 feet deep; they are provided with a false bottom on which are placed 300 lb. of iron. The solution is heated to 70° C. for 12 to 18 hours, and if all the copper is precipitated, the solution is drawn off and pumped up into tanks placed above the level of the agitation vats. It has been found that solutions containing 15 kilograms copper for every 100 gallons, give the best results.

When the precipitation vats contain from 4 to 5 tons of copper, the same is shovelled out and shipped and the precipitate contains from 75 to 80 per cent. copper. The purest portion of the cement copper is employed for the manufacture of blue vitriol, and this pure copper consists of:—

Cu	96·49
Fe	0·15
Fe_2O_3	0·97
Fe_2Cl_6	0·18
Cl	0·27
SO_3	0·20
SiO_2	1·04
Graphite	0·23

On the shores of the Escaut, near Antwerp, works were erected to treat the ores from the Vignoess Mines in Norway, which contain about 4 per cent. copper.* They are first utilised for the production of sulphuric acid, and their composition is as follows:—

Sulphur	41
Copper	4
Iron	32
Zinc	1·50
Carbonate of lime	1·50
Silica	20
	100

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* "La Metallurgie du Cuivre," par M. Roswag, Dunod, Paris.

After treatment in the sulphuric acid works they contain an average of 5 per cent. sulphur, and the loss in weight is about 25 per cent. There are daily treated 128 tons of pyrites leaving 96 tons of roasted ore; which has the following composition:—

Sulphur	5
Copper	5·50
Iron oxide	60·00
Silica	26·50
Zinc, lime, oxygen	3·00
	100

A. *The Roasting.* The ore is crushed in ball mills mixed with 20 to 25 per cent. of impure salt, according to the copper contents and after pulverisation and sifting the same is charged into 8 muffle furnaces, which are 12 metres long by 2·50 metres wide, and 4 furnaces which are 10 metres long and 4·50 metres wide, according the pattern shown in fig. 76.

They are charged by means of 3 ore hoppers and have 6 working doors, and consume 210 kilograms of coal per ton of mixture. The combustion gases pass into three large condensing towers.

The proportion of salt is arranged in such a manner as to convert all the sulphur into sodium sulphate, and an excess of 2 per cent. of salt is added to compensate for the volatilised chlorine. The reaction is as follows:—

$$ClNa + 4O + (CuS + 2CuO) = SO_3, NaO_4 + ClCu + Cu_2O.$$

Each furnace is charged with 3·75 tons and forms a layer of 4 centimetres on the hearth area; the new furnaces hold 4·50 tons and the ore layer is 3 centimetres on the hearth. The temperature is raised from 500 to 600° C., so as to avoid a cherry red heat; when the blue flame of the burning sulphur disappears the operation is finished. An assay should show that not more than 0·20 per cent. of sulphur is left before the ore is discharged from the furnace. The chloruration requires about 6 hours, which permits about 4 charges per furnace per day; and consequently each furnace roasts daily 15 tons of mixture, or 12 tons of ore.

The charge loses 5 per cent. in weight, and the percentage of salt added should be calculated in such a manner as not to chloridise all the copper, as some of the copper should remain as an oxide. If the operation is prolonged too much an oxychloride of copper is formed, which is insoluble. The composition of the ore when withdrawn from the furnace is as follows:—

Sodium chloride		$(ClNa)$	0·30	to	0·40
Cupric chloride		$(ClCu)$	3		
Sulphate of copper		$(CuSO_4)$	0·20	,,	0·30
Oxichloride of copper		$(ClCu_2O)$	0·60		
Oxide of copper		(CuO)	0·20		
Sulphide of copper		(CuS)	0·40		
Chloride and óxide of iron		$(ClFe, FeO)$	56	,,	57
Sulphate	of soda	$(NaSO_4$	19	,,	20
Silicate		$(NaSiO_4$	2		
Silica			17		

The roast gases are led into condensing towers filled with coke, and have a temperature of 130° to 150°, and escape from the towers at 12° to 18°. The liquid which runs from these towers has a density of 6½° B., and is utilised for the lixiviation of the chloridised material.

B. *The Cementation.* The roasted ore is allowed to cool down, as it was found that in the hot ore the chloride of copper collects into solid lumps, which dissolve with great difficulty when brought into contact with solutions. After cooling, the ore is elevated by chain elevators to the lixiviation tanks. There are 24 tanks in four rows of 6 each. Each tank is 25 metres long, 3·50 metres wide, and 3·50 metres deep, provided with a filter bottom composed of leached out ore (purple ore) and straw, and the solutions are conducted by means of troughs to the precipitating basins.

The ore undergoes three separate washings:—

1. By means of the waste liquors which are left after the copper is precipitated by iron; the same still contains 5 to 6 kilograms of copper per cubic metre, ferric chloride, which facilitates the solution of copper chloride and cupreous oxide, These liquors are heated to 80° C. by means of steam, and remain in contact with the ore for ten hours.

2. After this solution is filtered through, a second leaching is given by means of the liquid from the condensing towers, which if necessity requires can be strengthened by the addition of hydrochloric acid. These liquids are also heated to 80°

and the result of these two washings should give 20 cubic metres of solution from each tank, and after this solution is completely drained off the last washing is applied.

3. This consists in washing with hot water, and ought to finish the complete extraction of the chloridised material, and the residues ought only to contain 0·25 per cent. of copper.

The precipitation of the cupric chloride is effected in three series of basins, each composed of 7 vats, which all communicate, and one of which is generally being cleaned out. The vats each hold 9 cubic metres of solution, and the copper is precipitated on scrap iron while the solutions are heated by steam to 60°, so as to hasten the reaction, which requires 24 hours. The cement copper contains 80 to 85 per cent. of copper.

The waste liquors still contain 5 to 6 kilograms copper per cubic metre, and one-third of it is allowed to go to waste, while the other two-thirds circulates through the ore vats as mentioned before.

The consumption of iron is ton per ton of copper produced, which is very small in comparison with the consumption at Rio Tinto. The cement copper is washed on strong iron sieves with water under a pressure of two atmospheres; the sulphate of soda is dissolved, and any pieces of iron remain on the sieve, and to prevent the cement copper from becoming oxidised it is pressed into cakes in a hydraulic press, under a pressure of 50 atmospheres, and they retain 5 per cent. of water after being dried in the air. The residues are sold to the iron foundries at 12 francs per ton, which for 90 tons a day represents, less expense of loading into boats, 1053 francs, which are deducted from the cost sheets relating to the production of the copper.

The motive power consists of two boilers and an engine, which furnishes over 50 horse power nominal to the various machines and pumps employed. The *personnel* consists of 1 general manager and 3 superior officials, 10 overseers, mechanics, blacksmiths, carpenter; besides there are:

12 men in the crushing department,
28 ,, at the roasting furnaces,
12 ,, at the precipitation vats,
10 ,, charging and discharging,
8 ,, loading and discharging purple ore,
16 ,, maintaining the material,
43 ,, as generals,

or 143 men in all. In the roasting department 32 tons of coal are consumed daily, or 400 kilograms per ton of ore, and 10 tons are burnt under the boiler.

The loss of copper in these operations is as follows:—

1. Loss through volatilisation in the roasting furnace.

2. The copper contained in the residues (purple ore) amounting to 180 kilograms per 84 tons of ore, or 0·214 per cent.

3. Copper lost in precipitation, namely, 5 kilograms per cubic metre of solution, or 0·77 per cent.

The cost of production at Hemixheim is as follows:—On the treatment of 120 tons of mixture of salt and minerals for 24 hours, corresponding to 80 per cent. or 96 tons of ore. These calculations refer to one ton of roasted ore.

		francs.
a. Fuel . . .	Coal for the boilers, 104 kilos at 25 francs per ton, or . . .	2·60
,,	For the roasting operations, 400 kilos .	10·00
b. Reagents . .	Salt, 250 kilos at 21 francs per ton, or	5·25
,,	Iron, 50 kilos at 110 francs ,, ,,	5·50
c. Labour . .	Workmen of all description ,, ,,	6·25
,,	Supervision ,, ,,	1.35
d. General Expenses.	Various ,, ,,	2·57
	Cost per ton of ore	33.50

From 96 tons of roasted ore there are obtained 3 tons of cement copper.

The same contains 0·826 pure copper, and every month 90 tons cement copper are produced, or	74·30 tons pure copper.
The daily expense on 96 tons at 33·50 francs per ton	3216 francs.
The daily production is 3 tons cement at 0·826	2·47 tons pure copper.
At £65 or 1625 francs per ton 2·47 tons represents	4013·75 francs.
From which deduct expense as above .	3216·00 ,,
Which leaves a daily profit of . . .	797·75 ,,
Every ton of copper gives a profit . .	323 ,,
Every ton of roasted ore gives a profit .	8·31 ,,

By these figures it will be seen that the ores must be bought under 8·31 francs per ton to leave a profit, and taking the price of the Rio Tinto ores as a basis, the ores from Vignoess are worth 4·15 francs per ton.

Hunt and Douglas Process.*—This process is very similar to the Doetsch process, described at the beginning of Chapter VII. The theoretical reactions upon which it is founded consist in the transformation of the cupreous and cupric oxides by means of ferrous chlorides into cupreous and cupric chlorides, as shown by the following formulæ:—

1. In the case of cupric oxide:—

$$6CuO + 4FeCl = 2Cu_2Cl + 2CuCl + 2Fe_2O_3.$$

2. In the case of cupreous oxide:—

$$2Cu_2O + 2FeCl = 2CuCl + 2Fe_2O_3 + 2Cu.$$

3. In the case of metallic copper:—

$$2Cu + 2CuCl = 2Cu_2Cl.$$

4. In the case of cupreous and cupric oxides occurring mixed in the ore:—

$$6CuO + 3Cu_2O + 6FeCl = 3Fe_2O_3 + 6Cu_2Cl.$$

The cupreous chloride Cu_2Cl is insoluble in water, but soluble in salt solutions, and by decantation or filtration can be separated from the ferric oxide:—

5. $$6Cu_2Cl + 6Fe = 6FeCl + 12Cu.$$

Theoretically 45 parts of iron are required to obtain 100 parts of copper, as is shown by the following reaction:—

6. $$6CuCl + 6Fe = 6FeCl + 6Cu.$$

In practice 90 parts of iron are consumed or double of the theoretical quantity.

To carry out the process successfully, the copper ought to be present as an oxide and for this reason any sulphide ores must be first roasted, during which operation care must be taken not to produce the copper oxides at too high a temperature, as the ferrous chloride would not attack them. If the roasting is carried out at too low a temperature, copper sulphate is produced, which goes into solution and causes a great consumption of iron during the precipitation. Carbonate ores before being

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* Compte rendu. *Berg und Hüttenmännische Zeitung.* United States Patent, No. 227,902. May 25th, 1880.

brought into contact with the solution have to be heated, so as to drive off the carbonic acid, as otherwise a great effervescence would ensue, causing mechanical losses. Ferrous chloride should always be present in excess, so as to keep the cupreous chloride in solution and to prevent the formation of cupric oxychloride, which would take place in contact with the air.

The solution is prepared by dissolving 120 parts of sodium chloride in 1,000 parts of water and adding 280 parts of iron vitriol, which composition is sufficient to dissolve 90 parts of copper, provided the solution is maintained in a concentrated state and at an elevated temperature; and to keep up its efficiency 200 more parts of sodium chloride are added. After the solution of salt and iron vitriol is prepared, the sodium sulphate which forms is allowed to crystallise out, and the resulting mother liquors are syphoned off and are ready for use. In practice, the process is carried out as follows:—

The roasted ores are finely pulverised and are then brought into agitating vats and the solution is added, which is heated from 60 to 80° C. and left in contact from 3 to 4 days, according to the strength of the solution and the copper contents of the ore. From 60 to 70 parts of copper should be dissolved in 1,000 parts of water; and after the solution is drawn off, fresh solutions are added and the stirring continued.

In the precipitation tanks, the copper is precipitated very rapidly and it is not necessary to await a complete precipitation of the copper, as the waste liquors are used again for leaching fresh quantities of ore, and during the limited time the solutions are exposed to atmospheric influences only small quantities of basic salts are formed.

During precipitation the following reactions take place: if cupric and cupreous chlorides are present, they will form in contact with iron, ferric chloride,

$$2CuCl_2 + 2CuCl + 2Fe = Fe_2Cl_6 + 4Cu.$$

which in presence of metallic iron is again reduced to

$$Fe_2Cl_6 + Fe = 3FeCl_2.$$

The formation of oxychloride of iron cannot be prevented consequently a part of the chlorine gets lost, but this loss need not exceed 6 per cent., and for this reason an excess of sodium chloride should always be present in the solutions, and they should be frequently tested to determine their contents in ferrous chloride.

The cupric chloride has always a decomposing effect on copper sulphide.

$$2CuCl_2 + Cu_2S = 4CuCl + S.$$

The cupric chloride also exerts a chloridising action on silver and silver sulphides; and if this metal is present, it also goes into solution, and is precipitated by the copper, which in its turn is precipitated by iron.

The small quantity of iron which is required for precipitation, is a great advantage in this process, and when working on a large scale amounts only to 70 per cent. of the quantity of copper produced. Theoretically one iron (56) precipitates two copper ($2 \times 63{\cdot}4 = 126{\cdot}8$), causing a consumption in iron of

$$126{\cdot}8 : 56 = 100 : x.$$

$$x = 44{\cdot}16 \text{ iron for 100 parts copper.}$$

A chloridising roasting is not required, and the loss in copper is only 0·5 per cent., and the fuel consumption is small.

The disadvantages of this process are, that the iron oxides clog the filters and render filtration difficult, and that the silver is only precipitated when all the cupric chloride is reduced to cupreous chloride; also that the Claudet process cannot be employed for the precipitation of the silver when the solution contains cupreous chloride, as insoluble cupreous iodide is formed. According to Sterry Hunt, this difficulty can be overcome, by digesting the boiling solution with a soluble sulphide till all the copper is precipitated, when the silver with some copper remains in solution and can be precipitated by other means. The silver in case it precipitates as a sulphide, will be redissolved by the hot salt solution which contains cupric chlorides as it converts the silver into a chloride, which is soluble in salt solutions.

To avoid these difficulties, the following modification has been introduced: after an oxidising and sulphatising roasting, the ores are leached with dilute sulphuric acid, to the solution after settling and clearing, sufficient common salt is added to convert half the copper into cupric chloride. Sulphurous acid is pressed into the cupric chloride solution, which precipitates the copper as cupreous chloride, according to the following formulæ:—

$$CuCl_2 + CuSO_4 + SO_2 + 2H_2O = 2CuCl + 2H_2SO_4.$$

The cupreous chloride is separated from the solution and well washed, pieces of iron are placed into it and covered with water, till all the copper is reduced, and the freshly formed ferrous chloride is added to the copper sulphate solution instead of sodium chloride. Any surplus of sulphur dioxide is neutralised by adding some of the original sulphate solution, and after the precipitate of cupreous chloride has settled, the remaining liquors are used again for dissolving fresh quantities of ore. In this way the original solution is constantly regenerated.

When iron is expensive, milk of lime can be used as a precipitant, and on being boiled with the cupreous chloride, calcium chloride is formed.

If there is any silver in the ore, the same is converted into a chloride by the cupreous chloride in the solution, but it is not dissolved and remains in the residues, from which it can be extracted. The solution ought not to contain an excess of cupric chloride or sodium chloride, as both would dissolve the silver chloride, a portion of which would be precipitated with the cupreous chloride when the sulphur dioxide is pressed in, and of course this portion of the silver would be lost unless the copper is electrolytically refined.

If the solution only contains cupric chloride; on pressing in sulphur dioxide beside the cupreous chloride, hydrochloric

$$2CuCl_2 + SO_2 + 2H_2O = 2CuCl + H_2SO_4 + 2HCl,$$

acid is produced, which acid will keep silver chloride in solution; and for this reason, in preparing the first solution, an excess of sodium chloride should be avoided.

The metals of the zinc-iron group, which are present with the copper in the ore, also go into solution, but are not precipitated by the sulphurous acid gas, but they gradually become enriched in the solution and are eventually recovered. In the leaching of sulphide ores which have been roasted, the quantity of sulphuric acid gradually increases, and the same eventually becomes useless; the copper which the same contains is precipitated by sulphurous acid, and whatever traces of copper remain are thrown down by iron.

CHAPTER IX.

THE PRECIPITATION OF COPPER.

Process of Precipitation.—The copper, according to the solvents which are employed, is present in the solution either as a sulphate, or as a cupreous or cupric chloride. The precipitant usually employed is metallic iron in any shape or form, and all the old scrap heaps collected over the surrounding country are employed for this purpose. The graphite contained in the iron separates in this process and forms one of the impurities of the cement copper. The precipitation of copper by means of iron makes it desirable that the solution should only contain a small quantity of free acids, or iron oxide salts, otherwise a large quantity of iron will go into solution before the precipitation of the copper takes place.

Theoretically 88·8 parts of metallic iron are required to precipitate 100 parts of copper from copper sulphate and cupric chloride solution; whereas 44·4 parts iron are required for a cupreous chloride solution; but in practice the consumption is from 200 to 300 parts iron to 100 parts copper contained in sulphate solutions. The ferric sulphate in the solution decomposes in contact with the air into free sulphuric acid and ferrous sulphate. The free sulphuric acid dissolves iron, and the ferrous sulphate absorbs iron and becomes converted into ferric sulphate.

The ferrous chloride contained in hydrochloric acid solutions absorbs iron and becomes converted into ferric chloride. The disadvantage of the formation of basic salts is that they render the resulting cement copper impure, and it is therefore necessary to purify the solutions from the acid and iron salts before proceeding to the precipitation of the copper.

To prevent the formation of basic iron salts, it is advisable to allow the brine to act on the ores till the same is neutral, and to proceed with the precipitation of the copper as quickly as possible. Cement copper oxidises very rapidly in contact with the air, so that when ready for the furnace, it does not contain more than 80 per cent. of metallic copper.

It has also been proposed to neutralise the solution with lime, and to separate the basic iron salts by heating the same, or to reduce the ferric sulphate to ferrous sulphate by means of sulphurous acid; but these methods have only a very limited application. If the solution contains silver, this metal can be precipitated by copper, potassium iodide, or hydrogen sulphide. Milk of lime precipitates copper as a hydroxide from a cupric chloride solution, and as a cupreous oxide from a cupreous chloride solution; from sulphate solutions milk of lime precipitates also a hydroxide, which is contaminated with sulphate of lime or gypsum. The precipitates produced by milk of lime are voluminous, and can only be smelted with great difficulty, and for this reason is not employed in practice.

In solutions which contain copper chlorides, the greater the percentage of cupreous chlorides, the smaller will be the consumption of iron during precipitation.

$$CuCl_2 + Fe = Cu + FeCl_2.$$
$$Cu_2Cl_2 + Fe = 2Cu + FeCl_2.$$

If the ores submitted to a chloridising roasting contained silver, the solutions will contain the same as silver chloride. At the commencement of the precipitation the silver is thrown down with the copper, and it is advisable to collect the first precipitates by themselves and smelt them separately. In some cases the silver is precipitated in separate tanks from the first solutions by means of hydrogen sulphide, potassium iodide, or the sulphides of the alkaline metals or earth. After settling, the solution is drawn off and the copper precipitated.

The precipitation of the copper is facilitated by the heating of the solution, by agitating the same, or by exposing a large surface of iron. The heating can be done direct by means of steam, or by passing the same through pipes which are inside the precipitating vats. The agitation can be effected by means of stirrers, or by injecting compressed air, or by establishing a circulation of the solution from one vat to the other, by arranging them in terraces one above the other. The vats can be lined with sheet lead, so as to protect the timber from corrosion. The precipitation is completed when a clean piece of iron immersed in the liquor does not become coated with copper.

At Rio Tinto the sulphate solutions flow first into settling tanks, and from thence pass into the masonry precipitation vats, made of brick and covered with gypsum, coated with asphaltum or Portland cement. They are 78 feet long, 6 feet wide, and 3 feet deep, and are arranged in terraces, so that the solution can flow through a series of these vats. The waste liquors flow through a cement flume over a thousand yards in length, which has a fall for the first 2,000 feet of ¼ inch to the yard, but beyond that distance the fall is increased gradually from ½ to 1 inch per yard. The precipitation vats and flume are filled with iron ingots, and when the solution discharges from the flume, the same is perfectly freed of its copper. These waste liquors are pumped back from the collecting reservoirs and used again for leaching purposes on fresh ore charges, and the pumps which are utilised for this purpose are made of an alloy, composed of 80 parts copper, 15 parts lead, and 5 parts tin.

Owing to the presence of iron salts in the solution, the consumption of metallic iron is very high, and the cement copper is impure, owing to the presence of basic iron salts. It requires over 2 tons of iron to precipitate 1 ton of copper. After repeated cleanings, the cement copper only contains 60 to 85 per cent. copper, and is called "Cascara."

At Oker the precipitation of the copper takes place in vats, which are lead lined. The solution is heated with steam to hasten the precipitation of the copper by iron, and the heating has to be repeated according to the degree of concentration of the solution; on which also depends the time necessary for the precipitation, which may require from one to three days. One part copper requires one part iron, and the cement copper is cleaned up once a month.

At Natrona, in Pennsylvania,* all the copper solutions are run into the settling and storage tanks; the weak liquors being

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* "Mineral Industry," vol. viii., p. 197.

pumped or blown back with steam injectors to the lixiviation vats when required. Any solutions of 18° B. and upwards are left in the settling tanks until all the lead sulphate, etc., has settled out. The lead sulphate usually contains some gold, indeed an average of $100 per month is not an unusual recovery in the plant, and it is therefore essential for the recovery of this, as well as for other reasons, that everything that will settle out of the liquors be given time to settle in these tanks. After the lead sulphate, etc., has settled out of the strong liquors, they are run into other tanks, and the copper, silver, and gold contents are precipitated by means of clean, thin scrap iron from rolling mills. These tanks should have wooden slats, so placed as to form an open false bottom, about 2 feet above the real bottom, for the support of the scrap iron.

Live steam being let in the liquor during the process of precipitation, the heat therefrom serves to accelerate the process, and also serves to keep the liquor in motion, and wash off the copper from the iron as fast as precipitated. The copper then naturally finds its way between the slats to the bottom of the tank, and when it is desirable to remove it, the remaining scrap iron can readily be removed from the false bottom practically free from cement copper. The cement copper on the bottom of the tank after washing through perforated cast-iron plates set in frames over separate collecting tanks assays 90 per cent. Cu., 35 oz. Ag., and 0·15 oz. Au. per ton. The remaining chloride solutions are then run into the sewer, first through a series of tanks in the ground, which are filled with scrap iron, to recover any copper, etc., etc., that may be left in the waste chloride solutions and wash waters.

Purification of Cement Copper from Arsenical Compounds.—Mr. F. Claudet patented an invention which had for its object the removal of the arsenical compounds from the cement copper previously to smelting the same. For this purpose he either treats the precipitated copper when in the wet state or condition, as obtained from the precipitating vats, or when it exists in a partially or completely dried state or condition with a solution of caustic or carbonated alkali, or with mixtures of the same. He prefers for this purpose to employ a solution of caustic soda, or a solution of carbonate of soda, or a mixture of the same, which solutions may be employed either at an ordinary, or at an elevated temperature. By this means the arsenical compounds existing in the precipitated copper are converted into soluble arsenical salts, which are removed from the precipitated copper by the alkaline solution, and by subsequent washing, either with hot or with cold water. The precipitated copper is moistened with a strong alkaline solution, and then heated in a muffle furnace to dryness. Arsenical compounds are thus formed, which are then removed as soluble arsenical salts, by lixiviating the heated moisture with water at an elevated temperature.

At Agardo, in Italy, a large quantity of iron oxide salts, known as "brumini," precipitate with the cement copper, and Zoppi * reduces these salts by treating the solution with sulphur dioxide (sulphurous acid), whereby iron is saved in precipitating; the arsenic acid present is reduced to arsenious acid, and the arsenic is precipitated in the metallic state by iron, in which condition it can be washed away and separated from the cement copper. Zoppi erected a chimney near the precipitation vats, which is 9 metres high, and to a height of 4·5 metres has 12 horizontal partitions which only partially traverse the chimney, and by means of a pump the solution passes through this chimney in a shower and is then led into the precipitation vats; opposite the chimney are two kilns, and the sulphurous acid generated is drawn upward into the chimney and reduces the iron oxide salts. Any sulphuric acid which is formed in this operation condenses, and passes in the solution which dissolves some iron, but the quantity is very small in comparison to former losses of this metal.

The precipitation vats were constructed of timber on brick foundations, and they contained a heating apparatus made of an iron frame, but covered with sheet lead, as shown in Fig. 14 The vats are called caldaje, and the apparatus consists of a bell, *b*, fitting water tight at the bottom of the vat, *a*; through the chimney, *b'*, fuel is introduced on the grate, *f*, *b'* being closed with a cover when not in use; and the tube, *c'*, communicates the bell, *b*, with the box, *c*, where the warm air

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* *Berg und Hüttenmännische Zeitung*, 1876, p. 363; "Annales des Mines," 1876, ii. liv p. 190; Wagner's *Jahresbericht* for 1877, p. 171; *Die Metallurgie*, Balling, Berlin, 1885, p. 239.

circulates and at *d* escapes into the ventilator, *h*, which also carries off the steam from the solution; *e* is a tube for cleaning out any flue dust; *g* is the timber on which rests the iron for precipitating purposes; *l* is the ash pit, *i* is the pipe for the introduction of the solution; *k*, the pipe for the discharge of the solution after precipitation; *m*, the wooden framework on which the vats are built up; *n*, boards for covering the vats. The solution should cover the heating apparatus. Each caldaja has a length of 4 metres, is 3 metres wide, and 1·5 metres high; there is placed 7,000 lb. iron into each, and the solution is heated to 34° R., and this temperature is maintained for 3 days, on the fourth day the temperature is raised to 38°, and on the fifth day to 40° R., and 500 lb. fresh iron is introduced; the solution remains quiescent for 24 hours at a temperature of 35°, and the iron sulphate solution is with-

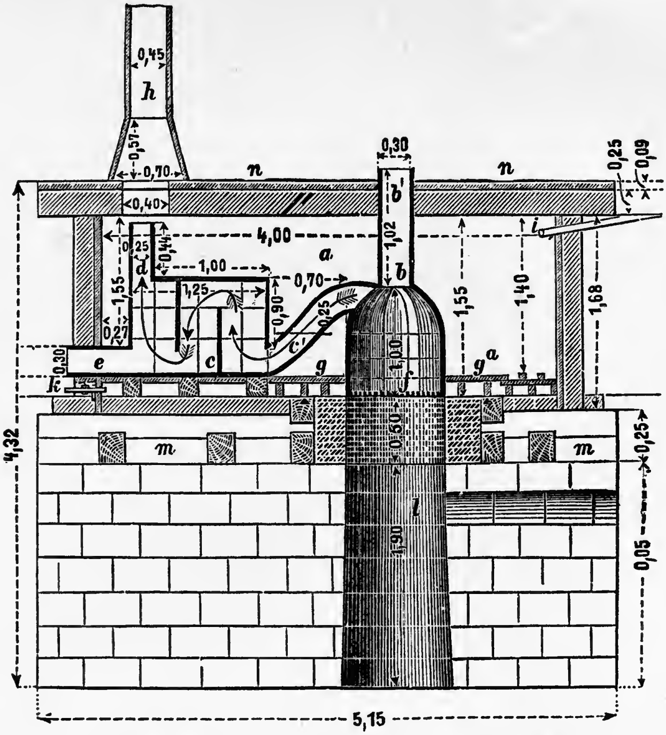

Fig. 14.—Italian Heating Apparatus for Precipitation of Copper.

drawn into crystallising kettles. The cement copper is collected in the usual manner. The caldaja is heated with peat, and 100 lb. copper require 10 to 12 cubic metres of peat; the consumption of iron, which for each part copper used to be 3·27 iron, is now reduced to 2·5 parts iron, and as no basic salts are present the production of vitriol has increased. One of Zoppi's apparatus reduces in one month as much solution as was formerly required for 40 cementations, and the loss of copper has fallen from 16 per cent. to 7·6 per cent.

Precipitation by Electrolysis.—The question naturally suggests itself, why copper should not be electrolytically precipitated, seeing it is refined so economically and successfully by means of electricity in so many establishments; but there is little analogy between the precipitation of copper from solutions and the refining of copper by means of electricity.

In refining copper the work to be done by the electric current is simply to transfer the copper from one pole of the cell to the other. This requires a current of very low voltage. In the case of decomposing a solution of copper sulphate, or other copper compound, the current must not only transfer the copper, but also break up the compound. The practice of the refining of copper on a large scale has demonstrated that 2½ pounds of copper are refined per horse power per hour. In precipitating copper, only about a quarter of a pound of copper is precipitated per horse power per hour. Thus when a comparison is made as to cost, it will readily be seen that nearly ten times more power is required for precipitation than for refining. Comparing labour in both cases, it is found that in precipitation work it is about one-and-a-half times that of refining; comparing the total cost of precipitation with that of refining, it is about six-and-a-half times greater. The cost of refining copper by electrolytic process being about £2 10*s*. per ton, the cost of precipitation would be about £16 per ton, and consequently prohibitive.

CHAPTER X.

THE REFINING OF CEMENT COPPER.

Where Refining is Necessary.—The cement copper is a mixture of metallic copper with basic iron salts, metallic iron particles, graphite, silica, antimony, arsenic; the same is washed first for the purpose of freeing it from its impurities. If the cement copper is pure, it is refined directly, otherwise it is melted first in the reverberatory furnace and then refined. If very impure, it can be mixed with raw ores and smelted for matte. In case the cement copper contains a large percentage of carbon, it has to be heated first to a red heat in a reverberatory till the carbon is burnt, by which a portion of the copper becomes oxidised. The same operation is employed with copper which contains arsenic, so as to drive the same away as arsenious acid.

The smelting of arsenical cement copper is best carried out in reverberatories, with a basic hearth lining; as not so much copper is slagged off; but in most cases it is smelted in the blister furnace. Owing to its bulk it is sometimes pressed into bricks.

The refining consists in an oxidising smelting, which is followed by the reduction of the cupreous oxide, and these operations are repeated till refined copper is obtained. The refining furnaces are very similar to the English reverberatories and two bottoms are smelted in; the upper one is thoroughly saturated with repeated small charges of metallic copper, which should be of the best quality.

Besides the working doors, special openings are made on both sides of the furnace for admitting the necessary air, and in some cases a blast of compressed air is employed, especially when dealing with impure copper.

The refined copper is ladled out of the furnaces and cast into ingots. The working door is near the flue, so that the cold air which enters by it can go up the chimney and has no cooling effect on the metal bath.

The best fuel for the purpose is wood, as the combustion gases do not contain any sulphur and do not exert a bad influence on the metal bath; bituminous coal is employed where wood is not obtainable.

The furnaces used for this purpose are strongly built, and thoroughly bound together; below the skimming door, which is at the chimney end, there is a heavy cast-iron plate; sometimes the entire bottom and sides of the furnace are incased in cast-iron plates.

The refining process takes about 24 hours, and is a very laborious operation which has to be carried out by skilled and experienced workmen.

The charge boils constantly, owing to the escape of anhydrous sulphuric acid, which is present if the copper has been precipitated from sulphate solutions, and this ebullition stirs up the molten mass even better than rabbling would, causing fresh surfaces to be presented to oxidation; suboxide of copper forms and exerts a powerful action upon the metalloids present, and which have a greater affinity for oxygen than for copper.

By continued rabbling and skimming, the injurious impurities are oxidised and removed either in the slag, or by volatilisation. When this point has been reached, the oxidation is concluded, and the molten bath of copper contains considerable suboxide, and to convert the latter into metallic copper, reduction must be resorted to. This is effected by covering the surface with charcoal and burying a long pole of green wood in the molten copper; large volumes of hydrocarbons and other reducing gases are thus evolved; which rapidly remove the excess of oxygen. This process is termed "poling."

When all the suboxide has been reduced, test samples taken from the furnace show a fibrous texture and silky lustre of a rose red colour, and the sample ingot does not contract on cooling, that is, the top remains flat. The copper has then reached its proper "pitch" and is ready for ladling.

Ladling is done as rapidly as possible, so as not to give the copper time to change its pitch; the fire should be previously attended to and everything arranged so that during ladling there will be an equally balanced oscillation between oxidising and reducing action in the furnace.

It takes very little to throw copper out of pitch, and any change is immediately shown by the appearance of the ingots. If, on cooling, the ingots contract, leaving a depression in the centre, it indicates that suboxide is forming, and ladling must be stopped and the charge poled a little; short sticks of green wood thrown on top of the copper assist in the reduction. If, on the other hand, the surface of the ingots rise and become convex, then the charcoal must be pushed back from the ladling door, and the charge rabbled. It only takes a few moments to bring the copper back to its proper pitch, and it is here that skilled labour is indispensable.

The size of the refining furnace must not exceed a certain limit, as it would be difficult to maintain during the ladling large quantities of copper at the same pitch. Large furnaces hold 8 to 10 tons and the largest 12 to 15 tons.

At Kadabek, in Russia, the refining furnaces are operated by naphtha, vaporised by compressed air. The refining is carried on in the usual way, except that air is blown on the copper bath to accelerate the oxidation. When the copper is impure the poling is discontinued, and the oxidation is carried beyond the cessation of ebullition, and then the copper is poled until it is tough. The consumption of naphtha per 100 lb. of pig is 33 lb. (330 kilograms per metric ton).

Purification of Cement Copper at Rio Tinto.*—The cement copper (or cascara) produced at these mines contains from 25 to 35 per cent. of impurities and the same is submitted to a mechanical preparation, after being first washed in tubs with very dilute sulphuric acid, to dissolve the ferrous salts. The cascara is then shovelled into inclined sluices with iron rifle bars in the bottom, so as to collect any pieces of iron which may be mixed with the cascara. These large pieces are sorted out by women and washed with acidulated water, and whatever copper is collected from them is added to the main mass of cascara. After the cascara has been sifted, the same is divided

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* "Annales des Mines," tome xvi. "Memoire sur l'Industrie du Cuivre dans la région d'H Huelva," par M. L. de Launay.

according to its density, in a sort of Long Tom by a current of water, where three grades are deposited:

a. La cascara cement (copper).

b. La grafita (scales of carbon and graphite from the pig iron).

c. La pucha (a sort of black mud).

a. La cascara is passed through a cylindrical sieve to be washed by means of a current of water which separates it into two parts; namely La Grafita, which remains in the cylinder and is added to *b*, and the pulverulent copper, which passes through the sieves.

This purified copper is then passed through a stamping battery and is carried by a current of water into troughs full of water, where a new separation, according to their density, takes place. Two products result from this operation: namely, copper, which is sent to the drying room to be dried and packed; and La Pucha.

b. La grafita is placed on jigging machines, which separate the copper in the sieves, and the grafita, which is sent to the smelting furnace to be incorporated with the rich ores which are smelted there in blast furnaces.

c. La pucha or the finest portion resulting from these operations, goes to the round buddles, which are convex and have a diameter of 3 metres 5 centimetres. A certain portion of copper separates in the centre, and the pucha, which is moulded into balls and dried, goes to the smelter.

Refining Furnaces at Mansfeld.*—These furnaces—shown in Figs. 15 and 16—are used for the refining of the residues from the Ziervogel extraction process, composed of copper oxide with some iron oxide. These are mixed with the necessary quantity of fine coal for their reduction. The charge is from 5 to 7½ tons, and in the first portion of the process the copper is reduced, and after that it is refined.

There is an opening at *c*, for the introduction of the charge; the hearth is made of quartz, which is smelted down with the admixture of some slags; *r*, is the fireplace; *d*, the stoke hole; *f*, the flue; *c*, a working door for the introduction of large pieces of copper; *b*, the working door through which the copper

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* "Handbuch der Metallhüttenkunde," von Dr. Carl Schnabel. Julius Springer, Berlin, 1894.

is ladled out; *e*, *e*, are two openings for the introduction of air, which is regulated by means of closely fitting stone dampers.

Copper Refining at Pittsburg.—The subjoined illustrations—Figs. 17, 18, 19—show a copper refining furnace in use at Pittsburg, Pennsylvania: *a* is the fireplace; *b*, the stokehole;

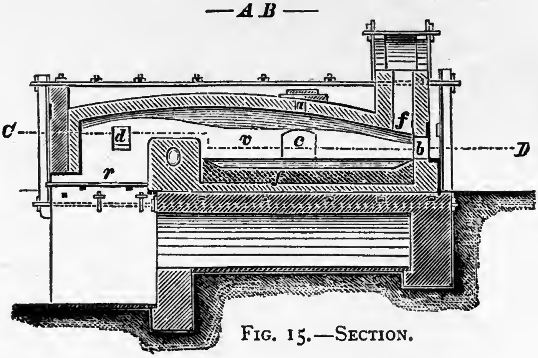


Fig. 15.—Section.

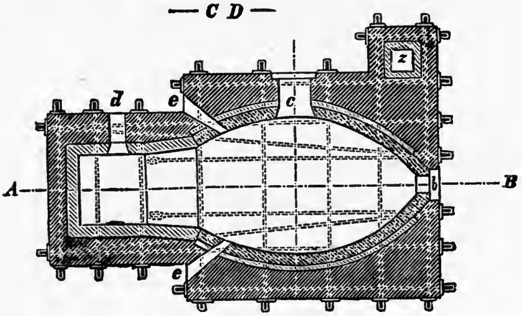


Fig. 16.—Plan.

Figs. 15 and 16.—Mansfield Refining Furnace.

m, the fire bridge; *c*, the hearth; *d*, the charging door; *e*, the working and ladling door; and *f*, the flue.

Boston and Colorado Refining Furnace.—In Figs. 20 to 24 is shown a refining furnace employed for cement copper at the Boston and Colorado Smelting Works.* The fireplace

* Eggleton, "Metallurgy of Gold, Silver, Mercury," page 143.

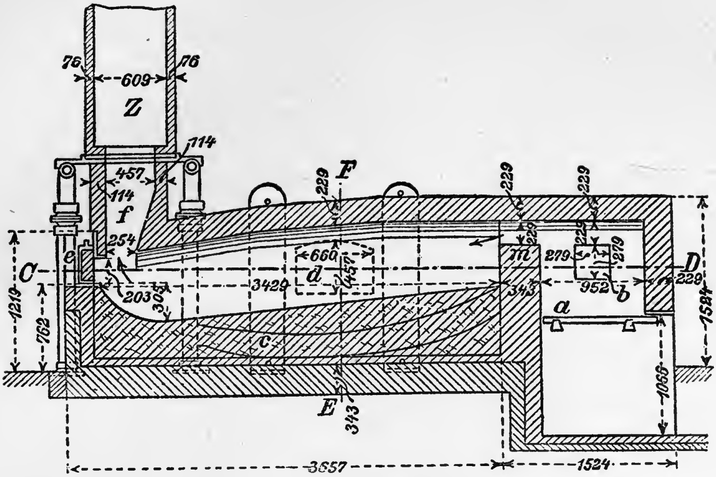


Fig. 17.—Longitudinal Section.

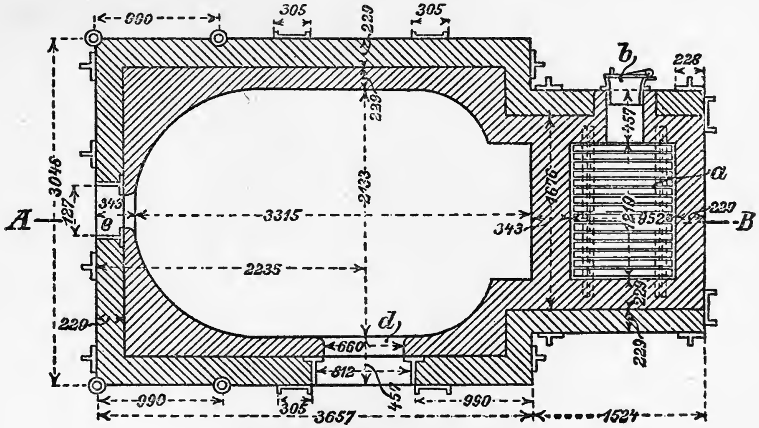
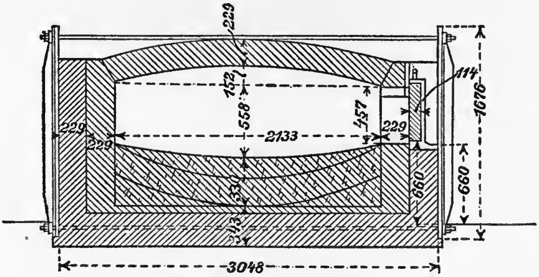


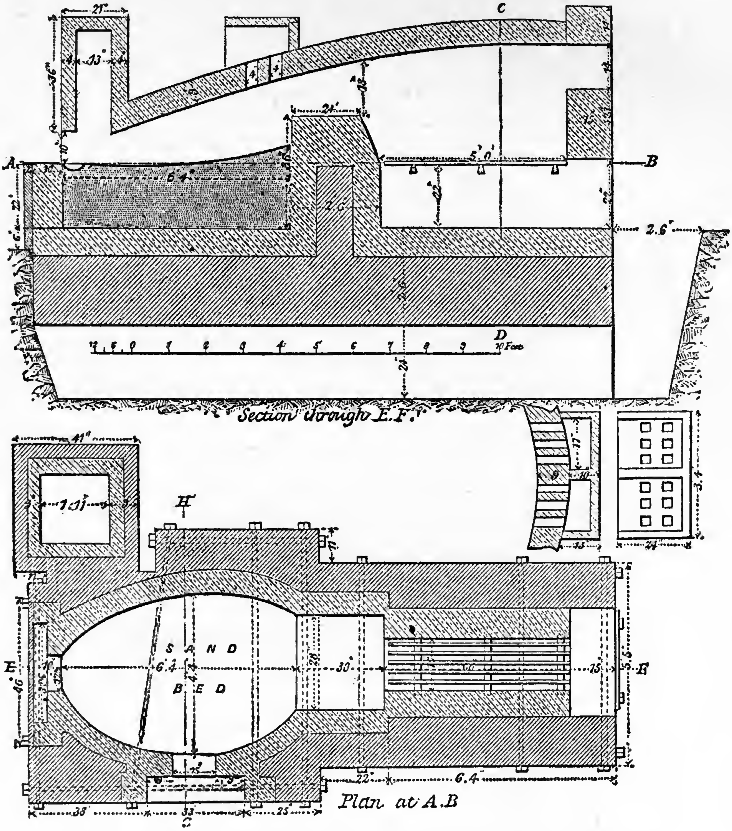
Fig. 18.—Horizontal Section.



Transverse Section.

Fig. 19.—Pittsburg Refining Furnace.

is 5 feet long, and 28 inches wide at the top of grate. The grate has the same length, but is only 17 inches wide. The bridge is 2 feet wide. The laboratory is 6 feet 4 inches long, and 4 feet 4 inches wide, and has two doors, one at the end, which is the charging door, and one on the side, which is the working door. Just over the bridge, Fig. 20, there are two rows of openings, *i*, for the introduction of air, these are covered with a hood to prevent the introduction of foreign substances. The furnace connects with the chimney by a flue, which is 2 feet square. The fireplace has 11·65 square feet, and the laboratory 21·79 square feet, so that the relation



Figs. 20 and 21.—Boston and Colorado Refining Furnace.

between them is nearly 1 : 2. This furnace runs once a month for eighteen or nineteen hours. A charge of 2500 lb. of copper

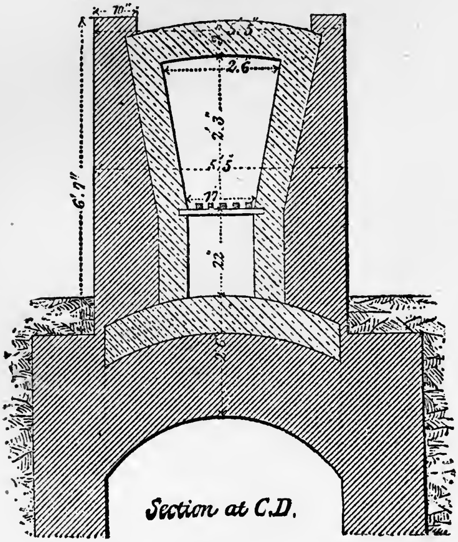


Fig. 22.

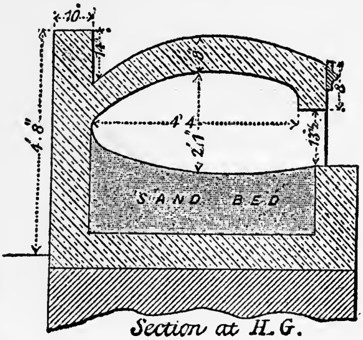
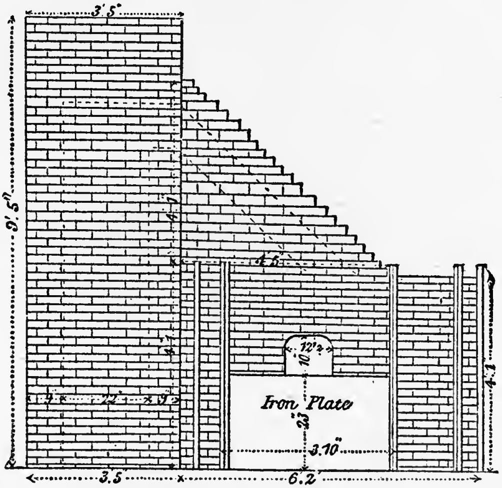


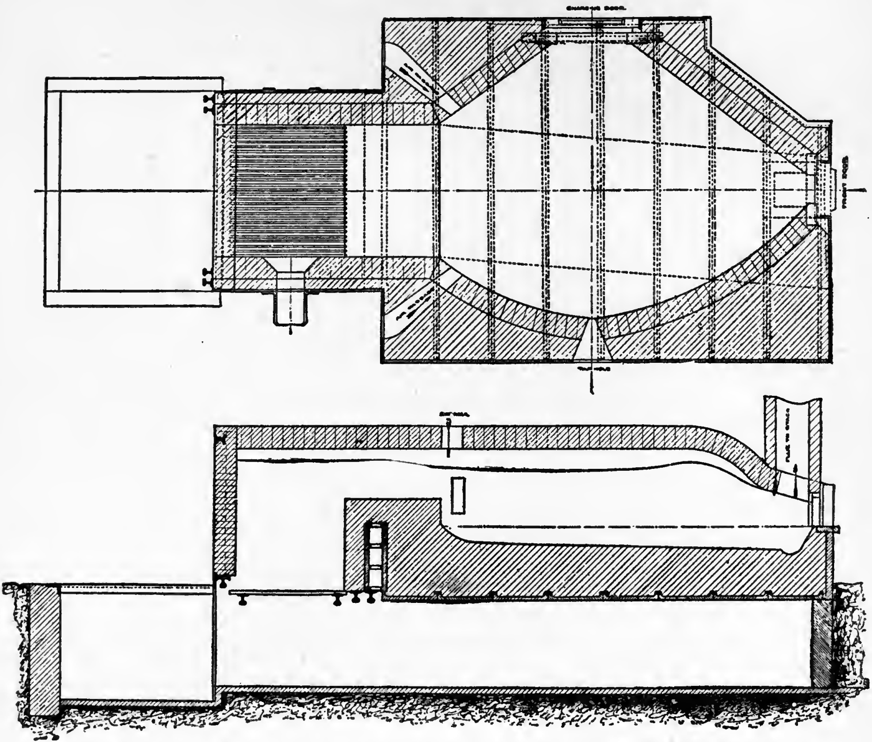
Fig. 23.

Fig. 24.



Sectional Views of the Boston and Colorado Refining Furnace.

mixed with 50 lb. of refuse charcoal is put in at 6 p.m. The fireman keeps up the fire during the night, and the refiner takes it at 7 a.m., and then skims off the slag and exposes the surface of the bath. Considerable sulphurous acid is given off, probably from the reduction of the sulphate of iron in the cement copper. The charge is worked for a "set" which takes three to four hours. This is done by striking the surface with the rabble and making waves. This is called beating the copper. The copper produced contains from two to three per cent. oxide of copper dissolved in it, but is not refined any further.



Figs. 25 and 26.—Copper Refining Furnace, H. L. Bridgman's Design.

Bridgman's Copper Refining Furnace.—Messrs. Fraser & Chalmers show in their catalogue a well designed refining furnace, designed by Mr. H. L. Bridgman. It is illustrated here in plan and section in Figs. 25, 26.

CHAPTER XI.

THE ELECTROLYTICAL TREATMENT OF COPPER ORES.

IN the practical application of electro-metallurgy it has not hitherto been found profitable to treat copper ores direct by electrolysis, or even coarse metal or ordinary matte; but as Messrs. Siemens and Halske and C. Hoepener claim that they can accomplish this with substantial financial success, the specifications of their methods will be given in the present chapter.

Siemens and Halske's Electrolytical Process.*—Copper has been produced electrolytically up to the present, by employing as anodes plates of impure copper or matte. On the anode, copper and iron are dissolved, and copper is precipitated on the cathode. The solution becomes impoverished, and has to be replaced by fresh solutions, which are prepared from ores with difficulty and with great expense. The preparation of the anodes from matte requires a previous smelting operation of the roasted sulphide copper ores; the casting of the anode plates is difficult and uncertain, and the electrolytic process is interrupted through the breaking to pieces of the anode plates.

The process now to be described consists in employing a solution in connection with insoluble anodes, and to separate by means of a non-metallic diaphragm the anodes from the cathodes. The solution to be electrolysed consists of iron vitriol and copper vitriol, to which some sulphuric acid is added, which assists the conductivity of the solution.

The solution is introduced in the bottom of the cells, and rises gradually, whereby a portion of the copper is deposited on

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* German Patent issued September 14th, 1886. No. 42,243.

Fig. 27.

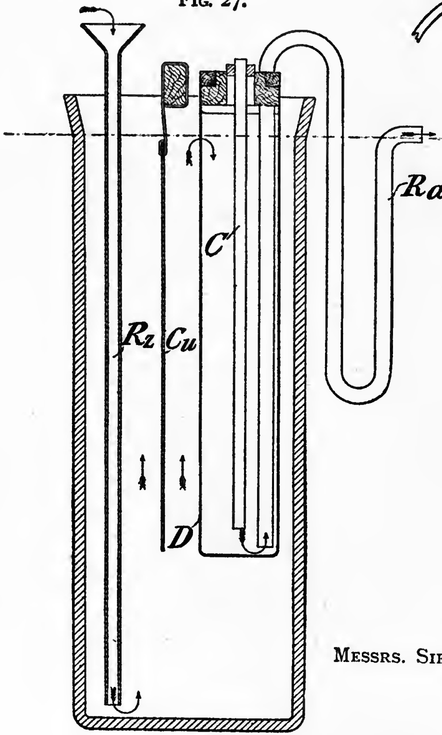
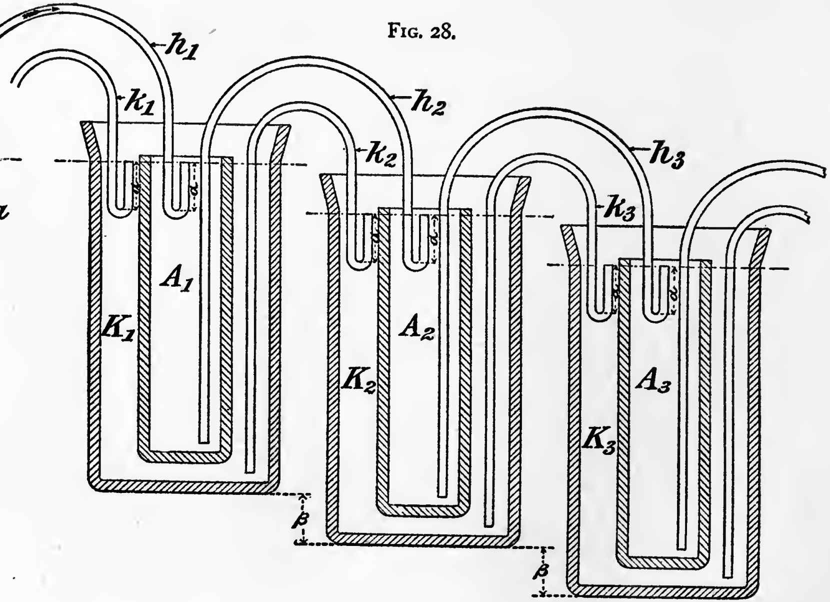


Fig. 28.



Messrs. Siemens and Halske's Apparatus for Electrolytical Treatment of Copper Ores.

the cathode by means of the electric current, and then flows over the edge into the anode cells, and runs out at the bottom. See Figs. 27 and 28.

During this operation the ferrous sulphate is first converted into basic ferric sulphate, and as the same takes up sulphuric acid from the decomposed copper vitriol, it changes into neutral ferric sulphate, which, owing to its higher specific gravity sinks to the bottom. The solution which flows off is poorer in copper, and consists of a solution of neutral ferric sulphate. This solution has the property to convert subsulphide of copper, sulphide of copper, copper oxide into copper vitriol; and, during this reaction, the ferric sulphate is reduced to ferrous sulphate, and the liberated oxygen oxidises the copper sulphides. During the preliminary roasting of the copper sulphides at a low temperature a product has been obtained, in which the copper is present as a subsulphide, the iron as an oxide, the last is a form, in which it is not attacked by ferric sulphate, and only very slightly by sulphuric acid, whereas the subsulphide of copper is easily dissolved by means of ferric sulphate solutions.

The process consists of the following operations:—The pulverised ores are roasted at a moderate temperature, preferably in the Gerstenhöfer furnace, till the iron is completely oxidised whereas the copper is present, partly as cupric sulphate, partly as cupric oxide, but mostly as subsulphide of copper. The roast product is first leached with the solutions which run off from the electrolytic vats.

The lixiviation is best carried out by passing the solution from one vessel to another, and in this manner the same becomes charged with copper vitriol, and does not contain any ferric oxide, and is pumped up into the electrolytic vats, where the copper is precipitated and the solution oxidised, and is then ready to be passed again through the filtering vessels, which contain the roasted ore. This is a continuous process, in which the solution can be employed till the same becomes impure through the foreign metals contained in the ore, which then renders the solution unfit for galvanic precipitation.

The chemical reactions which take place during the electrolysis and the lixiviation are shown in the following equations:—

1. Formula of the electrolysis—

$$x\,H_2SO_4 + 2CuSO_4 + 4FeSO_4 = 2Cu + 2Fe_2(SO_4)_3\,x\,H_2SO_4.$$

2. Formula of the lixiviation—

α. $x\,H_2SO_4 + Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S + x\,H_2SO_4$
β. $CuO + H_2SO_4 = CuSO_4 + H_2O$.
γ. $3Cu + Fe_2(SO_4)_3 = 3CuSO_4 + Fe_2O_3$.
δ. $CuO + 2FeSO_4 + H_2O = CuSO_4 + (Fe_2O_3 + SO_3) + H_2$.

In comparing the formulæ 1 and 2*a*, it will be seen that when the ore contains the copper as a subsulphide, the solution after passing the filtering vessels will contain the same quantity of copper vitriol, iron vitriol, and free sulphuric acid as before the electrolysis, and is therefore completely regenerated, and can be employed for the electrolysis. If the copper is partially present as an oxide, it will be seen from the equations 2 β, γ, δ, that in this case after the lixiviation the electrolytic solution is richer in copper, but poorer in iron and free sulphuric acid, as the same has been before the electrolysis.

Instead of roasted ore, unroasted matte can be employed, in which the copper is present as a subsulphide. In this case not only copper but also iron is dissolved, so that a constant solution of iron and copper could not be maintained.

It has to be mentioned that in this process no polarisation takes place, and whereas, when matte anodes are employed, there is a potential difference of 1·5 volts consumed, only a tension of about 0·7 volts is required with the same current density; and it is also noticed that no loss of current takes place in this process, whereas one-third of the current is lost in the other process.

The same system can be utilised for the extraction of zinc from zinc sulphide ores, by employing a solution of zinc vitriol and iron vitriol. There is formed in the electrolytic decomposition cells, zinc and iron sulphate, according to the following equations:—

$$ZnSO_4 + 2\,FeSO_4 = Zn + Fe_2(SO_4)_3.$$

The solution of iron sulphate has the property to dissolve zinc from ores which are slightly roasted, forming zinc vitriol and iron sulphate according to the following equation:—

$$ZnS + Fe_2(SO_4)_3 = ZnSO_4 + 2\,FeSO_4 + S.$$

A comparison of this with the previous equation demonstrates that, after the lixiviation of the slightly roasted zinc ores by means of the electrolytically oxidised solution, zinc and iron are present in the same proportion, as they were prior to the electrolysis. The potential difference between the anode and cathode in the electrolytic bath is about twice as much as in the copper process, owing to the tension difference between the zinc and carbon.

To insure a rapid circulation through the cells, which is essential for the success of the operation, the cells are placed in terraces (see Fig. 28), and the cathode divisions K_1 K_2 K_3 are put into communication with one another by the syphons k_1 k_2 k_3 as well as the anode divisions A_1 A_2 A_3 by means of the syphons h_1 h_2 h_3, and to maintain a uniform level in all the vessels independent of the flow, the ends of the syphons at *a* are turned up for a length which is equal to the difference in height and of each of the succeeding vessels.

The claim made in the patent is: For the electrolytic separation of copper and zinc, the lixiviation of the pulverised, roasted, or fused sulphide ore by means of ferric sulphate, which is produced in the solution itself, as the flow of the electrolyte, which is composed of copper or zinc sulphate and ferrous sulphate, is conducted in such a manner, as to pass first through the cathode cells, where the copper and zinc is precipitated, and then through the anode cells, which are separated by non-metallic diaphragms, and by means of electrolytic insoluble anodes the ferrous sulphate is converted into ferric sulphate and is now ready to be passed through the vats containing the ore, whereby the regenerated solution is prepared to go through the cathodes again.

Siemens and Halske's Modified Process.*—For dissolving the copper out of the pulverised ore, small and shallow troughs, *T*, are employed, made of wood or other suitable material lined with lead, which are provided with two wooden cylinders, *A*, arranged along the longitudinal axis of the troughs, and revolving in opposite directions, which act as stirrers and agitators, see Fig. 29.

As these cylinders run in opposite directions, they cause the solution to assume a rotating motion, which keeps the ore particles suspended. To assist the solution of the metals the

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* German patent No. 48,949, issued on January 3rd, 1889.

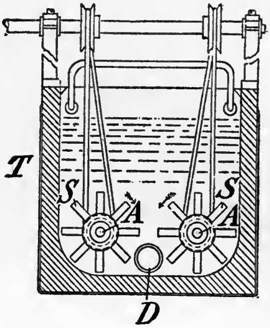

FIG. 29.—TRANSVERSE SECTION OF TROUGH.

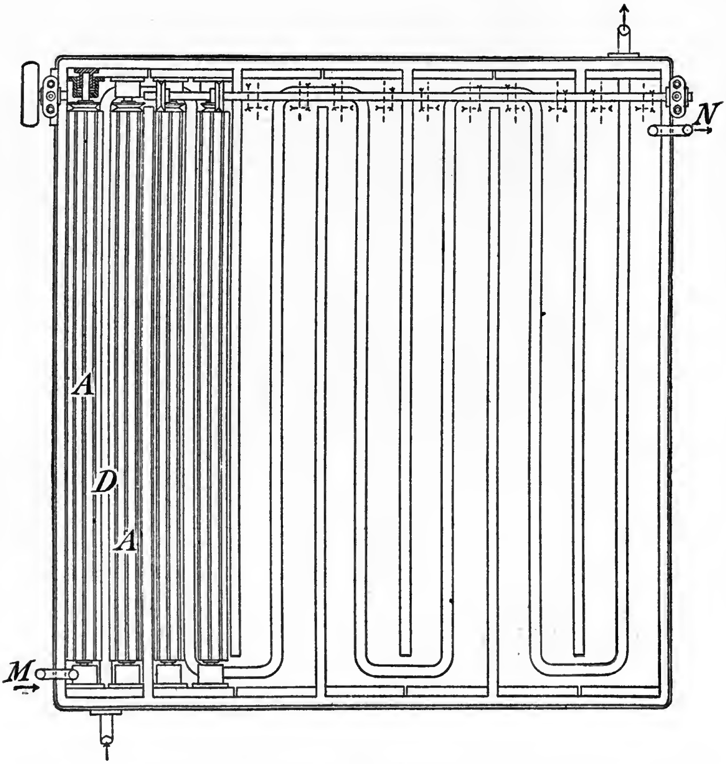

FIG. 30.—TROUGHS ARRANGED IN SERIES.

temperature of the bath is regulated by injecting steam through lead or copper pipes placed along the troughs.

To save space these troughs are arranged in series, as shown in Fig. 30, which represents a plan of a whole series arranged in a zigzag form. The cylinders are provided with stirrers, *S*, and motion is imparted by means of waterproof belts. The copper tube, *D*, passes through all the troughs for maintaining the temperature in the bath.

In the preceding patent, the electrolytic cells had been divided into two (positive and negative) compartments by a membrane; but these membranes are liable to become torn during electrolysis. The membranes have either too high an electrical resistance, or else they are not sufficiently durable, for they stretch and allow the solutions to escape either by diffusion or permeability. The following sketches (Figs. 31 and 32) show an electrolyte cell in which these evils are remedied.

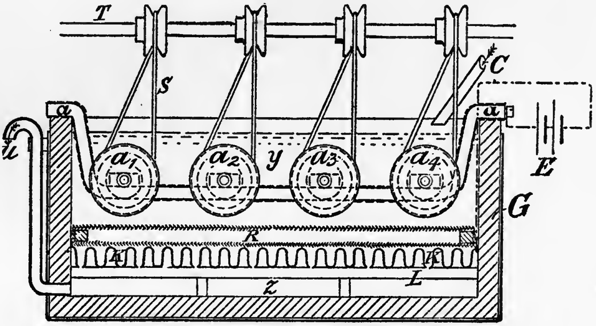

Fig. 31.—Section of Trough.

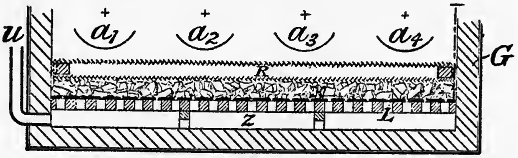

Fig. 32.—Bottom of Trough, Showing Anode.

A flat vessel, *G*, made of wood or other suitable material, and coated with lead, is provided with a perforated false bottom, *L*, on which the anode, *K*, is extended. The anode may consist, either of perforated lead plates covered with small fragments of retort carbon, or finally, of deeply corrugated lead plates containing perforations to allow of the passage of the electrolyte.

The horizontal anode is provided with the necessary electrical connections and is covered with a layer of some filtering material, *R*, that may serve to prevent the escape of the solution surrounding the anodes. The filter may be of felt or any other suitable organic or inorganic material.

The cathodes consist of the surfaces of the cylinders a_1, a_2, a_3, which are quite covered by the electrolyte, and are constantly maintained in slow revolution by the waterproof belts, *S*. These cylinders may be made of a wooden case coated with cement, or other material, and surrounded with a conducting material, which is electrically connected in any suitable way with the journals of the cylinders and the conductors, *a*.

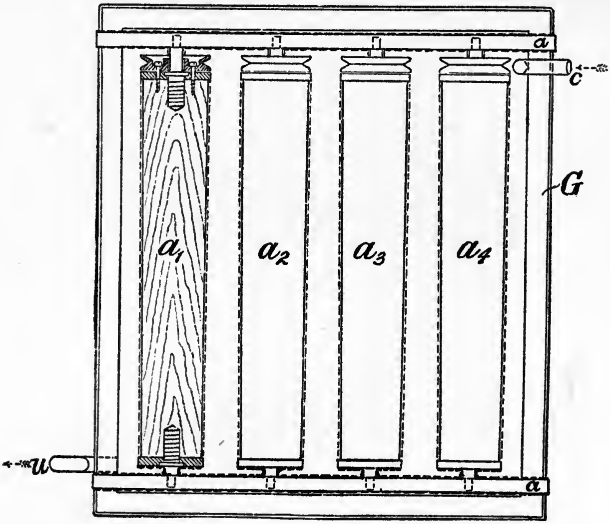

Fig. 33.—Plan, Showing Cathodes.

The regenerated solution, consisting of copper and ferrous sulphate solutions, is conveyed in a continuous stream into the liquid, which is already covering the cylinders. The rotation of the latter effects the continual mixture of the solution down to the partition separating it from the anode department. The tube, *u*, conveys the solution from the space beneath the filter at the same rate as the regenerated liquor is run into the upper compartment through *C*; and there is, in consequence of this, a constant but slow transference of the electrolyte through the filter from the cathode to the anode compartment. On the anode, the ferrous salt is reconverted into ferric sulphate by the liberated oxygen, and the ferric salt, having a higher specific gravity, sinks to the bottom, and is at once carried away through *u*, so that by properly regulating the inflow of liquid, the strength of the current, and the quantity of copper and iron in the solution, the result of the process should be, that the electrolyte in the upper compartment loses some two-thirds of the copper contained in it, while in the anode portion the whole of the ferrous salt is peroxidised to the ferric state. The solution is uninterruptedly conveyed from the anode cell to the extraction tank, and after acting upon the pulverised ore, it circulates through the whole system again.

C. Hoepener's Cuprous Chloride Process.—This method of using a chloride solution is based on the following well-known facts:—

Copper, silver, lead, and other metals are much more readily dissolved by a chloride than by a sulphate solution.

Chloride solutions are better conductors of the electric current.

They are also commercially cheaper.

A definite quantity of water will dissolve a much greater weight of any metal in a chloride state than this metal in any other combination.

Chloride solutions are also applicable to the extraction of gold.

They entirely prevent copper from becoming contaminated with sulphur or sulphates.

They allow the purification of the solution and the keeping of it perfectly free from iron, arsenic, antimony, bismuth, etc.

They will extract and allow an economic production of lead, zinc, silver, etc., and also of other valuable by-products.

The process is as follows:—

The ore, ground to a fineness of about 90 meshes, is automatically conveyed to the leaching drums, which have a capacity of 10,000 to 30,000 litres. Here it is mixed with a heated solution of cupric chloride, which contains before entering the drums 60 grams of copper to the litre, is saturated with common salt or chloride of sodium, and is left in contact with the ore from two to six hours, according to the nature of the treated mineral. Above the leaching drums is a tank filled with the necessary quantity of hot liquor to allow of continuous work.

The lixiviation takes place in two consecutive steps. At first, in one of the drums fresh cupric chloride solution is added to the ore that has been previously treated with the cupric chloride solution, to extract any remaining copper or other metals; then it is drawn off to another drum containing fresh ore. Here the cupric chloride solution is entirely reduced to cupreous chloride. After all the economic metals have been extracted from the ore the residue is taken out of the drums by means of a sand pump, transferred to filter presses, washed, and then dropped into cars and carried away. These tailings in careful work do not contain more than 0·2 per cent. of copper, and in many instances the percentage of copper remaining is even less than this.

The solution, after having been completely changed to the cupreous state in the drums, is drawn off into vats, allowed to clear, and then purified. Silver is precipitated by finely divided copper; lead, by the solution becoming cold; arsenic, antimony, bismuth, iron, etc., are precipitated either by oxide of copper or by lime.

The solution is now quite pure and contains 120 grams copper (as cupreous chloride) per litre, which is twice as much as its contents before extracting the copper from the ore.

The liquor now flows in two separate streams to the anodes and cathodes of the electrolytic baths. The one which passes along the cathodes deposits its copper on them in rose-coloured crystals and flows at last from the baths wholly or partly freed from the copper. The other stream which passes the anodes retains its copper, but chlorine in the nascent state converts its cupreous chloride into cupric chloride. After it leaves the baths this stream is usually mixed in a suitable tank with the stream coming from the cathodes. Since the latter solution has lost its copper, while the former has kept its 120 grams per litre, the mixed solution therefore now contains again 60 grams per litre in a state of cupric chloride. The original state of things has been re-established, that is, the solution is pumped back to the tanks above the leaching drums, heated, and returned to the latter to perform its work anew. The transferring of the solution from tank to tank is conveniently accomplished, either by means of a vacuum or compressed air machine. When the pure copper or cathode deposit is thick enough for removal the cathodes are taken out and replaced by new ones.

The electro-motive force required for the deposition of copper from a cupreous chloride (as a ferrous sulphate) solution by electrolysis is theoretically 0·5 volts, and practically 0·6 to 0·8 volt. From a copper sulphate solution one ampère precipitates per hour not more than 1·18 gram of copper, while from a cupreous chloride solution one ampère per hour precipitates twice the quantity, because one molecule of cupreous chloride contains double as much copper as one molecule of sulphate of copper. With 0·6 volt 1 horse-power produces per twenty-four hours as much as 60 kilograms, or 133 pounds of copper. This is, of course, the case only when comparatively large cathode surfaces are used. These in European practice are generally about one square metre per 25 ampères, or about one square foot per 3 ampères.

If steam power should be very expensive, as it is in some parts of the United States, it is advisable to use large surfaces of cathodes, and to electrolyse with low voltage. On the other hand, where power and fuel are cheap, it will be better to run with higher voltage and greater density of current, and thereby save considerably in cost of plant. This process allows a tenfold density of the current which is generally used in Europe and this not considering that, with the cupric sulphate electrolyte, only 1·18 gram of copper is precipitated per ampère, while with the cupreous chloride 2·36 grams per ampère are deposited. American refiners frequently run 10 ampères per square foot, instead of 2 or 3, as in Europe; but even compared with American practice, this chloride process can precipitate five or six times the quantity per square foot. Another advantage is that it extracts the copper directly from the ores, or low grade of mattes.

For lixiviation revolving drums are used made of wood, which do not require much motive power. The electrolytic baths consist of wood, and their partition construction permits a perfect and independent circulation of the solution essential to this process. The anodes are insoluble, and of such composition and quality that they will last for many years. Siemens and Halske, in their analogous sulphate process, claim that the depreciation of the carbon anodes does not amount to more than 10 per cent. a year. In a chloride of copper solution these anodes are even less liable to such a depreciation, owing to the fact that chlorine does not combine with carbon.

The residue is sometimes valuable on account of its gold contents or its free sulphur. In the former case the residue should be roasted alone, or with the addition of salt, and then lixiviated with a chloride solution containing free chlorine. Large quantities of limestone or iron carbonate in the ore interfere with the leaching process.

It is claimed that this is a better and cheaper electrolytic process, and especially adapted to localities where fuel and labour are expensive, and where it is desirable to produce pure copper from the ores or mattes. The following calculations show this:—

One horse-power in low voltage baths can produce up to 60 kilos of pure copper per day. Assume an ore containing 5 per cent. copper, and a steam engine of 100 horse-power, consuming 125 kilos of coal, and evaporating 1,000 kilos of water per hour. This is equivalent to 3 tons coal per 24 hours and 800 × 24 = 19,200 kilos of waste steam, which is certainly sufficient to heat the leaching solution. Assuming a daily production of 4,000 kilos copper, the 70 tons of cupric chloride solution would be required for its extraction.

For pumping and raising the solution, residue, mud, etc. not more than 6 horse-power per 24 hours will be required; the power necessary for driving the revolving drums for agitating the solution will be about 8 horse-power per 24 hours, or a total of 14 horse-power will be required for continuous lixiviation during 24 hours. As there are 100 horse-power to dispose of, this leaves 86 horse-power for the electrolytic production of 4,000 kilos or 4 metric tons of copper. As 1 horse-power can produce 60 kilos copper per day, therefore, with 86 horse-power, 86 × 60 = 5,160 kilos, or certainly 4,000 kilos can be deposited. These figures show that 4 tons of copper can be produced with 3 tons of coal, or, with a fair allowance, 1 ton of copper from 1 ton of coal.

CHAPTER XII.

THE MANUFACTURE OF COPPER VITRIOL.

AT most establishments copper vitriol forms a by-product, and is generally obtained as the result of the separation of the precious metals from copper. Cement copper is not largely employed in the production of copper vitriol. Dilute sulphuric acid is employed as a solvent; it does not dissolve silver, gold, or lead. When matte is to be converted into copper vitriol it is either treated direct, or by repeated smeltings is converted into metallic copper, which is granulated, and the granules are subjected to the action of air, and warm dilute sulphuric acid. The copper is oxidised by the air and dissolved by the acid, and yields a copper sulphate solution which is crystallised into a reasonably pure product, and mud residues which contain silver, gold, and impurities. A description of the process as carried out at various establishments may be given here.

Copper Vitriol Manufacture at Freiberg, Saxony.*— Copper sulphate is produced at the Muldenhütten and Halsbrücke from two sources—

1. Copper matte.
2. The cupriferous solution resulting from the precipitation of silver obtained in the parting process.

The concentrated matte, carrying from 70 to 75 per cent. of copper, and never more than 0·20 per cent. Fe, is dead roasted in reverberatory calciners and shelf burners; a charge of from

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* From "Mineral Industry," vol. v.: "Copper Sulphate Manufacture at Freiberg, Saxony," by Albert Doerr, p. 225.

1,100 to 1,600 lb. being thoroughly roasted in sixteen to twenty hours. Towards the close of the roasting, tests are made to ascertain if all the Cu_2S has been oxidised to Cu_2O. For this purpose a small portion of the matte is treated in a beaker with HNO_3; so long as brown fumes are given off, the matte is not thoroughly roasted. After the roasting is finished, the matte is ground in a ball mill and passed through sieves, the fines going he leaching vats and the coarse back to the roasting furnace.

The leaching vats, which are lined with hard (antimonial) ad, are 1·5 metre high and 1·2 metre wide. They are first charged with 440 lb. chamber acid (about 50° B.), water, and about 880 lb. of solution from previous lixiviations. The liquor is heated by steam, after which 220 lb. of the dead roasted matte are gradually added, the liquid being meanwhile constantly stirred. In from forty-five minutes to an hour, the Cu_2O is completely dissolved. After being allowed to settle, the solution is drawn off into filtering vats and thence to the crystallisation vats. The latter are made of wood lined with hard lead, and will hold about 2½ cubic metres of solution. Strips of hard lead are suspended in the solution from cross-pieces on top of the vats, to give more surface for the crystals of $CuSO_4 + 5H_2O$ to deposit on. After 8 to 10 days the crystallisation is considered finished, and the strips of lead, now quite covered with copper sulphate, are lifted out, the crystals are removed, and after being washed and dried are ready for the market.

The crystals from the bottoms and sides of the vats are impure, and are consequently dissolved in water heated by steam, and allowed to recrystallise. The solution for the second crystallisation must possess a strength of 32° to 34° B. Old solutions which have become too poor in copper are treated with scraps of metallic iron to precipitate cement copper, the iron going into solution as $FeSO_4$, which is crystallised out and sold. The cement copper is added to the charge of matte in the reverberatory.

In the dissolving vats there remains a slime which contains lead, copper, and antimony, and is rich in silver. This slime is collected, washed, and added to the charges of the blast furnaces which are running on rich ore.

A small amount of copper sulphate is also produced from the parting of silver and gold. The granulated silver from the cupellation furnace is dissolved in H_2SO_4, of 66°, from 900 to 1,100 lb. being dissolved at a charge, the time required being eight to ten hours. After being allowed to settle for ten to twelve hours the $AgSO_4$ solution is drawn off into filtering vats, and from thence to precipitation tanks, where it is diluted to about 20° B., and the silver precipitated with metallic copper, the solution being meanwhile heated with steam to about 70° C. The resulting $CuSO_4$ solution and the wash waters are then treated in the same manner as the matte solutions.

Manufacture of Copper Vitriol at Oker.*—A method is employed in the Harz for treating copper granules and solutions resulting from the desilverising of the copper by sulphuric acid. By wetting the granules of copper with warm diluted sulphuric acid, the surface becomes oxidised and the oxides dissolve in the acid, forming sulphate of copper in solution. The silver remains, being insoluble, forming a deposit in the solution. The other metals which are present, such as gold, will separate in the metallic condition; lead will become oxidised and give an insoluble sulphate; iron and nickel will also dissolve; arsenic and antimony dissolve slightly.

The sulphuric acid is stored in a lead-lined vat, *a* (Fig. 34), placed in the upper storey of the building, which acid is diluted with water or liquors from the crystallisation vats, and the same has a density of 25° to 30° Beaumé. The acid is heated by means of steam, which circulates in a lead coil, *b*, *b*, placed in the bottom of the vat, and is drawn off by means of the syphon, *c*, into the vats, *d*, where the solution of the copper granules takes place.

The solution vats, *d*, are round and lined with sheet lead, and have a false bottom, on which are placed first large pieces of copper, and these are covered with about a ton of copper granulations. At the lower end of the syphon, *c*, is a wide funnel-like opening, *g*, and when the faucet, *f*, is opened the acid comes out like a spray, and by swinging around the syphon with the handle, *h*, the granules are wetted down over their whole surface. These wettings are repeated at frequent intervals, so as to give the metal a chance to become oxidised. The air

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* "Le Harz Supérieur," Capacci, 1881.

necessary for the oxidation penetrates through the false bottom and the opening, *i*.

The copper solution, which is gradually formed, runs out by the spout, *i*, into the trough, *k*, which is also lined with sheet lead, and when six solution vats are used, this trough has a length of 110 metres. In this trough the blue vitriol crystallises and the insoluble residues deposit here.

The waters of crystallisation are collected in large vats and are utilised for the dilution of the acid, and are constantly regenerated, and in this way any copper which they may hold in solution is not lost.

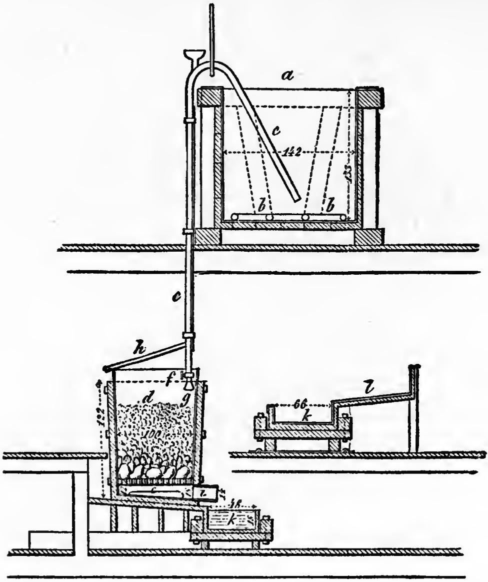

Fig. 34.—Arrangement of Vat used in Manufacture of Copper Vitriol.

The blue vitriol collected in the troughs has to be refined before the same is fit to be packed for shipment, and for this reason is submitted to a second crystallisation; and for this purpose the crystals are taken out from the trough, *k*, and placed on an inclined table, *l*, so that the water which is absorbed by them can drain away. They are then thrown into another solution vat which is 3·12 m. wide by 3·51 m. long and 0·61 m.

high; and they are dissolved in water mixed with the mother liquors, and these are heated by passing steam through lead coils placed around the sides of the vat. Sufficient crude blue vitriol is added till the solution marks 28° Beaumé. The liquor is now allowed to remain quiescent till all the solid material has settled and is then drawn off and passed through a vat filled with copper granules and collected in a crystallisation vat.

These vats are 3 m. long by 1·37 m. wide and 1·10 m. high, and contain each 4 cubic metres of solution. Strips of sheet lead are suspended in these vats which serve to facilitate and enlarge the surface of crystallisation for the sulphate crystals to adhere.

When the crystallisation is completed, the liquor is drawn off and used over again for dissolving the crude crystals. The refined crystals are collected in sieves where they are washed with the clear water and allowed to drain. After sifting out the fines the crystals are placed into drying rooms and then packed in barrels.

The nickel, which remains in solution in the waste liquors, becomes gradually concentrated, and at the end of a couple of years the nickel sulphate begins to crystallise out with the copper sulphate, and when this stage is reached, the waste liquors are drawn off into a special vat, where the copper sulphate is allowed to crystallise out first, and when it is noticed that the nickel sulphate begins to crystallise, the blue vitriol crystals are collected and the waste liquors remain quiescent till all the nickel sulphate has crystallised out of them. The crude crystals are collected and redissolved in clean water and re-crystallised.

The operations in 1876 gave the following results:—

The charge of copper granules amounted to	199·60 tons.
Which consumed in sulphuric acid	528·12 „
Coal for heating the boilers	370·20 „
„ „ „ „ sulphuric acid	177·55 „
„ „ „ „ drying room	24·90 „
Total coal consumption	572·65 „

The resulting products were :—

Copper sulphate (blue vitriol)	526·79 tons.
Nickel sulphate	11·60 „
Argentiferous residue	21·50 „

Production of Copper Vitriol from Granulated Matte.—It may be mentioned here, that when low-grade matte containing 10 to 15 per cent. of copper is granulated, by being tapped into water, hard polished granules are obtained, which, even by long exposure to a high temperature in the roasting furnace, are not altered. Quite satisfactory results are obtained in the case of richer matte, say from 30 to 50 per cent. copper, which is granulated in water ; and in many foreign works this is the only means provided for the preparation of the matte for the process of roasting.

At a certain plant in the United States the matte produced in cupolas was concentrated in a reverberatory, which was fired by crude petroleum, and the matte then granulated. The granules were roasted in an automatic reverberatory furnace for copper sulphates, which were then extracted by the usual leaching process, and the blue vitriol is crystallised out of the resulting brine.

In applying crude petroleum as a metallurgical fuel, the simplest and best way is to inject it in the form of spray by a jet of steam into the furnace, allowing the right amount of air to mix with it. Numerous injectors, or burners, have been devised for this purpose. If the steam jet has a fan-shaped opening, the greater part of the oil will be delivered at the sides, and a wide and short flame will result.

If a long, narrow flame is desired, the steam jet is given a concave opening, and most of the oil is then delivered on the centre of the steam jet and is propelled forward to a considerable distance.

Recovery of Bluestone.—In works for the electrolytic refining of copper, bluestone is recovered from the discarded electrolyte as follows :—

The solution is first boiled in lead-lined tanks with scrap copper, in the presence of steam and air, so as to neutralise the free acid and to increase the copper contents of the solution to the degree desired. It is then pumped to the crystallising tanks, in which bluestone is secured by allowing the copper sulphate to crystallise out on bands of lead suspended in the saturated solution. The mother liquor syphoned off contains most of the arsenic, and antimony originally present in the electrolyte, together with some remaining copper. To recover the latter, the mother liquor is treated in special tanks with sheets of scrap iron. This metal first precipitates out the copper, and then the arsenic, so that a black precipitate is finally secured, containing as much as 6 per cent. of metallic arsenic. The dirty precipitate may either be added to a furnace charge, to be worked up into base copper, or utilised in the manufacture of compounds of arsenic, such as Scheele's or Paris green, and crystallised arsenious acids.

At the Chicago Copper Refinery * the final impure solution remaining after the recovery of the bulk of the blue vitriol was concentrated by evaporation, so as to crystallise out the remainder of the blue vitriol and the arsenious acid. The bluestone was then leached out of the mixture by just sufficient water to effect its solution, without attacking the arsenious acid, which was subsequently collected and sold. Sulphuric acid, or iron vitriol, was finally recovered from the residual mother liquor.

Improvements in Treating Cupric Sulphate Solutions.—Ottokar Hofmann has patented a method for treating cupric sulphate solutions for the direct manufacture into blue vitriol, which he describes as follows:—

"If copper matte, or a sulphuretted copper ore after being subjected to an oxidising roasting, is treated with hot diluted sulphuric acid, a solution of cupric sulphate is obtained, which contains large quantities of iron besides more or less arsenic, antimony, nickel, cobalt, etc. Such an impure cupric sulphate solution is not suitable for the manufacture of blue vitriol because the impurities, especially the ferrous sulphate, also crystallise out of the concentrated solution and make the product of blue vitriol too impure for the market.

"In order to produce a pure solution, the impurities in the matte and ores have to be first eliminated, before they are

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* "Mineral Industry," vol. vi., p. 242.

subjected to the action of the dilute sulphuric acid; and this is accomplished by repeated roastings and smeltings, till the largest portion of the iron and other impurities are oxidised and go in the slag."

By the Hofmann method, *the crude cupric sulphate solution is refined*, and refining of the material is therefore not required.

The copper matte or sulphuretted copper ore is pulverised and oxidised by roasting, and treated with hot sulphuric acid, either in an agitating tank or in a leaching tank. The amount of sulphuric acid necessary for producing the solution depends upon the nature of the ore or matte. Attention has to be paid that the resulting cupric sulphate solution is neutral, or as nearly neutral as possible.

This process has been introduced in the works of the Consolidated Kansas City Smelting and Refining Co., at Argentine, Kansas, where it is in successful operation; the average daily production amounting to about 30 tons of blue vitriol. Mr. Hoffman describes the process as follows*:—

"*Crushing.* The copper matte is pulverised in a Krupp-Grusonwerks ball mill, having a capacity of 18 tons per 24 hours, to a fineness of 50 mesh per linear inch, and the wear and tear of iron in this machine amounts to only five per cent. per year.

"*Roasting.* The pulverised matte of 34 to 40 per cent. copper content is roasted, and for the benefit of subsequent operations, the roasting is conducted with great care, and with attention equally divided between the oxidation of the copper and the iron. The copper is to be converted into oxide and sulphate by roasting, and the formation of cupreous oxide should be avoided, as one-half only of its copper will dissolve in diluted sulphuric acid, while the other half will precipitate as metallic copper and will remain in the residues. The iron should be converted into an insoluble oxide, otherwise too much iron will go in solution, and the precipitate which results in the process of refining the solution will become voluminous and will retard the filtration. It is not advisable to conduct the roasting so that as much copper as possible will be converted into sulphate, because the roasted material will then contain too much soluble iron. In order to obtain the desired result, the

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* "Mineral Industry," vol. viii., p. 189.

roasting must be done in a furnace with excellent draught, and under the conditions of excess air in the furnace.

"At the beginning of the operation the temperature should not be raised above that produced by the combustion of the sulphur of the matte. During this period the charge assumes a rather bright appearance, an effect due more to light than to heat, and if excess of air is admitted to the furnace but few lumps will form, even with very leady copper matte.

"Gradually, as the oxidation advances, the surface of the charge becomes darker, especially near the air doors, and when the entire surface of the charge begins to darken, the fire is slightly increased to prevent cooling, as from this time on the supply of heat furnished by the oxidation decreases rapidly. If this condition is overlooked and the charge cools too much, it will be difficult to raise the temperature again to the proper degree.

"The roasting is continued at a moderate temperature until no more heat is evolved by the oxidation of the material, after which the temperature must be raised to a cherry red. A skilled roaster can readily determine this point by stirring the charge; if the particles thrown to the surface brighten, the roasting has not advanced far enough, but if the entire charge maintains a dead and uniform red colour, it shows that this part of the roasting has been completed and that it is time for an increase of temperature. This can now be done without danger of lumping the charge, because by this time the greater part of the sulphides has been oxidised.

"The increase of temperature is necessary for two reasons: first, to hasten the oxidation of the remaining sulphides, which would require a very long time at a low temperature; and second, to convert the iron as much as possible into the red oxide, in which state it is not soluble in diluted sulphuric acid. Care must be taken, however, to avoid too high a temperature, as the cupric sulphate formed, which is very desirable to have in the roasted matte, would then be decomposed. At a comparatively early stage of the roasting nearly all the copper is in a state in which it can be extracted by dilute sulphuric acid; about 75 per cent. of it is present as oxide and 25 per cent. as sulphate.

"The roasting, however, cannot be considered complete at this stage, because a large percentage of the iron is soluble in acid as well and would make the resultant cupric sulphate solution unnecessarily impure. The task for the roaster is to convert as much iron as possible into the insoluble oxide, without the decomposition of the cupric sulphate present. Cupric sulphate resists considerable heat, and it is possible to conduct the roasting in this way; but this increase of temperature requires judicious care, because if the heat is too high the cupric sulphate will be reduced to cupreous oxide, in which condition but one-half of the copper is soluble in diluted sulphuric acid.

"Should cupreous oxide be formed the amount of extractable copper will be greatly reduced. If, for instance, the extractable copper before raising the temperature was 97 per cent., after an excessive heat it will be reduced to 92, or even 90 per cent When the roasting is done in common reverberatory furnaces a mistake of this kind can be corrected by keeping the charge longer in the furnace and thus oxidise the cupreous to cupric oxide. In a mechanical roasting furnace, however, this cannot be done; but with experience and care the decomposition of the cupric sulphate can be avoided.

"A double-storey Pearce roasting furnace is used, giving very satisfactory and uniform results, both with regard to copper and iron. This satisfactory working was not attained until an extra fireplace was built between the last two fireplaces on the lower hearth. The space between these two fires in the original construction was too great, and the matte which arrived at the second fireplace had lost the larger part of its sulphur and did not have sufficient left to furnish the heat necessary for the maintenance of the required temperature. It was cooled below a red heat and the last fire, though kept very strong, was not sufficient to complete the roasting. The charge became hot in the immediate neighbourhood of the last fire, but as this is close to the discharge, the matte was not exposed long enough to this heat for the desired effect. After the addition of the extra fireplace it was easy to regulate the roasting operation and to obtain good uniform results.

"The present method of roasting with the altered furnace is as follows:—A moderate fire is kept on the upper hearth close to the drop slot, through which the matte falls to the hearth below. The other fireplace is used only at the start of the roasting, and when the charge is ignited the fire is discontinued so as to prevent it from becoming overheated. The remaining fire on the upper hearth is so regulated that the charge is dark red when it is dropped to the lower hearth.

"By far the greater part of the sulphur has to be oxidised on the upper hearth, otherwise too much work will be left for the hearth below, and it will be difficult to regulate the finishing part of the roasting properly. For this reason it is necessary to have an excess of air on the upper hearth, and all the doors, with the exception of the one next to the feed, should be kept open.

"A free access of air is of such great importance in the roasting process, whether oxidising or chloridising, that particular attention should be paid to this requirement in the constructing of a roasting plant, and care should be taken to provide the furnaces with sufficient draught. In fact an excess of draught should exist, so that the operator may regulate it by the use of the damper. In most plants dampers are useless, on account of a lack of draught, even when they are opened wide.

"It is not possible to avoid the formation of some lumps, especially in roasting leady matte, but, if the roasting is conducted properly, these will be small, soft, porous, and of well-roasted material. Roasted matte is always of coarser grain than the raw pulp, and for this reason, as well as on account of the lumps, it is necessary to pulverise the roasted material before treatment with sulphuric acid. The pulverised material should pass through a screen not coarser than fifty mesh to the linear inch."

To the pulverised material hot sulphuric acid is added, and this crude solution is charged into a suitable receptacle, most conveniently into a high tank or tower (Fig. 35), 16 feet high and 6 feet diameter, made of a cast-iron skeleton frame, and lined with heavy sheet lead, 20 lb. per square foot (see Fig. 2). The bottom of the tower is funnel-shaped. Through the lowest part of the latter enters, at A, a lead pipe, B, projecting 12 to 18 inches into the tower, and connected with an air compressor. To prevent the solution from flowing into the compressor, the pipe must ascend above the top of the tower, and then descend to the compressor. Near the inlet of the air pipe is the outlet or discharge pipe for the solution. By means of a steam coil, D, the solution in the tower can be heated.

When the tower is charged by means of the inlet pipe, E, with solution, steam is turned into the coil, and the solution heated to about 75° to 80° C.; then air is forced through the solution, and pulverised cupric oxide added in required quantities, which depend on the amount of impurities contained in the solution, and the amount of free acid, if any is present. As the roasted matte contains a large amount of cupric oxide, the same can be used to great advantage in place of pure cupric oxide. The ascending air keeps the particles of matte

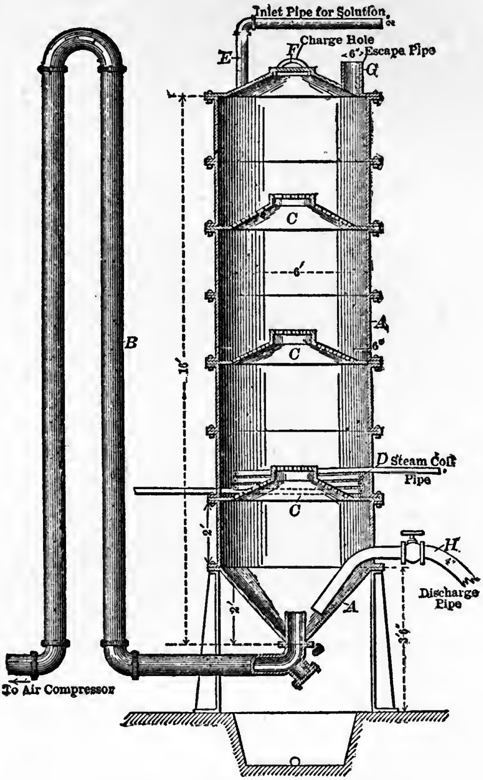


FIG. 35.—THE HOFMANN TOWER.

or cupric oxide suspended and in motion. After some three to four hours of operation, the above-named impurities, together with some basic sulphate of copper are precipitated. The end of the operation is ascertained by test for iron.

It is not practicable to dissolve the matte by filtration in tanks. The best method for the solution of the cupric oxide of the matte is accomplished in agitating tanks, and, unless the matte is in motion when the water or diluted sulphuric is applied, it will harden to such an extent that it will be necessary to use picks for its removal. This hardening greatly prevents free filtration and impairs the extraction. In addition to this objectionable feature there are others quite as bad, as the uneven concentration of the resulting solution, etc. If the dissolving is done in agitating tanks the process is under perfect control, and the extraction is accomplished in much less time and in a more thorough manner.

The agitating tanks are filled about two-thirds full with water, the agitator set in motion, and sulphuric acid added until the liquid is about 3 per cent. acid strength. The matte is then charged gradually, and at the same time a stream of acid is allowed to flow in, so as to maintain the acid strength during a portion of the charging. In this way the dissolving is accomplished with an acid strength of 3 per cent. or less, and still yields a strong solution of cupric sulphate. It is preferable to work with weak acid, because much less iron and other impurities will be dissolved than with stronger acid. When the solution has attained a certain strength the flow of sulphuric acid is stopped, and matte only is charged until the solution is neutral.

When the operation is drawing to an end, it is advisable to charge the matte at intervals, and to make frequent acid tests to avoid an excess of matte. The addition of sulphuric acid to the water and of the matte to the diluted acid produces heat, which aids the solution of the cupric oxide. This heat is not sufficient, and the temperature is further raised by a jet of steam. It is well to interrupt the charging of matte while neutralising as soon as the solution shows 1 per cent. free acid. If the agitation is then continued this 1 per cent. will be diminished, but if in half an hour after the last acid test, the percentage of free acid remains the same, more matte is added until the solution is neutral; in this way a mistake of adding a large excess of matte is avoided. When the solution is neutral, the pulp (solution and residues) is drawn through an outlet near the bottom into a large cast-iron pressure tank, and from thence by means of compressed air it is forced into a large filter press to separate the residues from the liquid. The cylindrical side of the pressure tank is lined with sheet lead, which is protected against mechanical wear by a wooden lining. The spherical bottom is lined with heavy hard-lead casting.

It is not advisable to make the cupric sulphate solution too concentrated, as it will partly crystallise when cooled moderately. These crystals will incrust the filter cloth of the press, blockade the pipes, incrust the sides and bottom of the receiving tanks, and interfere with the manipulation. A concentration when warm of about 24° to 26° B. gives good results.

The plates and frames of the press are made of wood, and are 4 × 4 feet in size.

The crude solution from the filter press contains, in addition to cupric sulphate, compounds of iron, arsenic, antimony, bismuth, cobalt, nickel, etc., and is conveyed to the receiving tanks for further treatment. No trace of silver can be found in the solution, as whatever silver is converted into sulphate during the roasting is precipitated in the agitating tank by the ferrous sulphate present in the solution. The residues are well washed in the press, to remove all copper solution. The wash water solution, which contains 1 per cent. copper, is collected in special tanks and used instead of water for the preparation of a new charge in the agitating tanks.

The residues contain all the silver, gold, and lead, of the original matte; they are of dark red colour, and consist mainly of iron oxide. This material is very desirable for the blast furnace, and is sent to that department for the extraction of the precious metals and the lead. A large portion of lead is converted into sulphate by the roasting, and therefore does not act as a consumer of acid. As the roasted matte contains 20 to 25 per cent. of its copper as sulphate, the total consumption of acid is much less than the equivalent amount of acid in the blue vitriol produced.

As mentioned before, the solution, by means of compressed air, is forced from the receiving tanks by means of a special cast-iron and leadlined pressure tank into the tower shown in fig. 35. Between every other section of the tower is inserted a perforated cone, C, made of hard lead and provided in the centre with a manhole and a lid well fastened to the cone. The perforations toward the periphery are larger than those nearer the centre.

When the tower is filled, steam is allowed to enter the coil to heat the solution, and at the same time air is forced in through pipe, B. The ascending air strikes the perforated cones, is divided into numerous streams, and imparts a violent boiling motion to the liquor. The cones help to retain the air in the solution. Part of the iron is precipitated as a basic salt by the action of the air, but never more than half of it is precipitated even if the treatment extends over several hours. When the solution is hot (75 to 80° C.) the roasted matte is added through the charge hole, F. The violent boiling motion of the solution keeps the matte in suspension, and after three to four hours the solution will be entirely free from iron, arsenic, antimony, bismuth, etc.

To observe and to regulate the progress of the operation the solution is tested from time to time for iron, by taking samples through a small cock inserted in the side of the tower. It is not necessary to test the solution for other impurities, because the iron predominates, and by the time all of it has been precipitated, no trace of the others will be found.

The chemical reaction of this process may be expressed by the following equation :—

$$2FeSO_4 + O + 2CuO = Fe_2O_3 + 2CuSO_4.$$

This shows us that the cupric oxide, which together with air, is used to precipitate the iron, combines with the sulphuric acid of the ferrous sulphate and goes in solution as cupric sulphate, and thus enriches the solution in copper.

A tower charge consists approximately of 3,000 gallons of solution. When the reaction is completed, after three to four hours, the refined liquor, the precipitate, and the residues of the added matte is discharged through the pipe, H, into an agitating tank at a lower level. From thence it is drawn to a pressure tank and forced through a filter press. The clear and refined solution from this press is conveyed to the evaporating tanks and concentrated by evaporation. The residues which consist principally of the precipitated impurities contain some undecomposed matte and some basic sulphate of copper; for this reason they are subjected to a short treatment with very dilute cold acid. The unwashed residues are removed from the press and charged into an agitating tank which contains a cold acid solution of 2·5 to 3 per cent. strength. This acid readily dissolves the basic sulphate of copper, while it reacts but slightly on the iron and not at all on the other impurities. The liquor of this charge passes to the crude solution and the residues to the matte residues. The refined solution is concentrated to the desired degree, and then conveyed to special tanks for crystallisation.

The solution, now freed from impurities, yields very pure crystals of blue vitriol of a brilliant colour. Unlike the blue vitriol which is found in the market, the crystals obtained by this process do not change their physical condition by exposure to light and air, even in the course of years. They retain their deep blue colour, remain hard and solid, and are affected by the direct sunlight only. The permanency of these crystals is caused by their production from a neutral solution.

PART III.

THE ROASTING OF COPPER ORE.

CHAPTER XIII.

HEAP ROASTING.

Arrangement of Roast Heaps.—When roasting ores in lump form the object to be attained is the formation of oxides, and the retention of a certain quantity of suphides in the roast product. If the ores are solid iron pyrites in admixture with copper sulphides which do not decrepitate on heating, they are submitted to what is called kernel roasting, whereby the copper contents are concentrated in the interior of each lump in the shape of a kernel of solid sulphide surrounded by concentric layers of oxides. The roast product is then treated by a combination process: namely, the oxidised outer part, after separation from the kernel, is subjected to some leaching action, and the kernel is smelted by itself in reverberatories or other furnaces. This method was carried out at Agordo.

The roast heaps are built up by placing the large lumps in the central portion of the same, and then piling on the smaller pieces, finishing with an outside covering of fines. Before building up a roast pile, a yard should be carefully prepared by levelling off a piece of ground and covering it several inches deep with broken stones, slags, and tailings, and then covering the same with a clayey loam. This should be rolled several times with a heavy roller, the surface being slightly dampened from time to time, until the entire area is as level and nearly as hard as a macadamised road. On top of this is placed a covering of fines and as this layer beneath the heaps becomes gradually roasted through, it should be removed with the coarse ore and sent to the furnaces.

In laying out a roast yard, the topographical features of the country have to be taken into consideration, so that the same shall be safe from inundations, and a good system of drainage should surround it. No hard and fast rules can be laid down, and every mine has to arrange its own plans to suit conveniences and local conditions.

In building up the roast piles, their height will depend on the character of the ore, and the richer the ore in sulphur the lower will the same be; ores carrying 30 to 40 per cent. of sulphur will be built up to a height of 7 feet and unless ores carry at least 15 per cent. they will not burn by themselves but require that fuel should be dispersed through the roast heap, besides the layer of wood on which the ore rests. The time required to burn a roast heap of 250 to 300 tons is from 50 to 75 days. The more perfectly the ore is roasted the better the result in the subsequent lixiviation, and if the ore is roasted for smelting operation, a well-roasted kiln will allow of the admixture of raw sulphides in the furnace charges and in the grading of the resulting matte.

The roast heaps are either rectangular or circular, one 24 feet wide by 40 feet long and 6 feet high will contain 240 tons.

When the roasting yard is prepared and covered with, say, 6 inches of fines, the fuel is arranged in regular layers, preferably cord wood, which should form a bed of 8 to 10 inches in depth, leaving at regular intervals canals, which are filled with brush and kindling wood for the circulation of air; and these communicate with chimneys in the centre line of the heap; these draught canals should be covered over in such a manner that they shall be neither choked nor destroyed by the superincumbent load. The chimneys are made by setting up vertically boards or sticks of wood in the centre line of the pile and their number depends on the length of the heap. On top of the fuel the ore is piled up, and it assumes the shape of a truncated pyramid, or a truncated cone. The main body of the roast heap is formed of the coarsest class of ore; the ragging is next placed upon the pile, forming a comparatively thick covering at the part nearest the ground, and gradually thinning out towards the top and on the upper surface of the sides. The fines are gradually added as an outside covering as the roasting proceeds, and the lower circumference of the pile should remain uncovered so as not to hamper the draught.

It is estimated that it takes about one cord of wood to roast

40 tons of ore. Too much fuel must not be used, or too great a heat will be generated and large masses of fused sulphides found collected at the bottom, impeding the circulation of the roast heap, and the result will be a badly roasted heap.

Fig. 36 and illustrations immediately following—showing the building up and construction of roast heaps—are reproduced from Plattner's "Metallurgischen Röstprozesse," published in 1856, since which date very little progress has been made in this department of the treatment of copper ores.

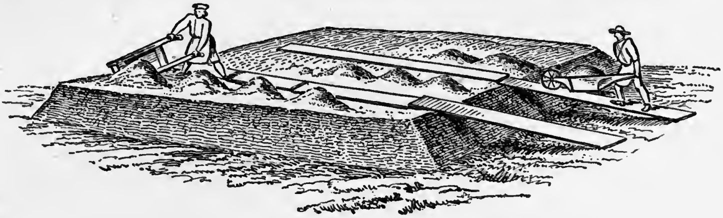


Fig. 36.—Building up a Roast Heap.

Fig. 37 shows a square roast heap, having at *a* an empty space which is filled with kindling wood and loosely covered with sticks of wood. The cord wood is shown evenly placed, and the air channels properly distanced. Lump ore, *c*, is now piled on to a height of 4½ feet, and arranged so as to leave a rim of 2 feet of uncovered cord wood all around the pile. In the centre the shaft, *b*, is formed by means of sticks of timber. On top of the coarse ore from 4 to 8 inches of ragging is placed, shown at *d*, and on top of this are placed the fines *e* and *f*. To regulate the burning of the heap, further additions of fines, *g*, are made.

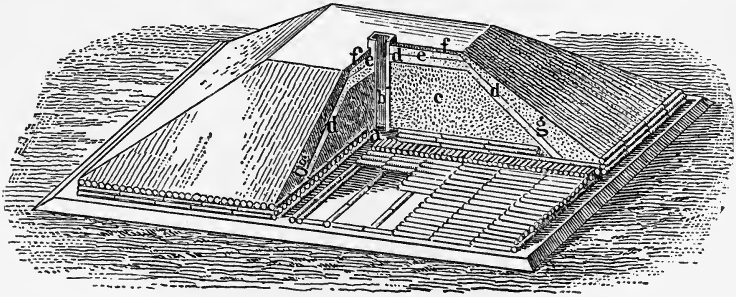


Fig. 37.—Construction of a Roast Heap.

Fig. 38 shows a heap when completed and ready to be set on fire.

The quantity of ore which is locked up in the roast heaps is in proportion to the capacity of the smelting plant; and supposing that it is a question of supplying a cupola of 200 tons daily capacity, it will be necessary to have a roast yard of a surface area of 100,000 square feet, capable of holding at least 80 roast heaps of 240 tons each, which would permit the withdrawal of at least 20 tons from 10 heaps daily, and when these heaps are cleared away in 12 days, 10 other heaps are broken into, while the cleared spaces are built up again with fresh heaps, leaving 60 heaps in operation. Taking 80 heaps of 240 tons, this represents 19,200 tons of ore which have to be constantly on the roast piles.

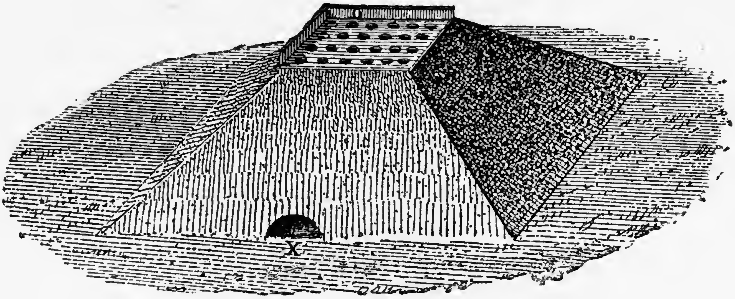


Fig. 38.—Roast Heap Completed.

An instance of a very peculiar arrangement of the roast heaps came to my notice at the United Verde Mine in Arizona, and one which suited the local conditions most admirably. The mine is opened by several adits to a depth of 600 feet and these penetrate the mine along the steep mountain slope of the Black Hills. As the ores are brought out from each adit, carefully prepared yards extend along the tramway track and below the same, and a special railway track which zigzags from the lowest level to the top of the hill carries the roasted ore to the smelter on top of the hill by electric traction. It is an unique sight to see these long smoking terraces extending from the base of the mountain to its summit, and probably nowhere else would a similar arrangement be required.

Where cone-shaped roast heaps are in use, the arrangement illustrated by Fig. 39 can be recommended. In the centre is a chimney, *a*, built up of bricks without mortar, resting on a solid foundation, and, as the same is being erected, small openings are left on the sides through which the products of combustion can escape, and to force the gases into the chimney, the kiln is well covered with fines, *b*. To provide the necessary air, small canals are placed at regular intervals around the periphery, and they all converge to the central chimney, *a*. One of these canals is seen at *c*, where the draught can be regulated by opening or closing the inlet. Of course, here, as with the pyramidical heap, the ore is built up on a layer or foundation of cord wood.

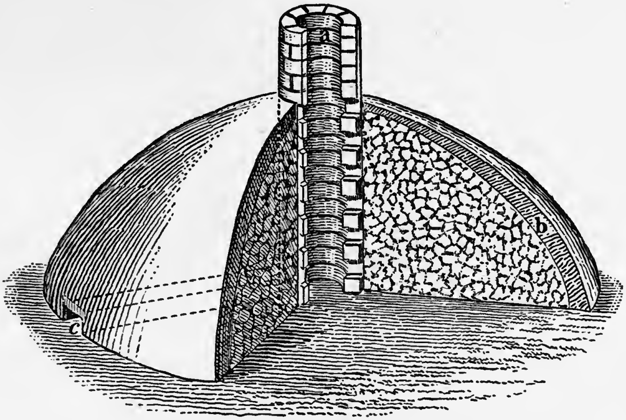


FIG. 39.—CONE-SHAPED ROAST HEAP.

If heap roasting is carried out in countries where the rainfall is heavy, the losses are very great, as so much sulphate of copper is leached out. The loss may reach the enormous figure of 30 per cent., as experienced by Mr. A. F. Wendt in heap roasting the Ducktown ores in Tennessee. He says: "All the experiments made on a total of nearly 3,000 tons of ore proved, beyond possibility of doubt, an average loss of more than one unit of copper, or over 20 pounds of ingot per ton of ore."

With the best of care and attention some portions of the roast heap will escape oxidation, this unroasted material being made up of the fines forming the cover, a large portion of which is agglutinated with the sublimed sulphur which has settled on it, and is therefore not fit for smelting or lixiviating. The sides, angles, and bottom of the heap are also generally poorly roasted.

The average cost of building up a roast heap when fuel is about $5 per cord, attending to same and tearing it down when roasted would be about 50 cents per ton.

After roasting, the copper in the roast product will be present as sulphide of copper, sulphate and oxide of copper. It is the sulphur which is combined with the iron that burns away, and the copper is the last metal (present in the ore heap) to part with its sulphur, whereas nearly the whole of the iron becomes oxidised.

The Guyer Desulphurising Kiln.—A very simple and expeditious method for desulphurising ores is described by Messrs. Fraser & Chalmers, and by them recommended for small plants where development of the property does not warrant expensive crushing and roasting machinery, and where the ores are suitable for heap or stall roasting. The method was devised by Capt. Henry Guyer, of Casapalca, Peru, where several of the kilns have been in operation for some time, with excellent results; one of these kilns roasting seven tons per day at a cost of 33 cents silver per ton, and in one kiln he roasted thirteen tons daily at a cost of 18 cents silver per ton. The original ore contained 27 per cent. of sulphur, and was reduced by roasting to 8·8 per cent.

Ores to be roasted in this furnace must be coarse—that is, from the size of corn to about the size of an egg—and should contain not less than 20 per cent. sulphur. The only fuel used is a few shovels daily of charcoal dust, shavings, or any rubbish that will burn. They are made of as small a capacity as two tons per day.

The furnace (Fig. 40) is very simple, consisting of a four-sided grizzley, constructed principally of grate bars fastened to a rectangle made of rails, which is supported on pipe columns; this is surmounted by a sheet-iron hood having a hole in the top for charging, and on one side for connection with a flue.

Sufficient ore should be thrown into the kiln to form a cone reaching to, and a short distance inside of, the grate bars upon which from 6 inches to 8 inches of fuel is to be placed.

This may consist of any refuse material which will ignite; upon this the ore to be roasted is piled, new ore being added as fast as the combustion is visible. This is continued until the kiln is filled to the top, when the roasting is permitted to continue for say 12 hours without further attention. At the end of this period the ore in the bottom is sufficiently roasted to be raked out, when any pieces that remain unroasted are thrown aside, to be returned to the kiln for retreatment. Should any of the ore become sufficiently fused to stick to the grate bars, it is removed by barring through the grate bars or through the top. It requires approximately from 8 to 10 hours between each roasting period.

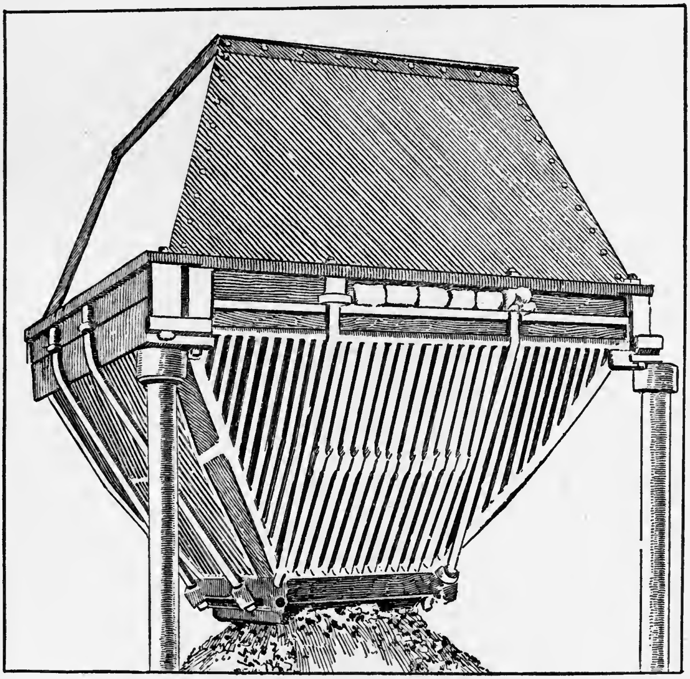


FIG. 40.—GUYER'S DESULPHURISING KILN.

At Casapalca the ores carry from 27 to 30 per cent. sulphur, the roasted ore averaging about 8 per cent. sulphur. With material of this description very little or no fuel is necessary. A complex ore of copper and lead (of the latter 15 per cent.)

seems to be specially adapted to this kiln, and all ores which are amenable to heap or stall roasting may be treated successfully by this kiln.

The kiln may be built of any capacity desired; units of 24 to 30 feet (length of one rail) will treat from 8 to 10 tons of ore per day of 24 hours. The flues which carry the fumes to the main stack require very little attention, as the sublimed sulphur may be burned out if the flues require cleaning. The arrangement most desirable seems to be to have a car running over the feeding openings of the kiln.

The cost of roasting is about equal to that of heap roasting, but the time required is very greatly reduced; instead of requiring several weeks, only as many days are necessary.

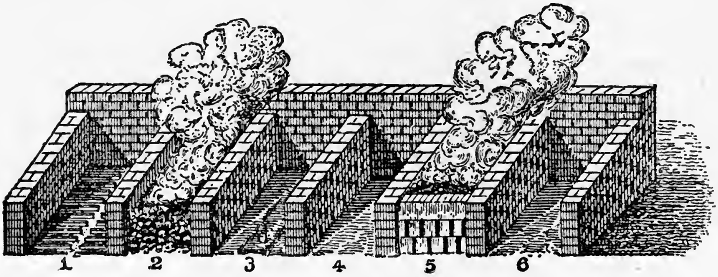


Fig. 41.—Open-Roast Stalls.

Stall Roasting.—An important improvement in the roasting of ores was the introduction of stalls, with the object of protecting the heaps against the elements, as well as concentrating the heat, and avoiding the tedious and laborious work of covering the sides and top of the heaps with fines. For this purpose square brick enclosures are erected, which are either open on top or covered with an arched roof, and their interior is connected by means of a flue with a chimney, which creates a draught and facilitates the oxidation of the ore.

The illustrations of open stalls here given are reproduced from some of the earlier text-books, but they show clearly enough the arrangements found in operation to this date with only slight modifications. Fig. 41 shows a series of stalls with level floors: d is a layer of wood in stall 1, leaving a canal in the centre; on this layer a second row of billet wood is placed, which covers the canal (see 3); 2 shows a stall on fire, still open in front; 5 is a stall closed in front, and in operation; 4 and 6 are empty stalls ready to be charged with ore.

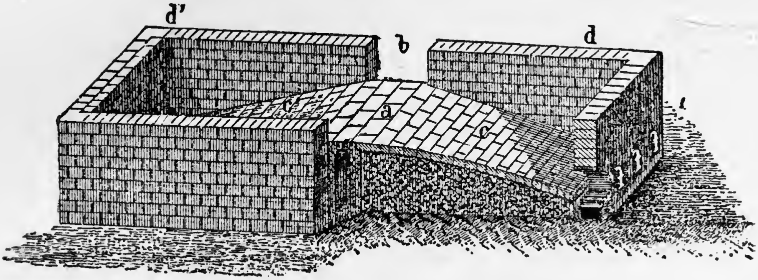


Fig. 42.—Roast Stall with Inclined Floors.

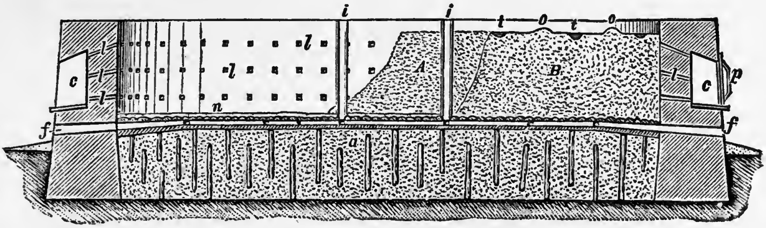


Fig. 43.—Section of Large Roast Stall.

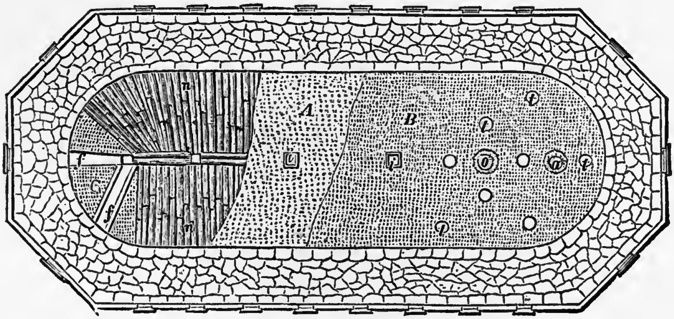


Fig. 44.—Plan of Large Roast Stall.

Fig. 42 represents a stall with inclined floors: *a* is the central part which is level and ends at *b*; lateral fireplaces allow the flame to circulate through vents which are built up by large pieces of ore, and the heap is piled up on the inclined planes, *c* and *c′*, made of brick, which in their turn rest on finely broken slag, the whole being surrounded by the walls, *d*, *d′*. The circulation of air becomes easily stopped up in the canals, as after the roasting they become obstructed and collapse.

If the roasting is to proceed slowly, as would be the case when it is desired to roast for sulphates, very large stalls are employed, as represented in Figs. 43 and 44, having the dimensions 11·7 metres long, 4·3 metres wide, and 2·5 metres high. The walls are 1·6 metres thick, and the canals, *l*, serve to conduct the sulphur vapours into the small chambers, *c*, called collectors, which are closed during the operation by iron doors, *p*.

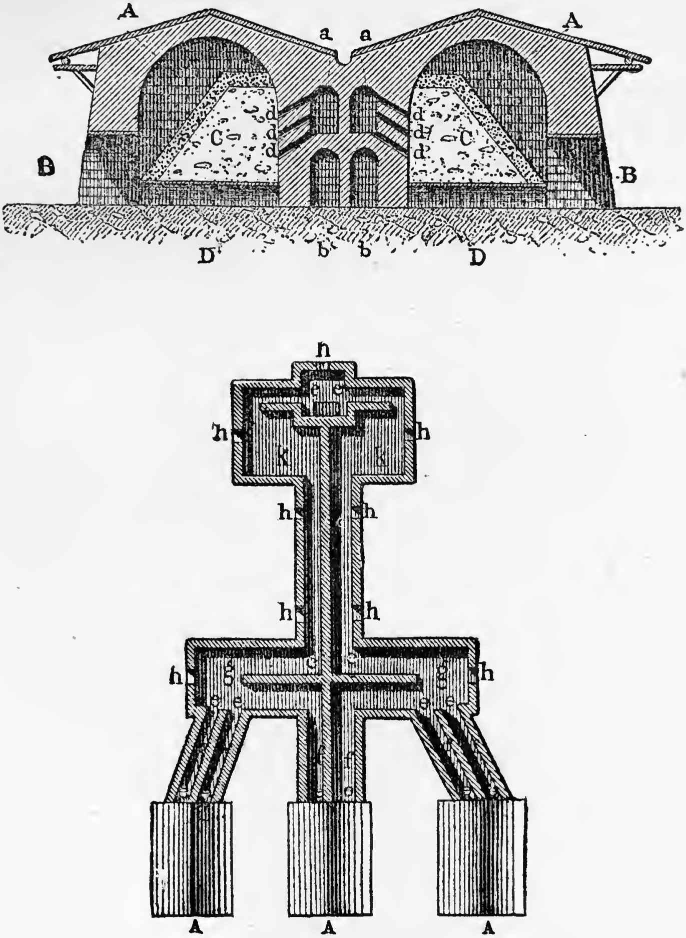
The floor, *a*, of the stalls consists of leached-out ore, in which are placed vertical pillars. The ore is first charged through the doors in the walls, and finished by being piled in from the top. On the floor is first placed a layer of wood, *n*, leaving at regular intervals small square spaces, *i*, which communicate with canals, *f*, which are covered with slate slabs, and these in their turn with vertical chimneys; and when the kiln is well on fire, the vents, *i*, are filled with fines. The heap is covered with fines and leached-out ores, in which are practised small cavities, *t*, to collect the sublimed sulphur. The roasting in these kilns takes from 6 to 8 months.

Kiln at Rio Tinto.*—Figs. 45 and 46 show a different form of kiln, formerly employed at the Rio Tinto mines.

The stalls, which are built in two rows, D, D, are 19 metres long, 4 metres wide, and 3 metres high, and are capable of holding 400 tons of ore each. B, B are openings, through which the ore is charged, and C shows the mineral charged on a bed of brush. On the top of the ore are placed the fines; *d*, *d*, *d* are the flues which communicate with the canals, *a*, *a*; and these in their turn communicate with the lower canals, *b*, *b*. These canals communicate with the flue, *f*, which is covered with slate

* "La Metallurgie du Cuivre," par M. Roswag. Dunod, Paris.

slabs, and leads to the condensing chambers. The first one is *g*, the second one is *h*, and then to the chamber, *k*, in which is a receiving basin to collect the condensed sulphur. Walled-up openings, *h*, *h*, serve to take out the sulphur when the operation is completed. The roasting in this apparatus takes about 5 months.



Figs. 45 and 46.—Kiln formerly in use at Rio Tinto.

Bohemian Stall.—The arrangement of stall adopted in Bohemia is shown in Fig. 47, in which the walls, A, are 7·55 metres long and 5·65 metres wide. One of the sides remains open, but is closed after the kiln is charged. The floor is inclined, covered with a layer of wood, on which is placed the ore heap, *m*, *m*. Openings in the back wall conduct the sulphur vapour into the condensing chambers, B, divided into three compartments, *e*, in which the fumes are forced to travel down one compartment, up the next, and then down again into the last, where most of the condensation takes place ; *b* is a low chimney for the escape of the fumes.

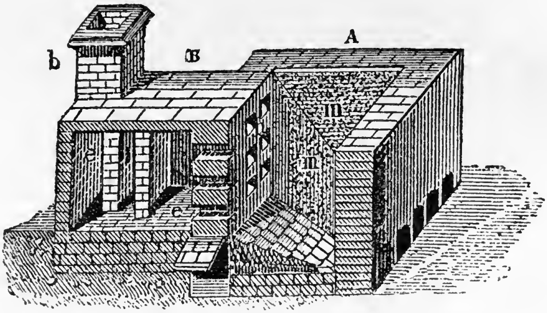


Fig. 47.—Bohemian Stall.

CHAPTER XIV.

KILNS FOR MANUFACTURE OF SULPHURIC ACID.[*]

ONE of the principal by-products in the hydro-metallurgical treatment of copper ores is sulphuric acid; and as the manufacture of sulphuric acid could be introduced with great advantage in some distant mining regions where such treatment of copper ores is in operation, a description of the kilns employed in the burning of pyritic ores will be given in this chapter. The pyrite burners are divided into two types, namely, burners for dealing with lump ores, and furnaces for roasting the "fines."

Lump ores are burned in shaft furnaces with or without grates. Some have fireplaces which are located outside the furnace, and some have their grates inside the furnace and are directly fired. Furnaces with sloping sides are preferable, as shafts with perpendicular sides get easily choked, impeding the draught. The disadvantage of these appliances is their limited capacity, as only a small quantity of ore can be burnt at one time.

Pyrite Burners without Grates.—A kiln of this description on a scale of $\frac{1}{50}$, having a height of 3 metres by 1 metre in width, is represented in the illustrations here given. Fig. 48 shows an elevation of the kiln, and to the right is a longitudinal section along the line C D of fig. 50. Fig. 49 is a vertical section along the line E F, of the plan, Fig. 50, which shows the inclined

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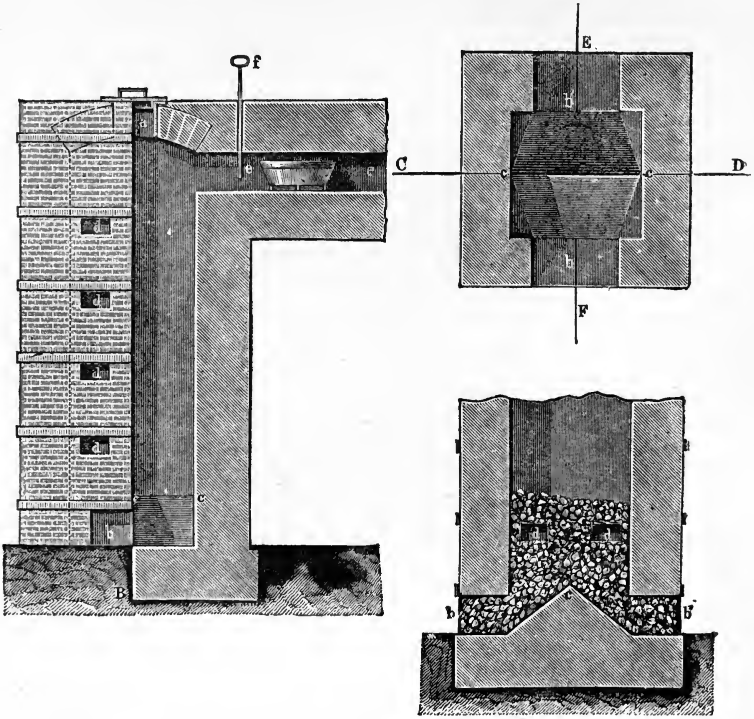
[*] From Dr. George Lunge, "Handbuch der Soda Industrie," who gives a full description of the manufacture of sulphuric acid. Braunschweig, 1879.

sides of the bottom of the kiln, as these facilitate the withdrawal of the ore from the openings, *b*, *b'*.

The ore is charged through the opening, *a*, which is closed by means of a cast-iron cover, and the air necessary for the combustion of the sulphur is admitted by the openings, *b*, *b'*, and *d*, in the side walls, where its admission is regulated by squarely fitting bricks; and these openings also serve for the introduction of iron bars, to break up any clinkers which may have formed.



Figs. 48, 49, and 50.—Pyrite Burners. Kiln without Grates.

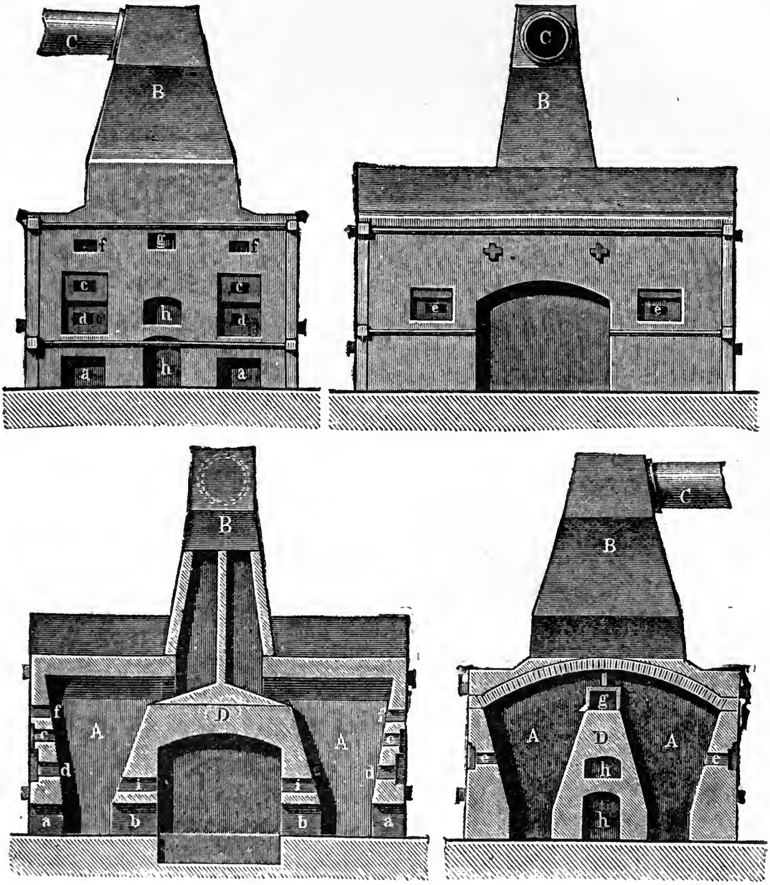
The height to which the kilns ought to be charged depends on the quality of the material, and the more difficult the material burns, the higher the same ought to be in the furnace. During the operation, special attention must be given to prevent the sublimation of the sulphur, and for this purpose plenty of air must be admitted into the upper part of the furnace. The gases pass through the flue into the lead acid chambers. In some factories the gases first pass through dust chambers. If it is desired to introduce the nitric acid produced by the decomposition of the saltpetre and sulphuric acid, these materials are placed in earthenware pots through openings, which are afterwards well luted, into the canal, *e*, in which the temperature is high enough to cause the decomposition. It is usual to build six of these furnaces in one block, namely three in front and three at the back, all discharging into one flue, *ee*, to hold the saltpetre pots, and in which is a damper, *f*, for the regulation of the draught, the flue connects with a canal 1 metre in diameter to conduct the sulphurous acid vapours.

The square section of these kilns is not recommended, as the ores easily bake together and prevent an easy admission of the air. For this reason kilns *with sloping sides*, on which the ores slide down with greater ease, are to be preferred. The larger surface which is exposed facilitates the burning of the ores, and the heat does not concentrate in the centre of the mass so as to cause the ore to fuse, with the consequence that the furnace becomes clogged.

Such a furnace is shown in Figs. 51 to 54. Four of these furnaces are generally built into one block. A, A, the roast shafts, having at the bottom a square section of 0·64 metre and on top of 1·28 metre, are 2 metres high; B is the vault to conduct the gases into the flue, C. Each shaft has in front four openings, on the sides one, and inside two; *f*, *f*, serve as openings for charging the furnace; *a*, *a*, *b*, *b*, to discharge the roasted product and for the admission of air; *c*, *e*, *d*, *i*, to stir up the ore, and to increase the draught if required. The arch under the pillar, D, can be reached through the passages, *h*, *h*; the pillar also carries the saltpetre pots, which are introduced at *g*. Each furnace is recharged every eight hours, therefore every two hours a new furnace comes into operation.

The square burners have been replaced at Freiberg, Saxony, by oblong kilns, which have a height of 8 feet, are 8 feet long and 3½ wide on top and 6 ft. 8 in. long by 1 ft. 8 in. wide at the bottom. This shape of furnace is adaptable for ores poor in sulphur and consequently difficult to burn, and in this style of furnace not all the sulphur is burned.

In the previous pages it has been shown that washed or leached sulphides enter largely into the manufacture of sulphuric acid, and as they have been exposed for a number of years to the action of weather, mechanically they are in such a condition as to crumble very readily, and should therefore be screened through a one-inch mesh before being used in lump burners. This of course necessitates the use of fine burners also, and the tendency at present is to erect fine burners, as they have been very much improved, and types of fine

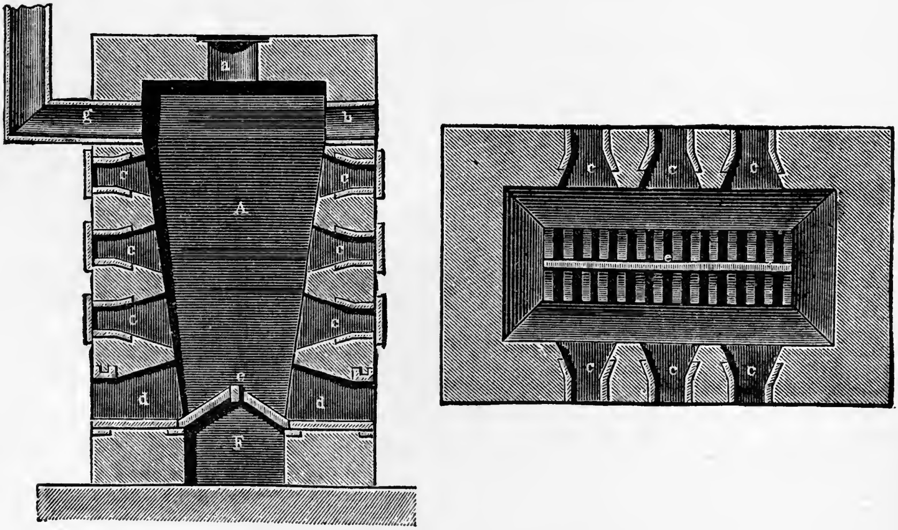


Figs. 51, 52, 53, and 54.—Pyrite Burners. Elevation and Section of Kiln without Grates having Sloping Sides.

burners are in use which will handle such part of the product as will pass a screen of one-inch mesh, giving as complete a roast as most lump burners.

The ores are therefore divided into two classes when burned for the manufacture of sulphuric acid: (1) Ores which are prepared for burning on grates, or in kilns without grates, in lump form, or (2), Ores which are fines resulting from the preparation of the lumps, and which can be burnt to best advantage on fire-clay shelves in shallow layers without auxiliary heat, or in muffle furnaces. In rare instances only are combination burners employed, namely, those in which the burning lump ores supply heat to burn the fines.

Pyrite Burners with Grates.—These are a decided improvement over kilns without grates, as they permit of due regulation of the draught. With a closed ashpit only a definite quantity of air need be admitted into the pit, which is equally distributed under the grate and rises over the whole area of



Figs. 55 and 56.—Kiln with Grates.

the burner, effecting a better combustion of the sulphur. The operation of drawing out the burnt ore is more regular, and no raw ore is left behind; it also prevents the formation of fused masses or "scars" in the burner. By the introduction of the grates into the burners the height of the ore column was diminished, which is a great advantage with easily fusible ores, although in some localities the other extreme, namely, too low layers of pyrites has been resorted to. By employing kilns with grates a better roasting is effected, the gases are richer in sulphur, with the result that the work in the lead chambers proceeds better, a larger quantity of sulphuric acid is obtained and the consumption of nitric acid is smaller. The production of fused saws and slags in the furnace is also diminished. In Figs. 55 and 56 is shown a kiln with grates, which has been used in Freiberg for the roasting of matte containing 20 to 21 per cent. sulphur and has a capacity of 900 to 1,000 kilograms in 24 hours. A is the shaft; *a* is the charge opening, 12 inches in diameter, covered with an iron plate; *b*, three large openings, 15 inches long, 12 inches high; *c*, three rows of canals, which are 8 inches long and 4 inches high; *d*, three discharge openings on each side of the furnace, 24 inches long and 12 inches high; *e* is the grate, F is a canal for the introduction of air under the grate; and *g*, the canal for the escape of the sulphurous vapours.

The Freiberg Pyrite Burner.—A transition from the metallurgical kilns to the burners of to-day is represented by the Freiberg kilns for roasting coarse metal, shown in the accom-

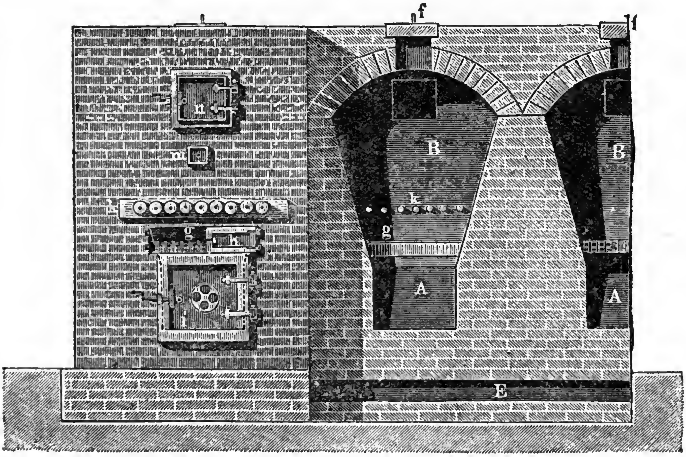
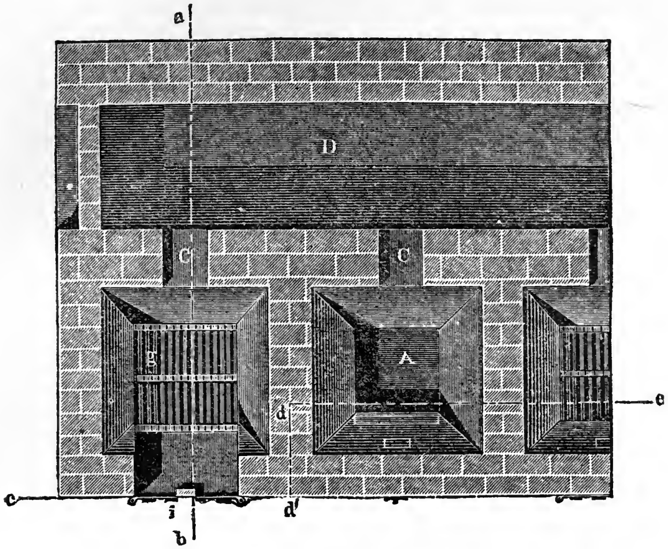
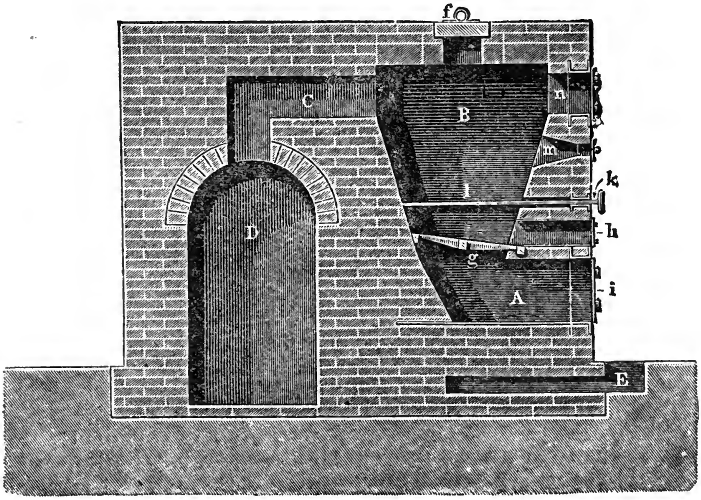


FIG. 57.—FREIBERG PYRITE BURNER. Elevation.



Plan.



Section.

FIGS. 58 AND 59.—FREIBERG PYRITE BURNER.

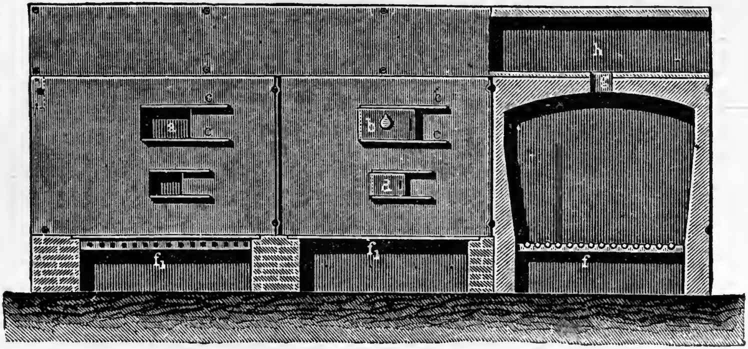
panying illustrations. Fig. 57 shows the appliance in elevation on a scale of 1 to 50; Fig. 58 in plan; and Fig. 59 in section.

This burner is specially adapted for easily burning ore, B is the shaft, *f* the charging hole, furnished with a tightly closing cover. The grate, *g*, is inclined, in order to facilitate the drawing through *h*. The smaller pieces fall through the grates into the ashpit, *A*, and are emptied from time to time through the door, *i*, furnished with holes for the supply of air. About 10 inches above the grate the front wall of the burner is pierced by a horizontal row of holes, *k*, in which stuffing boxes are fixed for movable round iron bars, *l*. These can be used for loosening the ore; they also serve for supporting the higher lying portion of ore on withdrawing the cinders. The door, *m*, serves for observing the combustion (which, however, can only be judged of properly from the top), and for introducing a poker in case the ore must be broken up. The larger opening, *n*, likewise with a door, serves for the same purpose. The gases from C pass first into the large main flue, D, which at Freiberg is 330 feet in length, here they deposit dust, and especially arsenic, and then pass on to the acid chambers. The canal, E, serves for keeping the ground moisture from the burners.

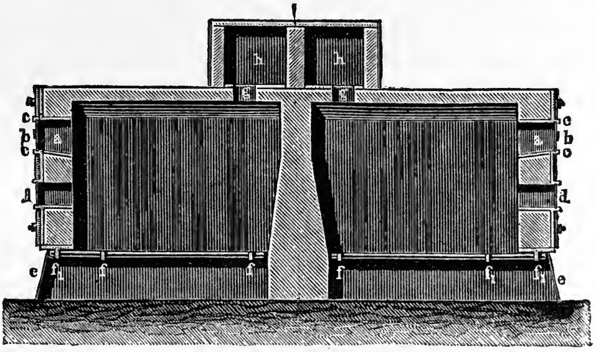
The English Pyrite Burners* have a moderate horizontal section, say 4 feet long in front by 4½ feet in depth, on the grate surface. The inner walls are sometimes vertical, usually the side and back walls slope upward as far as the working door, and then become vertical again. The front wall is covered with iron plates, in which are left the openings for the working doors. The ashpits have also vertical walls, but generally they slope downward so as to facilitate their cleaning out. The depth of the ashpit varies from 16 to 24 inches; the level of the working door, which determines the height of the charge, varies between 20 to 30 inches above the grate. From the top of the ore charge to the centre of the arch a height of 18 to 24 inches is left. They are generally constructed back to back which saves a wall, keeps the heat together, and permits one canal to be utilised for two rows of burners.

The gas canals are built on top of them, and communicate with the shafts by means of openings 4 to 5 inches square. The grate bars which are employed are so constructed that they allow of an easy regulation of the draught and the discharge of the furnace.

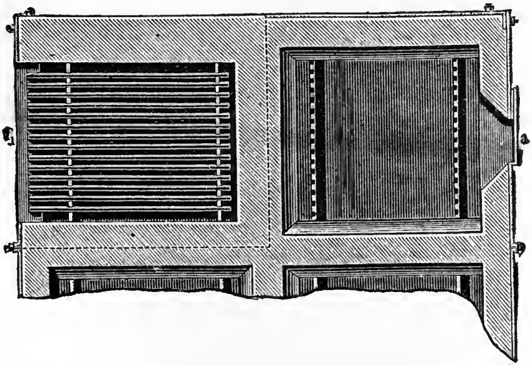
* Dr. George Lunge.



Plan and Section.



Transverse Section.



Plan at Grates.

Figs. 60, 61, and 62.—The English Pyrite Burner.

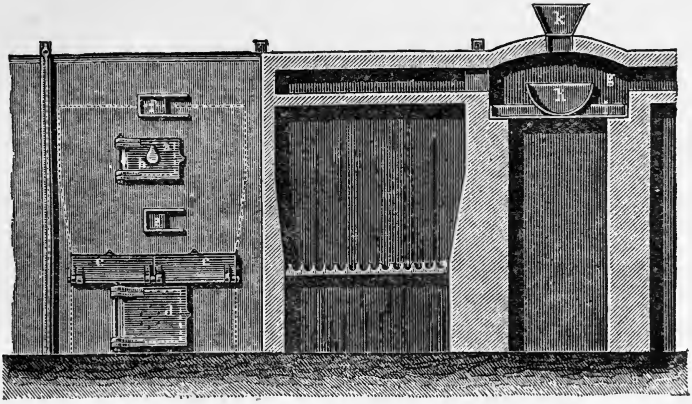
The portion of the kilns which are exposed to heat are lined with fire-bricks, laid in fire-clay; but in the colder portions the mortar is mixed with tar. They have to be strongly braced.

These kilns are generally constructed in groups. Ordinarily 12 to 24 of them are served by the same shift, and the work is so regulated that the kilns are filled and emptied in rotation, so as to maintain a uniform gas development. As will be seen from the plans and sections, each kiln is independent of the other, and have no communication with one another; but by means of flues built in the arches they empty into the main canal. Each shaft ought also to have its own damper.

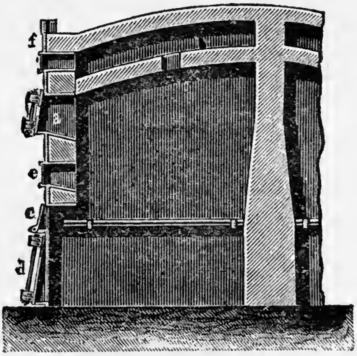
The Figs. 60, 61, and 62 show a simple construction of burner, which can be made with open sand castings. In Fig. 60 are two burners in front elevation, and one in section. In the left-hand furnace the doors of the working opening and ashpit are taken away. Fig. 61 is a cross-section, showing two rows back to back; *a* is the working opening, with the door, *b*, which slides in the grooved ledges, *c*, *c*, cast to the front plates. The small door, *d*, only to be used exceptionally, is arranged in precisely the same way. The openings of the brickwork are protected by iron plates; *e* is a movable cover of the ashpit, provided with air holes; *f*, *f* are the grate bars, the front bearer, *f*, at the same time carries the bottom plate for the front wall, and is perforated with round holes; whilst *f*, *f* are cut out in semicircles. The arches are sprung parallel with the working doors, and by the draught holes, *g*, *g*, are in connection with the gas flues, *h*, *h*. The latter, like the burners, are encased in metal plates; they are covered by fire-tiles.

To operate such a burner it is necessary to lay on the grates (Fig. 62) a layer of roasted lump ore, and on top of it the fuel is dumped and set on fire. After 12 to 24 hours the kiln becomes red-hot, and the pyrites are charged. In a short time they commence to burn, and the sulphur gases are let into the lead chambers by opening the damper leading to them, which is kept shut down during the heating of the kiln. Care must be taken to give sufficient air during the operation; otherwise, instead of producing sulphurous acid, sublimed sulphur will be obtained in the flues and chambers.

Improved Form of Kiln.—Another English pyrite burner, of improved construction, is shown in Figs. 63 and 64, in front elevation, longitudinal and transverse section: *a* is the working door, with a slide, *b*, to observe the working of the furnace ; the working door is fixed to an iron frame, which is set at an angle into the brickwork. In the same manner the doors, *c*, *c*, of the grate are arranged, and *d* for the ashpit ; whereas the small working door, *e*, and the door, *f*, of the flue, which is seldom opened, are arranged in the same manner as the doors in Fig. 65. At *g* is shown the canal for holding the saltpetre pots, *h*, resting on the plate, *i* ; and at *k* is a funnel for the introduction of the sulphuric acid and saltpetre into the pots.



Elevation and Section.



Transverse Section.

FIGS. 63 AND 64.—IMPROVED ENGLISH PYRITE BURNER.

Operation of the Pyrite Burners.*—When newly constructed and before they are put into operation, it is first of all necessary to dry them by a slow fire; and to effect this the grate is covered to a depth of four or more inches with lumps of roasted ore; the damper in the flue is closed and the working door is opened. Some kindling wood, cord wood, and coals are charged and set on fire, which is kept burning from 12 to 24 hours; at the expiration of which the first charge of raw ore is given, and the sulphur will be set on fire by closing the working door and opening the damper of the flue, so that the sulphurous gases can pass into the lead chambers.

In some of the English factories, the dampers and other openings are closed on Saturday night and opened again Sunday night, and the furnaces keep their heat so well, that the sulphur of the fresh charges takes fire at once without the addition of any fresh fuel. It has been found that, even after four to six days' interruption, the heat in the furnaces can be maintained, without the addition of fuel, if all the openings are well luted with clay.

In these operations a complete desulphurisation is not aimed at in the burners, but the work is considered satisfactory, if from 4 to 6 per cent. sulphur remains in the residues. The success in the manipulation of the pyrites depends on the skill of the workmen, who ought to stir up the ore occasionally, and who ought to see to it that the ores are regularly distributed over the whole area of the furnace; and for this purpose the grates should be turned at regular intervals, and any large lumps of ore should be broken before charging them into the furnace, and by maintaining a regular draught, the formation of "saws" is prevented. These consist mainly of monosulphide of iron, FeS, and are produced through overheating the bisulphide FeS_2 in the absence of air, which also generates free sulphur. The FeS, being easily fusible, forms large lumps, which ought to be broken up through the working doors. Rich ores should not be burnt in high kilns, but poor ores can be burnt to advantage in shallow ones. If the draught is poor, it will manifest itself at once, by the escape of the gases from every opening; but the draught should not be too strong, as too much air will pass into the acid chambers.

The admission of air is regulated as follows:—After a fresh

* From Dr. George Lunge, "Handbuch der Soda Industrie."

charge has been placed in the burner, the quantity of air required is limited, till the same is well alight, which takes about an hour, after which more air is admitted, and when most of the sulphur is burnt, and hardly any flame is noticed, the draught is cut off and the latent heat of the furnace is allowed to act by itself. Two hours before it is time to charge the furnace afresh, the working door is opened, the charge well stirred, and any lumps of slag removed. If the blue flames appear, it is a sign that the roasting is not complete and more air is admitted. After this, the working door is closed, the small grate doors are opened, the grate bars turned and the cinders discharged. The fresh ore charge should be placed into the furnace as rapidly as possible, and the process follows again its usual course.

After charging afresh the furnace becomes dark, but gradually blue flames appear, disappearing after a few hours; the mass of ore meanwhile has become hot and is bright red. Afterwards the charge becomes cold again, and the glow is hardly noticeable. If a furnace works well, it should be so hot on the outside, about 6 inches below the working door, that one cannot place a hand on it; further down, it should be cooler; and immediately above the grate bars, it should be cold.

It also happens that, owing to bad draught, or an excess of draught, a furnace goes "cold," and the fresh charge has taken no fire at all; in which case hot pyrites are taken from the other furnaces and charged into it.

Where the quantity of pyrite fines is large, and no provision has been made to roast them separately, and it is desired to burn them together with the lump ore, it is customary to form them into balls or bricks, and for this purpose the powdered material is intimately mixed with plastic clay. They are then moulded and dried by the heat given off by the burners.

At the Freiberg works the fines are wetted down with dilute sulphuric acid, a few per cent. of clay is added, and the mass is intimately incorporated and then moulded. The bricks or balls are placed on cast-iron plates, on top of the dust chambers which are connected with the burners. The bricks made in this manner do not fall to pieces so easily as the lump ore does during roasting. The addition of clay, however, has the disadvantage that it retards the burning of some of the sulphur in the artificially formed lumps.

When the ores contain zinc blende and galena, these are converted into zinc and lead sulphate during the burning, and consequently are not completely desulphurised, as these compounds only decompose at a white heat, which is not attained in the pyrite burners; they therefore remain as such in the residues. When the pyrites contain gypsum or carbonate of lime, a corresponding quantity of calcium sulphate remains in the residues.

The principal improvements which have been introduced in these burners are: (1) The use of an air jacket which serves either to prevent radiation of heat, keeping the burner room cool and rendering the work of serving the burners less arduous, at the same time conserving heat for concentration of acid in pans on the top of the burners. (2) The method of holding in position the grate bars so that they may be drawn and replaced. (3) In making all the flues and openings into flues airtight, since all air admitted to the burners or flues, except where it will aid combustion and will be under complete control, is of great detriment to the process, and renders its proper regulation difficult.

CHAPTER XV.

FURNACES FOR ROASTING FINE MATERIAL.

THE furnaces employed for this purpose—both for oxidising and for chloridising roasting—may be divided into half-a-dozen classes, as follows:—

(1) *Ordinary reverberatories*, or open hearth furnaces, which heat the product by a direct flame; or, to prevent the material from becoming overheated when an easily fusible ore is being treated, a modification is sometimes introduced, whereby a protecting curtain extends from the bridge to about the middle of the furnace, so as to prevent contact of the flame with the ore.

(2) *Reverberatories* in which the material is first heated from below, and then from above, direct.

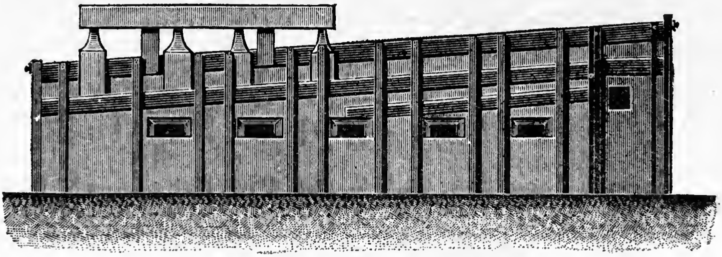
(3) *Muffle furnaces*, in which the material is heated through the brick work.

(4) *Reverberatories* with a rotating hearth and mechanical stirrers, as arranged by Gibb and Geltsharp.

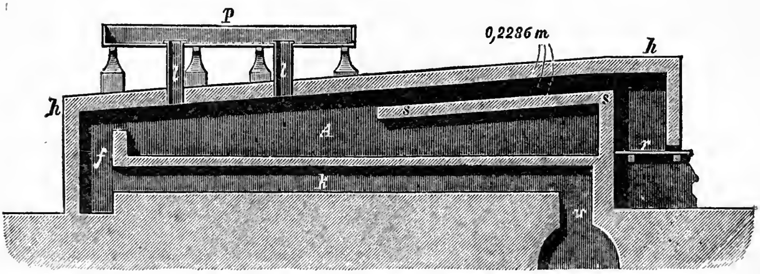
(5) *Shaft and shelf furnaces* of various types, like Perret and Olivier's and Helbig's, Maletra's, and others. In the shelf furnaces, a number of short hearths of moderate width are superimposed one above another, the ore being fed to the top hearth, and moved down one hearth to another below until the ore is discharged, burnt out, from the lowest hearth, or the shelves are all charged simultaneously, and roasted at one and the same time; and as the shelves are placed a short distance

one from the other, the heat is localised by reflection as fully as possible.

(6) *Mechanical roasting furnaces.* These have been brought to a great state of perfection, and several of them will be found fully described in the present chapter.



Elevation.



Longitudinal Section, showing Protecting Curtain.

Figs. 65 and 66.—Reverberatory Furnace of the Bede Metal Company.

Reverberatory Furnaces.—Furnaces of this class employed by the Bede Metal Company at Hebburn-on-Tyne, in England, are shown in the accompanying illustrations, Figs. 65 to 68.*

It will be noticed that in these furnaces a protecting arch or curtain extends from the fire bridge nearly to the middle

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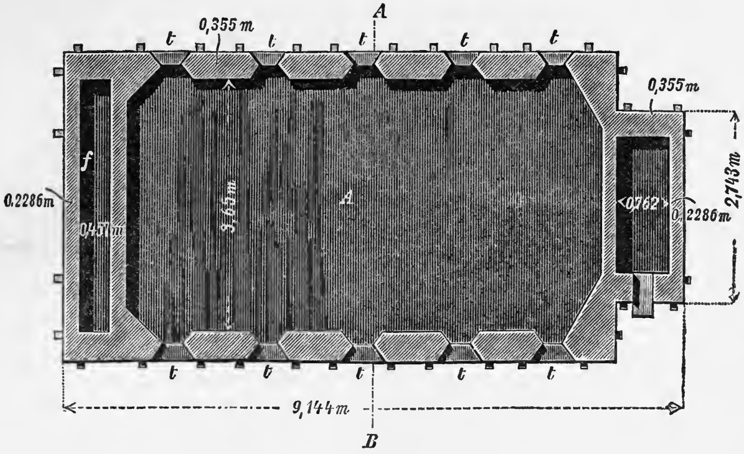
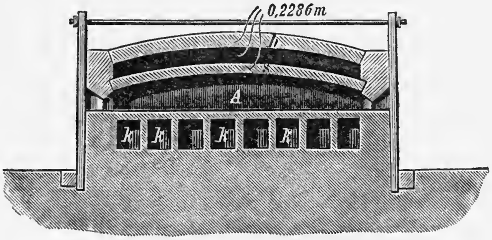
* Carl A. Balling, "Die Metallhüttenkunde," Berlin, 1885; *Dingler's Journal*, Bd. 204, p. 308; *Berg und Hüttenmännische Zeitung*, 1872, p. 345, and 1882, p. 232.

of the furnace, which prevents the ore from becoming too strongly heated. At *r* is the fireplace; the flame passes into the space between the curtain and the main arch, *h*, and then over the hearth, *A*; and from thence the flame passes through the flue, *f*, into eight canals, *k*, which are under the hearth floor, and then passes into a subterranean flue, *u*, which leads to the acid condensing tower. The working doors are shown at *t*, *t*; *p* is an iron pan for preheating the ores, and *l*, *l*, are tubes, through which the ores are dropped into the furnace, which holds 2·8 tons; and the roasting lasts 8 hours.



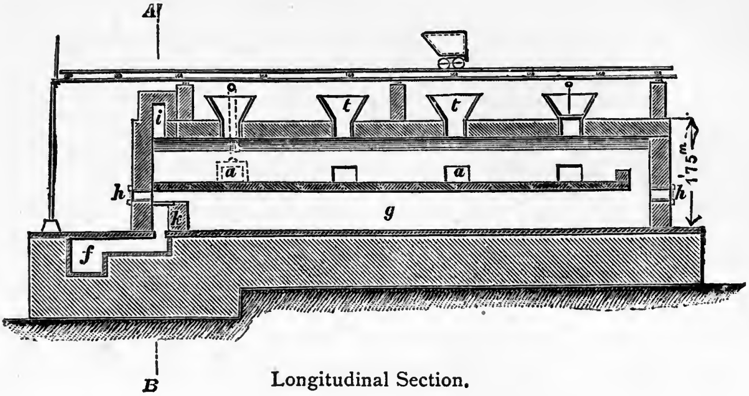
Plan.



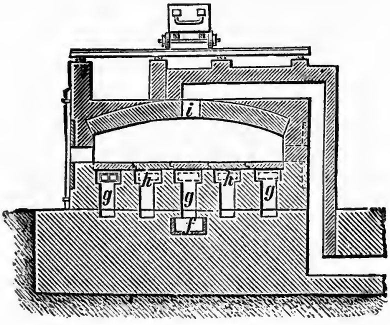
Transverse Section.

FIGS. 67 AND 68.—REVERBERATORY FURNACE OF THE BEDE METAL COMPANY.

At Widnes, in Lancashire, a furnace is employed (shown in Figs. 69 and 70), which is fired by gas. A similar furnace was formerly in use at Oker.



Longitudinal Section.



Transverse Section.

Figs. 69 and 70.—Roasting Furnace at Widnes.

From the gas generator, not shown in the drawing, the gase pass into a canal, *k*, through which it is distributed into five canals, *g*, which are built in longitudinally under the hearth, and they mix here with atmospheric air which is admitted at *h* by means of dampers and set alight, and then passes into the working space. Through the flue, *i*, the roast gases pass into a canal, which leads to the condensing tower filled with coke, where the volatile chlorides are absorbed. These furnaces have four working doors, *a*, on each side, and four hoppers, *t*, for charging the ore; they have a capacity of 2·5 tons, and two charges are roasted in 24 hours.

Reverberatories with Rotating Hearths.—An example of this class of furnace, also employed by the Bede Metal Company, is illustrated in Figs. 71 to 74.*

The movable hearth consists of a round pan made of boiler iron *z*, *z*, which is lined with fire bricks, *y*. The pan rests on the shaft, *w*, rotating in the socket, and is fixed with a box supported by the two iron tubes, *x*. The socket which rotates the pin forming the end of the shaft, *w*, is constantly oiled by a small pump operated from the main engine; the surplus oil running back into its reservoir. The rotation of the hearth is effected by means of an endless chain working in the groove of the pan. The chain is kept in motion by means of the shaft, *v*, *v*, which is turned by the pulleys, *u*, *T*. The rotating hearth has above it the arched dome, *s*, and the sides, *r*, are made of brick. *R* is the fireplace and *M* the flue, through which the gases pass into the condensing tower.

Between the pan and the brickwork of the furnace is a space an inch wide, which permits the free movement of the hearth, and also the admission of the air that is required for the roasting. The charging is effected through the opening, *O*, in the arch of the furnace, which can be closed when not in use. The stirring of the ore is effected by means of the plough, *P*, which moves slowly in a radial direction backward and forward. By the simultaneous rotation of the hearth and the movement of the plough, which at every single revolution of the hearth passes from the centre to the periphery, the roast product is sufficiently stirred to come in contact with the air. The movement of the plough is effected by means of the endless screw, *K*, working into the toothed gear, *A*, *L*. The toothed wheel, *L*, transmits the movement by means of a crank pin and connecting rod, *N*, to a lever, which by means of the cross head, *g*, puts the plough, *P*, in a straight-line motion communicated to it by the rod, *D*.

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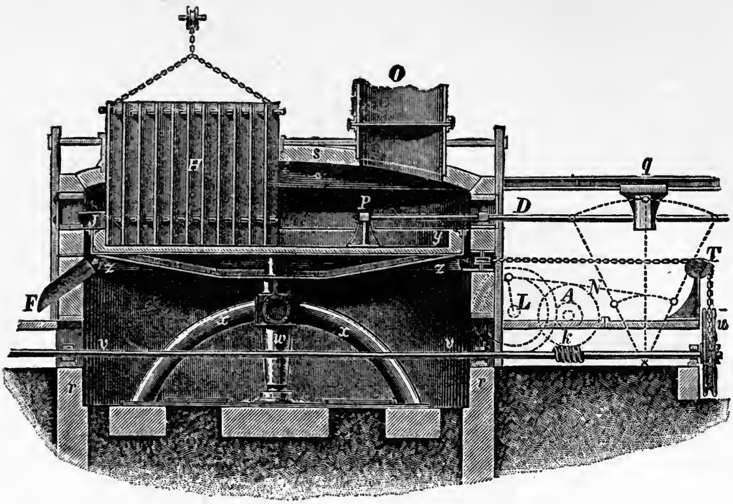
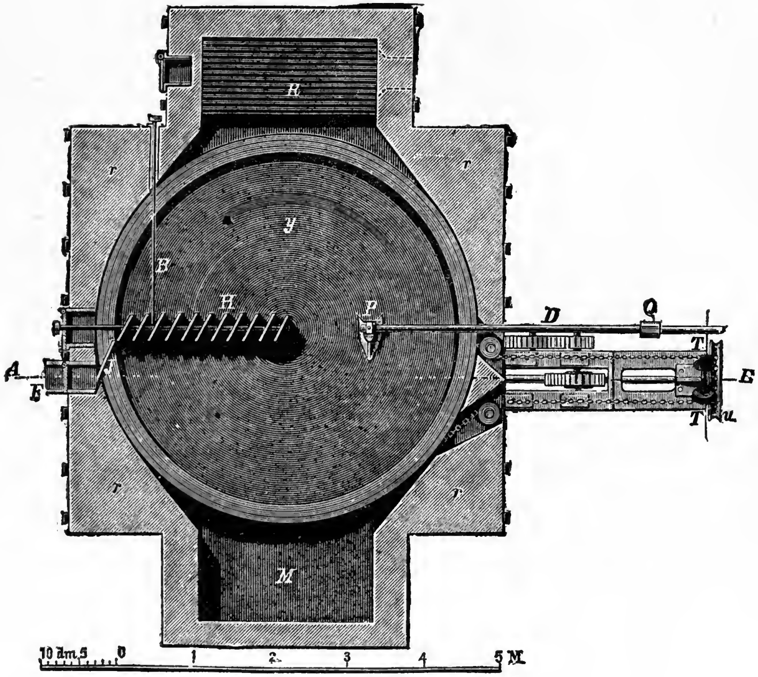
* *Dingler's Journal*, 204, p. 308; *Berg und Hüttenmännische Zeitung* 1872, p. 345, and 1882, p. 232; Jun, *Contarets Annaler*, 1882, 2; Dr. C. Schabel, "Die Metallhüttenkunde," 1894.



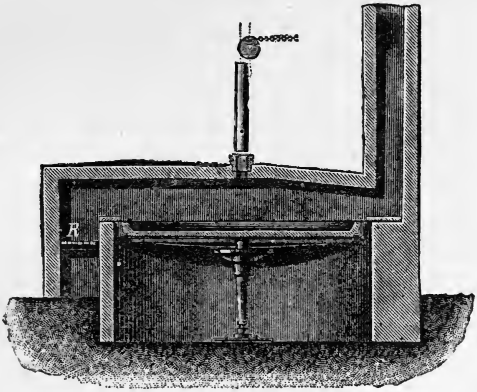
Section.



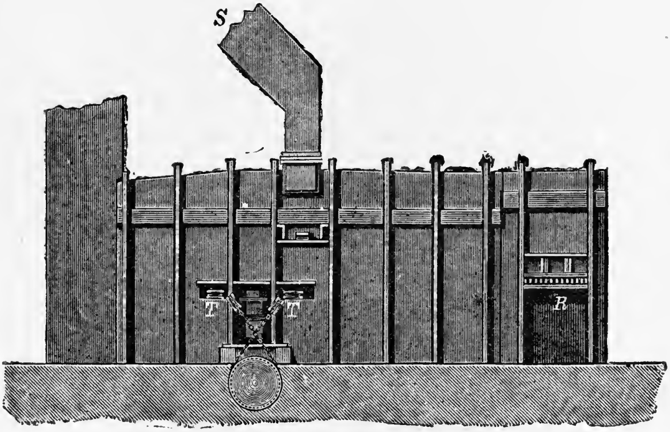
Plan.

FIGS. 71 AND 72.—ROASTING FURNACE WITH ROTATING HEARTH, AS USED BY THE BEDE METAL COMPANY.

The discharging of the furnace takes place by means of a grating, *H*, which is suspended during the roasting operation



Transverse Section.



Elevation.

Figs. 73 and 74.—Roasting Furnace with Rotating Hearth, as used by the Bede Metal Company.

outside of the furnace, and when the same is to be discharged, it is passed through an opening by means of a chain on to the hearth; the opening can be closed when not in use. The grating is composed of a series of strong, boiler-iron plates, placed parallel to one another. They are fastened together and placed in such a manner that they stand diagonally in the furnace. The grate is held in position by the iron bar, *B*.

As the hearth rotates, the ore passes through the interstices between the plates and is pushed ahead, owing to the diagonal position of the plates, in such a manner that it is pushed to the periphery of the hearth, till it arrives at the plate, *J*, where a certain quantity passes out of the gutter, *F*, at every revolution. The cast-iron plough is renewed every 14 days.

Twelve of these furnaces were operated by two steam engines, each of 18 effective horse-power. In one furnace in 9 hours, 5 tons of ore are roasted with 7½ per cent. salt. They give an even roasting as their operation does not depend on the skill of the workmen; and give a larger quantity of salts soluble in water than the furnaces operated by hand labour

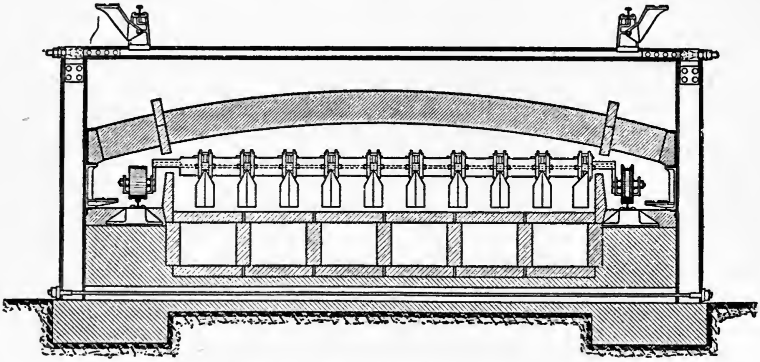
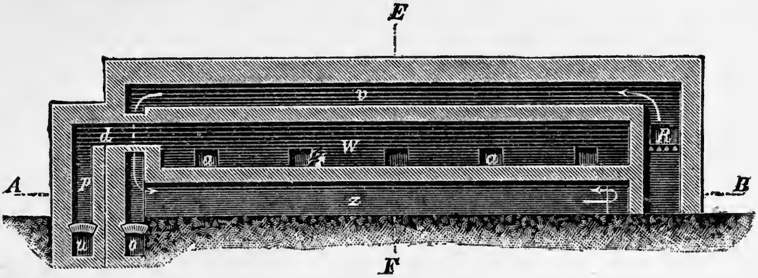


FIG. 75.—MUFFLE FURNACE WITH MECHANICAL STIRRERS (FRASER & CHALMERS).

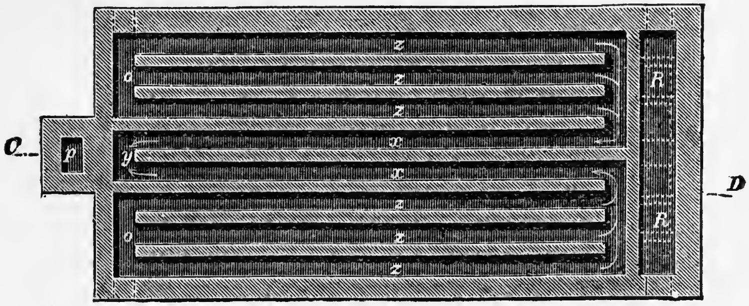
Muffle Furnaces.—These furnaces are closed reverberatories, so constructed that the products of combustion from the fuel are not allowed to mix with the gases evolved from the ore. Such a furnace may consist of one long continuous muffle, or several muffles arranged in tiers, one above the other.

Muffle furnaces are used for roasting pyritic ores when it is desired to collect the sulphurous acid fumes free from any admixture with foul gases and excess of air, for the manufacture of sulphuric acid. They are also constructed with mechanical stirring gear, and are then of large capacity.

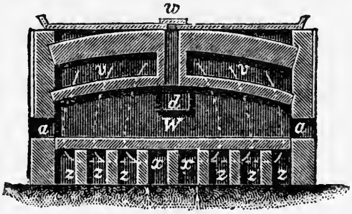
The high cost of their construction, and the greater consumption of fuel, are adverse to their general employment; and although under certain circumstances, when a gentle and regular heat is required, they offer certain advantages, it is only rarely that they are found in actual use.



Longitudinal Section.



Plan.



End Elevation.

Figs. 76 to 78.—Muffle Furnace used by the Tharsis Company.

Fig. 75 shows a cross-section through a Brown muffle furnace, as constructed by Messrs. Fraser & Chalmers. The hearth is arranged to be heated by "producer" gas. The large spaces directly beneath the hearth are combustion chambers where the fuel gases are burnt. In other respects the furnace is like the Brown "straight roaster," described hereafter.

A muffled furnace employed by the Tharsis Sulphur and Copper Company is shown in Figs. 76 to 78. *R*, *R*, are two fireplaces, *W* is the muffle. The flame passes first in the canals, *v*, above the muffle, then passes downwards and through the canals, *z*, *z*, under the muffle in an opposite direction, and in two branches through the canals, *x*, *x*, and the vertical canal, *y*, into the flue, *o*, to the chimney. The roast gases, which contain chlorine and hydrochloric acid, pass from the muffle through the flue, *d*, and the vertical canal, *p*, into the canal, *u*, leading to the condensing towers; *a*, *a*, are working doors on both sides. On top of the furnace is an iron basin in which the ore and salt are heated; and these are dropped through the openings, *w*, into the muffle. These furnaces require twice as much fuel as the reverberatories, but they furnish concentrated roast gases. It requires 12 hours to roast a charge. The liquors, which are obtained in the condensing towers consist of diluted hydrochloric and sulphuric acid. The sulphurous acid from the roast gases is converted by the chlorine into sulphuric acid.

As already intimated, the operation of muffle furnaces is costly, and in many localities they have been altered in such a way that the burning of the lump ore is effected in a separate furnace, and the heat generated by this operation conducted around the muffles which contained the fine ore.

Such a furnace has been designed by Perret and Olivier, in which the lump ore is burnt on a grate in the lower portion of the shaft; and the upper portion of the shaft is arranged to receive a number of fireclay tiles, placed one above the other. The fine ore is put upon them in layers two inches thick, and is ignited and burnt off by the hot gases given off in the burner below.

Other furnaces have been designed which do away with the burning of the lump ore and burn only the fines; and among them are those of Gerstenhöfer, Hasenclever, Maletra.

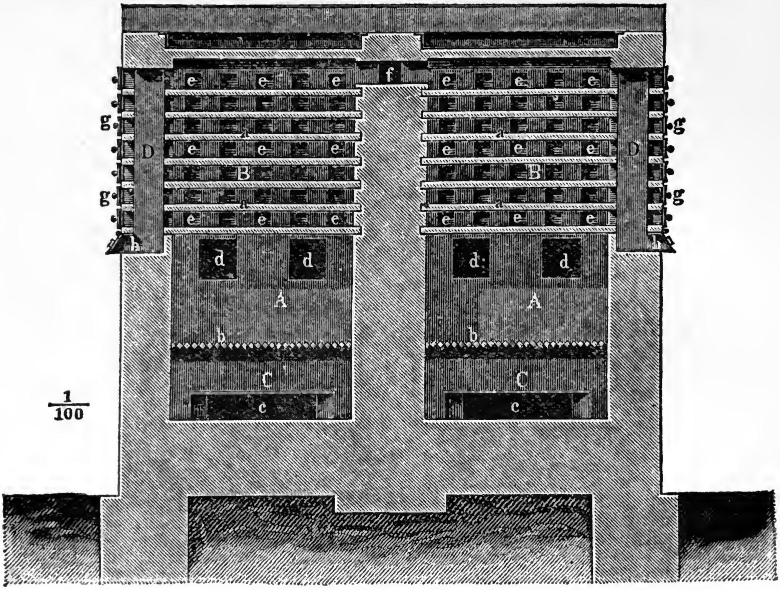
These furnaces are applied for the roasting of sulphides where the utilisation of the fumes for the manufacture of sulphuric acid forms a part of the process of calcination. Their design is such, that the gases arising from the oxidation of the ores are kept separate from the products of combustion of the fuel, and a high degree of perfection has been arrived at in their construction.

Shaft and Shelf Furnaces.—A shelf furnace designed by Perret and Olivier is shown in Figs. 79 and 80, on a scale of $\frac{1}{100}$, Fig. 79 being a longitudinal section, and Fig. 80 a vertical section.

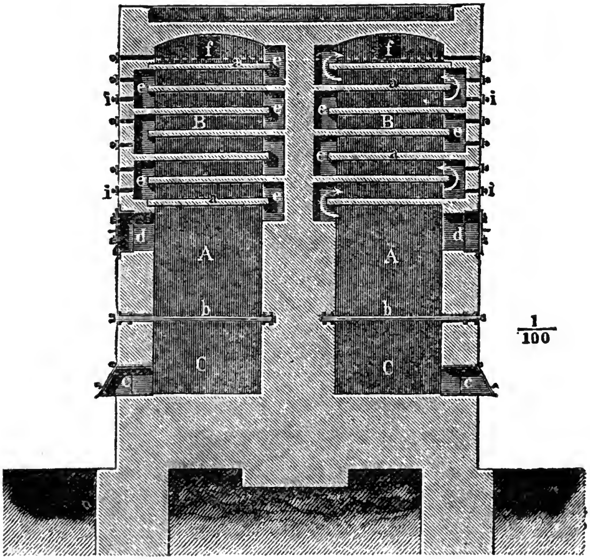
Four of these furnaces are built into a block. In the lower portion, A, are burnt the lump pyrites on the grate, *b*; *C*, is the ashpit with the working door, *c*, and the admission of air is regulated by means of small ventilators. The openings, *d*, serve for the introduction of the ore. The upper portion, B, serves for the roasting of the fines. A series of fireproof tiles, 3 inches thick, are arranged in shelves, and the fines are placed on them 2 inches thick, and these are set on fire by the burning of the lump ores in the lower portion of the furnace. The hot gases from *A*, pass through canals, *e*, in the walls of the furnace which are shown in the figures, over the shelves in the direction of the arrows, and the gases pass through the flue, *f*, to the lead chambers.

The small holes, *i*, Fig. 80, which are closed with clay stoppers, serve for observing the roasting. The openings, *g*, Fig. 79, which are covered with iron plates serve for the introduction of the "fines," and also to discharge them after roasting into the canal, *D*. During the operation of roasting, the canal, *D*, is filled to the top with roasted ore, and this forces the gases to take the course indicated by the arrows over the various tiles. When the furnace has to be charged again, the canal, *D*, has to be emptied, through the door, *h*, and then the door is closed again and the fines from the lowest tile are drawn first into the canal, *D*, whose dimensions are so figured out, that it will hold the charge on the tile to the level of the same. Now the lowest tile is charged with fresh "fines" and the corresponding opening, *g*, is closed, and the roasted ore from the second shelf is drawn into the canal, *D*, and the same is filled to the level of this second shelf. In this manner the operation is continued, till all the shelves are covered with fresh ore. Experience shows that 50 parts fines are roasted by 50 parts lump pyrites. The sulphur remaining in the ore amounts to 5 per cent.

The furnace shown here has seven shelves and is 6 metres high from the floor level. The distances between the shelves has been reduced in some constructions from 20 centimetres to 10 centimetres, with a corresponding reduction in the height of the furnace.



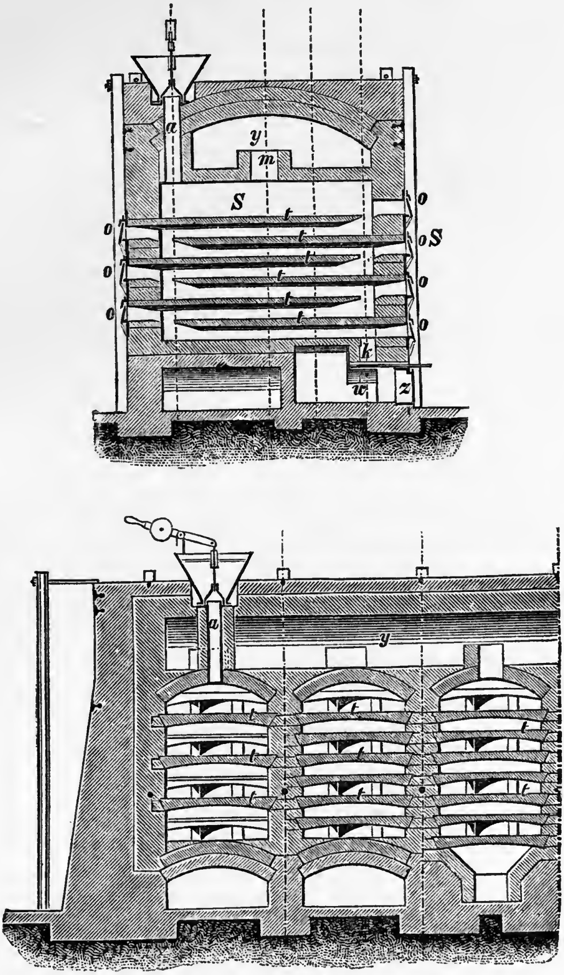
Longitudinal Section.



Vertical Section.

Figs. 79 and 80.—Perret and Olivier's Shelf Furnace.

Maletra's Furnace.—This is also a shelf furnace, constructed with fire-clay tiles, which are placed at certain distances one from the other, and arranged in such a manner that the ore, which is charged on the top shelf, has to pass over all the other shelves and is finally discharged in a roasted condition. Before the furnace is put in operation the same is brought to



Figs. 81 and 82.—Maletra's Furnace.

a red heat, by burning fuel in the same on all the shelves, and when thoroughly heated the furnace is charged with ore, and the roasting proceeds by itself, as through the oxidation of the sulphides the necessary roasting temperature is maintained. Consequently a combination of a shelf with a lump furnace is not intended in this construction.

Every shelf has its own working door, and the construction of the furnace is shown in the Figs. 81 to 83: *S* is the shaft; *t*, *t* are the shelves; *a* is the opening, provided with a hopper, for the charging of the ore on the top shelf; *o*, *o* are the working doors for the respective shelves, and these are opened when stirring the ore or when transferring it from one shelf to the other. The roasted ore is drawn through the opening, *k*, into the space, *w*, from whence it is withdrawn through *z*. The roast gases pass through the opening, *m*, into the canal, *y*, which leads them into the dust chambers, *f* (Fig. 83), and from them into the canal, *p*, which leads to the acid chambers.

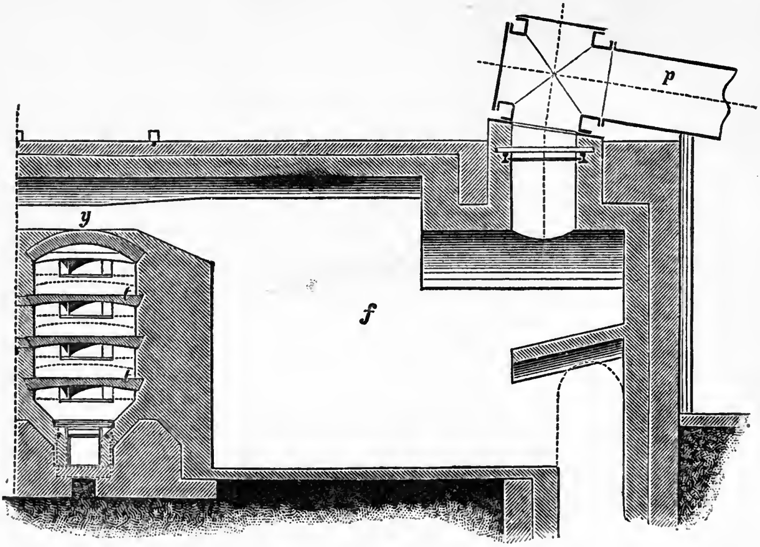


Fig. 83.—Maletra's Furnace.

CHAPTER XVI.

MECHANICAL ROASTING FURNACES.

THE most important types of this class of furnace are the Herreshoff roasting furnace, the Pearce turret furnace, the improved Spence furnace, and the Brown horseshoe furnace ; and among the mechanical furnaces should also be classed the various types of revolving cylinders with continuous discharge, like the White-Howell ; as well as the Bruckner cylinders with intermittent discharge.

The Herreshoff Roasting Furnace.—This furnace consists of a series of superposed chambers or floors, furnished with rakes or stirrers and feeders, by means of which the materials under treatment are fed continuously through the series of chambers, whilst being submitted to the burning or calcining process.

As will be seen from Fig. 84, the rakes are fixed to a main shaft, passing vertically the chambers, which are provided with openings or passages from chamber to chamber, alternately at the centre and at the periphery, so that the materials are passed by the rakes across each floor and from chamber to chamber, until finally delivered out of the furnace by an outlet in the bottom.

Fig. 84 represents a vertical transverse section through the furnace. Fig. 85 is a plan with a view of the floor thereof, taken on the line 2, 2 of Fig. 84. Fig. 86 is a plan view of a tile forming part of the trays, and Fig. 87 a section thereof on the line 4, 4 of Fig. 86. Fig. 88 is a centrepiece or keystone for the tile tray hereinafter referred to, of which the tile shown in Fig. 86 forms a part. Fig. 89 is a plan view of another form of tile for constructing another form of tray. Fig. 90 is a section thereof on line 7, 7 of Fig. 89. Fig. 91 is a view of a keystone for the tile

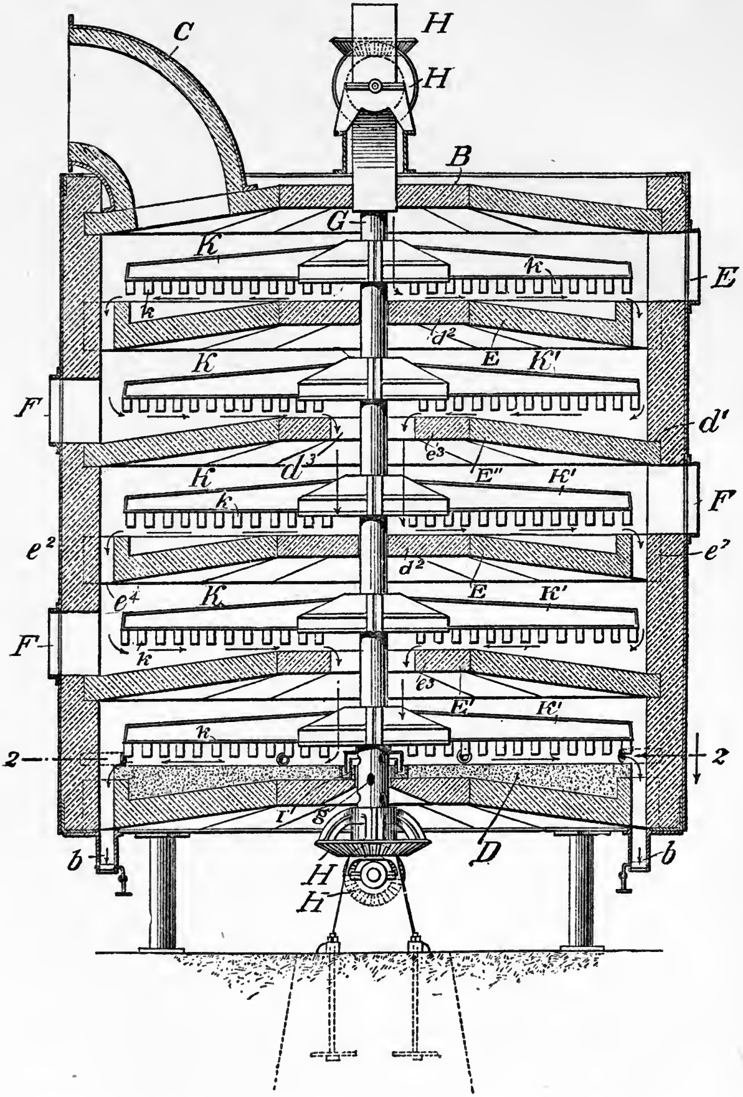


FIG. 84.—HERRESHOFF ROASTING FURNACE. Vertical Transverse Section.

arch or tray constructed of the species of tile shown in Figs. 89 and 90. Fig. 92 is a plan view of a stirrer, showing the details of the stirrer arms in dotted lines. Fig. 93 is a side view thereof,

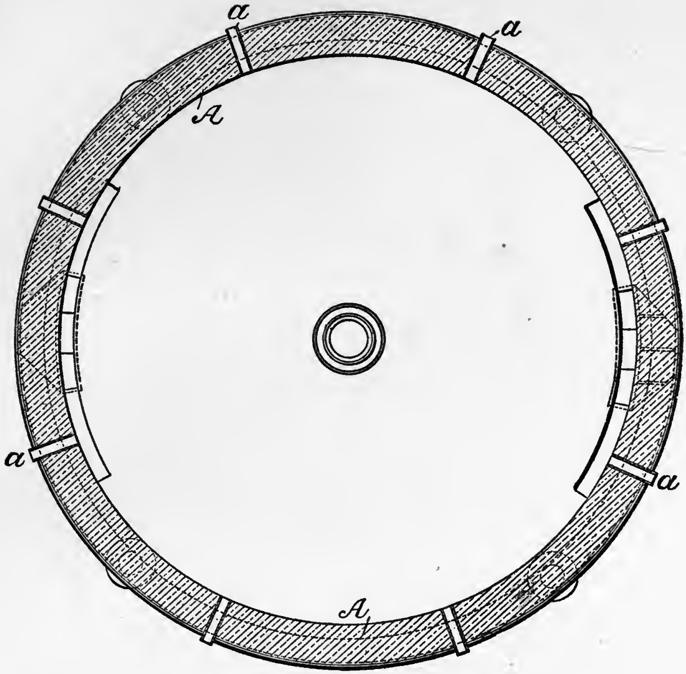


Fig. 85.—Plan.

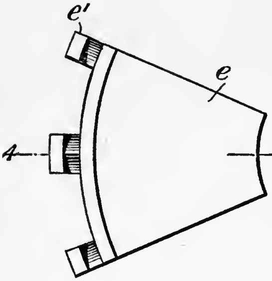


Fig. 86.

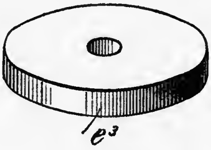


Fig. 88.

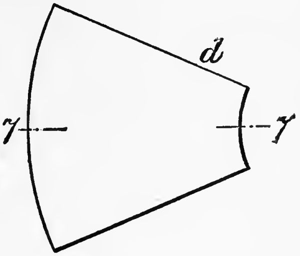


Fig. 89.

Fig. 87.

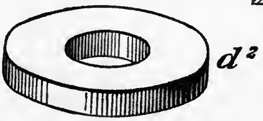


Fig. 91.

Fig. 90.

Figs.—86 to 91.—Herreshoff Roasting Furnace. Details.

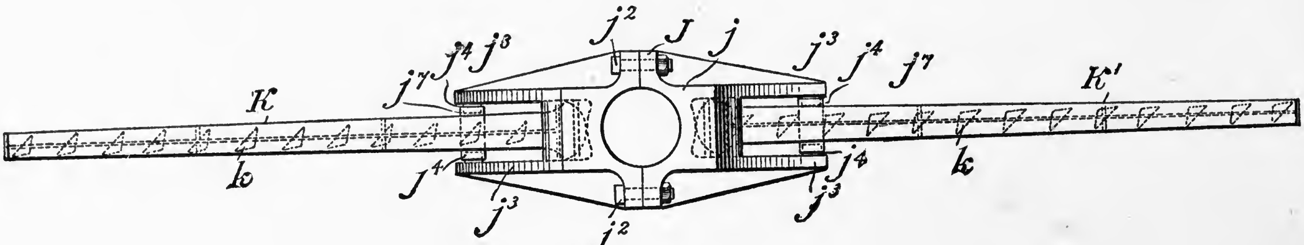


FIG. 92.

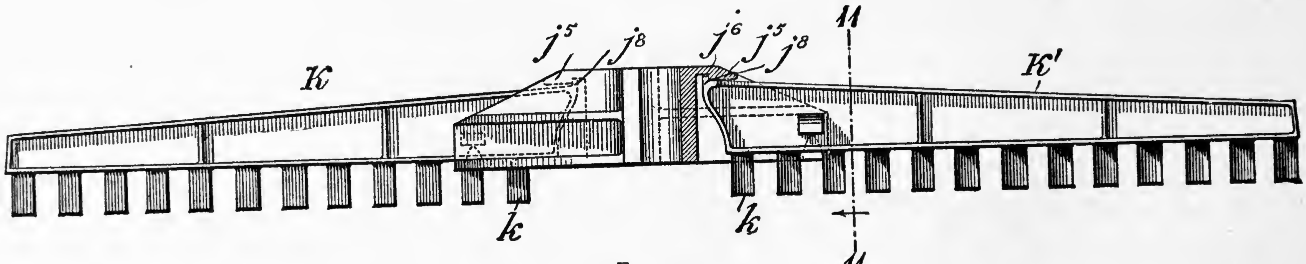


FIG. 93.

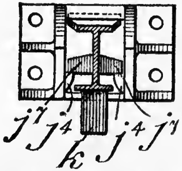


FIG. 94.

FIGS. 92, 93, 94.—HERRESHOFF ROASTING FURNACE. Details.

partly in section, the section being taken through the hub of the stirrer, and serving to exhibit the detailed construction and connection of a stirrer arm with a hub. Fig. 94 is a section on line 11, 11 of Fig. 93, looking in the direction of the arrow.

The furnace is cylindrical, and A represents the walls. B is the roof, which is pierced for the reception of an exit pipe, C.

D is the floor of the furnace, and E, E′ are trays or roasting floors superposed one above the other. These roasting floors are differently constructed, according to the location of their exit passages.

The floors, *E*, are constructed of tiles, *e*, which are provided with projections, e^1. These tiles, *e*, have their projections, e^1, built into the wall, *A*, of the furnace, as shown at e^2, and bear against a keystone, e^3, placed in the centre of the furnace. There is a space or passage, e^4, formed by the walls of the furnace and the edges of the tiles, *e*. The floors or trays, *E′* are constructed from the tiles, *d*, shown in Fig. 89.

These tiles, *d*, have their edges built into the wall, *A*, of the furnace, as shown at d', and bear against an annular keystone, d^2, at the centre of the furnace.

It will thus be observed that the several floors or roasting-trays are in communication, the passages for such communication being at the edges of the floors, E, and at the centres of the floors, *E′*.

Openings, *F*, are provided in the wall of the furnace opposite each of the several floors or trays. These openings are suitably closed or covered during operation of the furnace, but may be opened at any time to admit of the ready removal or insertion of a stirrer arm. The lowermost floor of the furnace is provided with exit pipes, *a*, which are pierced laterally through the walls of the furnace, and with draw-off pipes, *b*, which open downward.

The vertical shaft is hollow, so that a large quantity of air is drawn up through it, this amount being increased by the introduction of a sheet-iron stack extended above the top of the furnace. The shafts or pipes employed are 14 inches in diameter. Between each shelf there is a cross channel passing through the shaft at right angles, which is 4 inches wide and 5 inches high, and allows an ample space around it for the passage of the ascending air. Into this channel or socket the arms are inserted. In the top of the channel, at the centre of the vertical shaft, is a pocket running across the channel. Into this a rib at the inner and top edge of the arm locks when the arm is forced into its proper position. The details of the stirring-arms are shown in Figs. 92, 93, and 94.

The central shaft revolves one revolution in two minutes, and the plunger in the feeding apparatus makes two strokes in the same time.

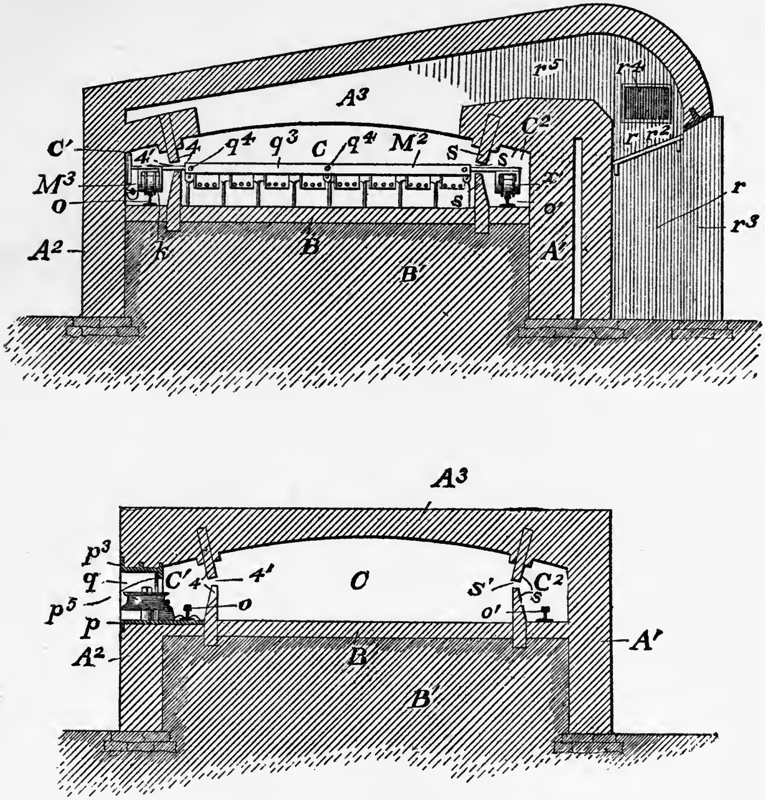
The outside casing of the furnace is ¼-inch steel, and is strongly riveted. The lining inside of this is of red brick, 8 inches in thickness. The outside diameter of the furnace is about 10 feet, and the height about the same.

Each furnace requires from $\frac{1}{10}$ to ¼ horse-power. The principal renewal is due to the corroding or burning out of the arms. Each arm weighs about 100 lb. The life of the central shaft would seem to be almost indefinite, inasmuch as it never reaches a low red heat. No fuel is required after the furnace is once started. The ores ordinarily used are either iron pyrites or iron pyrites containing copper pyrites. Roasting goes on quite satisfactorily with ores containing as low as 30 per cent. of sulphur, and even in some cases as low as 25 per cent. The usual amount of 44 per cent. of ore roasted in a furnace of this size is over 7,000 lb. The roasted ore contains from 2½ to 3½ per cent. of sulphur.

The Brown Roasting Furnace is a single hearth reverberatory, annular in shape, forming a large circle, having an outer diameter of 60 to 80 feet. The hearth proper occupies about four-fifths of the circle, the remaining one-fifth being cut out, and the free space thus formed being used to cool the rabbles. By means of projecting tiles in roof and floor, a narrow gallery is formed on either side of the hearth, which is shown at *S* (Fig. 95), covered with a low arch. In the conduits, C^2 (Fig. 96), formed by the slotted walls and the exterior walls of the furnace, are placed rails, *o*, upon which run trucks, *k*, supporting a stirrer arm, M^2, projecting through the slots. Fastened to that portion of the arm which extends over the hearth are stirrer shoes, resembling miniature ploughshares, which dip down into the ore, lying in a thin layer on the hearth.

The furnace at the fireplace is constructed as shown in fig. 95.

The ashpit is at r, the combustion chamber is at r^1, which are divided from each other by an inclined grate, r^2, the ashpit having a draft and cleaning opening, r^3, and the combustion chamber a fuel feed opening, r^4. Each fire chamber has a flue, r^5, leading to the roasting chamber, *C*, through the roof of the latter. Extending at short intervals through the wall, A^2, at the hearth, *B*, is a series of openings, q, into which are fitted boxes, p. Each box, p (see Fig. 97), is formed with a base plate, p^1, side plates, p^2, and top plate, p^3, and is firmly incased in the wall. Fastened to the base plate, p^1, of each box is a



FIGS. 95 AND 96.—THE BROWN ROASTING FURNACE. Sections.

vertical pin, p^4, upon which a guide wheel, q^1, preferably in the form of a sheave, is mounted to rotate in the horizontal plane. The sheaves, q^1, project a short distance into the chamber, C^1, and the base plates, p^1, extend across or nearly across the chamber, C^1, to the partition, *t*. At the inner side of the box is a removable back plate, p^5, which extends from the top plate down nearly to the sheave. The base plates are constructed to afford rail chairs, on which is mounted a continuous track rail, *o*. Extending around the partition, *s*, in the chamber, C^2, is a continuous rail, o^1.

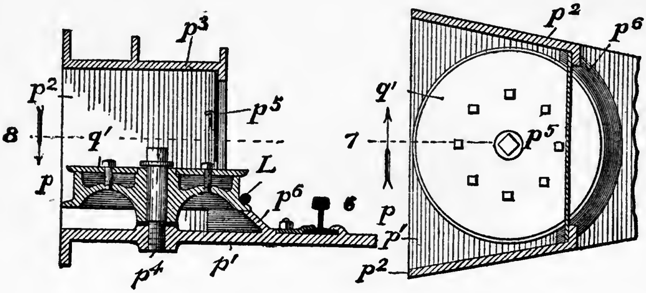


FIG. 97.—BROWN ROASTING FURNACE. Details of Boxes.

The slotted walls are formed by fireclay tiling, which projects upward from the hearth, and by firebrick which project downward (see *S*, Figs. 95 and 96)

The skew-backs of the arch are steel channels supported on short columns, the spaces between the columns being 3 feet 6 inches long by 12 inches high these openings extending the entire length of the hearth, forming a continuous slot on both sides; they are closed by sheet-iron doors lined with asbestos. This construction permits of ready access to the hearth at any point for repairs, etc., without having to tear down the brick construction to get to the interior of the furnace. From the ground to the hearth the furnace may be conveniently built of uncut stone, and the rest of the furnace constructed of brick, the structure bound together by steel I-beams.

Fireboxes, in number and position to suit the length of the furnace and the character of the ore, are provided.

The stirrer carriages are drawn by an endless steel wire

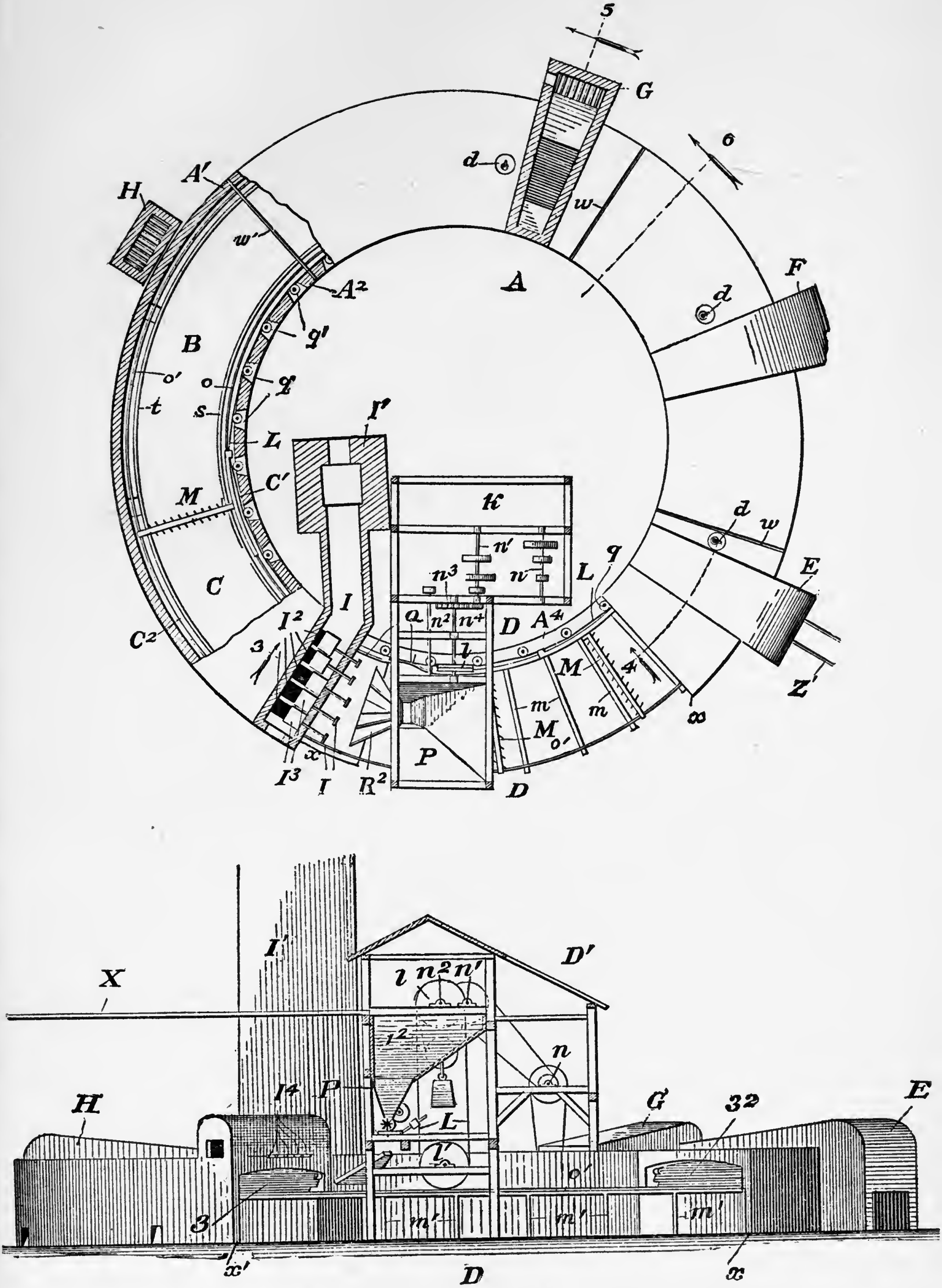


FIG. 98.—THE BROWN ROASTING FURNACE. Plan and Elevation.

rope, which runs in the inner conduit, and is supported on small horizontal grooved wheels placed sufficiently near each other to cause the rope to conform to the curve of the furnace; the rope is driven and kept taut by passing it around a system of wheels driven by a small slidevalve engine provided for that purpose.

Fig. 98 represents a circular furnace. At *E*, *F*, *G*, *H* are the furnaces, located at intervals, around the outer wall, *A*. At the break or open space, *D*, is a frame work, D^1, which supports the ore-feeding mechanism. In the space enclosed by the furnace structure is an engine, indicated at *K*, from which the various moving parts of the construction are operated. Journaled in the framework, D^1, are a drive shaft, *n*, which is belted to the engine, not shown, a shaft, n^1, belted to the shaft, *n*, and a shaft, n^2, carrying a gear wheel, n^3, driven by a pinion, n^4, on the shaft, n^1.

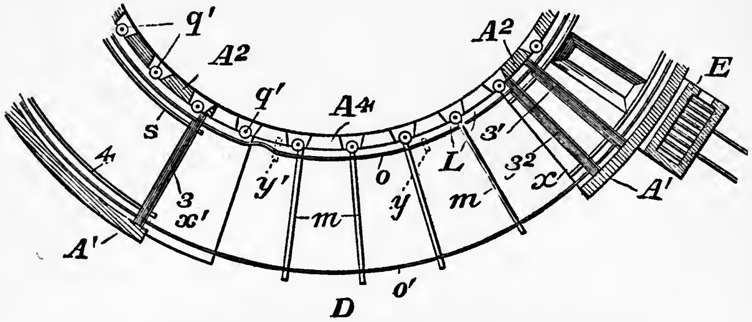


Fig. 99.—Open Space of the Brown Roasting Furnace.

A wall, A^4 Fig. 99, forming the continuation of the wall A^2, extends to the height of the plane at the openings, *q*, across the break, *D*, and the same supports the sheaves, q^1, as indicated in Fig. 98, which complete the circle described by the series of sheaves. The wall, A^4, also supports the rail, *o*, where the latter extends across the break. Forming part of the framework, D^1, are beams, *m*, resting at their inner ends on the wall, A^4, and supported at their outer ends upon posts, m^1. The beams, *m*, also support the track, o^1, where it extends across the break, *D*.

L is an endless cable, which extends around the wall, A^2, in the chamber, C^1, against the sheaves, q^1. The shaft, n^2, in the framework carries a drum, l, and below and parallel with the shaft, n^2, is a shaft carrying a drum, l^1, which extends at the lowest part of its circumference in the plane of the sheaves, q^1. From the sheaves, q^1, at one side of the drum, l^1, the cable passes, as indicated in Fig. 98, under the drum, l^1, to and over the drum, l, thence under the weighted pulley, l^2, back to and over the drum, l^1, to the sheave, q^1, at the opposite side. The weighted pulley, l^2, is suspended from the cable, and thus operates as a tightener for the latter.

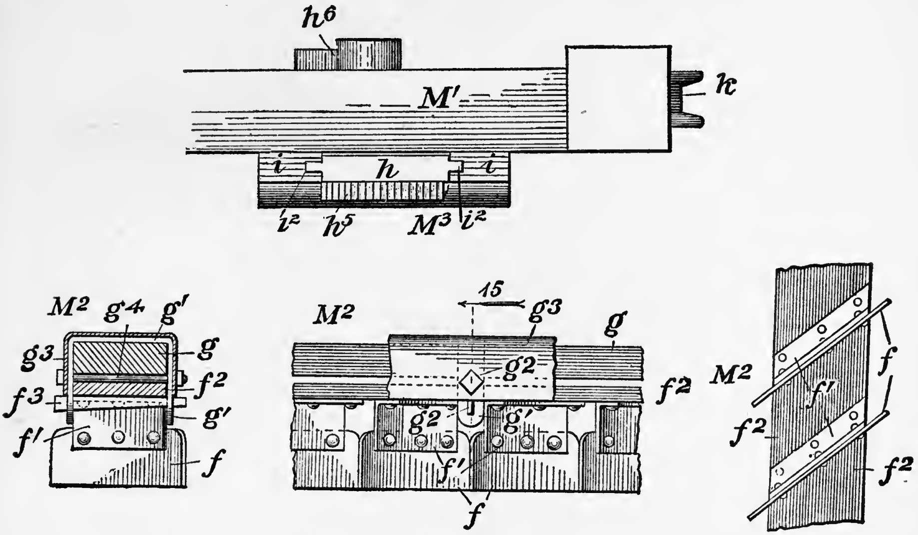
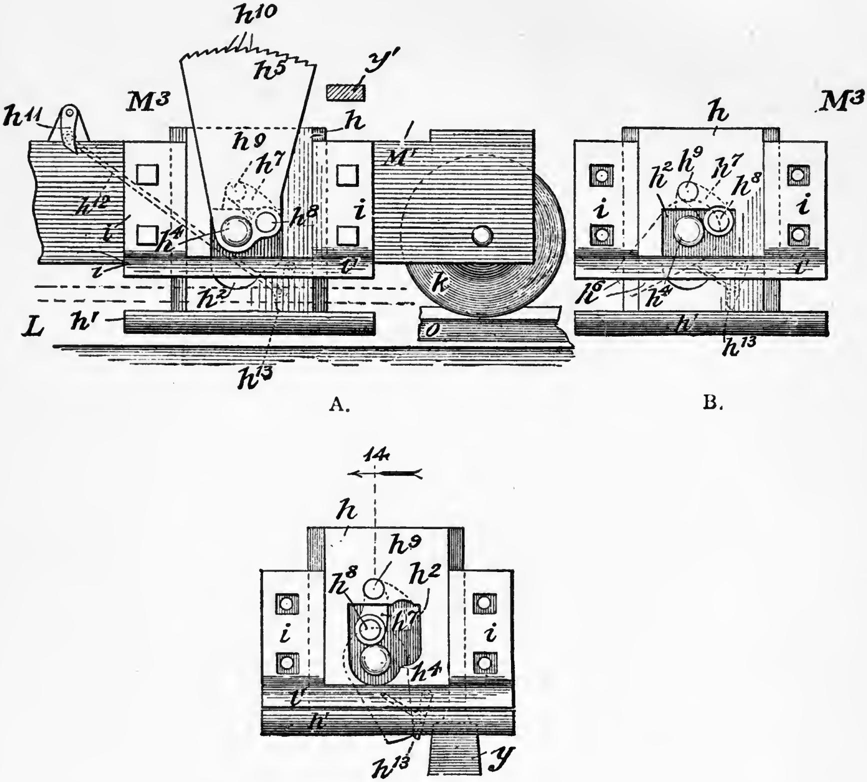


FIG. 100.—STIRRER CARRIER FRAMES OF THE BROWN ROASTING FURNACE.

The stirrer carrier frames, M, M, are of T shape, each comprising a head bar, M^1, and an arm, M^2 (see Fig. 100).

The head bar, M^1, may be L shaped in cross section, and curved longitudinally to conform approximately to the circle described by the track rail, o. It is provided at opposite ends with grooved wheels, k, see A, Fig. 102, which travel upon the rail, o. The partitions, s, S^1 are separated by longitudinal slots, t^1, s^1, see Figs. 95 and 96, just large enough to permit the arms, M^2, which extend from the chamber, C^2, to move without obstruction from the partitions. At the ends of the arms, M^2, are grooved wheels, k^1, which travel upon the track, *o*.

Near the forward end of each head bar, M^1, is the cable-gripping mechanism, M^3. The gripping mechanism comprises a fixed part, formed with two side plates, *i*, *i*, secured to the



A. B.

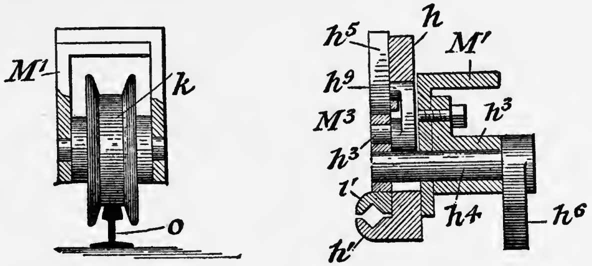
C.

FIG. 101.—CABLE-GRIPPING MECHANISM OF THE BROWN ROASTING FURNACE.

side of the bar, M^1, and a cross plate or bar, i^1, which affords the upper gripping jaw, and a movable part comprising a plate *h*, which slides in vertical guide grooves, i^2, in the plates, *i*, and has a flange, h^1, at its lower edge affording the lower gripping jaw. Through the plate, *h*, is an opening, h^2, of the form shown partly by dotted lines in A, B, and by full lines in C, Fig. 101.

On the bar, M^1, is a bearing, h^3, for a short horizontal rack shaft, h^4. The shaft, h^4, extends through the opening, h^2, in the plate, h, an upward extending switch finger, h^5, and, at the opposite side of the bar, M^1, a downward extending switch finger, h^6. In the opening, h^2, is the link, h^7, pivotally connected at one end to the finger, h^5, at h^8, and pivotally connected at its opposite end to the plate, h, at h^9.

In the open space, D, near the end, x, of the roasting chamber is the stop, y, in the path, when the gripping jaws are closed, of the switch-finger, h^6; and in the open space, D, near the end, x^1, of the roasting chamber is a stop, y^1, in the path, when the gripping jaws are open, of the switch-finger, h^5. In the movement of a stirrer frame, M, when it enters the open space, D, its switch finger, h^6, strikes the stop, y, causing the shaft, h^4, to rock, to turn the switch-finger, h^5, to the raised position shown in A, Fig. 101, and draw down the link, h^7, and plate, h, to open the gripping jaws; and in the further progressive movement of the stirrer frame toward the end, x^1, of the roasting chamber, the switch-finger, h^5, strikes the stop, y^1, turns the rock shaft, h^4, and finger, h^6, to the positions shown in B, C, Fig. 101, and B, Fig. 102, forcing up the link, h^7, and plate, h, to close the jaws, h^1, i^1. The jaws of the gripping mechanism are in position to engage the cable as they close, and in opening they release the cable.



A. B.

FIG. 102.—CABLE-GRIPPING MECHANISM OF THE BROWN ROASTING FURNACE.

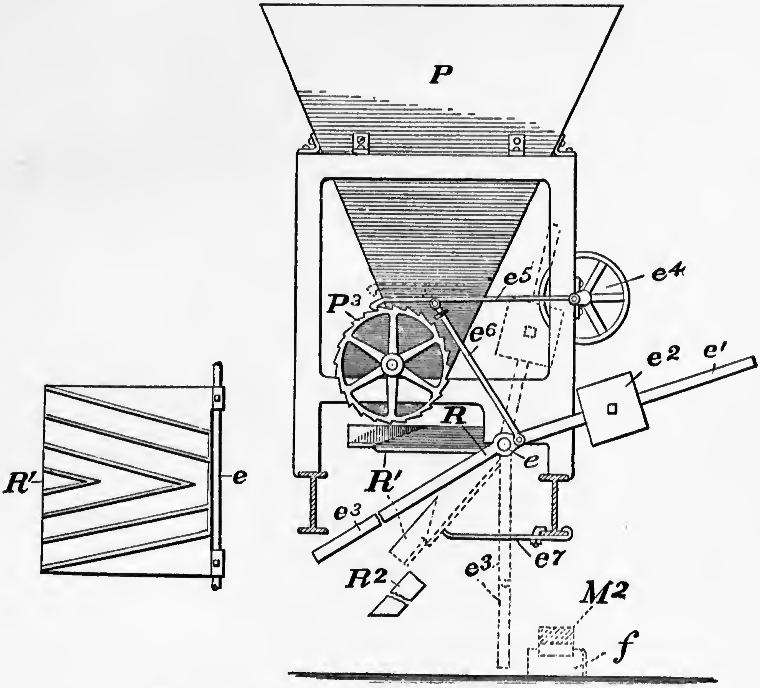
The switch-finger, h^5, is provided on its upper end with teeth, h^{10}, which are engaged by a pawl, h^{11}, pivoted on the head, M^1 (A, Fig. 101), the effect of which is to insure the holding of the switch-finger and attendant mechanism in gripping position after it has been acted upon by the stop y^1. Just before reaching the stop, *y*, the pawl is released through the medium of the rod, h^{12} which is tripped by impact with the stop, *y*, thus permitting the parts to be thrown out of gripping position when the finger, h^{6}, comes into contact with the stop, *y*. For this purpose the rod, h^{12}, is pivotally connected to the pawl, h^{11}, and projects obliquely downwards to a point slightly in advance of the finger, h^{6}, where it is pivotally connected to a wiper, h^{13}, pivoted on the fixed jaw, i^{1}. Thus when the wiper comes into contact with the stop, *y*, the pawl, h^{11}, is lifted out of engagement with the teeth, and it drops back to its normal position when the stop has been passed.

The arm, M^{2}, of each stirrer frame, comprises a bar, *g*, which is fastened at one end to the bar, M^{1}, preferably midway of the length of the latter, extending therefrom at a right angle, to the track, o^{1}, upon which its wheel, k^{1}, travels. In the annular space between the circles described by the partitions, *t*, *s*, the bar, *g*, is provided with, say, three clips, g^{1}, which extend across the top and down the sides of the bar, and are formed below the plane of the under side of the bar with key openings, g^{2}. Extending over the bar, *g*, and clips, g^{1}, is a shield, g^{3}, held in place by bolts, g^{4}, which pass across the underside of the bar, *g*. The stirrer blades, *f*, are fastened to angle-iron braces, f^{1}, secured to the under surface of a bar, f^{2} (*D*, Fig. 101). The stirrer blades extend parallel with each other and obliquely with relation to the bar, f^{2}. The bar, f^{2}, fits between the sides of the clips, against the cross-bolts, g^{4}, and is held firmly in place by keys, f^{3}, driven across its under surface through the key-openings, g^{2}.

The ore to be roasted may be conveyed to the furnace in dumping cars travelling upon a track, *X*, above the furnace and which enters the frame work, D^{1}; and is dumped into the hopper, *P* (Fig. 104).

The lower end of the hopper is closed by a wheel, P^{3}, mounted upon journals in the framework to rotate in the vertical plane, and provided lengthwise with radial partitions, affording segmental pockets, open at the circumference and closed at the end. Around the wheel at one end is a ratchet, P^{3}. Below this wheel, and pivoted upon a shaft, *e*, is a dumping lever, *R*, one arm of which, e^{1}, carries an adjustable weight, e^{2}, the other arm, e^{3}, being free. Integral with the lever, *R*, is a fan-shaped platform, R^1, held by the counterweight, e^2, normally in the horizontal plane across the underside of the wheel, P^3.

Rotating in the framework is a shaft carrying a crank, e^4, and pivoted at one end to the crank is a pawl, e^5, which at its free end engages a tooth of the ratchet, P^3. Pivoted at one end to the arm, e^1, of the lever and at its opposite end to the pawl, e^5, is a link, e^6. The lever, R, swings from the position shown by full lines in Fig. 104, wherein the platform, R^1, extends across the underside of the wheel, P^1, and the pawl, e^5, engages the ratchet, P^3, to the position indicated by dotted lines, wherein the platform, R^1, rests against a stop, e^7, on the framework, the pawl is out of engagement with the ratchet, and the arm, e^3, extends downward into the path of the stirrer arms, M^2.



Figs. 103 and 104.—Ore Hopper of the Brown Roasting Furnace.

In operation the ore to be roasted is dumped into the hopper, P, and fills those pockets, P^3, of the wheel, which at the time register with the discharge end of the hopper. The crank, e^4

rotates continuously and causes the pawl with each revolution to reciprocate and move the wheel around the distance of one tooth of the ratchet, P^3. As a pocket passes across the hopper it is filled with ore, which, as the pocket leaves the hopper, is dumped upon the platform, R^1. When sufficient ore has been deposited upon the platform to overcome the weight, e^2, the lever upsets, and the ore is discharged from the platform, R^1, upon a stationary inclined platform, R^2, which terminates over the hearth end, x^1, of the roasting chamber just above the path of the stirrer arms. The lateral edges of the platform, R^1, diverge, whereby it is widest at the discharge end, and on the surface of the platform are ribs forming the said surface into a series of radially diverging chutes, which spread the ore as it runs therefrom over the platform, R^2: see Fig. 104.

The latter platform is also formed with diverging chutes, causing the ore to be distributed uniformly across the hearth. When the lever, R, is upset as described, the pawl, e^6, is raised, through the medium of the link, e^5, and the wheel, P^3, remains stationary. The weight, e^2, is swung to a point above the fulcrum of the lever whereby the latter remains balanced in its upset position with its arm, e^3, extending into the path of the stirrer arms as before described. In the movement of a stirrer arm below the lever, it impinges against the arm, e^3, and turns the lever until the weight, e^2, overbalances the latter and swings the platform, R^1, to the horizontal plane, and the pawl into engagement with the ratchet, P^3. By adjusting the weight, e^2, upon the lever, the quantity of ore discharged upon the hearth with each operation may be regulated, and the frequency of the charges may be regulated by timing the travel of the stirrer arms, as hereinafter described.

The cable travels continuously, and two, four, six or more stirrer carrier frames may be employed, according to circumstances. The stirrer blades are set obliquely to their direction of travel, the blades of alternate, that is to say, of every second one of the carriers pointing in the direction of the partition, t, and the blades of the intervening carriers toward the partition, s, this arrangement being usual in furnaces of this character. At the end, x^1, of the roasting chamber is a vertically swinging self-closing door, z, and between the firebox, E, and the end, x, are two similar doors, z^1 and z^2. When a stirrer frame grips the cable it strikes against and opens the door, *z*, which closes when released, and moves into the furnace, carrying in the ore deposited upon the hearth by the feed.

In Fig. 98, two stirrers are shown at rest in the open space, *D* one just released from the cable and the other ready to engage the latter. When a stirrer frame advances from the end, *x*, it strikes the rearmost stirrer in the open space, and advances it and the foremost stirrer until the latter grips the cable and advances into the furnace. In practice the stirrers may follow each other, say one minute apart, causing the feed mechanism to deposit ore upon the hearth at intervals of a minute, and each stirrer to remain in the open space two minutes to cool. The time may of course be varied as desired. The construction of the stirrer arms gives an air-space around the bar, *g*, except at the points where the clips, g^1, and bolts, g^4, intervene, the bar, *g*, is thus protected from the heat of the roasting chamber, and as the shield, g^3, is cooled off regularly at the open space, as described, the stirrer arms will last an indefinite time. In the event that any of the stirrer blades become seriously injured by the heat of the roasting chamber or contact with the ore, the bar, f^2, carrying the blades may be quickly removed, when the stirrer reaches the open space, by knocking out the keys, f^3 and replaced by another bar, f^2, without stopping the operation of the stirring mechanism.

As a safeguard against binding of the cable, in the event of its becoming slack at any time, and dropping from the sheaves, q^1, there is provided upon each base plate, p^1, beyond the back plate, p^5, and below the sheave, an inclined guard projection, p^6, in the arc of the circle described by the lower edge of the sheave and close to said edge, upon which the cable will drop in the event of its leaving the sheave, and which will guide the cable to the sheave when the slack is taken up.

When the ore has been advanced by the stirrer around the roasting chamber it may be discharged through an opening, *Z*, in the hearth and into cars which move upon a track, Z^1, Fig. 105, below. As the stirrers pass from the roasting chamber, the door Z^1 closes before the door Z^2 opens, and undue access of air is thus prevented.

In the roof of the roasting chamber, adjacent to each firebox, is an opening, *d*, closed by a removable lid. In the event of the accumulation of matte at a firebox, a bar may be inserted through the adjacent opening, *d*, and the matte loosened. This is a very desirable feature, particularly when lead ores are to be roasted. The openings are placed adjacent to the fireboxes, because those are the hottest parts of the roasting chamber, and where the matte would form. In the straight furnace the best width for the roasting hearth is 10 feet, and for the curved hearth 8 feet. The straight furnace may vary from 60 to 180 feet in length, and the diameter of the round ones may be from 50 feet upwards. In localities where economy in floor space need not be considered, the round or the elliptical type may be used, being simpler in construction, and costing less per square foot of hearth area than the straight furnace.

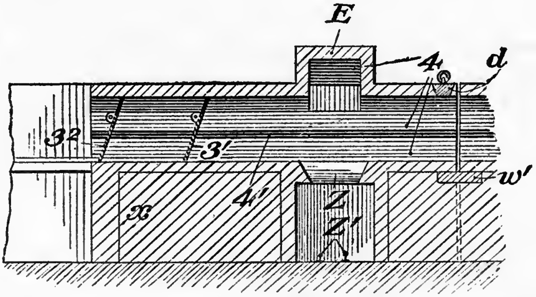


FIG. 105.—DISCHARGE OPENING OF THE BROWN ROASTING FURNACE.

Silicious ores, containing from $\frac{1}{2}$ to $3\frac{1}{2}$ per cent. of sulphur will require from 13 to 15 square feet of hearth area per ton.

Mattes, which usually contain from 18 to 20 per cent. of sulphur, when it is required to bring the sulphur down to about 4 per cent., need about 45 square feet.

Sulphide ores roasted for smelting purposes require 33 to 35 square feet; for roasting iron sulphide concentrates, which carry from 35 to 45 per cent. down to $\frac{5}{10}$ per cent. of sulphur, from 55 to 60 square feet per ton. From 100 to 135 lb. of coal are required per ton of silicious ore, and half that amount for concentrates roasted down to about 4 per cent. of sulphur.

When it is necessary to roast sulphide ores and mattes to below 1 per cent. of sulphur a higher heat and more fuel will be required, the fuel expense increasing in proportion to the perfectness of the roasting.

The Pearce Turret Furnace, manufactured by the Stearns-Roger Manufacturing Company, of Denver, Colorado, may be described as a long, narrow hearth, bent around a circle, the circumference of which is a little greater than the length of the hearth, so that the two ends do not quite meet. At this broken part the roasted ore is discharged. The fresh ore is automatically fed from a hopper at the other side of the break, and is gradually stirred and moved forward by rabbles attached to hollow, air-cooled arms, revolving around a stationary, central column.

In the centre of the circle stands this iron column, which acts as a vertical axle for the revolving framework. This fram carries four pipe arms, radiating horizontally from the column, and projecting through the inner wall of the hearth. On the end of the pipe arms are blades for the rabbling of the ore. The wall of the hearth forming the inner circle is provided with a continuous slot for the sweeping passage of the two revolving arms, and this slot is closed by an endless steel tape, which revolves bodily with the rabble arms, being continuously pressed against the slot, so as to mostly exclude the cold air. The entrance of outside air is still further counteracted by the employment of a slight blast under the grate and through the hollow rabble arms, which balances the tendency of the draught to suck air into the furnace, cools all the exposed iron surfaces, and enables the metallurgist to introduce an accurately gauged quantity of air for the purposes of combustion and oxidation. The inner skewback wall, that is to say the wall immediately above the flue, is hung from heavy I-beams, whose extremities are supported by the central column, and by the outer walls of the furnace. The bracing of the furnace is exceedingly simple and effective, consisting merely of circular iron bands from the outside, while any distortion is prevented by radial struts, like the spokes of a wheel, between the lintels and the central column. Two or three fireplaces are spaced around the outer circumference of the circle at appropriate points, the entering flame being kept from immediate contact with the ore by short curtain arches.

The ore is moved along the hearth by the rotating pipe arms in the direction opposite to the movement of the gases. The ore is stirred once in 40 seconds, or a total of 540 times, during the 6 hours that it requires to pass from the feed to the discharge opening. Of course the time of roasting and number of stirrings can be regulated to suit the requirements of the material under treatment.

The width of the hearth is either 6 or 7 feet, and the diameter of the enclosed circular space is 19½ feet, and of the furnace over all 36 feet. The fireplaces project 6 feet further, and the entire furnace can stand in a quadrangle, 36 by 42 feet, thus occupying 1512 square feet.

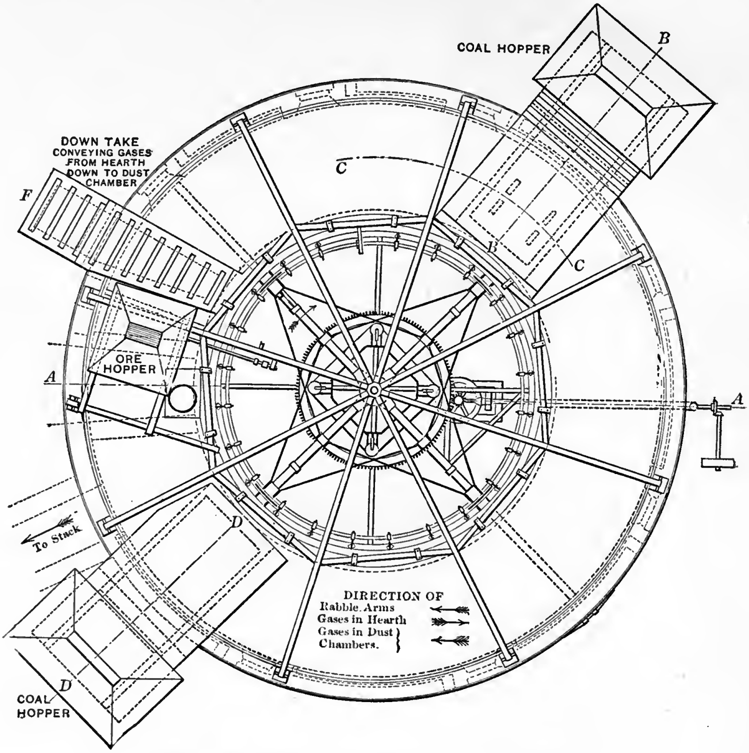


FIG. 106.—PEARCE TURRET CALCINER. Plan.

Figs. 106 to 114 illustrate the Pearce turret furnace. *A* is the hearth, forming a circle with a wedge-shaped piece removed for the discharge of the roasted ore. This hearth is generally constructed over a dust chamber through which the gases pass in a direction contrary to that in which they move upon the

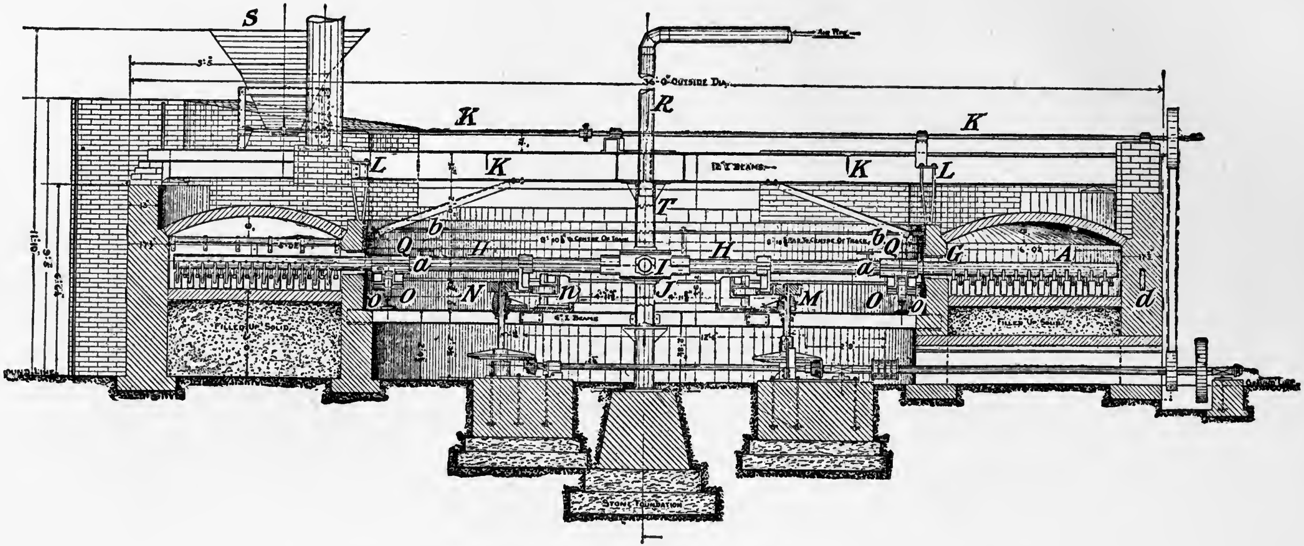


Fig. 107.—Single Hearth Furnace of Pearce Turret Calciner. Vertical Section.

hearth. *D* is the first fireplace, and *B* the second one, the gases moving around the hearth to the flue and downtake, F, through which they pass to the dust chamber. The inner hearth wall has a continuous slot, *G*, for the passage of the spoke-like rabble arms, *H*, which have their hub, *J*, around the central column, *I*. This column is stationary, and is hollow, to admit of the passage of a light blast of air to the wind box (hub), *J*. The superior portion of the inner wall and skewback cannot be built up in the usual manner, and is therefore hung from the eight 12-inch I-beams, *K*, by means of stirrups, *k*, and the cross beams, *L*.

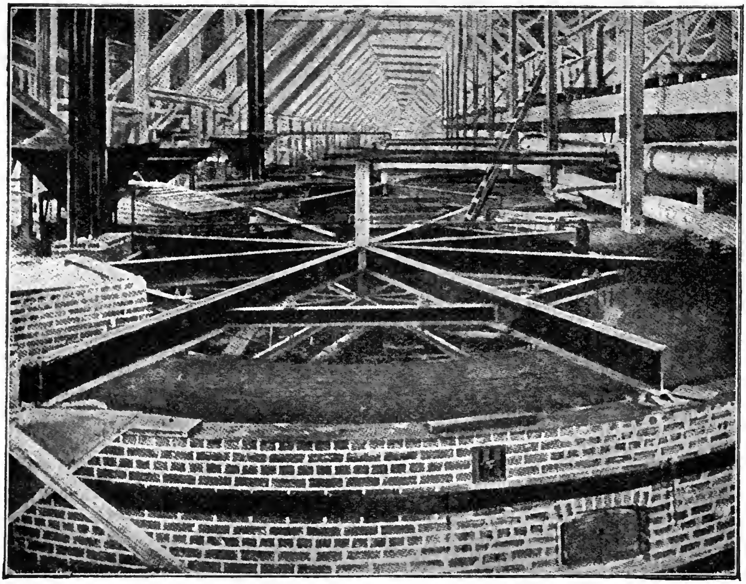


FIG. 108.—PEARCE TURRET FURNACE. Top View.

The rabble arms, *H*, are strongly held by means of the straining rods, *h*, and are revolved by the pinion, *M*, which meshes into the bull wheel, *N*. The wheel is centred by the rollers, *n*, and the entire weight of the rabble arms and driving gear is taken by the conical rollers, *O*, running on the circular track, *o*; no weight at all comes upon the hub, *J*. A 5-inch pipe, *P*, protects the driving shaft, *p*, where it traverses the dust chamber. The rabble arms have a joint at *Q*, so that they can be adjusted to suit the wearing of the plough blades. The blast coming through the pipe, *R*, the central column, *I*, and the wind box, *J*, continues through the rabble arms, *H* (which consist of 5-inch gas pipe), and, cooling that portion of the arms which is exposed to the heat of the gases, streams out into the hearth through openings and little pipes, thus cooling the ploughs and furnishing hot air for the oxidation of the ore. On the first portion of the

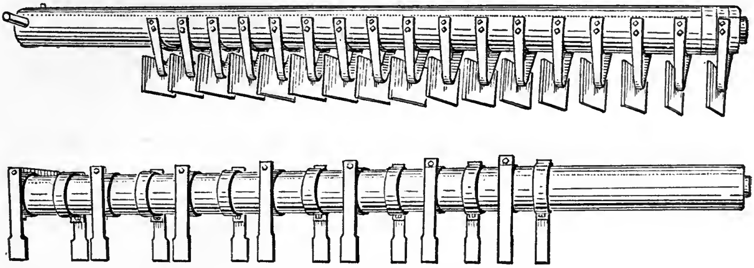


FIG. 109.—RABBLE ARMS OF PEARCE TURRET FURNACE.

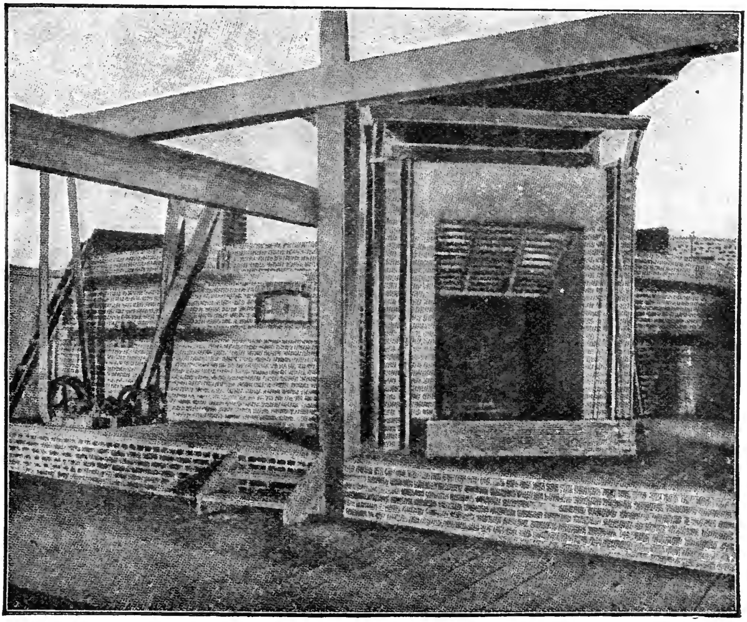


FIG. 110.—FIREPLACES WITH STEP GRATES OF PEARCE TURRET FURNACE.

hearth, where the fresh ore is being gradually heated, no air is desired. The blast is, therefore, cut off opposite the ore hopper by means of the butterfly valves, *a*, *a*, which are closed by the stop, *b*, and again opened at *c*. Heated air is also introduced through the exterior wall of the hearth by means of the intramural passages, *d*.

The ore is dropped upon the hearth from the hopper, *S*, by an automatic feed, is gradually advanced by the ploughs in a direction opposite to the gases, until it is discharged at *B*, into a car. The 12-inch I-beams, *K*, take their bearings on the central column and on the main outside wall of the furnace. See the Top View Battery of furnaces at Argo, in Colorado, Fig. 108.

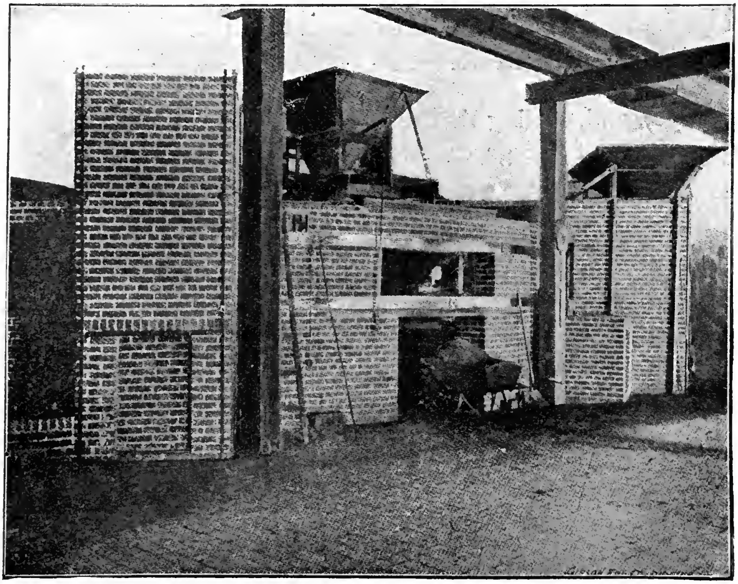


FIG. 111.—FEEDING HOPPER AND DISCHARGE OPENINGS OF PEARCE TURRET FURNACE.

The ploughs or rabble blades are made in two forms—rectangular sections of plate steel—$\frac{1}{4}$ inch or $\frac{3}{8}$ inch thick, set vertically on an angle with the line of the arms, or pieces of bar iron set vertically and clamped to the arms. The greater length

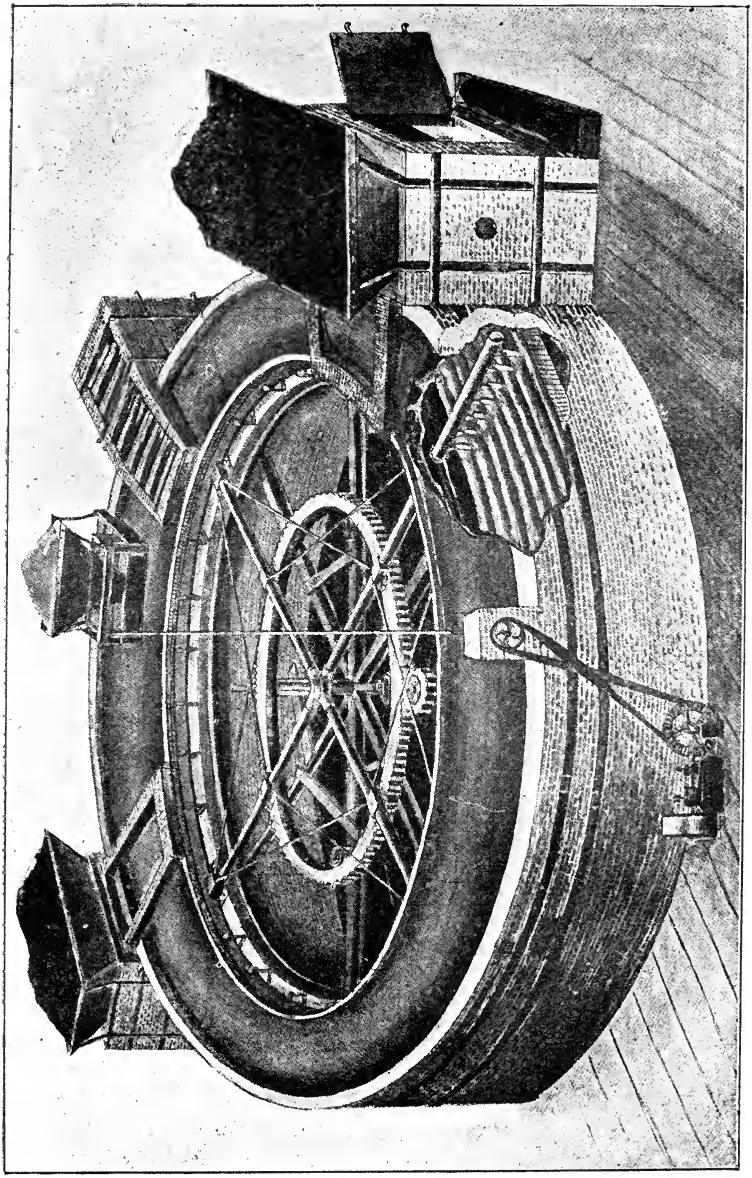


Fig. 112.—Pearce Turret Furnace. Perspective View.

of the outer circumference of the hearth, as compared with the inner, seems to have no ill-effect on the result, the roasting being

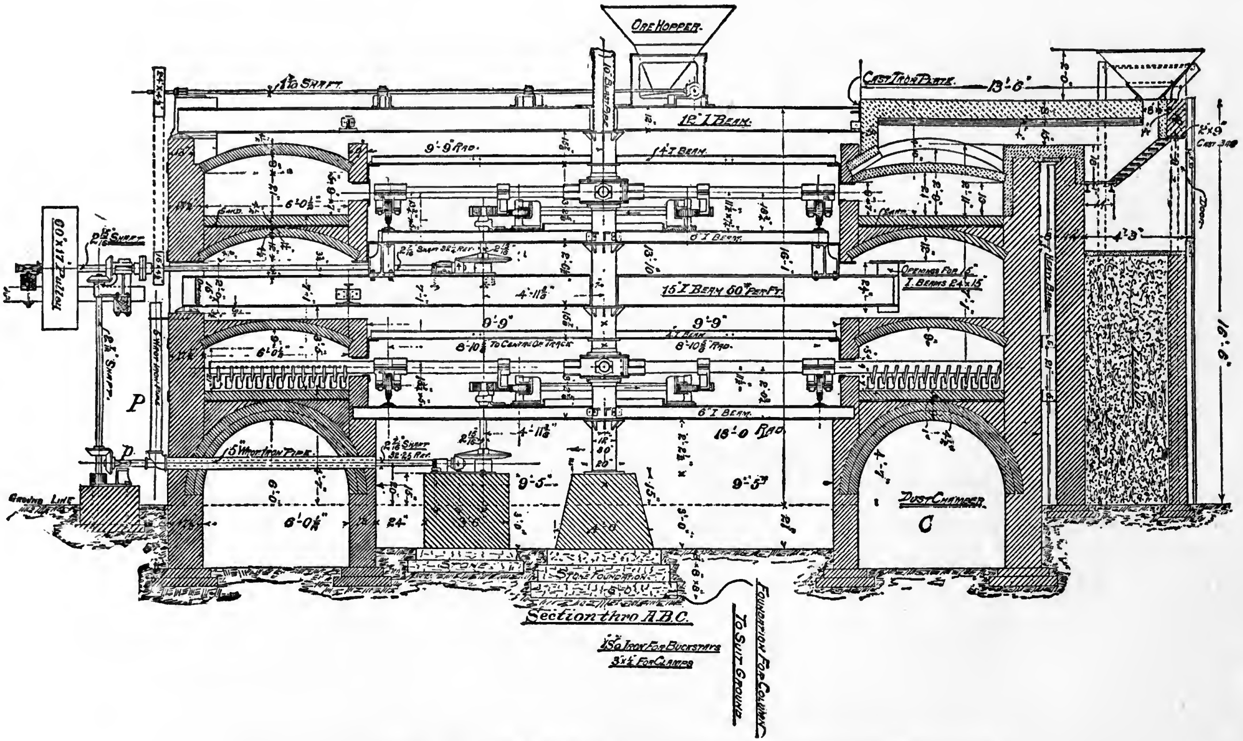


FIG. 113.—VERTICAL SECTION THROUGH TWO-HEARTH PEARCE TURRET FURNACE.

absolutely uniform over the entire width of the furnace, and the length of each individual plough blade increasing slightly towards the outer circle, so that it can move the ore the slightly greater distance demanded by the increased size of the circle. The ploughs or blades last four to six weeks on pyrites containing 40 per cent. of sulphur. The rabble arms that carry the ploughs are of 5-inch pipe, and last a year. When the ploughs require renewal, the section of the pipe arm extending over the hearth is unjointed on the column side of the inner wall, and a new section with ploughs attached is substituted—an operation requiring a very few minutes.

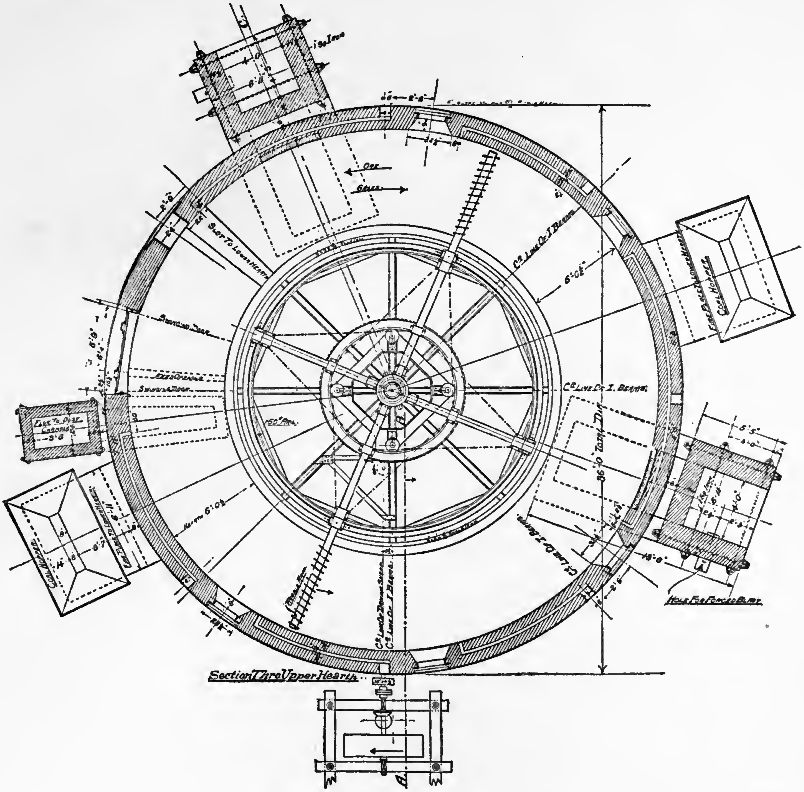


FIG. 114.—HORIZONTAL SECTION ABOVE HEARTH OF PEARCE TURRET FURNACE.

The fireboxes burn slack coal, and are provided with a step grate shown in the figure. The fireplace, *E*, nearest the feed is provided with a curtain arch, as the ore is easily fusible at this stage of the roasting. The discharge vault is provided with a light stack, *Z*, to carry off the fumes.

To regulate the amount of ore handled, the automatic feed may be adjusted, or the speed of the rotating arms may be increased or diminished, or both. The access of air is controlled absolutely by the rabble doors in the outside wall, by the amount forced through the hollow arms when air is used for cooling, and by the forced blast used under the grates. The control of air used may be reduced to the accuracy of a specific number of cubic feet per minute. By the double doors either side of the discharge vault, the steel shields over the slot, and the doors in the outer wall, the air can be almost totally excluded, if desired. About two-horse-power is required to run the furnace and blast.

For chloridising, salt can be fed at any point, thereby saving the large loss occasioned by mixing with the raw ore, as in other forms of furnaces.

A perspective view of the Pearce single turret furnace is shown in fig. 112.

The Colorado Smelting and Mining Company, of Butte, has erected double-decked turret furnaces, the upper hearth of which is supported upon an arch that takes its peripheral bearing upon the main external wall of the furnace, while its inner skewback is supported by the same interior wall that has been already described as hanging from the heavy radial 12-in. I-beams. The inner wall above the slot of the upper hearth is hung from a second set of I-beams, 6 feet higher than the set belonging to the lower hearth. Each hearth is provided with two fireplaces, and by this means the capacity of the furnace is more than doubled as compared with the single hearth calciner; a great saving in labour and fuel being effected.

CHAPTER XVII.

GAS GENERATORS.

IN connection with the roasting of ores, the economic utilisation of fuel has to be considered; and from a theoretical standpoint, the ideal way is first to convert the coal into gas in a producer, and then to burn this gas with air in the combustion chamber. A great number of appliances have been patented, but only those of simple construction, and applicable to roasting furnaces, will be mentioned here.

Operation of Gas Generators.—The generator gas contains as its principal constituent carbonic oxide, and is obtained through the volatilisation of solid fuel with the assistance of air. The fuel is placed in the generator, and partially burned by means of air which is admitted from below. The generator gas is composed of carbonic oxide, nitrogen, small quantities of carbonic acid and hydrogen, and carburetted hydrogen gas (marsh gas); and, according to its volume, can be represented by the following percentages:—

Nitrogen	64
Carbonic acid	4
Carbonic oxide	24
Hydrogen	6
Carburetted hydrogen	2

The oxygen of the atmosphere in contact with the burning material forms carbonic acid; in the upper portions of the fuel column, where the oxygen meets a higher temperature, carbonic oxide is produced. The heat, which is disengaged through the oxidation of the carbon, is taken up by the gases, which set the whole mass of fuel aglow; and in this way, while the carbonic acid gas passes through the incandescent mass, it is converted into carbonic oxide. The height of the column of carbon must be sufficient to consume the oxygen of the air. The result of the carbonisation is a mixture of carbonic oxide, nitrogen, some carbonic acid, and small quantities of hydrogen. The last is produced by the decomposition of any moisture in the fuel.

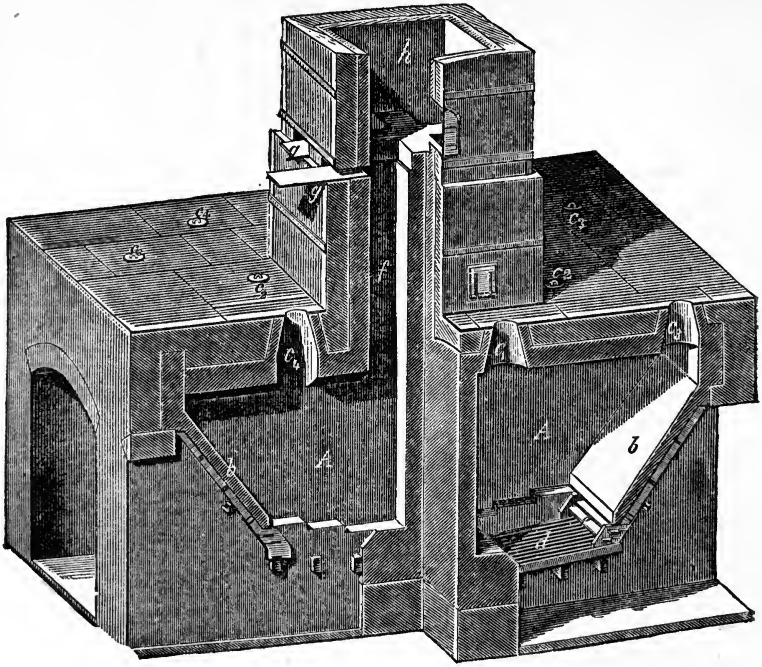


FIG. 115.—SIEMENS GAS GENERATOR.

The carbonic acid does not burn, and by its reduction to carbonic oxide causes a loss of heat; and therefore its production at a high temperature in the generator must be prevented, and the height of the column of fuel must not be too low, as otherwise too much carbonic acid is produced.

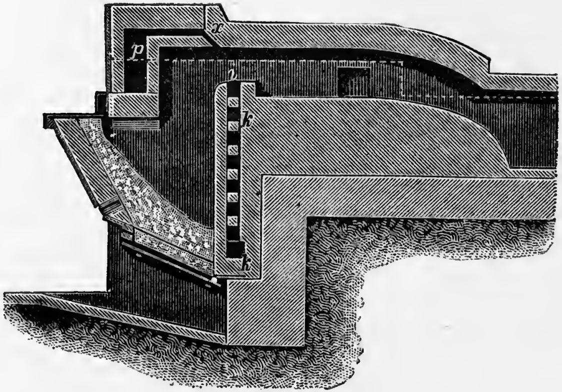


Fig. 116.

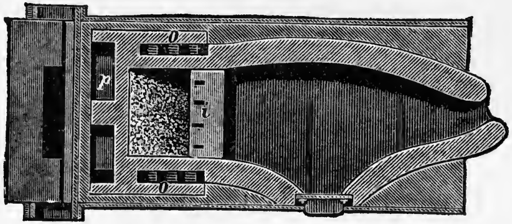


Fig. 117.

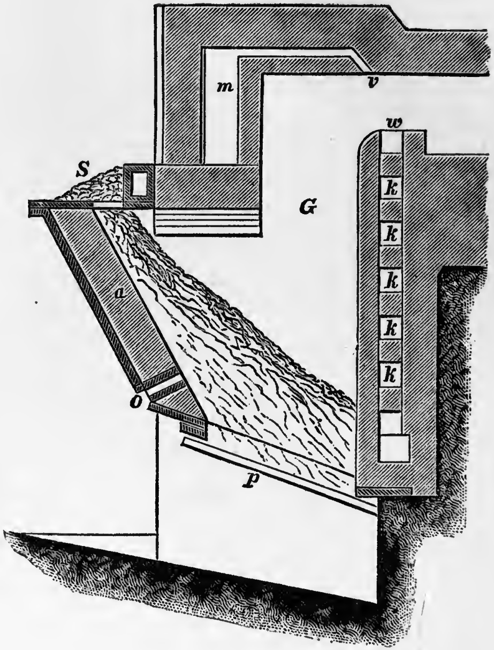


Fig. 118.

The Bœtius Gas Generator.

Single compartment generators are either vertical shafts, or shafts with inclined sides. They are provided with openings for the feeding of the fuel, for the discharge of the ashes, for the introduction of the air required for the volatilisation, for the discharge of the gases, and for observing the operation in the furnace. When wood is employed, the shaft is larger than would be the case when coal is used. The grate is usually inclined, and the fuel rests on the same and on the inclined sides of the generator.

The **Siemens Generator.**—The generators are generally placed close to furnaces in which the gases are to be burned.

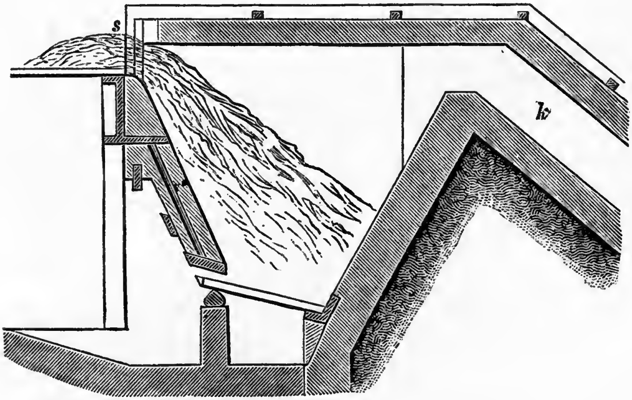


Fig. 119.—The Bicheroux Generator.

An isolated generator designed by Siemens is shown in Fig. 115. In it the front wall is inclined, and consequently the shaft, A, is narrow in the bottom. The front wall, b, ends in the bottom in a step grate, e, which adjoins a horizontal grate, d. The top of the generators are formed by arches in which are four openings, C^1, C^2, C^3, C^4, for the introduction of the fuel, and also to introduce iron bars to detach clinkers and to remove obstructions. Some generators have special openings for this purpose. On the inclined side, b, the coal becomes carbonised, and on the grate below the same becomes volatilised. The gases pass through the canal, f, into the chamber, h, into a conduit, in which tar and water precipitate. Generally four of these generators are in a block as shown in the figure. The canals, *f*, can be closed by a damper, *g*.

The **Bœtius Generator** is shown in Figs. 116, 117, and 118. The front wall, *a*, is inclined, on which the fuel slides down on the grate, *p*. The charge hole is at *s*, and in the lower portion is an opening, *o*, which serves for the introduction of air into the generator and also for the raking out of clinkers.

The gases pass through the canal, *G*, into the furnace. The air, which is required for the combustion, is preheated in the canals, *k* and *m*. The air which is heated in *k*, *k*, passes through *w* to the gases, and the heated air from *m* passes through *v* into the furnace. The air which passes through the canals, *k*, comes out at *i*, as shown in plan, Fig. 117. The air which passed through the canals, *o*, passes out through *p*, and escapes through the slit, *v*, in Fig. 118, or *x* in Fig. 116. The generator gas is thereby furnished with heated air from two channels.

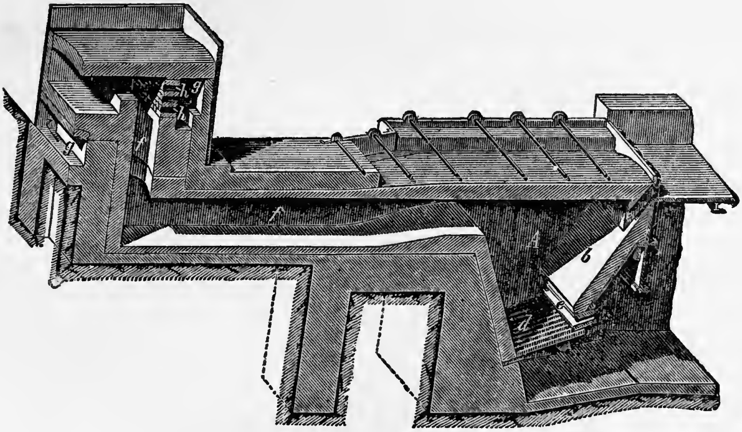


FIG. 120.—THE BICHEROUX GENERATOR.

The **Bicheroux Generator**, Figs. 119 and 120, is very similar to the Bœtius, with the difference that the front and back walls are inclined, giving it more capacity. In consequence of this arrangement the generator cannot be built contiguous to the furnace, but is connected by means of a canal, *k*. The fuel is introduced through *s*.

In this generator, the heating of the air takes place within the walls of the furnace; thence it passes into the canal, *g*, and through *h* into *f*, where it mingles with the furnace gases.

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