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ZINC

T. E. Lones

ZINC
AND ITS ALLOYS

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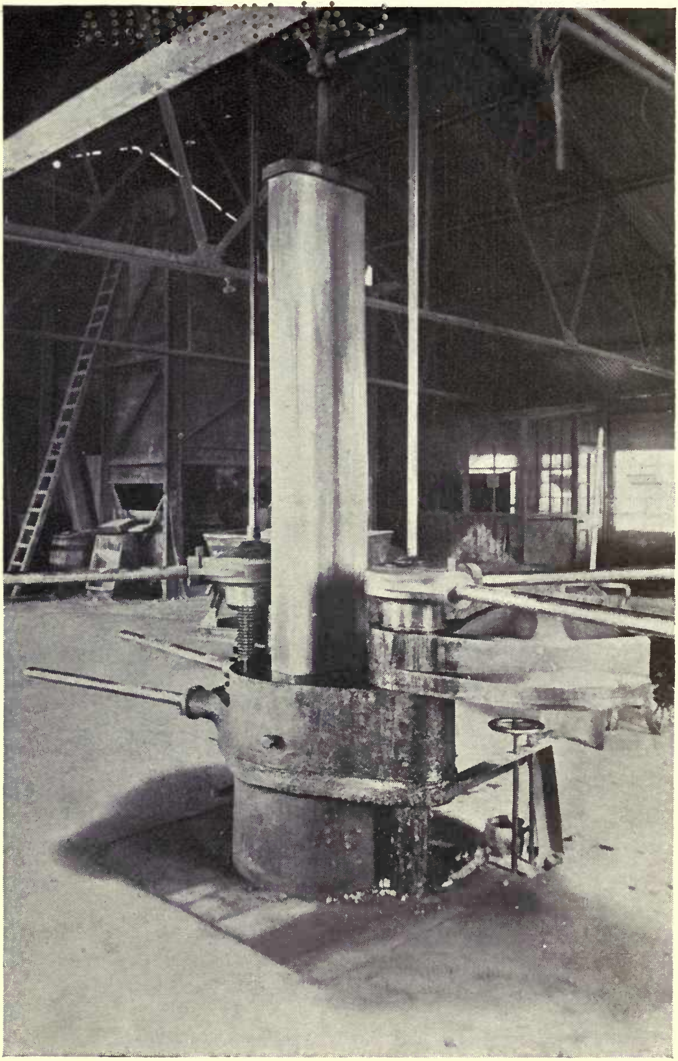

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PITMAN'S COMMON COMMODITIES
AND INDUSTRIES

ZINC
AND ITS ALLOYS

BY

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London
Sir Isaac Pitman & Sons, Ltd., 1 Amen Corner, E.C.4
Bath, Melbourne, and New York

Printed by Sir Isaac Pitman
& Sons, Ltd., London, Bath,
Melbourne and New York

PREFACE

DURING the past five years, the zinc industry has undergone a development which, before the War, would have been thought possible only in romance. Much of this development has been due to the demands of the war, and the circumstances connected therewith have been duly noticed and commented on by the leading newspapers and technical journals.

These circumstances show how, during a long period of peace, control of an important industry may be lost to a dangerous extent. Before the month of August, 1914, less than one-third of the zinc used in this country was produced at home, the rest having been imported chiefly from Germany and Belgium. Further, most of the important yield of zinc concentrates obtained in the Australian Broken Hill district was at the disposal of German merchants and found its way to German and other continental smelters. A small part only was sent to England and smelted there.

Soon after the outbreak of war, an embarrassing state of things arose in the zinc industry. The demand for zinc for use in making cartridge-case and other brass increased rapidly. This country had difficulties in obtaining the zinc it required, the supplies from Germany and Belgium having been stopped. Larger amounts of Broken Hill concentrates could be obtained, but many smelting-furnaces which had been working on calamine and other rich ores were not well adapted for these concentrates and there was also great difficulty in obtaining a sufficient supply of labour skilled in zinc-smelting. Still, after overcoming numerous difficulties, many smelters succeeded in effecting a large increase in the home production of zinc. Most of the balance of zinc required by this country was, however, supplied by America, where the zinc industry has long been an important one.

Such has been the general course of recent events in the zinc industry. There have also been important developments in the processes of extracting and utilizing the metal. These are dealt with in the course of this book, the most important probably being those connected with the production of electrolytic zinc.

Full use has been made of information available in many books and technical publications among which may be mentioned

The Metallurgy of Zinc and Cadmium, W. R. INGALLS, New York and London, 1903.
The Mining Journal, London.
Transactions of the Institution of Mining and Metallurgy, London.
The Engineering and Mining Journal, New York.
The Mineral Industry, 1892–1917, New York and London.
Mining and Scientific Press, San Francisco.
The Canadian Mining Journal, Toronto.
Australian Mining and Engineering Review, Melbourne.

The author is grateful to his friends Mr. E. W. Hulme, B.A., Mr. R. Jenkins, M.I.M.E., and Mr. A. R. Wright, F.S.A., all of The Patent Office, who furnished much valuable information relating to the history of zinc and its alloys and read the MS. and proof sheets.

THE AUTHOR.

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CHAPTER I

ZINC: ITS HISTORY, PROPERTIES, AND USES

History of Zinc. The history of zinc begins in very early times. There is conclusive evidence that the ancient Greeks, Romans, and Arabians used ores and condensed furnace-fumes containing zinc in the production of alloys and medicinal preparations.

It has also been asserted that they were acquainted with zinc in its metallic state. This assertion is based mainly on an oft-quoted passage from Strabo's description of Andeira in Mysia, in which he describes the production of "false silver" (*pseudargyros*), and on recorded discoveries of antiquities said to be of metallic zinc.

The passage from Strabo is too vague to enable a definite opinion to be formed, but it is interesting to note that deposits of blende or zinc sulphide with iron pyrites and galena or lead sulphide occur near Balia, not far from the site of Andeira.

In 1772, a small metallic bar was found in Champagne, in the ruins of an old Roman town. M. Grignon, who examined the bar, concluded that it was of zinc, and stated that the bar had been worked to some extent and that, in the vicinity of the Roman town, there was an iron mine containing a great deal of zinc—(*Bulletin des fouilles, etc.*, 1774, p. XI).

A relic, stated to be made of zinc, has also been recorded from Pompeii.

A more valuable record is that by M. Salzmann of the discovery of some bracelets in the ruins of Camirus, in the Isle of Rhodes. His words are worth quoting. He says: "The silver trinkets are sometimes solid, sometimes plated. Certain bracelets, for example, are made of a hollow silver ring filled, not with tin, as I believed at first, but really with zinc"—(*Revue Archéologique,* Paris, 1861, p. 472).

It is, in fact, probable that metallic zinc was known to the Ancients, although its production and use was only occasional, and the nature of the metal was but little understood.

For the mediaeval period it is necessary to consult the works of the alchemists for information about zinc, but inferences drawn from these works are often unsatisfactory. The production of brass, the yellow or gold-coloured alloy of copper and zinc, was well known to them, and this knowledge gave rise to a belief that by means of zinc-bearing substances it might be possible to transmute copper into gold. This belief induced them to keep the results of their researches secret, and when they wrote on the subject they often tried to confuse rather than enlighten their readers.

The word *zinck* first occurs in the works said to have been written in the fifteenth century by Basil Valentine; in the 3rd Book of the Strasburg edition (1645) of the *Last Testament of Basil Valentine,* occurs a mention of ores, metals, minerals, *zincks,* etc., but there is nothing to show that metallic zinc was meant. The first, in fact, to give the name *zinck* to the metallic form of the metal was Paracelsus (1490-1541); many passages in his works show that he was acquainted with the metallic nature of zinc and knew that it was fusible but not malleable.

For many years after the time of Paracelsus, zinc continued to be a rare metal in Europe. In India, however, metallic zinc was extracted long before the time of Paracelsus, and the Hindus were acquainted with a method of extracting the metal by a process of distillation downwards, or *per descensum,* into a vessel containing water—(*A History of Hindu Chemistry,* Praphulla Chandra Rây, London, Vol. I, 1902). Not only is the history of zinc in India of great interest for its own sake, but that history, as well as that of China, is closely bound up with the history of zinc in this country.

During the seventeenth and eighteenth centuries, large quantities of zinc or spelter, the term usually employed for commercial unworked zinc, were imported from the East, under various names, such as calaem, tutaneg, spiauter, and Indian tin. The account-books of the various companies trading to India, Sumatra, and China give a great deal of information about this trade, but the time of its commencement is not known. It was before the year 1611, for in the beginning of the seventeenth century, a Portuguese ship carrying spelter, was seized by the Dutch, and this spelter found its way to Paris and other places—(Savot's *Discours sur les médailles antiques,* 1627, p. 109), and, in a letter dated Sept. 14th, 1611, Libavius clearly shows that at that date the calaem of Malabar was known to him, and says that it seems to be the same as zinc.

During this period of importation from the East, many attempts were made in this country and on the Continent to produce spelter. Some of these attempts were successful, even in the early part of the seventeenth century, but the processes adopted were usually kept secret. Goslar, in the Harz, and Carinthia were among the places where spelter was produced. Libavius, in his letter referred to above, says that he was desirous of seeing the metal called zinc by the Carniolians and Tyrolese ; although he does not say so, it is probable that the zinc to which he referred was that produced in Carinthia, the zinc and other mines of which have been worked for many centuries. At a later time, Dr. Isaac Lawson wrote that zinc was obtained from the East and Germany—(*Dissert. de Nihilo,* 1737). This suggests that substantial quantities of the metal were being produced on the Continent in the first half of the eighteenth century. It is known, however, that Libavius did not succeed in obtaining the zinc he desired so much to see and that he had to be content with the zinc imported from the East. In his time, and later, the zinc produced in some, if not all, the zinc-ore districts of Europe was probably little more than a laboratory curiosity, but it became, in Lawson's time, an article of export trade. These details will enable the relative importance of an event in the history of zinc, which will next be described, to be more clearly understood.

About the year 1740, John and William Champion, sons of Nehemiah Champion of Bristol, set up works near that city for obtaining spelter by a process of distillation *per descensum.* For that period, these works were large and their output, according to Dr. R. Watson, who knew the works well, was about 200 tons of spelter per year. It was intended to produce such quantities of spelter as would free this country from dependence on importation from the East. It appears, however, from William Champion's Petition, presented to the House of Commons in 1750 for prolongation of his patent rights, that the importers of East Indian spelter determined to ruin the enterprise, for, by bringing in large supplies of spelter, they forced the price down from £260 a ton to £48 a ton, still leaving a substantial profit to themselves, but preventing Bristol spelter from being made at a profit. The Champions suffered, but the works were carried on, with various changes in ownership and products of manufacture, until the year 1880.

According to William Champion's statements in his Petition, he had travelled in most parts of Europe in order to find out a successful process of making spelter, and John Champion, according to the traditions of the Bristol district, went to Holland, obtained work as a labourer, and, having learned the secret of making brass and spelter, returned to Bristol with Continental workmen, and set up smelting works at Warmley. There is another story, not consistent with the above narration, that Dr. Lawson introduced from India or China the process carried out at the Bristol works.

On the Continent, the earliest commercially important zinc-smelting works appear to have been those built by Dillinger, in Carinthia, in 1799. Shortly afterwards, in 1799 or 1800, zinc-smelting works were built by Ruhberg in Upper Silesia. About the year 1809, zinc-smelting furnaces were built by Dony near Liége, but commercial progress was slow until the formation of the world-renowned Vieille Montagne Company in 1837.

The first zinc-smelting works of Swansea were set up in 1835 by the firm of Vivian & Co. From about this time the zinc industry made rapid progress. In 1838, the rich zinc ores of New Jersey were smelted for the production of spelter at the Arsenal at Washington. A few years later these ores were smelted on a large scale in New Jersey and Pennsylvania, but difficulties arising from corrosion of the smelting-retorts by the iron in the ore, smelting for spelter was largely given up, and the ores were treated, mainly for the production of zinc white, by the Wetherill process, introduced in 1856. In later years, the development of the zinc industry in Kansas, Missouri, Colorado, Wisconsin, and other States has brought America into the foremost position as a producer of spelter.

Probably in no part of the world has greater enterprise been shown than in the Broken Hill district, Australia. Its rich lead-zinc-silver ores began to be worked in 1893 for lead and silver, and vast quantities of tailings accumulated; these tailings contained about 18 per cent. of zinc. In 1905, for the purpose of working these tailings, Zinc Corporation, Limited, was formed, and, after the difficulties at first met with had been overcome, the operations of this company had considerable commercial success. It would probably not be an exaggeration to say that all the zinc ore concentrates needed by this country for its supply of zinc could be furnished by the Broken Hill district. It should be mentioned, however, that in recent years, a part of these concentrates has been smelted at Port Pirie, S. Australia, and the Electrolytic Zinc Company of Australia has taken steps to treat large quantities of the Broken Hill ore at works situated near Hobart, Tasmania.

In Canada, also, there has been a considerable development of the zinc industry in recent years, although transport is often difficult, and the ores are usually of a complex nature and difficult to concentrate. The chief ore deposits are in the Rocky Mountain districts of British Columbia and Alberta, and here as long ago as 1904, attempts were made to smelt the zinc ores. Since 1916, electrolytic zinc has been successfully produced at Trail, British Columbia, by the Consolidated Mining and Smelting Company of Canada.

This outline of the history of zinc would be incomplete without reference to a few other recent developments of considerable interest. For a long time, Sardinia and many parts of Italy have mined large quantities of zinc ore for export. About the year 1900, however, the Montepioni Company began to extract zinc from the Sardinian ores, and, in 1917, zinc-smelting works were put in operation near Savona, in Northern Italy. In Japan there has been an extensive development of the zinc industry in the last few years. Zinc-smelting operations were begun in 1911 with the setting up of two zinc-smelting furnaces, and many plants have also been established for producing zinc by electrolytic methods.

Properties of Zinc. Zinc is a bluish-white metal with a bright lustre when polished. Its specific gravity varies from about 6·8 (cast zinc) to about 7·4 (drawn, hammered, or rolled zinc). The pure metal is harder than aluminium but softer than silver, it is malleable and can be hammered or rolled into thin sheets. Spelter, or commercial zinc, is brittle but, when heated to a temperature between 100°C. and 150°C., it is malleable ; at a temperature of about 200°C. it again becomes brittle.

The want of malleability of commercial zinc was the chief obstacle to its use in the arts in the early days of the zinc industry. As late as the year 1805, it was called a semi- or half-metal in contradistinction to malleable metals like gold, silver, and copper, which were called whole or entire metals. When it was discovered, by Sylvester and Hobson of Sheffield, early in the last century, that zinc became malleable by the heat treatment set out above, its extensive use in the arts was assured, and proposals for making it into sheets, rods, wire, forks, spoons, plates, etc., soon followed.

Compared with lead or tin, zinc is a strong metal; its tensile strength varies from about 3,000 lbs. per square inch (cast zinc) to about 15,000 lbs. per square inch (rolled and carefully annealed zinc).

The heat conductivity of zinc is about one-half that of silver; its coefficient of linear expansion by heat = 0·000029 and its specific heat = 0·094. Its electrical conductivity is about one-fourth that of silver.

When heated to about 420°C. the metal fuses and can then be run into castings which reproduce well the intricate parts of the interior of the mould. If the molten metal is allowed to cool in an iron pot or fireclay vessel until a crust of solidified zinc is formed, and this crust is then broken and the metal poured out, the metal which adheres to the surface of the pot or vessel will be found in the form of long hexagonal prisms. The boiling point of zinc is about 930°C., which is below the melting points of silver and copper.

Zinc burns in the air at a temperature of about 500°C. with a bluish-white flame and formation of fumes of zinc oxide. Pure zinc dissolves in nitric acid, but only very slowly in sulphuric and hydrochloric acids. Commercial zinc dissolves readily in nitric acid, sulphuric acid, hydrochloric acid, and hot solutions of the alkalies.

In consequence of the strong electro-positive nature of zinc, it can effect the precipitation of many metals from their solutions; gold, silver, and platinum are often precipitated by means of zinc employed for this purpose in cyaniding and other processes for extracting these precious metals.

A very important property of zinc from an industrial point of view is its resistance to the action of the atmosphere. Dry air scarcely affects zinc at all, but in damp air, which contains carbonic acid gas, the exposed surface of the metal is converted into a basic carbonate of zinc, which protects the metal from further change.

Another very important property of zinc is that of alloying readily with other metals, especially copper, aluminium, and antimony, with or without other metals or elements, to form many useful alloys.

A property of zinc, also of great commercial importance, is its capability of being very easily soldered, thus enabling large castings or any complicated structures, for which the use of zinc is suitable, to be built up of small castings or parts.

In concluding this short account of the properties of zinc, some information will be given about the composition of commercial zinc or spelter. The elements which occur in spelter are very numerous; among them may be mentioned iron, lead, cadmium, arsenic, antimony, bismuth, copper, silver, sulphur, gallium, indium, thallium, and other rare metals.

Different brands of spelter vary very greatly, not only in the nature of the elements, other than zinc, which they contain, but also in the quantities of these elements. There are many brands of spelter produced to-day which contain not less than 99·9 per cent. of pure zinc, leaving only a small margin for the presence of any other elements. In September last, there were at King's College, London, ingots of electrolytic zinc, exhibited by Messrs. Chance & Hunt, Oldbury; these ingots were cast with the words and figures: "Lightning Brand, 99·95." Even without this information, the high quality of the metal was evident from its appearance on fractured surfaces with their large, glistening pale electric-blue crystal faces, like mirrors, free from specks of any kind. Spelter of such quality is by no means exceptional, especially at the present time when there is a demand for spelter of the highest possible purity for making many special alloys, and there is, consequently, a large output of re-distilled, high grade, and electrolytic spelters all of a high degree of purity to meet such demand.

The following are examples of the composition of a few kinds of spelter—

	Zn.	Pb.	Fe.	Cu.	Cd.	As.
American high grade	99·96	0·02	0·02	—	—	—
Electrolytic . . .	99·95	0·03	0·01	0·01	—	—
Silesian . . .	98·92	1·03	0·02	—	0·02	0·01

Lead and iron are the elements which occur most often as impurities in spelter. Lead may be present in any quantity up to about 3 per cent. It increases the ductility and malleability of the metal and its presence is beneficial in some cases, *e.g.*, spelter containing about 1 per cent. of lead is thereby rendered better for rolling, and the presence of about 2 per cent. of lead is an advantage in spelter intended for the production of zinc shavings for use in cyaniding processes. Iron when present in zinc hardens the metal and renders it less malleable. A quantity of iron from about 0·01 to 0·05 per cent. is not uncommon in spelter. Cadmium is found in some spelters, but usually only in very small amount. For most purposes, spelter is not any the worse for containing a small amount of cadmium, but its presence is unwelcome in spelter for use in certain alloys, such as cartridge-case brass. Copper, arsenic, and antimony when present in spelter render it brittle. The rare elements, gallium and indium, have been found to occur in spelter obtained from the blende of Oklahoma, Missouri, and Kansas; thallium has also been found in some spelters.

Uses of Zinc. It is not remarkable that zinc, which can be obtained in large quantities and has such useful properties, has become of very great commercial importance. In recent years, the demand for spelter has increased enormously. In the early part of last century, the total output of spelter in the world, excluding India and China, was probably only a few thousand tons per year, in 1873 it was not less than 150,000 tons, in 1893 it was nearly 400,000 tons, and in 1913 the output was about 1,000,000 tons; of this enormous quantity the United States produced about 325,000 tons, and this country about 50,000 tons.

In normal times, the spelter used in the galvanizing trade accounts for about one-half of the total consumption. Galvanized iron and steel sheets, so largely used in the construction of permanent as well as temporary buildings, galvanized tubes, rods, wire, wire netting, fencing standards and bars, bolts, nuts, nails, staples, fish-plates, railway rail chairs, locks, water cisterns, spouts and gutters, chimney cowls, ventilating pipes, mica-valve gratings for sanitary pipes, baths, and buckets, are only a few of the articles thus protected by a coating of zinc against the action of the atmosphere and water.

Another very important use of spelter is in the manufacture of brass and other alloys. For this purpose, probably not less than a quarter of the total output of spelter is necessary in normal times. Recently, the consumption of spelter for making alloys for war purposes has been exceptionally great.

A third very important use of spelter is in making rolled zinc sheets chiefly for the construction of roofs, zinc-lined boxes and drawers, and many articles of domestic use, also in the printing trade for zinc printing plates.

There are other important uses of spelter, *e.g.*, in the form of rods, plates, or gratings as electrodes for electric batteries and in accumulators, in the form of shavings, which are turned off zinc discs, for precipitating gold from cyanide solutions, and in the form of ingots for desilverizing lead, during the refining of the lead by the Parkes process. A certain amount of spelter is also used in the production of castings, *e.g.*, statues, figures of animals, ornamental boxes, and other articles are sometimes cast, or built up by soldering together a number of small zinc castings. Many of these uses are of importance, because zinc is, in a special degree, the metal most suitable for them.

There are also some other important uses of zinc. A large amount is used, especially in Europe, for making oxide of zinc or zinc white, for which there is a great demand in the colour and paint trade. In the United States very little of the metal is consumed for the production of zinc white, the greater part of the zinc white obtained being made directly from the rich zinc ores of New Jersey. Zinc chloride, zinc sulphate, and other zinc salts are also usually obtained by treatment of the metal. Zinc dust, called also *blue powder*, from its colour and form, is largely used in precipitating gold from its cyanide solutions, in decomposing nitrobenzol, and in dyeing. This zinc dust consists of small particles of zinc having a thin coating of oxide of zinc, and is obtained during the smelting of the zinc ores for the production of spelter, or is made by reducing zinc ores by means of carbon, the zinc vapours produced being oxidized by a blast of air.

CHAPTER II

ZINC ORES AND OTHER SOURCES OF ZINC

UNLIKE gold, silver, copper, and several other metals, zinc very rarely occurs in nature in a metallic state. Such an occurrence of zinc has been recorded, however, in basalt from the neighbourhood of Melbourne—(*Comptes Rendus*, Vol. 55, p. 218).

The chief natural sources of zinc are the sulphide (blende and wurtzite), the carbonates (smithsonite or zinc spar and hydrozincite or zinc bloom), the silicates (willemite and hemimorphite or electric calamine), and the oxide (zincite or red zinc ore and franklinite, which contains zinc oxide together with oxides of iron and manganese). Some of the above-mentioned ores are called by the old name *calamine*, but the meaning of this name varies in different countries; in this country, *calamine* means the carbonate or zinc spar, in the United States it usually means the silicate, and on the Continent it often means the carbonate and the silicate, both willemite and hemimorphite.

The want of agreement in the use of the term *calamine* causes confusion and sometimes serious difficulty. By the revised tariff of 1896, in the United States, a 20 per cent *ad valorem* duty was put on minerals containing metallic values, but *calamine* was excepted. The meaning of the term *calamine* came in question, and it was some time before it was decided officially that *calamine* meant not only the silicate but also the carbonate of zinc.

Besides zinc ores the chief sources of zinc are the slags and residues from earlier smelting operations, dross and skimmings from galvanizing baths, and zinc fumes condensed and collected during the treatment of zinc ores and other ores associated with zinc ores.

Spelter obtained from zinc ores is called virgin or primary spelter, and that obtained from dross, skimmings, and like sources is called remelted or secondary spelter.

Smithsonite used to be the most important source of zinc, but in recent years most of the zinc obtained in the world has been obtained from blende, for the supplies of smithsonite suitable for smelting have been exhausted to a large extent. Blende is more difficult to treat than smithsonite, and does not yield so pure a metal. In zinc ore districts, where both minerals occur in large quantities, the greater part of the smithsonite, usually a product of alteration of pre-existing blende, has been found in the superficial parts of the deposit. Being easily accessible, rich in zinc, and easy to smelt, the best smithsonite deposits were naturally the first to be worked, and the blende deposits were largely neglected. It is true that, as early as the year 1758, John Champion of Bristol patented a process for concentrating, roasting, and smelting blende, black jack, mock jack, or red stone, which had not, he says, been used before for the production of zinc. The use of blende, however, developed very slowly. It was used as an addition to low grade smithsonite ores or by itself and at length, about the year 1880, became the most important ore of zinc.

In consequence of its great commercial importance, a more detailed description of blende will be given than of the other minerals mentioned above.

Blende, also called sphalerite, jack, black jack, or zincblende (to distinguish it clearly from a few other minerals, *e.g.*, pitch-blende), is found in crystals, crystalline aggregates, granular masses, compact masses, in which the grains are so small that they cannot be easily detected except when prepared for examination by the microscope, and sometimes in grape-bunch (botryoidal), kidney (reniform), or icicle-like (stalactitic) forms. The crystals of blende are of the cubic or regular system of crystallization, and are often of very complicated structure and distorted. Usually, the mineral has a resinous lustre. Colourless and transparent crystals occur, but only rarely; usually, blende is white, green, yellow, brown, red, or black. Yellow and brown crystals, large and of great beauty, occur at Binnenthal, in Switzerland, and yellow, transparent crystals near Santander, in Spain. Crystals of blende are sometimes three inches across.

Blende is sulphide of zinc, ZnS, and, in its purest form, contains about 67 per cent. of zinc, and 33 per cent. of sulphur. Usually, it contains appreciable quantities of other elements, especially iron, cadmium, manganese, lead, arsenic, silver, and also some rare metals. Thallium has been found in blende from the Joplin district and germanium in blendes from that district and Wisconsin. Blende is commonly associated with other zinc ores and with sulphide of iron (pyrites and marcasite) and sulphide of lead (galena); other minerals less commonly associated with it are siderite or carbonate of iron, barytes or sulphate of barium, and calcite or carbonate of lime.

Wurtzite is a brownish-black mineral which, like blende, is sulphide of zinc, ZnS, but crystallizes in a different system, the hexagonal. Iron and cadmium are commonly found in wurtzite. It has been obtained from Bolivia and from Przibram, in Bohemia.

Smithsonite occurs usually in rhombohedral forms, when found in crystals, but most commonly occurs in reniform, botryoidal, and stalactitic masses, or in friable masses resembling chalk; this form of the mineral is called *dry-bone ore,* in America. Smithsonite is carbonate of zinc, $ZnCO_3$, with about 52 per cent. of zinc, when pure. It is usually grey, yellow, or brown. Smithsonite has been found in numerous localities; among these may be mentioned the famous Vieille Montagne, the Mendip Hills, Upper Silesia, Santander and Carthagena in Spain, Laurium in Greece, and Sardinia.

Hydrozincite or zinc bloom is a hydrated carbonate of zinc containing about 14 per cent. of water. White or whitish in colour, it usually resembles chalk. It has been found in large quantities in a few localities, the chief being Santander in Spain and Bleiberg in Carinthia.

Willemite occurs in rhombohedral crystals and in granular and fibrous masses. It is silicate of zinc, Zn_2SiO_4, with about 60 per cent. of zinc. Its colour is white, green, yellow, or brown. When the mineral contains a substantial amount of manganese, it is called troostite; this variety sometimes occurs in crystals several inches long. New Jersey is the most important locality for willemite and troostite.

Hemimorphite or electric calamine is hydrated silicate of zinc with about 7 per cent. of water. Its crystals, which are sometimes columnar or tabular, are often brilliant. This mineral has remarkable electric properties. Many minerals become electrically charged when heated, or are what is called thermo-electric. Hemimorphite, however, is not only thermo-electric, but also polar thermo-electric, for one end of a crystal of the mineral becomes positively and the other end negatively charged when heated. Fig. 1 shows such a crystal, and it will be noticed that the upper end is flat and the lower end pointed. On heating and examining such a crystal, it will be found that the flat end becomes positively and the pointed end negatively charged. The colour of hemimorphite is usually white or light yellow, brown, red, green, or blue. Large quantities of this mineral have been found at Bleiberg, and in Silesia, Virginia, New Jersey, Kansas, and Missouri.

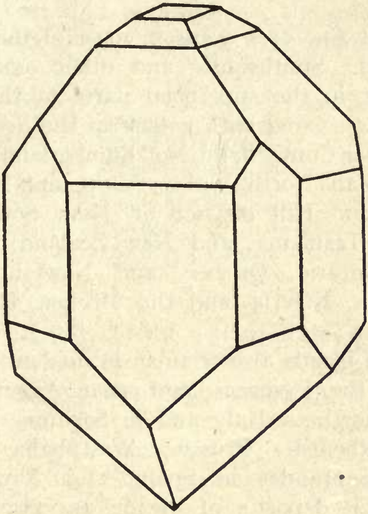

FIG. 1

CRYSTAL OF ELECTRIC CALAMINE

Franklinite is of very variable composition, but an average specimen contains 46 per cent. of iron, 10 per cent of manganese, 18 per cent. of zinc, and 25 per cent. of oxygen. Its crystals are black and often as much as two inches across. Franklinite is magnetic. It occurs in large quantities in New Jersey, where it is worked for the production of zinc oxide, spelter, and ferro-manganese.

Zincite or red zinc ore occurs occasionally in hexagonal crystals, but usually in masses associated with franklinite and troostite. Its colour is red or orange-yellow. Zincite is oxide of zinc, ZnO, with about 80 per cent. of zinc.

Deposits of zinc ores occur in most of the countries of the world. Smithsonite and other oxidized ores usually occur in the superficial parts of the deposits and blende associated with galena in the deeper parts. Blende occurs in Cumberland, Northumberland, Leadhills, the Isle of Man, North Wales, Salop, and Derbyshire, in the Broken Hill district of New South Wales, Queensland, Tasmania, and New Zealand, in British Columbia, Ontario, Quebec, and Newfoundland, in Upper Burma, Nigeria, and the Broken Hill district of Rhodesia.

Deposits of blende also occur in France in the departments near the Pyrenees and near Angouleme and Rennes, in northern Italy and in Sardinia, in Silesia, Carinthia, Rhenish Prussia, Westphalia, Laurium in Greece, Santander in Spain, and Ammeberg in Sweden. Rich deposits of blende are also found in Kansas, Missouri, Colorado, Wisconsin, Montana, Idaho, and many other States of America, and also in Mexico and Bolivia; the deposits of the Joplin district, extending over adjacent parts of Kansas and Missouri, are exceptionally rich and yield concentrates with 60 per cent. or more of zinc. Deposits of blende are also found in Algiers, Japan, and Eastern Siberia.

Oxidized zinc ores occur in Vieille Montagne, in Silesia, in France, in the departments of Var, Gard, Drome, and the departments near the Pyrenees, in Santander, Carthagena, and Linares, in Spain, in Poland, Silesia, Sardinia, Algiers, Greece, Tunis, at Gebel Rosas in Eygpt, at Broken Hill, Rhodesia, and in New Jersey, Wisconsin, Arkansas, and several other States of Americia.

Statistics of the annual output of zinc ores from various countries show that, for the year 1913, the last year unaffected by the war, the amounts of ore in tons produced or exported were approximately as follows—

United States	1,000,000
Germany	700,000
Australasia	580,000
Spain	190,000
Italy	160,000
Algiers	90,000
Greece	57,000
Sweden	56,000
France	50,000
Japan	50,000
Austria	40,000
Tunis	37,000
Mexico	20,000
Great Britain	18,000
Canada	10,000
China	10,000

The above figures for the United States do not include the zinc ore mined for zinc white manufacture; those for Australasia represent approximately the production for the Broken Hill district, the quantity obtained elsewhere being comparatively small. The figures given for Spain and China represent approximately the amounts of zinc ore exported.

In connection with the zinc industry of this country, the zinc ores of Broken Hill are of considerable importance. At Broken Hill, there is an extensive saddle-shaped deposit of blende, galena, iron pyrites, calcite, rhodonite, garnets, and other minerals in gneiss, mica-schist, and other hard rocks, the blende and galena being often so intimately mixed that the one mineral cannot be distinguished from the other in the mass. In the earlier years of Broken Hill mining, the deposit was worked for lead and silver, the zinc being neglected. Enormous dumps or deposits of tailings and slimes accumulated from the lead-silver concentrating plants. These dumps, rich in zinc ore, were estimated in 1903, by the New South Wales department of mines, to amount to 5,687,000 tons, containing 18·6 per cent. of zinc. In 1905, Zinc Corporation Limited was formed to work these dumps, and, since that time, after the adoption of flotation processes of concentration, to be described later, immense quantities of zinc concentrates ready for smelting have become available.

Several months ago, the Board of Trade and the Zinc Producers Association Proprietary, of Australia, agreed to the purchase by the British Government of the stocks of Australian zinc concentrates existing at the end of the year 1917 to a maximum extent of 250,000 tons per annum for the period of the war and one year after, and a considerable amount per annum for nine years subsequently. This is one of the most important industrial transactions ever negotiated.

CHAPTER III

DRESSING ZINC ORES

AFTER having been obtained by mining operations, which do not fall within the scope of this book, the zinc ores are dressed or treated by concentrating and separating processes to prepare them for smelting. The ores are associated not only with *gangue,* such as iron pyrites, calcite, chert, quartzite, and other minerals and rocks of little or no commercial value, but usually also with lead ores and sometimes with silver ores. The dressing processes, therefore, have for their object not only the separation of the zinc, lead, and silver ores, often called the *values,* from the gangue, but also the separation of the zinc ores from lead and silver ores. In many cases, these processes are of a complex nature, especially if the association of the values and gangue is very intimate.

Much of the success of the dressing operations depends on the extent to which the ores are disintegrated and sized so as to obtain the mineral constituents of the ores in particles which do not differ greatly in size and can then be concentrated and separated by means of water currents. This concentration and separation is possible when the mineral particles are of substantially different specific gravities. When the specific gravities of two or more minerals it is desired to separate are substantially the same, their separation is effected by magnetic and other means. Examples of some of these means will be given in a later part of this chapter.

The selection of a system of dressing suitable for the ores of a particular deposit is a very important problem. The nature of a suitable system depends not only on the kind of ore to be treated but also on many local conditions. A sulphide ore usually requires a more complicated treatment than a carbonate ore, and a complex sulphide ore in which blende is intimately mixed with galena, pyrites, and other minerals, requires a still more complicated treatment. The local conditions are also of great importance in influencing a choice of dressing processes; such conditions are, *e.g.*, the available supplies of skilled labour, water, and fuel, the conditions of transport, the extent and richness of the ore deposit, and the conditions of ownership under which it is worked. When an ore deposit is small, or held under onerous conditions, there is little inducement to sink much capital in setting up an elaborate dressing-plant.

Separating by the Action of Water Currents. The dressing of many kinds of zinc ores comprises the following operations: grading or sizing by means of screens and trommels, sorting and picking by hand, breaking down by means of Blake, Gates, or other rock-breakers, crushing to a smaller size by means of crushing-rolls, and subjecting the crushed and graded or sized ores to the action of currents of water in jigs and classifiers and on shaking tables of various kinds. Many of these operations are not carried out once for all; the first operation, *e.g.*, to which the ores are usually subjected is that of sizing by means of some kind of screen, but this is by no means the only sizing operation to which the ores are subjected as the dressing proceeds. This will be more fully understood when an example of dressing certain zinc ores has been given. Before giving such example, however, the chief types of dressing apparatus employed will be described.

Screening and sizing is effected by fixed screens, one kind being called a *grizzly*, and by moving screens, the most important of which are the rotary screens usually called *trommels.* The larger material which passes over the screens without falling through is called the *oversize* and the smaller material which falls through is called the *undersize.*

The grizzly is a strongly built screen of parallel iron bars usually secured together by long bolts passing through apertures in the bars. Distance tubes or washers may be threaded on the bolts to keep the bars apart, or the bars may have their ends shouldered for the same purpose. The bars are tapered downwards or otherwise shaped in cross section to minimize the risk of the grizzly being choked by lumps of ore just large enough to enter the slots between the bars. To enable the ore to slide down continuously, but not too quickly for efficient screening, the grizzly is inclined at an angle of about 30°.

Rotary screens or trommels are very largely used in dressing zinc ores. They are cylindrical or conical drum sieves secured to spider frames on a rotary shaft, or the drums may be mounted to rotate upon external rollers. Cylindrical trommels are inclined a few degrees to the horizontal, but conical trommels are mounted horizontally. Trommels are used for ores in which the constituent pieces are not more than two inches across, and they work well on dry ores, the particles of which are as small as $\frac{1}{16}$ inch ; if the ores are moist, so as to be sticky, the trommel meshes become clogged when working such fine ores, and in such cases the trommel should be worked with a free supply of water.

Trommels vary much in size and arrangement. A set of trommels may consist of two, three, or more simple trommels, arranged in descending series as regards the size of mesh, each trommel yielding one oversize and one undersize, or the set may include one or more compound trommels, like that shown in Fig. 2, which yields one oversize and two undersizes. In this trommel, the ore is fed along a shoot A and passes successively through the wire gauze section B and perforated sheet iron section C, the oversize being discharged by a shoot D. The undersize from the section B is discharged by a shoot E and that from the section C by a shoot F.

There are also complex trommels built up of concentric perforated sheet iron or gauze drums, the innermost drum having the largest sieve apertures to which the ores are first fed.

Hand-sorting and picking, or culling, is an operation of importance, especially when treating zinc ores in which the association of the mineral constituents is not too intimate. When the ores are passing over the first grizzly employed in the dressing operations, a great deal of valuable work can be done by selecting and throwing out lumps of gangue as waste and collecting lumps of clean blende or galena. In some cases hand-sorting, and picking is done on the oversize from screens and trommels which treat the ores after they have been disintegrated by rock-breakers. To assist in this work, picking tables and belts are often employed. A picking-table is usually an annular table mounted upon a vertical shaft rotated slowly by toothed gearing. The ore is fed to the table at one point, and is picked over by boys, standing round the table, the residue being swept off by a scraper fixed over the table near the feed point. A picking-belt is endless and travels over rollers which support it horizontally. The belt itself consists of india-rubber belting or is formed of a number of iron or wooden strips connected together. The belt may be two feet or more in width and the ore fed to it at one end is picked over by boys, standing at each side of the belt.

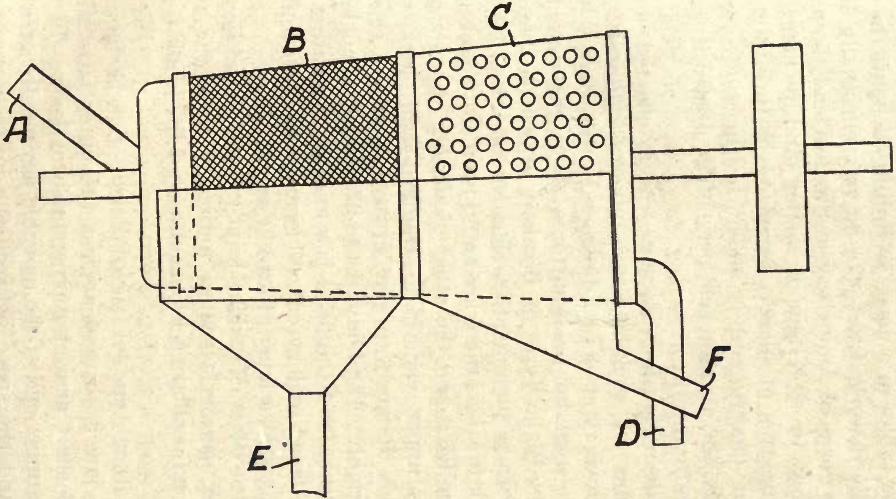

FIG. 2

COMPOUND TROMMEL

Under capable supervision by experienced men and with the tables in a clear, well-diffused light, the ores, especially if worked wet, can be very effectually culled. The zinc ores of Ammeberg in Sweden lend themselves admirably to a system of sorting and picking. The large quantity of blende separated in this way is of excellent quality and is added to the zinc ore concentrates, the average zinc percentage of which is thus raised substantially.

The disintegration of zinc ores is effected mainly by means of rock-breakers and crushing-rolls. The best known type of rock-breaker is the Blake, which was first used for breaking ores about the year 1861.

In the Blake type of breaker, of which there are many forms, such as the Marsden and the Hadfield and Jack breaker, there are two downwardly converging jaws, one fixed and the other oscillating about a pivot near its upper end. The Hadfield and Jack rock-breaker is designed to give great strength in relation to its weight. The body of the breaker is a toughened steel casting, and the fixed jaw and the oscillating jaw are each faced with a removable manganese-steel plate, bedded against a layer of lead or spelter.

In the Blake-Marsden lever-motion breaker, the oscillating jaw is actuated indirectly from the main shaft by an oscillating lever connected by a link to the jaw.

In another type of rock-breaker, the Dodge, the movable jaw is secured against the outer face of the upturned short arm of a powerful bent lever. In this type, the upper end of the movable jaw has the greatest motion and the space between the lower parts of the fixed and movable jaws is constant. In a third type of breaker, the Gates, the ore is fed between the inner surface of a strong conical casting and the outer surface of a conical gyrating head. The Comet rock-breaker, made by Messrs. Fraser & Chalmers, is of this type.

The broken products obtained from any of these types of ore-breakers are well adapted for treatment in the jigs.

Crushing-rolls for disintegrating zinc ores are pairs of rolls mounted on horizontal shafts in bearings which are forced towards each other by weighted levers or powerful springs. The rolls are usually formed of chilled iron shells detachably secured to inner cores; they are geared together, for it has been found that when only one of the rolls is positively driven not only is the output less but the wear of the roll surfaces is greater and more uneven than when both rolls are positively driven. Usually, the rolls are set a short distance apart and the first-motion roll has flanges embracing the second-motion roll or follower.

The jig is a wet-separating apparatus arranged to subject the disintegrated and sized ore to the action of water moving alternately upwards and downwards in rapid succession. The manner in which this separating process, called jigging or hutching, is effected will be explained by reference to Fig. 3, which shows the Cooley jig, a simple form of jig used for many years in America, especially for treating the rich zinc-lead ores of the Joplin district. A strong wooden box has its upper part divided into two compartments by a transverse wall *A*. In one compartment works a loosely fitting piston *B*, actuated by means of an eccentric and rod; in the other compartment is fitted a horizontal screen *C*. A pyramidal chamber, the hutch, is formed in the lower part of the box, one side of this chamber being formed by the front wall of the box which is stepped as shown in Fig. 3. The walls of the box are built up of battens, 2 in. × 4 in. in cross section, cotton wick being laid between the battens to ensure the formation

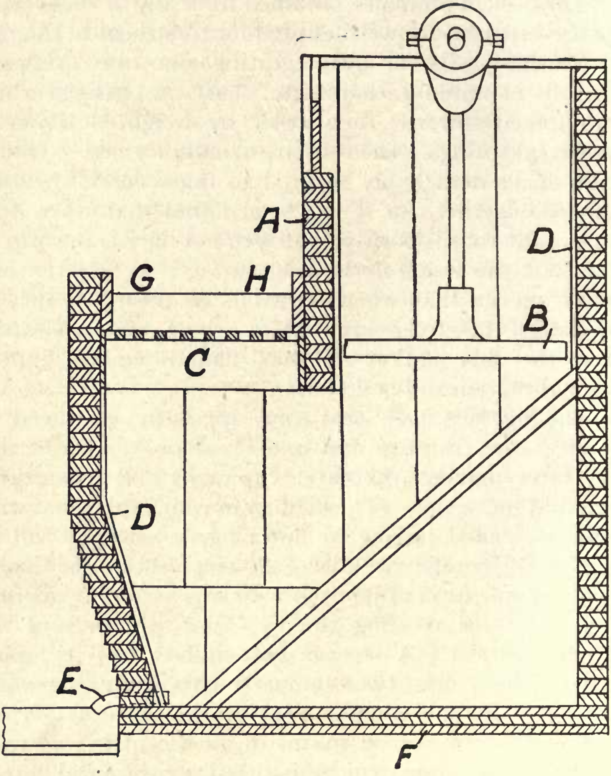

FIG. 3

COOLEY JIG

of tight joints; the parts of the walls exposed to the action of the water are lined by wooden boarding *D*, one inch thick. A discharge pipe *E*, provided with a cock, is fitted to the bottom of the hutch. The box is built up on a strong foundation formed by three layers of boarding *F*, one inch thick, nailed together.

When the jig is working, it is kept filled with water by a trough discharging into the piston compartment, and ore pulp, *i.e.*, ore mixed with water, is discharged above the sieve. It will be evident that, during the motion of the piston, currents of water pass through the sieve, first in one direction and then in the other. An upward current will cause the particles of ore to be lifted, but at different rates depending mainly on differences in the specific gravities of the particles. During the first part of the motion, heavy particles, such as those of galena, will lag behind the lighter particles. The resistance of the water to the upward motion of the particles, due not only to its inertia but also its viscosity, tends to equalize the velocities of the particles, but long before such equalization can take place the piston begins its upstroke and the water current is reversed. The upward motion of the particles is soon arrested and their downward motion commences, but the heavy particles sink faster than the light ones. This cycle of operations is repeated many times a minute with the result that the heavier particles tend to rest upon the sieve and the lighter ones to flow away with the water over the edge *GH* of the sieve compartment. Besides the heavy concentrate on the sieve, a certain amount of heavy concentrate passes through the holes of the sieve into the hutch and may be drawn off through the pipe *E*.

It will be evident from the above description that the jig can be worked to yield three products, viz. (1), coarse concentrates above the sieve; (2), fine concentrates, or hutch-work, which has passed through the sieve, and (3), tailings, or gangue mixed with a smaller or larger quantity of values. In many cases, however, jigs are worked to produce (3) and either (1) or (2) as main products.

In order to produce tailings and hutch-work, the screen is covered with a bed of galena or other heavy material, the pieces of which are too large to pass through the screen, and the holes in the screen are much larger than the largest particles of ore treated. This method of working is called the English or the Harz method, or the method of jigging through the sieve. It is suitable for the finer sizes of ore, say up to $\frac{3}{8}$ in. maximum size.

The Cooley is an example of the so-called Harz type of jig, the distinguishing feature of which is that the motion of the piston during its upstroke is the same as that during its downstroke. The Cooley is usually a large jig, its sieve being from 24 in. × 32 in. to 32 in. × 42 in. in area.

Many jigs, especially those arranged to work coarse-sized ores, from $\frac{1}{4}$ in. to $1\frac{1}{2}$ in. or even larger, are constructed to yield tailings, a heavy concentrate on the sieve, and, incidentally, a little hutch-work. Fig. 4 shows such a jig, invented by Henry Foust in 1907, and used largely in the Joplin district and other parts of America. The Fig. explains itself to a large extent, but it will be noticed that there are two piston compartments in order to ensure uniformity of action of the water currents beneath the surface of the large screen *S*.

The two pistons are compelled to reciprocate in unison by a connecting-rod *R* attached to crank pins carried by two wheels *W* on the shafts *T*. Another important feature of this jig is the arrangement for automatically discharging the concentrates from the sieve. This

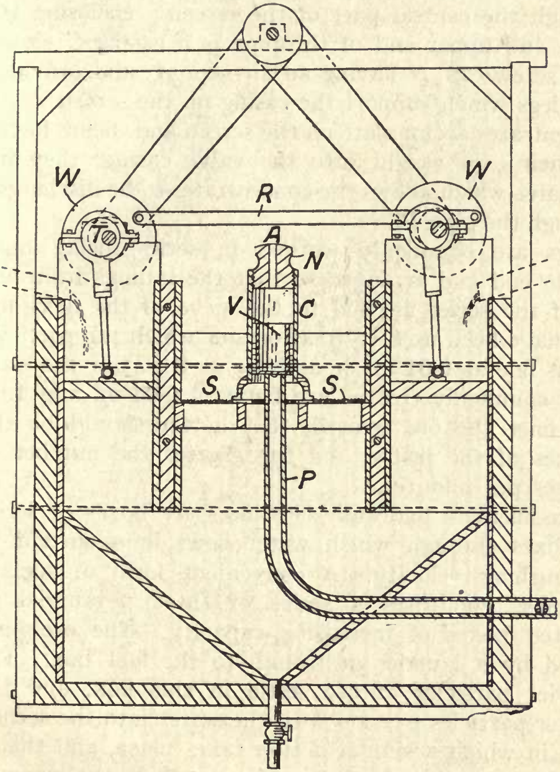

Fig. 4

FOUST'S JIG

arrangement comprises a valve *V* resting on the upper end of a discharge pipe *P*, which projects upwards through the central part of the screen; enclosing the valve and upper end of the pipe is a casing *C* closed by a screw cap *N* having an air-vent *A*, and provided with legs which support the casing on the screen. The concentrates accumulate on the screen and, being forced by their own weight into the valve casing, they lift the valve which allows the concentrates to be discharged through the pipe *P*.

Jigs are commonly worked in series, being built end to end and arranged so that the tailings from one jig of the series are fed to the sieve of the next jig. Jigs have been used to treat ores of which the particles are as fine as 0·01 in. or as large as 3 in., but the sizes most commonly treated are between 0·04 in. and 1 in. The finer the ore treated, the shorter should be the strokes of the piston and the greater the number of strokes per minute.

Classifiers, or hydraulic classifiers, are boxes or series of boxes through which water flows in a current of diminishing velocity. A convenient form of such a classifier, comprises a series of three pyramidal or pointed boxes of increasing capacity. The ore pulp is fed by a launder or trough to the first box. The heavier particles of ore settle in this box, and the lighter particles pass on with the water into the second box, in which a similar action takes place, and this is repeated in the third box from which the gangue, consisting of light and very small particles, flows away through a trough.

Classifiers are used for treating ore pulp too fine for treatment except in fine-sand jigs or on Wilfley tables. The size of the particles of such pulp is usually not greater then $\frac{1}{25}$ in. or 1 millimetre.

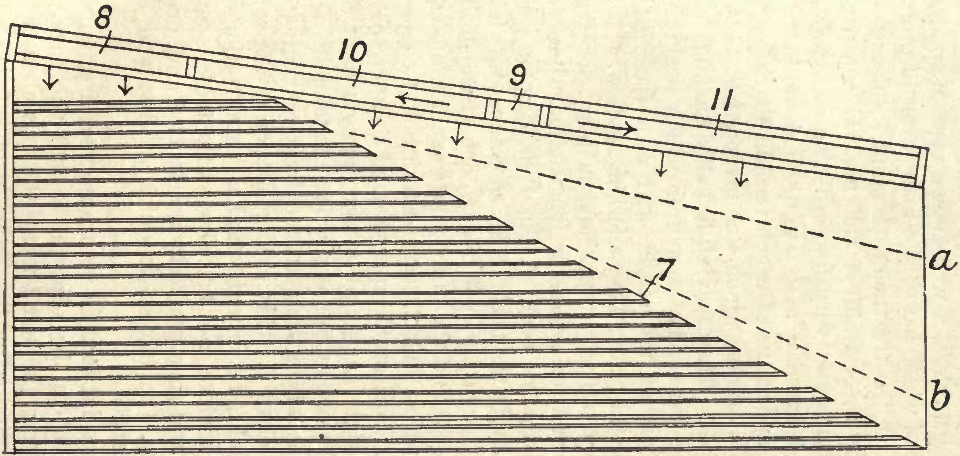

FIG. 5

WILFLEY TABLE

The Wilfley table is a well-known type of apparatus, the adoption of which has solved many difficult problems connected with the treatment of complex sulphide ores, in which the association of the mineral constituents is very intimate and very fine crushing is required to break up such intimate association. This table belongs to a type of apparatus of which the old Rittinger table and the Frue Vanner, which was invented in 1874, are other examples. They may all be called shaking tables, but the Frue Vanner has a motion which is similar in both directions of the stroke and is a true shaking motion, while the others have a jerking motion.

The Wilfley table is trapezoidal in plan, see Fig. 5, and is supported on rollers or longitudinal slides upon a strong framework bed. A rapid shaking or jerking motion is given to the table in the direction of its length by means of toggle levers 4, Fig. 6, one of which abuts against a post 3, and the other abuts against one end of a draw and thrust link 2, secured to a bolt 1 connected to the table. Adjustable springs tend to force the link towards the right hand and, under the control of these springs, the jerking motion is given to the table by means of the toggles, which are actuated by a connecting-rod 5 and crank shaft 6. This jerking motion is one which has been found to be very effectual in concentrating ores, viz., a motion which is at first slow as the table is forced to the right and then gradually accelerated and, on the return stroke, the motion is quick at first and then gradually retarded.

The table is inclined in its transverse direction and the inclination can be adjusted to suit the nature of the ore treated ; the bolt 1 forms the axis about which the table is tilted when this adjustment is being made. The upper surface of the table is covered with linoleum on which is secured a series of parallel wooden riffles

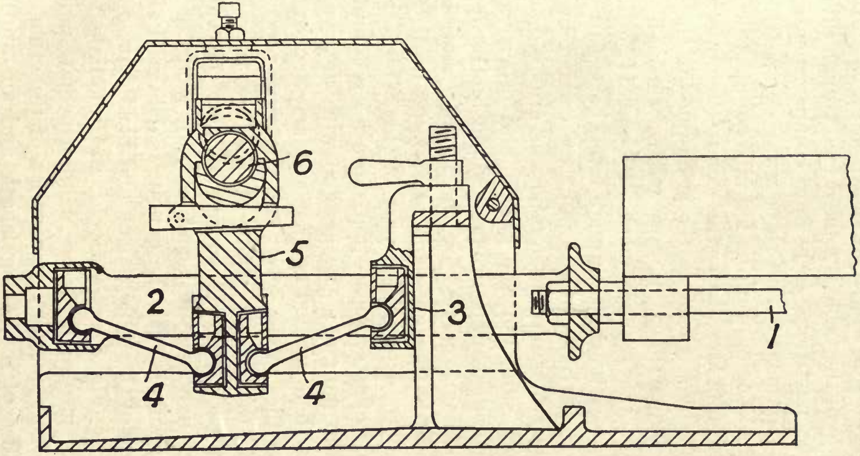

FIG. 6

JERKING-MECHANISM FOR WILFLEY TABLE

or bars 7 of increasing length, as shown in Fig. 5. Above the higher side of the table is a fixed feed trough divided by transverse partitions into four compartments, an ore-pulp compartment 8, and three water compartments 9, 10, and 11. The ore-pulp is fed into compartment 8, and passes through lateral apertures on to the uppermost corner of the table. Clean water is supplied to the central water compartment 9 and passes through end apertures into the compartments 10 and 11, whence it streams across the table through lateral apertures.

The lightest particles of the pulp are carried by the water over the riffles across the table and are discharged from its lower side, but the galena and other values together with some gangue are first caught by the uppermost riffles and are carried by the jerking motion of the table towards its right-hand or tail end until they reach the smooth or unriffled part of the table. Here the clean water effects a separation, more or less complete, of values from gangue; the gangue with any values it contains is then washed against and arrested by the next longest riffles of the series and the same processes are repeated, the lighter parts of the ore travelling over or past each riffle in succession and the values being separated on the adjacent smooth parts of the table. The result is that the gangue is delivered along the lower edge of the table, galena and blende are delivered at *a* and *b*, Fig. 5, respectively, and middlings, depending on the nature of the ore, at intermediate points. This use, in combination, of a series of directing and retarding riffles of increasing length and an unriffled surface, where the values and gangue are separated from each other, is an important feature of the Wilfley table.

Many forms of shaking table have been introduced in recent years and have been found to be efficient in treating the fine ores from the classifiers and also slimes, unavoidably produced by the crushing-rolls, which used to be treated on special slime tables or buddles. The shaking tables have also been found to do work previously effected by the fine-grade jigs.

An apparatus specially suitable for treating slimes is the vanner, a well-known form of which is the Frue Vanner, comprising an endless travelling rubber belt, about 4 ft. wide with raised edges. The frame carrying the belt is shaken rapidly from side to side and is slightly inclined upwards so that the belt travels against the flow of ore pulp, which is fed in a thin stream on to the upper end of the belt. Separation of the values from the gangue is facilitated by the shaking of the frame and the heavy values tend to cling to the belt to a greater extent than the gangue minerals. The separated values are carried forwards by the belt into a tank of water in which the lower leaf of the belt travels. Vanners are very efficient for treating slimes in which the largest particles are less than $\frac{1}{160}$ in. in diameter.

The various forms of apparatus used in dressing zinc ores by the action of water currents having been described, the manner in which these forms of apparatus are arranged so as to constitute a complete dressing-plant will be explained by describing the treatment of a blende-galena ore previously sized by passing over a grizzly, the ore being associated chiefly with calcite, quartz, and some pyrites. The ore is, in fact, a complex sulphide ore, but not one presenting great difficulties.

The grizzly is 12 ft. long, 5 ft. wide, and the bars are 1·5 in. apart. The undersize falls into an ore bin which also receives the oversize after this has passed through a Blake rock-breaker. The size of this breaker, represented in the usual way by the dimensions of its feed opening, is 12 in. × 7 in.; its crank shaft makes

180 revolutions per minute. After treatment on a picking-belt which travels 45 ft. per minute, the ore is delivered to crushing-rolls, which are 12 in. wide and 30 in. diameter ; the number of revolutions of the rolls may be 10 per minute.

The crushed ore is carried by an elevator to a compound conical trommel 6 ft. long and 3 ft. in diameter at its larger end. A convenient size for the holes in the larger screen of the trommel is 0·5 in., and for the mesh of the smaller screen 0·3 in. The oversize from the trommel passes to the first sieve of a three-cell jig of the Harz type, the undersize from the coarse sieve of the trommel passes to the first sieve of another three-cell jig, and the undersize from the fine sieve of the trommel is led to a compound cylindrical trommel, the screen meshes of which may be 0·22 and 0·16 in., respectively.

The oversize from this trommel passes to the first sieve of a four-cell jig, the undersize from the coarse sieve of the trommel passes to the first sieve of a second four-cell jig, and the undersize from the fine sieve of the trommel is conducted to the first pointed-box of a three-cell classifier. The deposits of fine ore thrown down successively in the pointed boxes are respectively led to the three four-cell jigs of a series of finer-grain jigs.

The eccentric shafts of the coarser-grain jigs make about 100 revolutions per minute and the stroke of the pistons is about 1½ in. ; the finer-grain jigs work faster than this and have shorter strokes. They are adjusted to give the following products from the ores assumed to be treated : Clean galena is obtained from the first cell of each jig and is led to the galena bin, and clean gangue (calcite, etc.) flows to waste from the last cell. Blende is obtained from the last cells of the three-cell jigs and is led to the blende bin. The second cells of these three-cell jigs yield products intermediate in specific gravity to galena and blende and called "middlings"; in the case of the ore assumed to be treated, these middlings consist chiefly of pyrites, galena, blende, and some calcite and quartz, but more or less bound together. These middlings, called coarse middlings, are reground by a set of coarse middlings rollers and returned to the elevator, to be fed again to the first trommel.

Similarly, the first cell of each four-cell jig yields galena and the third yields blende to be conducted to the galena bin and the blende bin respectively. The second and the fourth cells of each jig yield middlings, but of finer grain than the middlings from the three-cell jigs. The fine middlings are crushed by a set of fine-middlings rollers and returned to the second trommel.

The overflow from the classifier passes to a four-cell classifier, the deposits from which are led to the Wilfley tables, yielding galena, blende, and tailings. These tables are 12 ft. long and 7 ft. in maximum width; the number of jerks is 240 per minute.

Magnetic Processes of Separation. The successful separation and concentration of zinc ores by the methods so far described depends mainly on the differences of specific gravity of the constituent minerals. When these differences are not only appreciable but also considerable, such methods present no difficulties, but in other cases they are, from a commercial point of view, unsatisfactory. When zinc ores contain siderite, limonite, and, in some cases, iron pyrites, methods employing magnetic separators are often used.

Excepting pyrites or sulphide of iron, most minerals containing iron and manganese are paramagnetic, while calcite, quartz, chert, limestone, and zinc ores (excepting those containing iron and manganese) are diamagnetic. These differences in magnetic properties are utilized in dressing zinc ores. The ores are sometimes calcined or calcined and roasted before being subjected to the action of the magnets, for by such preliminary treatment, the pyrites can be converted into a magnetic form, and the siderite and limonite into magnetic oxide of iron, Fe_3O_4; these magnetic bodies can then be removed by ordinary magnetic separators.

The treatment of zinc ores containing pyrites, FeS_2, by the method indicated above requires considerable care and does not appear, until recently, to have been carried out on a large scale. In recent years, the zinc ores of the Platteville District, Wisconsin, have been calcined by the Campbell process in a rotary calciner, using oil fuel and provided with effective means for excluding air. The calcining temperature, a dull red, is kept well under control, and the calcination is completed in a very short time, say one or two minutes. Mr. Campbell states, in his British Specification, No. 6811 of 1903, that he had discovered that iron pyrites could be rendered magnetic by the action of heat without the removal of an appreciable part of the sulphur. This discovery is the basis of his process.

The separation of siderite from zinc ore has been carried out in Spain, at Przibram in Bohemia, and elsewhere. The ore is calcined and roasted at a red heat, with admission of air, when ferrous oxide is first formed and is then oxidized to magnetic oxide of iron. The air admission is regulated so as to prevent over-oxidation of the iron with formation of ferric oxide instead of the magnetic oxide.

Limonite, Fe_2O_3, can be converted into the magnetic oxide by calcining and roasting in presence of a small quantity of coal dust. This process has been carried out by the Montepioni Company, in Sardinia, in treating zinc ores containing electric calamine, limonite, dolomite, and clay. After having been calcined and roasted, the cooled ore was treated by a series of Ferraris electromagnetic separators, in which the ore was fed by a travelling band beneath the magnet poles, and the magnetic particles were attracted to the lower side of a belt travelling beneath the poles in a direction at right angles to the feed belt.

Another example of these methods of separation may be mentioned. At the Lehigh Zinc Company's works, South Bethlehem, Pennsylvania, franklinite used to be separated by roasting the zinc ores at a red heat with anthracite in a rotary cylindrical chamber, cooling and sizing the roasted ores, and separating the magnetic franklinite by Wenström separators. Each of these comprised a rotary horizontal copper drum within which was a fixed concentric series of magnets; the ore was fed to the peripheral surface of the drum which attracted the magnetic particles and carried them upwards out of the magnetic field.

The conversion of siderite, limonite, etc., into strongly magnetic bodies by calcination or calcination and roasting required great care in carrying out the process, especially as regards regulation of temperature and mode of working to avoid fritting of the ore and to ensure the production of a uniformly roasted product. On account of the difficulties of working, the processes described have been superseded to a large extent by the use of separators capable of removing feebly magnetic minerals from crushed and sized ores without other treatment. To Mr. J. P. Wetherill, general manager of the Lehigh Zinc Company, was due the introduction of these separators. The date of the introduction was 1896, and it marks an important forward step in the history of the zinc industry. Broadly speaking, the process consisted in crushing the ore so as to break up the intimate association of its constituents and then passing the ore through a magnetic field of such high condensation that feebly magnetic minerals, such as hematite, limonite, siderite, and garnets were deflected into a path different from that of the remainder of the ore. The ore was fed into the field between the opposed poles of electro-magnets, so as to enter from opposite sides of the field and pass through the zones of greatest attraction adjacent to the pole edges, thus avoiding the central zone of substantially equal attraction midway of the poles. The magnetic particles were arrested in the zones of greatest attraction and diverted into receptacles provided for them,

In an early form of Wetherill's separator (British Patent, No. 4805 of 1896) the pole-pieces were elongated and their adjacent ends, which were detachable, were tapered to effect a condensation of the magnetic lines of force. Conveyors of fine linen or canvas travelled over the pole-pieces and over pulleys mounted on shafts. The ore was fed from hoppers in a thin layer, regulated by means of vertically adjustable rollers, to a shoot above the conveyor, which carried the ore to the tips of the pole-pieces. The feed of ore into the magnetic field was therefore lateral and not central. The magnetic particles were momentarily arrested and then deflected during the motion of the belt over the tip of the corresponding pole-piece, and were directed by convergent adjustable plates into one of two lateral receptacles, while the non-magnetic material fell directly into a central receptacle.

Many modifications of this apparatus have been designed to carry out as completely as possible the

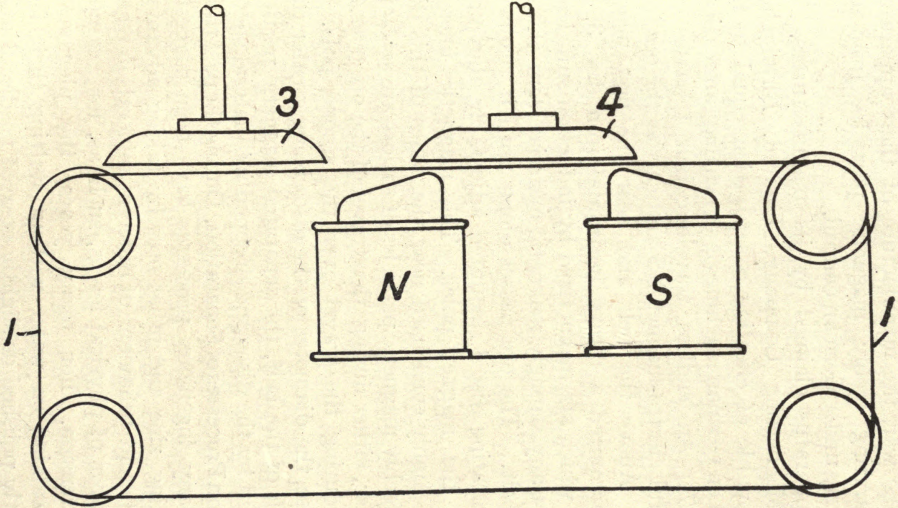

FIG. 7

ELECTRO-MAGNETIC SEPARATOR

principles of magnetic separation described above. Before the war, the manufacture of these apparatuses for separating feebly magnetic particles from ores was largely under German control.

An apparatus claimed by its manufacturers, The Rapid Magnetting Company, Limited, Birmingham, to be capable of effecting a separation equal to that obtained on German machines is shown diagrammatically in Fig. 7. An endless travelling belt 1 passes over a powerful electro-magnet NS and carries the ore to be treated. Above the belt and near the first magnet pole is mounted a rotary horizontal iron disc 3, the edges of which are magnetized by induction sufficiently to attract any strongly magnetic material from the ore on the belt. The ore passes along until it reaches a second rotating disc 4, mounted adjustably above and between the magnet poles. The magnetic lines of force are highly condensed near the edges of this disc, and the feebly magnetic particles of the ore are attracted to the disc, either during the travel of the ore over the first or during the travel over the second pole. In every case, the diameter of the discs being greater than the width of the belt, the separated magnetic particles are carried by the discs and dropped into lateral shoots.

Flotation Processes of Separation. During the past thirty years, many ingenious processes have been suggested for treating zinc and other ores by taking advantage of the different behaviour of different minerals in regard to a number of physical forces, such as, for example, surface tension. For many years, the phenomena of flies walking on water without wetting their feet, of perfectly polished or slightly greased needles floating on water, or of plates of mica, often of large size, resting on the rising and falling waves near a shore of micaceous sands, had attracted attention and were long regarded as interesting and curious. Between the mere observation of such phenomena and the practical realization of their employment in dressing zinc ores there was, however, a long journey. The first step of that journey was taken by William Haynes who, in his British Patent Specification, No. 488 of 1860, recognized that oil has a greater affinity for sulphide minerals than for their associated gangue minerals, and proposed to agitate ores with water and oil with a view to causing the oil to adhere to the sulphide minerals and carry them to the surface.

The next specially important step was taken by Miss Carrie J. Emerson. The full history of her discovery reads like a romance. She busied herself washing some greasy sacks which had contained some ore concentrates and, during the washing of the sacks in soapsuds, she noticed that the concentrates rose to the surface with the oily and soapy froth. This process, suitably modified, was tried commercially at Baker City, Oregon, and at Denver, in 1889.

In 1898, a process was described (F. E. Elmore's British Patent Specification, No. 21948 of 1898), for mixing ores with a large quantity of water and with thick oil, agitating the mixture, and allowing it to run into a settling vat. The quantity of water used was several times greater than the weight of ore treated, and the agitation of the mixture was gentle, being insufficient to produce a uniform mixture of the oil and ore pulp. A thick oil, *e.g.*, a thick tarry residue from mineral oil, was employed. This process was extensively used, more particularly for treating copper ores.

Two processes having much in common but differing greatly from those so far described were patented by C. V. Potter and G. D. Delprat, respectively. In Potter's process (British Patent Specification, No. 1146 of 1902) the ore was heated in an acid solution of 1 to 10 per cent. strength, and in Delprat's process (British Patent Specification, No. 26279 of 1902) a hot solution of salt cake or sulphate of soda and sulphuric acid was used. In Potter's process, sulphuric acid was used on account of its cheapness ; the specific gravity of Delprat's solution was about 1·4 and the solution was, preferably, at a temperature below its boiling point. Bubbles of gas evolved in the liquids assisted the flotation of the sulphides, but the specifications do not mention this. Both processes, the interests in which have been combined so that they are spoken of together as the Potter-Delprat process, have been carried out at Broken Hill, Australia.

A long step forward was taken by A. Froment, of Traversella, Italy, whose British Patent Specification, No. 12778 of 1902 describes a process of mixing and agitating the ore for a short time with water, an ordinary oil, a small amount of sulphuric acid, and some limestone. This is a true oil and gas flotation process. The sulphides adhere to the oil and form spherules which become attached to the bubbles of gas formed by the action of the acid on the limestone.

Another process involving the introduction of a distinctly novel idea was patented by A. E. Cattermole, in British Patent Specification, No. 26295 of 1902. Oil and soap were mixed with the ore pulp in proportions suitable for effecting an aggregation of the sulphide minerals into lumps or granules which subsided, while the gangue flowed away with the current. Instead of using a large quantity of oil, the amount used was so small that the granules formed were specifically heavier than the gangue ; for example, the quantity of oil was between 4 and 6 per cent. of the weight of the values.

In their British Patent Specification, No. 20419 of 1903, H. L. Sulman and H. F. K. Picard, utilizing the property possessed by films or bubbles of air or other gas of attaching themselves to oiled particles of sulphide ore, described the introduction into the ore pulp of bubbles of air or other gas previously charged with a spray of oil or with vapour of a volatile oil.

A process introducing a novel method of working was patented by F. E. Elmore, in British Specification, No. 17816 of 1904. In this process the ore pulp is treated with a small quantity of oil under a partial vacuum, the treatment resulting in the evolution of gas bubbles from the liquid mixture. This process has been applied with very great success, and has given excellent results at Broken Hill, Australia.

Nearly all the processes so far described depend for their success on the formation of a froth carrying the values, but A. J. F. De Bavay proposed, in his British Patent Specification, No. 18660 of 1904, to float a thin layer of zinc-blende ore-pulp in a pasty condition by means of a small stream of water on to the surface of a vessel of water, relying on the action of surface tension to cause the sulphides to float. This may be compared with the phenomenon of floating plates of mica previously mentioned.

An important process was patented by Messrs. Sulman, Picard and Ballot, in British Specification, No. 7803 of 1905, and this was followed by other processes described in Specifications, Nos. 28173 of 1908 (Sulman and Picard) 2359 of 1909 (Greenway, Sulman, and Higgins), and 4911 of 1909 (Hoover), which have given excellent results. In Specification, No. 7803 of 1905, the inventors state that they had found that when the oily substance mixed with the ore pulp was only a fraction of 1 per cent. of the weight of ore, granulation did not take place, that, after vigorous agitation, the oil-coated particles rose to the surface in a froth, that the action of the process was improved by warming the pulp and adding a small amount of acid, and that very finely pulverized ores or slimes were more easily included in the froth than larger mineral particles. The process described by the inventors consisted in mixing warm ore pulp, the ore having been finely pulverized, with acidified water and a small quantity of oil, such as oleic acid or petrol, and agitating the mixture so as to form a froth.

This process and also modifications of it described in the three later Specifications mentioned in the preceding paragraph were carried out successfully by Minerals Separation Limited, a Company formed to work and develop flotation processes. The following is a description of their amyl-alcohol process, to which Specification No. 28,173 of 1908 relates. Simple as the process appears when inspected, it deals easily with a large amount of pulverized ore with the production of a dense thick scum carrying the blende and galena of the ore. The nature of the process will be understood by reference to Fig. 8. Finely powdered ore is delivered by a shoot 1, together with four parts by weight of water, into the first cell of a three-cell agitating apparatus 2. Water containing about 0·2 per cent. of sulphuric acid is delivered to the cell from a vessel 3 and a solution of amyl-alcohol, containing as little as 0·002 per cent. of the alcohol, is delivered from a vessel 4. Each cell is provided with a rotary agitator 5, by which the liquid is vigorously agitated so as to disseminate a large quantity of air throughout it. The agitated mixture delivered from the last cell is deflected upwards by an inclined board 6 into a pointed-box 7, and presents a dense, thick scum which flows over the surface of the water and into a launder 8, provided with a pipe 9, for delivering the blende and galena. The gangue settles in the pointed-box and is discharged through a pipe 10.

The remarkable feature about the process is the formation of a thick, dense scum carrying the values

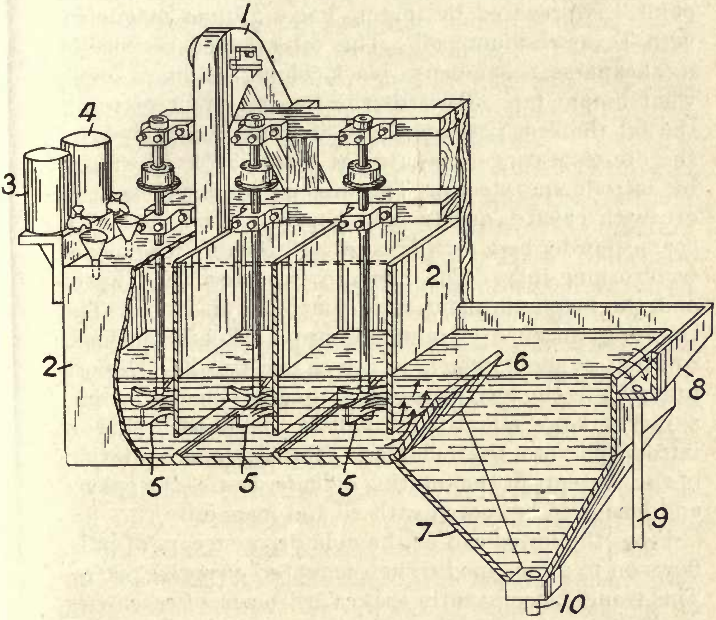

FIG. 8

FROTH-FLOTATION APPARATUS

by the use of such a small amount of reagents. The quantity of acid used is very small, while the quantity of amyl-alcohol is very trifling, a smell of pear drops being distinctly perceptible, but by no means strong, in the atmosphere about the apparatus.

An ingenious process, utilizing magnetism as well as surface tension phenomena for treating blende-galena ores, was patented in British Specifications, Nos. 12962 of 1908 (Lockwood & Samuel), 16229 of 1909 (Lockwood & Samuel), and 25369 of 1911 (Murex Magnetic Company, Limited, and Lockwood). A "magnetic paint" is prepared by mixing finely ground magnetite with Texas residuum oil. This oil, selected because of its cheapness, is of a dense, black colour, and like a somewhat limpid tar. Towards the freezing-point of water the oil thickens; consequently it is necessary to keep the ore-separating apparatus at about 70°F in winter, by introducing steam. The ore, *e.g.*, a blende-galena ore with calcite, quartz, and barytes, is crushed to a coarse powder by a rock-breaker and then to fine powder by crushing-rolls. The fine ore is mixed with water and the magnetic paint is run into the mixture. The resulting mixture is pumped into a slightly inclined rotating cylinder which is driven electrically. Before pumping in the mixture of ore pulp and magnetic paint, a rather large quantity of ballast and leaden shot is introduced into the cylinder. The vigorous agitation of the contents of the rotating cylinder causes the galena and blende to be coated with oil and magnetite.

From the lower end of the cylinder a stream of pulp flows on to an inclined trough mounted on spring plates. This trough is constantly shaken by means of eccentrics and delivers the pulp beneath a band travelling at right angles to the trough and under a vertically adjustable powerful magnet. This magnet attracts the oiled particles out of the pulp to the underside of the belt, the appearance beneath the belt being that of "rain going upwards." The pulp with the gangue is discharged from the lower end of the trough, and the oiled blende and galena particles travel on the underside of the band out of the magnetic field. The process of oiling needs to be carefully carried out to prevent some of the gangue minerals being oiled and coated with magnetite grains.

Another process, which may be mentioned, depending on the phenomenon of surface tension, is Macquisten's, described in British Patent Specification, No. 25204 of 1904. Flotation of the sulphide minerals of an ore is effected during their passage through Macquisten's tube, a rotary nearly horizontal cylinder provided with an internal helix by which the ore pulp fed into the tube is pushed forwards as the cylinder rotates.

In Callow's process, patented in America, oil and air are introduced into and mixed with the ore pulp in a vertical cylindrical vessel, whence the mixture flows into two cells in succession. These cells have perforations in their bases through which air is forced into the pulp so as to form a froth carrying the values.

By the various processes described, blende and galena together are separated from the ore and, if the blende and galena are sufficiently free from gangue minerals, nothing remains but to separate the blende from the galena, *e.g.*, by ordinary wet-separating processes.

This reference to the separation of blende from galena and such gangue as may be present introduces us to an important development of the flotation process, viz., the selective separation of the blende, galena, and other sulphides from an ore during the carrying out of the flotation process itself. On account of the great difference between the capabilities of being oiled possessed by galena and blende on the one hand and by gangue minerals on the other, the separation of galena and blende from the gangue is comparatively simple, but the difference between galena and blende in this respect is comparatively small. Blende is, however, less amenable to oiling than galena, and it has been found that they can be separated by modifying the method of carrying out the flotation processes so as to separate the galena from the blende and gangue, and then carrying out another flotation process to separate the blende from the gangue.

Many modifications may be made in the process to effect the above-mentioned results. The nature of the oiling agent, the nature and amount of free acid present, the temperature of the pulp, and many other conditions exercise an important effect and have been utilized by various inventors to effect the desired selective action.

In Cattermole's British Patent Specification, No. 26296 of 1902, which relates not to selective separation of galena and blende during the carrying out of the flotation process itself but to the liberation of the blende from the galena of the granules obtained in his flotation process, the different degrees to which different sulphides can be oiled is clearly recognized. He proposed to break down the association of the oiled blende and galena particles by agitating the granules with a solution of soap and an alkali, the strength of the solution being such that the blende was liberated from the granules but not the galena.

Several other processes have been patented and worked commercially for effecting a true selective separation of the mineral constituents of zinc ores. A few of them will be described. British Patent Specification, No. 1789 of 1909 (Horwood), describes a process of roasting so as to leave the blende substantially unaltered but convert the superficial parts of galena, copper pyrites, and iron pyrites present into oxides or sulphates; the roasted ore is then treated by ordinary flotation processes, when the blende is oiled and carried away by the scum. The roast is effected at a temperature of between 300°C. and 400°C.

In the working of the Murex process already described, it was found that, when using shot and ballast in the rotary oiling cylinder, the agitation could be continued so as to oil not only the galena and blende but also substantial parts of the gangue minerals. By using quartz grains, instead of the shot and ballast, and adding silicate of soda solution to the oily mixture the process could be worked with the result that the galena only was oiled. This important discovery, therefore, rendered possible the separation of the galena from the blende and gangue by means of the magnets ; the blende could then be separated by an ordinary magnetic oiling process. British Specification, No. 13208 of 1911 (Murex Magnetic Company, Limited, and Lockwood), relates to this process of effecting a selective separation.

Another process for effecting selective separation of blende and galena is described in Australian Patent Specification, No. 5040 of 1912 (Lyster), and British Patent Specification, No. 11939 of 1913 (Lyster). This process is carried out by treating the ore pulp with a solution of sulphates, chlorides, or nitrates of calcium, magnesium, sodium, or potassium, or mixtures of these, so as to produce an alkaline or neutral, solution ; the oiling reagent preferably employed is eucalyptus oil.

Another development of the flotation processes is directed to rendering them suitable for separating smithsonite and other oxidized zinc ores from associated gangue minerals. In British Patent Specification, No. 26019 of 1909 (Sulman & Picard), it is proposed to treat the ore pulp with sulphuretted hydrogen, or soluble sulphides, in order to convert the superficial parts of the smithsonite and other oxidized zinc ores into sulphide and then subject the treated pulp to the action of an ordinary flotation process.

A later process for effecting the separation of oxidized ores from their gangue is described in British Patent Specification, No. 105627 (Sulman, Edser, and Minerals Separation, Limited). The process, as claimed, is not limited to the treatment of the ores of any particular metal and, in the description of the process for the treatment of an oxidized ore, given by way of example, an ore of copper is selected. In order to cause the values to float with the froth, the finely ground ore was mixed with soft water, and small quantities of silicic acid solution, sodium oleate solution, sodium resinate solution, and paraffin oil. This mixture was agitated for one minute and the resulting froth removed. Without any further addition of reagents, a second and then a third froth were formed and removed. The three froths yielded a total of nearly 80 per cent. of the copper contents of the ore treated.

CHAPTER IV

CALCINING AND ROASTING ZINC ORES

AFTER concentration in the manner already described, zinc ores are usually calcined and roasted to prepare them for smelting or reduction to the metallic state. This calcination and roasting is necessary in the case of blende ores in order to eliminate their sulphur and convert their zinc into oxide of zinc suitable for reduction by means of carbon or other reducing agent. In European zinc works, calamine ores, both carbonate and silicate, are usually calcined before being smelted, but in America they are rarely so treated.

The nature of the calcining and roasting processes will be better understood from a consideration of the chemical changes which take place during the processes. Calcination is a heating process by which chemical constituents are eliminated from the ores, and roasting is a heating process by which chemical constituents are combined with the ores. The process of preparing blende for smelting is both a calcining and a roasting process, for sulphur is eliminated in the form of sulphurous acid gas and oxygen is caused to combine with the zinc to form zinc oxide.

The chemical changes which take place during the calcining and roasting of blende are more complicated than would appear from the following account which, however, represents the principal reactions. The sulphur of the blende burns with production of sulphurous acid gas and, at the same time, the zinc of the ore is oxidized, as represented by the following equation—

$$2\,ZnS + 2O_2 = Zn_2 + 2\,SO_2 \quad . \quad . \quad .(1)$$

A certain amount of sulphuric anhydride is also formed and unites with some of the zinc oxide to form sulphate of zinc, according to the equation—

$$ZnO + SO_3 = Zn\ SO_4 \quad . \quad . \quad . \quad . \quad . (2)$$

At a bright red heat the sulphate of zinc is decomposed with production of basic sulphates of zinc, the composition of which appears to be variable and may be represented by the formula $x.ZnO, ZnSO_4$. Finally, at the high temperature to which the ore is raised towards the end of the process, these basic sulphates are decomposed into zinc oxide, sulphurous acid gas, and oxygen.

The earlier stages of the calcining and roasting process require temperatures between 700°C. and 800°C., but the later stages require a temperature of 900°C. or more.

When carbonate ores (usually called calamine in this country) are treated, the operation is a calcination represented by the equation : $Zn\ CO_3 = ZnO + CO_2$. A dull red heat is sufficient to effect this calcination.

When silicate ores are calcined, hygroscopic moisture is driven off and, in the case of the hydrated silicate, water of crystallization is also eliminated.

The calcination and roasting of blende is necessary, as stated already, to prepare it for smelting ; carbonate and silicate ores, on the other hand, may be smelted raw. There are important reasons, however, why these ores, especially the carbonate ores, should be calcined. In the first place, they are rendered less compact and more capable of being acted upon by the reducing-agent employed in the smelting process. Again, calcination renders the ores perfectly dry by removal of moisture, which is present in the raw ore to an extent of 5 or more per cent. of its weight, and eliminates the water of crystallization present in hydrated ores. By using such perfectly dry calcined ore in the smelting furnace, loss of heat required for driving off water from the ore, if used raw, is avoided, and it is also easier to regulate the heat in the smelting retorts. The elimination of water vapour and, in the case of zinc carbonate ores, carbonic acid gas, during the calcining process contributes greatly to the success of the smelting process, for, without calcination, the water vapour and carbonic acid gas would be driven off in the smelting retorts and would tend to oxidize the metallic zinc vapour produced during the smelting process. There is another advantage attending the calcination of zinc ores, and especially carbonate ores. Theoretically, carbonate of zinc loses about 35 per cent. of its weight through loss of carbonic acid gas. In practice, during calcination, some of the carbonic acid gas is not driven off, but the loss of weight due to elimination of carbonic acid gas and moisture is commonly not less than a third, so that a ton (2,240 lbs.) of carbonate ore may weigh, after calcination, only about 1,500 lbs. This is a great consideration in connection with the cost of transport of the ore, and of special importance to smelters in this country, since so much of the ore is imported, and this consideration applies, in different degrees, to all zinc ores.

In order to save freightage costs, it is usual to calcine carbonate and other zinc ores at or near the mines. Most of the zinc ores imported from Spain, Sardinia, Algeria, Tunis, and Greece are calcined before shipment.

Carbonate and silicate ores are calcined in vertical kilns, reverberatory furnaces, or rotary calciners. The kilns, which have been used extensively in Belgium, Silesia, Spain, and Sardinia, are particularly suitable for calcining coarse ores. These kilns are about 16 ft. high and 7 ft. in diameter at the widest parts of their vertical sections, which are usually conical or oval. Some of the kilns are provided with firegrates at or near their bases, while others are without firegrates, the ores and fuel being charged into the kilns in alternating layers. The fuel generally employed is coal or, as in Sardinia, charcoal.

These vertical kilns have been superseded to a large extent by reverberatory furnaces, which are especially well suited for calcining ores in a finely divided state, but may be used also for coarse ores. In one form, which has been used largely in Belgium and Silesia, the hearth has working doors along one side and is heated by means of a fireplace at one end. The hearth varies in size in different furnaces, but is usually about 16 ft. long and 8 ft. wide. In another kind of reverberatory furnace, there are two superposed hearths heated by means of a fireplace, the flames from which travel over the lower and then over the upper hearth to a chimney. The ore is charged on to the upper hearth, rabbled and heated for some hours, and then pushed through an aperture in the upper hearth on to the lower hearth, where the calcining process is finished.

The Montepioni Company, Sardinia, use the Ferraris furnace, which is heated by means of a gas producer and is of large dimensions; the hearth of this furnace, which may be 40 ft. long, is inclined at an angle of about 20° from its lower or discharging end to its upper or charging end. Rotary calciners of the Oxland-Hocking type are also used by the Montepioni Company; in these calciners, the ores are fed into the upper end of an inclined rotary cylinder having a fireplace at its lower end. The ore travels in about six hours to the lower end of the cylinder and is discharged through a gap between the fireplace and the lower edge of the cylinder. This type of calciner, for treating zinc and also copper, tin, and arsenical ores, was patented by Oxland and Hocking in 1868.

The calcining and roasting of blende is more difficult than the calcining of carbonate and silicate ores of zinc, for, in order to eliminate the sulphur of the blende as completely as possible, a high temperature is necessary and also repeated rabbling to expose every particle of blende to the roasting action. In many localities, it is also necessary to prevent the sulphurous gases from escaping into the atmosphere, and arrangements have to be made to render these gases harmless, or to collect and utilize them.

In the earlier years of extracting zinc from blende, the sulphurous acid gases were allowed to escape freely into the atmosphere, but successful attempts have been made, since the year 1872, to collect and utilize them, especially in the manufacture of sulphuric acid. Many years before, suggestions and attempts to do this had been made in this country and on the Continent. British Patent Specification, No. 13999 of 1852 (Graham) describes the roasting of blende, with recovery of sulphurous acid gas for use in making sulphuric acid, and Crockford, in his British Patent Specification, No. 1376 of 1858, also describes a process for the same purpose.

Where recovery of the sulphurous acid gas is not imperative or is not desired, blende is usually roasted in reverberatory furnaces in which the hot gases from the fireplace, together with a plentiful supply of air, pass freely over the ore, burning off the sulphur and oxidizing the zinc. With furnaces of this kind it is easy to drive off practically all the sulphur and convert the zinc into oxide of zinc, thus effecting what is called a "dead roast."

A simple form of furnace of the so-called Freiberg type, for roasting blende ores, has a single long hearth with a fireplace at one end and a chimney at the other, the working doors being provided along one side of the hearth. Two such furnaces may be built side by side, thus saving heat which would otherwise be lost mainly by radiation and convection. The hearth is about 7 ft. wide, and may be 35 ft. long, but varies greatly, being longer in furnaces for roasting ores with a high percentage of sulphur, the combustion of which assists in maintaining the furnace temperature, and shorter in furnaces for roasting ores with a low percentage of sulphur. Sometimes the hearth is about 14 ft. wide, and has working doors at both sides.

A more common type of blende-roasting furnace is the double-hearth reverberatory, with two superposed hearths worked in the manner already described when dealing with similar furnaces used for calamine ores. Each hearth may be 7 ft. wide and 20 ft. long, and four such furnaces are usually built in one structure, called a *massive,* with fireplaces and a common chimney at the contiguous parts of the hearths.

A blende-roasting furnace, called the shelf-burner or shelf roaster, is often employed in the United States, and has four or more superposed hearths, which differ from those of the double-hearth furnaces described above in having their working doors in their ends instead of along their sides. Several shelf-burners or roasters are usually built together to form a massive with heating and chimney arrangements in the centre.

The furnaces so far described have their charges rabbled by hand. There are also many kinds of blende-roasting furnaces which are reverberatory but provided with mechanical means for rabbling and moving the charge over the hearth. One of these is the Ropp furnace, which has been used in America, especially in Kansas and Missouri. The construction of this furnace is shown diagrammatically in plan in Fig. 9. The hearth *A* is very large, often 150 ft. long and 14 ft.

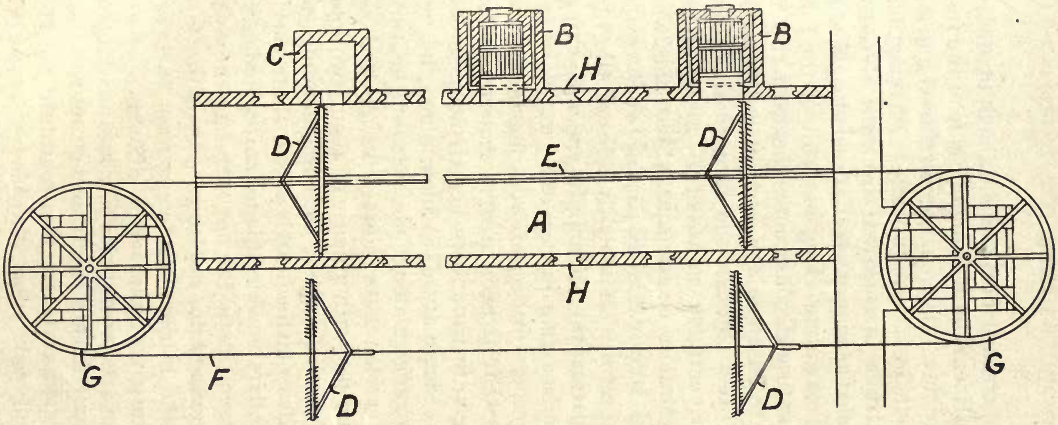

FIG. 9

ROPP ROASTING FURNACE

wide, its temperature being maintained by means of a series of fireplaces *B* built along one side of the furnace; *C* is the smoke flue. The charge is rabbled and moved along the hearth by a series of rakes *D* having inclined blades; these rakes are carried by vertical rods supported on wheeled carriages which travel along a continuous trackway, extending along one side of the furnace, and through a tunnel constructed beneath the centre of the hearth. To allow the vertical rods supporting the rakes to travel through the furnace, the hearth is formed with a central narrow slot *E*, along which the rods travel. Motion is transmitted to the wheeled carriages by a steel cable *F* passing over two large pulleys *G*. Apertures *H* in both sides of the furnace serve for regulating the air supply and inspecting the progress of the roasting process.

Another reverberatory blende-roasting furnace, which has been somewhat largely used in America, is known as the Zellweger furnace. Its hearth may be 130 ft. long, and its temperature is maintained by means of fireplaces arranged along one side of the furnace. A heavy shaft carries at its ends two large wheels which are rolled to and fro, with a pause of about two minutes at the end of each traverse, in corresponding wheel pits at the sides of the hearth. The shaft carries a series of loose collars on which blades are secured radially; these blades serve to stir the ore. During the traverse of the shaft towards the discharge end of the furnace the action of the blades is different from their action during the return traverse. This difference of action is due to the collars having a locking-means which locks them to the shaft during the traverse towards the discharge end and leaves them free to rotate during the return traverse; as a result the blades carry the ore towards the discharge end of the furnace, but do little more than agitate it when the shaft travels towards the feed end. The fuel consumption of the Zellweger furnace is considerable.

In both the Ropp furnace and the Zellweger furnace the agitating means is exposed to the action of the furnace heat and gases during a large part of the roasting process ; in the next furnace described, the agitating means is scarcely so exposed. This furnace has been used for roasting blende at the works of Messrs. Fry, Everett, & Company, at Swansea, and is called the Godfrey furnace. It has an annular rotary hearth, covered by a roof, except in one sector which is open and accommodates a radially arranged agitator. The ore fed to the hearth is calcined and roasted as it travels round with the hearth, but is stirred up and freely exposed to the air when it reaches the agitator.

There remains to be described an important class of roasting furnaces in which the blende is calcined and roasted with recovery of sulphurous acid gas for use in making sulphuric acid. These furnaces have been used to a large extent in Germany, Belgium, France, and the United States, and also at several works in this country.

It has been found that the gas leaving the roasting chambers and intended for use in making sulphuric acid should contain not less than about 5 per cent. of sulphurous acid gas. To obtain such a gas, admixture of the heating gases with the sulphurous gases should be prevented as far as possible ; at the same time, sufficient air must be admitted to burn off the sulphur and oxidize the zinc. The calcining and roasting chambers, all or some of them, are therefore muffled or shut off from the heating gases, and arrangements are made for supplying the necessary air. This air is preheated, sometimes to a high temperature, by passing through air passages in the masonary of the furnace, or through hollow stirring apparatus employed for rabbling the ore.

The Hasenclever-Helbig furnace is said to have been the first successfully used, about the year 1874, for calcining and roasting blende with recovery of sulphurous gases. It had two muffled hearths, one inclined and the other horizontal, and also a horizontal reverberatory hearth heated directly by the hot gases from a fireplace or gas producer ; the roof of this reverberatory hearth formed the floor of the horizontal muffled hearth. The ore was fed into the upper end of the inclined hearth down which it travelled into one end of the horizontal muffled hearth, and was worked by hand towards a discharge aperture through which it fell on to the reverberatory hearth. Baffles projecting downwards from the roof of the inclined hearth regulated the descent of the ore, and its feed to the horizontal muffled hearth was controlled by a rotary fluted drum. It is said that this early form of blende-roasting furnace recovered about 60 per cent. of the sulphur contained in the blende.

The Hasenclever-Helbig was superseded by the Eichhorn-Liebig roasting furnace. This furnace is described in the German Patent Specification, No. 21032 (1882), which shows six superposed hearths along which the blende is caused to travel in succession. These hearths are heated by producer gas traversing flues built in the masonry between the hearths and extending transversely to them. The ore remains on each hearth about six hours. Air admitted to the roasting chambers is preheated by circulation through passages in the masonry below the lowest heating-flues.

The Eichhorn-Liebig has been superseded to a large extent by the Rhenania furnace, sometimes called the Hasenclever furnace. In this furnace, shown in Fig. 10,

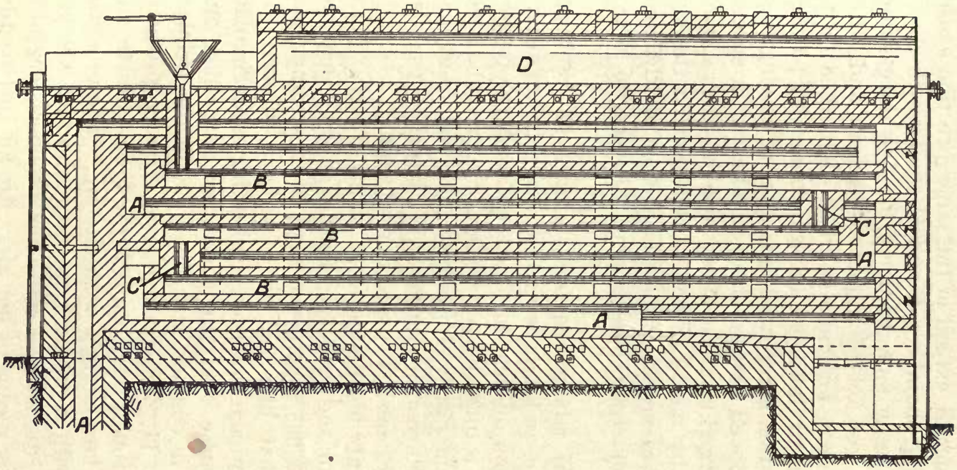

FIG. 10

RHENANIA ROASTING FURNACE

the heating flues *A* extend in the same direction as the muffled roasting-chambers *B* and alternate with them, there being three or four chambers *B* ; *D* is the gas flue. The ore is fed on to the uppermost hearth and, after remaining thereon for some hours is discharged on to the second hearth through a vertical connecting passage *C* ; this operation is repeated until the ore having been rabbled and moved forward along each hearth in succession, is discharged from the lowest hearth. The rabbling is performed by means of hand tools inserted through working doors in one side of the furnace. Two Rhenania furnaces, or sometimes four, are built together to form a massive.

The manual labour required, mainly for rabbling, is considerable, and four or five cwts. of coal are needed to roast one ton of blende. The sulphur in the roasted ore, however, is often below one per cent., and the gases yielded contain nearly 7 per cent. of sulphurous acid gas. The Rhenania furnace is largely used in Westphalia, Rhenish Prussia, and Belgium.

An excellent blende-roasting furnace, very much used in Belgium and France, is that designed by Delplace, of Namur. It has superposed shelves, the arrangement being somewhat like that of a Maletra furnace. In the Maletra furnace, however, the heating gases circulate in zig-zag course over the shelves in succession and therefore are in contact with the ore. In the Delplace furnace, Fig. 11, the heating-gases from a producer 1 circulate through flues beneath the lowest hearth and do not come into contact with the ore. The producer is provided with a muffle 2, in which the fuel is coked before being discharged into the producer chamber to be burnt by means of hot air. Air for the roasting chambers and for the producer is heated by circulation through passages, shown by dotted lines in the lower

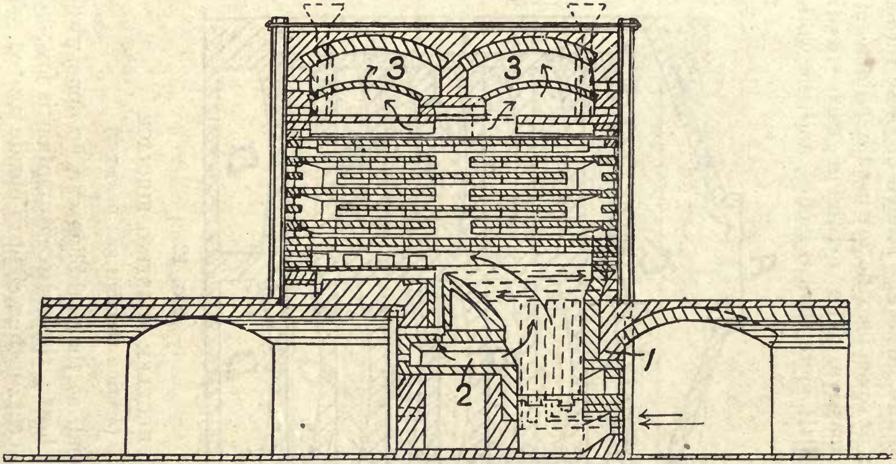

FIG. 11

DELPLACE ROASTING FURNACE

part of Fig. 11. Dust chambers 3 are provided in the upper part of the furnace. Twelve of these furnaces, each with six or seven hearths, are usually built together to form a massive. The depth of each roasting-chamber is little more than 6 inches, and the working doors are small so that rabbling can be done without great loss of heat; the coal consumption is low, being about 12 per cent. of the weight of blende treated. The sulphur of the blende is reduced to a low percentage, and the roast gases contain nearly 7 per cent. of sulphurous acid gas by volume.

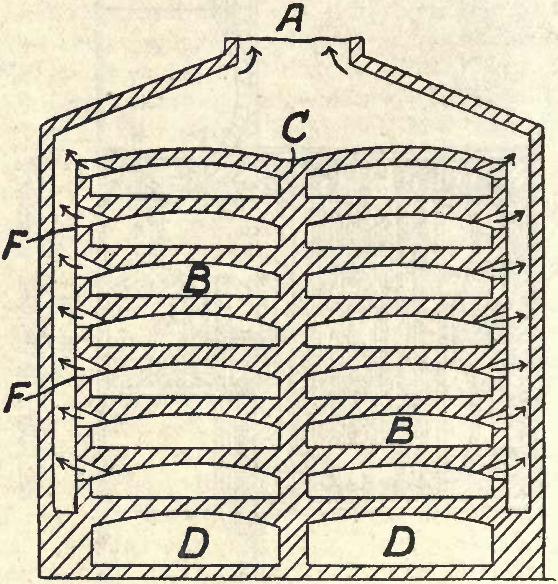

FIG. 12

HEGELER ROASTING FURNACE
(Section through gas passages)

The muffled furnaces so far described for roasting blende have their charges rabbled by hand. The next to be described, the Hegeler furnace, has mechanical means for rabbling. It was the first mechanical furnace used with success in America for roasting blende. That was more than 35 years ago; to-day, the Hegeler furnace, with various modifications, is used almost exclusively in the United States, and is also used in Australia. The essential features of the furnace are shown in the United States Patent Specification, No. 303571 (1884), from which Figs. 12, 13, and 14 have been taken, Fig. 12 being a cross-section in a plane through the flue *A* leading to the sulphuric acid chamber;

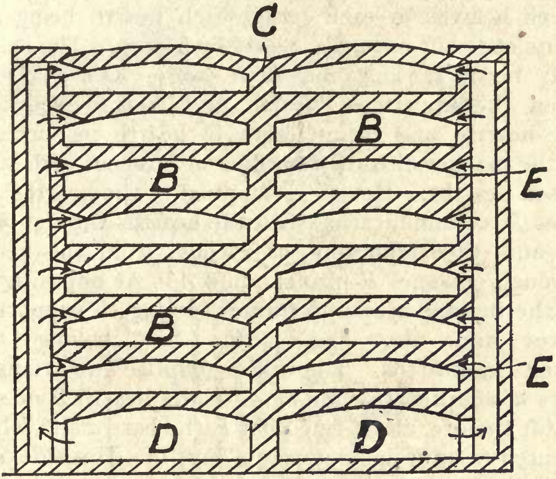

FIG. 13

HEGELER ROASTING FURNACE

(Section through air passages)

Fig. 13 a cross-section in a plane through some of the air passages; and Fig. 14 a view of part of an ore charge being agitated and moved forwards by one of the rakes used in this furnace.

A massive foundation supports a double series of hearths *B* separated by a central wall *C*; there are seven hearths in each series, each hearth being open at its ends but normally closed by a door. The hearths may be 50 ft. long and 12 ft. wide. Ore is charged upon the uppermost hearth and is traversed along the hearths and from hearth to hearth in succession in the manner already described in furnaces with superposed hearths. Hot air is supplied to the hearths from flues *D*, communicating with the hearths through inlets *E*, and the sulphurous gases pass from the hearths through passages *F* into the flue *A*. At opposite ends of the furnace are large frames serving to support the rakes and also the means for moving them along the hearths. The rakes comprise two triangular bars *a*, adapted to slide close to the hearth floor so as to lift the ore, and a tined bar *b*, the bars *a* and *b* being secured to an iron side piece *c*, Fig. 14. This side piece, and the corresponding one at the opposite end of the rake, are connected by rods to a length of gas-piping, or to a chain or cable for moving the rake over the hearth. Hegeler furnaces reduce the sulphur of the ore, which usually contains 25 to 30 per cent. of sulphur, to about 1·2 per cent., and the sulphurous gases produced contain about 5 per cent. of sulphurous acid gas by volume.

The Ridge blende-roasting furnace has five long superposed hearths, each of which is swept over by several rakes mounted on vertical rotary hollow shafts cooled by water currents. The uppermost hearth serves to dry the ore which is heated during this process

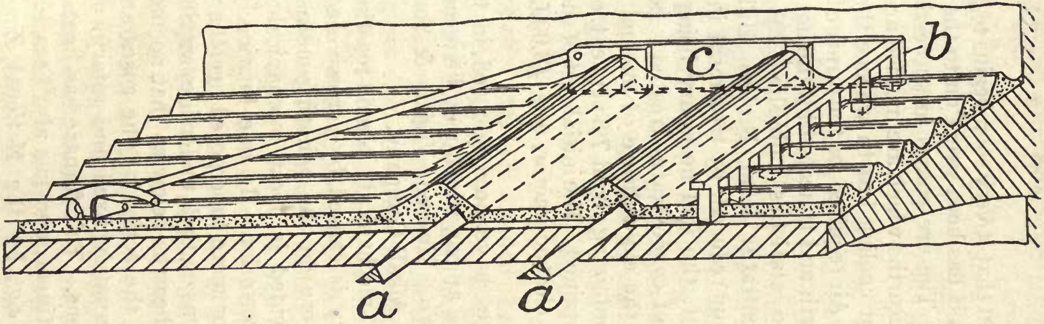

FIG. 14

HEGELER AGITATING-APPARATUS

to such an extent that it very soon begins to yield sulphurous gases when it has been swept on to the first roasting hearth below. The ore passes in succession along the three roasting hearths which are muffled and is delivered to the lowest or cooling hearth whence the roasted ore is discharged. Air required for the furnace flows through the cooling-hearth and is heated by the hot roasted ore.

According to statistics published by Mr. Ridge, flotation concentrates from Broken Hill, Australia, had their sulphur reduced, by treatment in his furnace, to 1·25 per cent., the fuel necessary being 8 per cent. of the weight of concentrates treated; both the cost of repairs and the expenditure of manual labour were small. Gases containing about 7·5 per cent. of sulphurous acid gas were obtained. The initial cost of such a furnace, complete with electric motor, was £3,000, before the war.

Ridge furnaces have been adopted in this country at several works, among which may be mentioned those of Dillwyn & Co., Limited, Vivian & Sons, Limited, and the United Alkali Company.

In working mechanical blende-roasting furnaces a great difficulty is caused by corrosive action of the gases and the ore on the agitating-means employed. Means are provided in most mechanical furnaces to minimize this corrosion. In one furnace, the Spirlet, there are three or more superposed hearths which carry fireclay projections on their undersides serving to agitate the ore on the hearths below so that no metallic parts are exposed to the action of the gases and ore; the hearths are alternately fixed and rotary, or rotary in opposite directions. This furnace has been extensively used on the continent, and has also been set up in the United States, *e.g.*, by the National Zinc Company and the Granby Mining and Smelting Company.

Many other forms of mechanical blende-roasting furnaces have been introduced; of these furnaces, two will be described, viz., the Wedge and the Merton furnaces.

The Wedge furnace, manufactured by the Wedge Mechanical Furnace Company of Philadelphia, has been used, in some of its forms, for roasting copper, lead, zinc and other ores to adapt them for leaching, and has been adapted recently to effect a dead roasting of zinc blende. This type of furnace has a number of superposed annular hearths swept by agitating arms, cooled by air or water and mounted on a central hollow shaft of large diameter to allow access to the agitator fittings. In the form described in United States Patent Specification, No. 1170375 (1916), there is a lower series of reverberatory hearths separated from an upper series of muffled hearths by horizontal flues communicating with the uppermost reverberatory hearth below and with a chimney flue above. The air supplied to the muffled hearths is preheated by the hot gases from the reverberatory hearths.

The greater part of the sulphur of the blende is eliminated without being mixed with the heating gases, and nearly all the remaining sulphur, amounting to about 4 per cent. of the whole, is driven off in the highly heated reverberatory section of the furnace.

The Merton furnace has a series of long superposed hearths, over which the ore is rabbled by sets of agitating arms carried by vertical water-cooled shafts passing through the furnace. A recent form of the Merton furnace has an upper drying-hearth, three muffled roasting-hearths in which most of the sulphur is eliminated from the blende, a fifth hearth exposed to the heating gases to effect the elimination of as much of the remaining sulphur as possible, and a sixth or cooling hearth. In the ordinary Merton furnace, the ore is rabbled along practically the whole length of the hearths in succession, but in the new Merton furnace the ore feed is split, one half being fed to one set of agitators and the other half to the other set. In this case each half of the ore is rabbled over only a part of the total length of each hearth.

The Merton furnaces have been used in South Wales and Australia.

During the future development of the zinc industry, the use of mechanical types of roasting furnaces, such as, for example, the Ridge, the Spirlet, the Wedge, and the Merton, will greatly increase.

CHAPTER V

ZINC SMELTING

A PROCESS of heating a mixture of calcined and roasted zinc ores with carbon so as to produce zinc vapour, which is then condensed, is the one followed in producing by far the largest proportion of the World's output of zinc. In its essential features, the process employed is the same, whether conducted in the great smelting furnaces of Europe and America, with their hundreds of retorts, or in the small furnaces employed in some of the provinces of China.

The ores mixed with anthracite or other solid carbonaceous material are charged into comparatively small retorts or muffles, arranged in a nearly horizontal position, and heated to a very bright red heat, when the following reactions probably take place: $2\,ZnO + C_2 = Zn_2 + 2\,CO$, and $2\,ZnO + 2\,CO = Zn_2 + 2\,CO_2$. There is probably, in fact, a reduction effected by solid carbon and also one effected by carbonic-oxide gas (CO), formed during the first-mentioned reaction, and also by reaction between the carbon and any oxygen which happens to be in the retort or muffle. The gases and metallic-zinc vapour evolved from the charge are led into a suitable condenser and the zinc vapour is cooled therein and condensed to molten zinc.

Such is the general nature of the zinc-smelting process, as it is usually called. It is intermittent, that is, the process is interrupted periodically for discharging and cleaning the retorts or muffles, introducing fresh charges, and arranging the condensers and other fittings ready for continuing the smelting operations. Further, a large consumption of fuel is necessary, for the high temperature required in the retorts or muffles must be obtained and maintained by transmission of heat through their rather thick walls of fireclay, which is not a good conductor of heat. Then, again, the use of such large numbers of comparatively small retorts or muffles necessitates the employment of a large amount of labour, although this varies considerably with the type of smelting furnace employed.

For its main purpose, viz., the production from zinc ores of a high percentage of zinc or spelter of good quality, the simple process described above is excellent and, up to the present, has not been superseded to any large extent by other methods of smelting. Many processes for doing this have been suggested, and some of these will be described towards the end of this chapter.

Two processes of zinc smelting, no longer practised, are of great historical importance, and will be described before the processes in general use at the present time. The two processes referred to are known as the English process and the Carinthian process. Both were processes of distillation downwards or *per descensum*.

The English process, which was first carried out at Champion's works, near Bristol, about the year 1740, continued to be practised until about the year 1865. The furnace employed resembled the well-known glass house or glass-melting furnace in external form. Its massive foundation, called the *cave*, was formed with arched passages and supported a masonry structure which enclosed the smelting-pot chamber and supported the large conical dome serving as a chimney. The masonry structure, referred to above, was usually octagonal in plan, and was built up of pillars which converged inwards and upwards to the base of the dome, archways being left between the pillars to allow access to the smelting-pot chamber. The *cave* was about 20 ft. square, and the total height of the furnace about 40 ft.

In a passage formed diametrically across the *cave* and communicating with the smelting-pot chamber through a large slot in the floor of the latter, was a fireplace from which the flames and hot gases circulated through the chamber and escaped through passages in its roof into the dome ; these passages were provided with dampers.

The smelting-pot chamber had an arched roof springing from side walls having passages which were normally closed during the smelting operations. The pots were 4 ft. high and 2 ft. 6 inches wide and usually three of them were set along each side of the fireplace ; they were conical in form, the maximum diameter being near the top. Each had a central hole in its base, registering with a corresponding aperature in the roof of the *cave*. To the lower part of each aperture was secured a short, conical tube to which was detachably connected a conical tube, about 8 ft. long ; these tubes projected vertically downwards into the *cave* and formed the condenser.

When charging a pot, a piece of charcoal was placed in the aperature in its base and then a mixture of about 3 cwt. of calcined ore and 2 cwt. of anthracite or coke and bituminous coal was charged into the pot, and its cover secured by luting.

During the heating of the charges, the vapours given off at the lower ends of the short condenser tubes burnt with a *brown blaze*, if the ores contained cadmium, which distils at a lower temperature than zinc. When the temperature reached a very bright red heat, a bluish-white flame of burning carbonic oxide gas and zinc vapour appeared at the lower end of the tube and then the long tube was attached and conducted the vapour downwards, condensation taking place during the passage ; the condensed zinc was delivered into receivers placed beneath the condensers.

The time occupied in working off a charge was about three days and the consumption of fuel was very great, being more than 20 tons of coal for every ton of zinc obtained ; the expenditure of manual labour necessary was, however, comparatively small. The pots lasted about four months. They were usually made of good fireclay and old burnt-out pots from which all pieces of fused slag had been carefully removed, the whole being ground fine in admixture with water, and moulded by hand. After the pots were moulded, they were dried and carefully annealed by being heated slowly to a high temperature and then cooled. Similarly, a new pot, intended to replace an old one in the furnace, was first carefully heated to a bright red heat and then placed in position in the smelting-pot chamber, through one of the passages in its side-walls.

The condensed product obtained was very impure, the zinc having zinc oxide and other substances mechanically mixed with it. The product was known as *rough spelter,* and was remelted in fireclay pots, when the impurities, rising to the surface, were removed by skimming. The skimmed-off impurities were called *sweeps* and were added to subsequent smelting-charges.

The Carinthian process is said to have been used in Hungary as well as in Carinthia. About a hundred small conical tubes or retorts were set vertically in the heating chamber of the smelting furnace, the large ends of the retorts being uppermost. At their upper ends the retorts were closed, and tubes were attached to their lower ends to conduct the zinc vapours into a common condensing chamber having an iron plate for its base on to which the condensed zinc fell. The

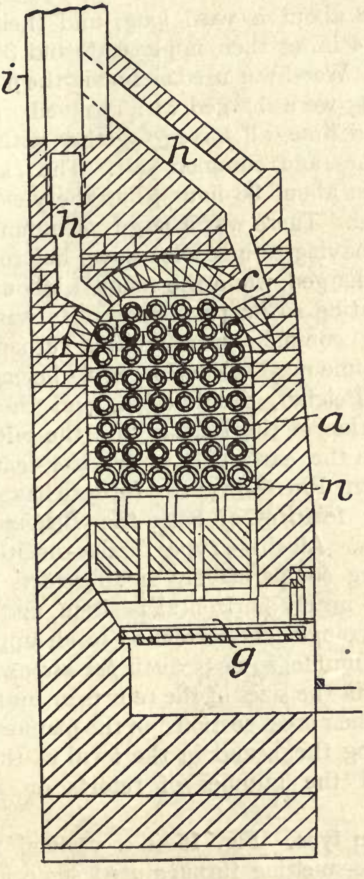

FIG. 15

BELGIAN SMELTING FURNACE
(Section across retorts)

retorts were about a yard long, and their diameters were about 4 in. at their upper ends and 3 in. at their lower ends. Wood was used as fuel in the fireplace.

The retorts were charged with calcined ore, powdered charcoal, and lime, all mixed together with a solution of wood ashes and common salt. The charges were worked off in about 36 hours, but the yield of spelter was not good. There was a large consumption of fuel, the furnace having to be cooled down before the retorts could be recharged, while the manual labour necessary for manipulating so many small retorts was excessive.

The most common zinc-smelting furnaces used at the present time may be considered to belong to three types, the Belgian, the Silesian, and the Rhenish; the introduction of the Belgian and the Silesian types dates back to the early part of the last century, while the more recent Rhenish type of furnace has some of the characteristic features of both the Belgian and the Silesian types. All these types of zinc-smelting furnace agree in using comparatively small retorts or muffles arranged in a nearly horizontal position, and in having condensing arrangements attached to an upper part of the retort or muffle, so as to distil *per ascensum*. They differ mainly in the sizes of the retorts or muffles and in the forms of their cross sections, in the manner of setting and supporting them, and in the form of the heating-chamber and the number of retorts or muffles it contains.

The Belgian type. Fig. 15 is a vertical section of a Belgian zinc-smelting furnace used some forty years ago by the Vieille Montagne Company, and Fig. 16 is a vertical section in a plane at right angles to the plane of the section in Fig. 15. The retorts *a* were supported at their back ends in recesses formed in the back wall *b* of the arched-heating-chamber *c*, and were inclined

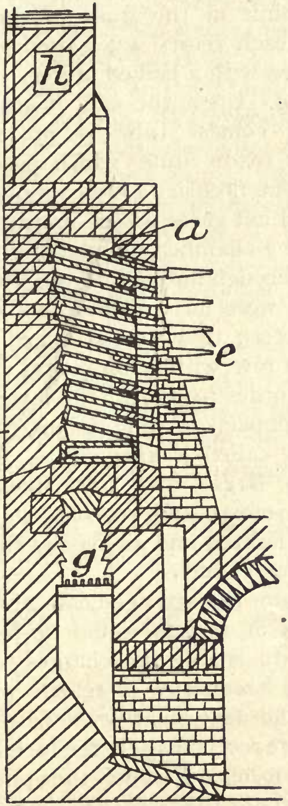

FIG. 16

BELGIAN SMELTING FURNACE
(Section along retorts)

downwards with their front ends supported by cast-iron ledges built in the front of the chamber. The back end of each retort was closed and its front end open, but fitted with a bellied fireclay condenser secured by clay luting. Upon the end of each condenser was a detachable conical tube or *prolong e,* serving to condense zinc oxide fumes which passed through the condenser. The fireplace *g* was supplied with coal and the flames and hot gases passed upwards through flues into the heating-chamber, circulated around the retorts, and escaped through flues *h* into the chimney *i*.

The retorts were forty inches long and seven inches internal diameter ; they were arranged in six rows of six retorts in each row, with a top row of four retorts under the arch. In order to protect the lowest row of retorts from direct impact of the flames, an additional row or retorts *n*, called *cannons,* was provided. These *cannons* were larger and had thicker walls than the ordinary retorts and received no charges ; their walls were perforated and air passed through them into the combustion chamber.

It follows from the arrangements of retorts described that the rows of retorts would be heated unequally, and, in order to enable the charges to be worked off uniformly, the lowest row of retorts was most heavily charged and the uppermost was charged most lightly, the intermediate rows being charged to an extent dependent on their positions. Further, the upper rows of retorts received as parts of their charges some of the zinc *fume* previously taken from the condenser tubes *e,* and also roasted ore containing an unduly large amount of oxide of iron, which would form readily fusible slags if charged into the lower retorts.

The calcined ore to be smelted was ground fine, mixed with half its weight of small coal, and ladled into the retorts through the fireclay condensers. During the heating of the retorts, the clear, lambent flame of burning carbonic oxide soon appeared and, as the heat increased this flame became luminous and of a bluish-white colour due to burning zinc vapour ; the *prolongs e* were then attached, and distillation and condensation of the zinc vapour continued until the charges were exhausted. Most of the zinc condensed in the fireclay condensers and was ladled out from time to time, the product being called *rough zinc* and requiring to be purified in the manner already described, when dealing with the English process.

The Belgian process, carried out in the manner described, required a consumption of about 6 tons of coal for every ton of zinc obtained, and was therefore much more economical than the English process. On the other hand, the expenditure of manual labour was considerable.

The Silesian type. Fig. 17 is a vertical section showing a Silesian zinc-smelting furnace used near Swansea some forty years ago. The muffles *a* were  -shaped in cross-section and about 3 ft. long, 18 in. high, and 8 in. wide. They were made by moulding, drying, and annealing a carefully prepared mixture of fireclay with powdered pieces of old muffles freed from all vitrefied parts. The muffles were laid, in two linear rows of twelve each, along opposite sides of the fireplace *b*, and rested on the bed of the combustion chamber with their flat lower surfaces supported throughout. A bent clay condensing-tube *c* was secured to the outer and upper part of each muffle ; a cast-iron tube *d* was attached to the tube *c*, and a sheet-iron tube *e* was connected to the tube *d* and conducted the condensed zinc to a receiver *f*. An inspection aperture formed in the bend of the condensing-tube *c* was provided with a removable cover. In the front of each muffle, below the tube *c*, was an opening through which the residues could be withdrawn after the charge had been exhausted.

The roof of the combustion chamber was formed by a long and wide arch *h*, and the chamber communicated with some small lateral archways *i* formed in the walls of the furnace; beneath each of these archways a pair of muffles was arranged, so that there were six archways and six pairs of muffles on each face of the furnace. The flames and hot gases circulated about the exposed parts of the muffles and passed upwards, through vertical flues *k*, into flues *n* extending along the top of the furnace and communicating with a chimney at one end of it. During the working of the furnace,

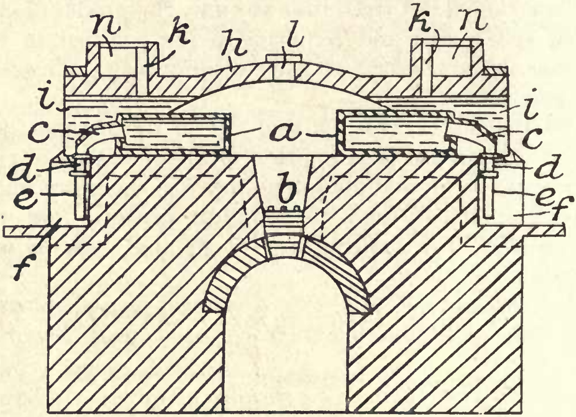

FIG. 17

SILESIAN SMELTING FURNACE

tools for use in luting any cracks formed in the muffles could be inserted through openings *l* in the furnace roof. Sheet iron doors provided with inspection holes normally closed the archways *i* during the working of the furnace. The fireplace extended about half-way along the furnace so that the muffles were not heated equally and those near the fireplace end were charged more heavily than those which were at the chimney end. An average charge was about 60 lbs. of calcined ore, 6 lbs. of sweeps, and 22 lbs. of coal-dust mixed with 9 lbs. of coke.

The period of distillation was about 15 hours, and about 24 hours were needed to work off the charges, clear out the residues, repair or replace defective muffles, and recharge them. The life of a muffle was from 2 to 3 months, according to its position in the furnace. Not less than 10 tons of coal was consumed for every ton of zinc produced.

The Rhenish type. The early Rhenish furnace did not differ greatly from furnaces of the Silesian type. There were, however, two rows of muffles on each side of the fireplace, an upper row and a lower row, the lower muffles resting flat on the bed of the heating-chamber, as in the Silesian furnace, and the upper muffles being supported at their front and back ends only, like retorts in a Belgian furnace. The flames and hot gases from the fireplace circulated around the muffles and then passed down vertical flues on their way to the chimney. The structure of the Rhenish furnace itself was similar to that of the Silesian, except that the arch was relatively higher to accommodate the double rows of muffles. The muffles were similar in form to the Silesian, but smaller in cross-section, and straight condenser tubes were employed.

The structural details of the early Belgian, Silesian, and Rhenish furnaces have undergone many changes, so that although most of the zinc-smelting furnaces at work to-day may be classed with one of the types described above, they include features characterizing one or both of the other two types, and, more frequently, details of structure which were not in any of the early Belgian, Silesian, or Rhenish furnaces.

Important changes were introduced by the Vieille Montagne Company, about the year 1871, when building a number of Belgian furnaces at Engis. Two furnaces were built back to back, and two of these double furnaces were built end-on so as to form a *massive* of four single furnaces, with two fireplaces, one for each double furnace, extending underneath the central main wall against which the back ends of the retorts rested. The flames and hot gases passed upwards through long transverse ports in the heating-chamber floors, and finally escaped into the chimneys, of which there were three, a single one at each end and a double one at the centre of the *massive*. Each *massive* contained about 200 retorts, some of these being circular and others elliptical in cross-section.

In America, furnaces very similar to the Belgian furnace used to be employed extensively, but those of New Jersey and other eastern States employing anthracite, had shallow fireplaces and ashpits. Each double furnace had a large number of retorts, *e.g.*, one at Jersey City had 252 retorts, each heating-chamber having 7 rows of superposed retorts with 18 retorts in every row.

Many changes have been made in the heating arrangements to adapt the furnaces to use producer gas and natural gas instead of solid fuel burnt close to the retorts. During recent years, some furnaces have been designed for oil-firing and a few for coal-dust firing.

One very important advantage resulting from the use of gaseous fuel is the facility of regulating the heat of the heating-chamber and effecting an economy of fuel. Its use has also enabled larger furnaces to be worked with

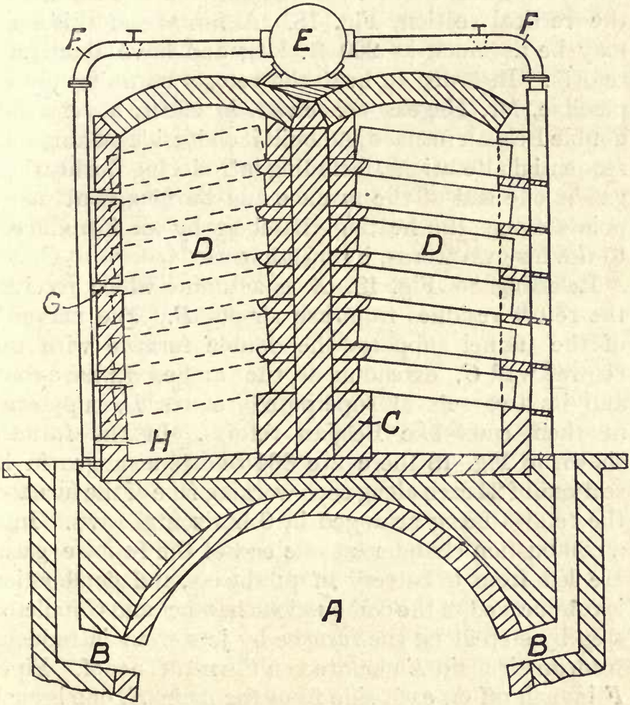

FIG. 18

HEGELER SMELTING FURNACE

success. One of the most important modifications of the Belgian gas-fired furnace was introduced in 1872 by Mr. E. C. Hegeler, of the Matthiessen and Hegeler Zinc Company, Lasalle, Illinois. This type of furnace, modified in many of its details and fired by producer or natural gas, is almost universally employed to-day in the United States.

The essential features of the furnace are shown in the vertical section, Fig. 18. A furnace of this kind may be as much as 200 ft. long and have about 900 retorts. In order to heat the retorts as uniformly as possible, Mr. Hegeler conceived, in effect, a very tall double Belgian furnace and built it on its side making consequential alterations, including introducing the heating-gas at one end of the furnace and burning it at many points along the heating chambers by air introduced, to use his own words, by instalments.

Referring to Fig. 18, *A* is a tunnel which receives the retort residues from ash shoots *B*. The masonry of the tunnel supports the double furnace with the central wall *C*, extending to the arched furnace-roof, and its two sets of superposed retorts *D*, supported at their ends like Belgian retorts. In the furnace shown in Fig. 18 there are 864 retorts arranged in 18 sections of 24 each along each working face of the furnace, the retorts being arranged in 6 horizontal rows. Into a combustion chamber at one end of the furnace, gases are led from a battery of producers, and combustion is commenced in the combustion chamber and completed step by step along the furnace by jets of air introduced from an air main *E* mounted on the furnace roof. Pipes *F* branch off on each side from the main *E*, one branch pipe *F* being provided between every pair of sections of retorts, and a number of air nozzles *G* deliver air through ports *H* in the furnace walls.

The earliest forms of Hegeler furnace had a very high arched roof, the central wall separating the retort chambers did not extend to the furnace roof, and, instead of a tunnel, as shown in Fig. 18, there were a central gas channel and two side flues for receiving the waste gases from the combustion chamber.

In Kansas and a few other States where natural gas is used, some of the furnaces employed are of the so-called "blow furnace" type, which are modified Hegeler furnaces. In these "blow furnaces" the gas is not admitted at one end but at intervals along the sides of the furnace through a large number of gas pipes, the air being similarly admitted from an air main mounted along the top of the furnace arch.

A furnace of the Belgian type, designed by Emile Dor-Delattre of Budel, Holland, has come into use on the Continent during recent years. It is shown in Figs. 19 and 20, Fig. 19 being a cross-section on line *A B*, Fig. 20, and Fig. 20 a longitudinal section of one end of the furnace, on the line *C D*, Fig. 19. It is provided with Siemens regenerators at one end of the furnace, and is designed mainly to facilitate access to the air and gas passages, to enable the supplies of gas and air to the burners to be regulated satisfactorily, and to overcome one of the great difficulties attendant on the use of regenerators, viz., unequal heating of the retorts. The combustion chambers *a a'*, each containing six rows of superposed retorts, communicate through flues *c*. In the roof of the furnace are two pairs of passages *d e* and *d' e'* of which *d d'* are air passages communicating with the air regenerators and *e e'* are gas passages communicating with the gas regenerators. Long and narrow burner passages *f f'* convey air and gas from the regenerators and products of combustion in the usual way. The flow of air and gas or of products of combustion is regulated by means of movable slabs *n n'* to which access is easily obtained through openings *o o'* in the furnace walls. Each burner opening serves for 6 vertical rows of retorts, each opening being over the axis of a retort.

The early form of the Silesian furnace has been considerably modified. The Silesian furnace was adopted

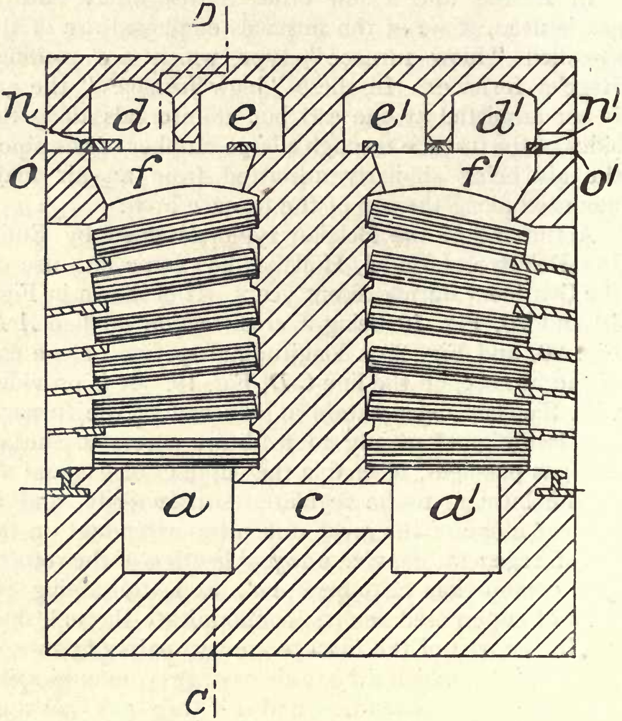

FIG. 19

DOR-DELATTRE SMELTING FURNACE
(Cross section)

long ago by the Vieille Montagne Company and was used for a long time, but in an altered form which, on account of the introduction of some features of the Belgian furnace, was called Belgian-Silesian. The flames and hot gases passed from the fireplace into the combustion chamber and escaped by vertical flues into chimney flues

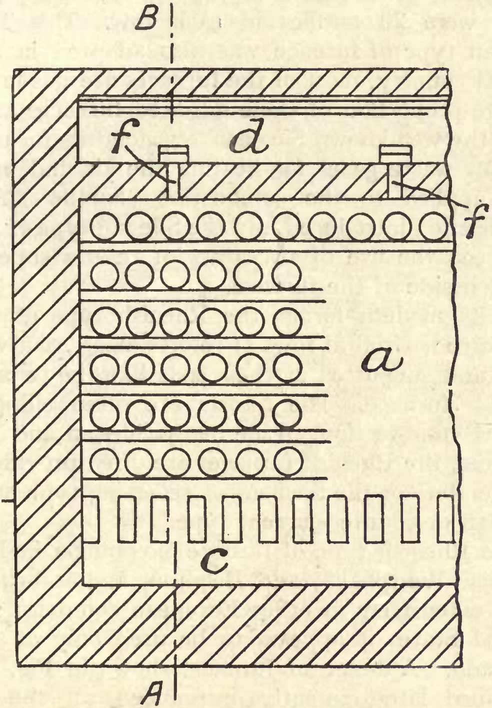

FIG. 20

DOR-DELATTRE SMELTING FURNACE
(Longitudinal section)

beneath the hearth. Further, the beds on which the muffles rested were slightly inclined downwards towards the working faces of the furnace, and the typical bent condenser was replaced by condensers of the kind used in Belgian furnaces. The number of muffles on each side of the furnace was greatly increased, because the Belgian coal used gave a long flame ; in some cases there were 20 muffles in each row. This Belgian-Silesian type of furnace was also adopted in Silesia ; in that country, most of the furnaces are gas-fired and a large proportion of these gas-fired furnaces are built upon the well-known Siemens regenerators for utilizing the hot waste gases for heating the air and producer gas supplied to the combustion chamber. Another modification introduced into the Silesian type of furnace has been the use of two rows of retorts superposed, on each side of the furnace.

In its modern forms, the Rhenish type of furnace has three horizontal rows of retorts along each working front and supported at their ends like the retorts of a Belgian furnace. The retorts are often elliptical or oval in cross-section. Like many Silesian and Belgian furnaces, the Rhenish furnaces are often provided with regenerators of the Siemens or reversing type or of the Gorman or counter-current type.

The Rhenish type of furnace is common in Rhenish Prussia, Westphalia, and Belgium, and is being used more extensively in other European countries ; in the United States it appears to be used only at Pueblo, Colorado. A design of furnace, shown in Fig. 21, and described later, recently introduced at the Crown Spelter Company's works, Swansea, is a Rhenish Belgian furnace with reversing regenerative arrangements.

Modern zinc-smelting practice will be exemplified by the following accounts of some of the more recent plants in different countries.

The English Crown Spelter Company's Works, Swansea. The newest design of a smelting furnace introduced at these works is one patented by the Manager of the

Company, Mr. Edwin Ruck, of Swansea. This furnace is shown in vertical section in Fig. 21. The furnace has 204 retorts of which only 6 are shown in Fig. 21. Along each working-face are 102 retorts arranged in three horizontal rows. The chief object of the design is to enable the furnace to be heated satisfactorily by gas with regenerative working.

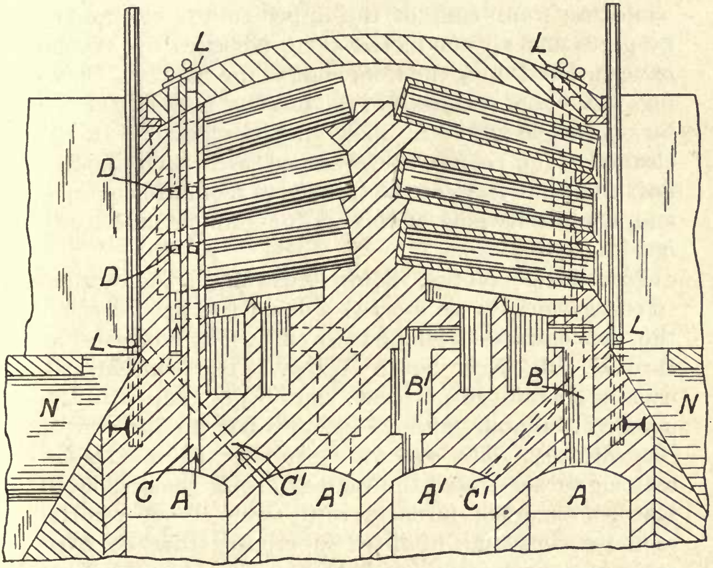

FIG. 21

RUCK SMELTING FURNACE

According to the inventor, it had not been possible to work satisfactorily zinc-smelting furnaces having more than two horizontal rows of retorts, when Siemens regenerators were used, because of the difficulty of heating properly the front ends of the retorts in the upper rows. In order to do this, in the new furnaces, part of the hot gases and air from the regenerators pass into the combustion chamber through the flues *B′ B* communicating respectively with the gas and air regenerators *A′ A*, while the front ends of the upper retorts are heated by gases and air conducted along passages *C′ C* which have outlets *D* near the front ends of the retorts. Openings in the roof and walls of the furnace, normally closed by removable bricks *L*, allow the passages *C′ C* to be cleaned. The retorts are arranged with their mouths near the front faces of the furnace to facilitate charging and also discharging of the residues, which slide freely into the ash pockets *N*.

Port Pirie Works, South Australia. These zinc-smelting works were erected a few years ago to smelt the concentrates obtained by flotation processes at Broken Hill, New South Wales. The concentrates usually contain 46 per cent. zinc, 8 per cent. lead, 30 per cent. sulphur, and 13 oz. of silver to the ton of concentrate. This concentrate is roasted in Hegeler roasting furnaces and the roasted ore is smelted in 10 Rhenish smelting furnaces with two sets of retorts, each set consisting of three superposed rows of 24 in each row, giving a total of 144 retorts per furnace. Each furnace is heated by gas from a producer. The retorts are 5 ft. 6 in. long and are elliptical in cross-section, being 13 in. by 7 in.

The Donora Works, Pittsburg. These works belong to the American Steel and Wire Company, an auxiliary of the United States Steel Corporation. They were built in a remarkably short time in 1915. A line of railway extends alongside the smelting furnaces and serves to take in ore and coal and convey away the spelter. The roasting department of the works has six Hegeler furnaces, seven hearths high, each hearth being about 80 ft. long. These furnaces are heated by producer gas. When roasting Australian concentrates, the sulphur was reduced to about 1·5 per cent., and a temperature of 1,000°C. was registered on the second hearth. The gases contained 4·5 per cent. of sulphurous acid gas. Raking of the charges was effected every $\frac{3}{4}$ hour. There are ten Hegeler smelting furnaces each with 912 retorts, 456 on each working face, arranged in six horizontal rows. The retorts are cylindrical, and measure 52 in. in length, and 8 in. internal diameter. A new feature of the Donora furnaces is the provision of air flues beneath the floors of the combustion chambers to provide preheated air for the first sections of the furnaces. These works at Pittsburg, with others at St. Louis, Missouri, and Cherryvale, Kansas, furnish the United States Steel Corporation with most of the spelter they require for use in their galvanizing works.

In the construction of the building at Pittsburg, reinforced concrete was extensively used. The various departments of the works are connected by overhead telpherage systems serving to convey material from one department to another, and the ground of the works is thus kept free, to a large extent, from rails and switches.

The National Zinc Company's Works at Bartlesville, Oklahoma. These are large works using natural gas for heating the furnaces. The roasting department has four Zellweger furnaces. The smelting department has the usual type of blow-furnace with burners for admitting gas and air to the combustion chambers. The retorts are cylindrical and are cleaned out, at the end of a distillation, by means of a spray of water, any adhering slag being removed by scrapers. Mechanical discharging means was tried but found to be unsuitable, because the retorts were shaken too much during the action of the discharger. They are charged, however, mechanically by means of Saeger's charging apparatus, having eight conveyors.

The Montepioni Company's Works, Vado Ligure, near Savona, Italy. The company built smelting works in the year 1917, near a large coking plant, the superfluous gas from which is used in heating the smelting furnaces. This appears to be the first instance of such use for gas from a coking plant. Twelve zinc smelting furnaces were intended to be erected, and three had been built by September, 1917. They are of Rhenish type with 216 oval retorts, 1·56m. long and 0·30m. × 0·20m. cross-section. The furnaces are worked in connection with regenerators built beneath them.

Having described the essential structural features of the chief kinds of zinc-smelting furnaces employed in the zinc industry, the operations carried out in working such furnaces will next be described. These operations are the same, generally speaking, for all types of furnace and may be considered under the headings: (1) Preparation of the charges for the retorts, (2) Charging the retorts, (3) Distilling the charges, and (4) Discharging and cleaning the retorts.

Preparation of the Charges for the Retorts. The calcined calamine ores or the calcined and roasted blende ores are mixed by means of hand tools or mechanical mixers with the reducing agent, which is preferably anthracite of good quality, or, if this is not available, a mixture of good quality coke and lean bituminous coal. Coke is not suitable by itself, because it does not contain sufficient hydrocarbons, for it has been found that hydrocarbons should be present in the reducing-agent to an amount corresponding with that occurring in good anthracite. A little common salt is usually added to the mixture of ore and reducing-agent to minimize the production of blue powder during the distillation process, or, as it is sometimes expressed, to obtain a better yield of spelter.

Roasted blende ore is used in a finer state of subdivision than calcined calamine ore, the particles of the former being not larger than about $\frac{1}{12}$ in. and those of the latter not larger than about $\frac{1}{6}$ in. The use of a mixture of both kinds of ore is quite usual in some smelting-charges, and when such a mixture is used it is so regulated as to give a charge which will not be liable to form easily fusible slags likely to corrode through or "butcher" the retorts. The practice of mixing different kinds of ores is determined mainly by the nature of the ores which are available for smelting. Silicate ores, which would be difficult to smelt by themselves, are conveniently treated by mixing them with roasted blende or calcined carbonate ores.

The amount of reducing-agent to be added is largely in excess of that theoretically necessary. Theoretically, twelve parts by weight of carbon are necessary to reduce about eighty parts of zinc oxide. The amount of carbonaceous material employed in practice is, however, about one-half in weight that of the ore treated. During the past few years, attempts have been made to reduce the amount of carbonaceous material by moulding the ore and reducing-agent, very intimately mixed together, so as to form compact briquettes. In this way, the reducing-agent is enabled to act more efficiently by reason of its more intimate association with the particles of ore, and, incidentally, this method of preparing the charges renders it possible to deal with very fine ores and a larger space is rendered available in the retorts to receive the charges.

To obtain good results in smelting zinc ores, it is necessary to guard against using a charge containing too much iron, managanese, lead, or suphur. The ore should contain, preferably, not more than two per cent. of its weight of iron, and it is usual to deduct from the purchase price of the ore a certain sum for every percentage of iron present above 2 per cent. or sometimes even less than 2 per cent. Manganese acts very much like iron in the charge, and it is usual to regulate the mixture of the ores by having regard to the sum of the percentages of the two metals. A mixture containing 10 per cent. of iron and manganese cannot be smelted satisfactorily, as a general rule, except in strong, highly refractory retorts. If sulphur is present in the charge to a greater extent than one per cent., the iron or iron and manganese together should be correspondingly less in amount.

With respect to the amount of lead in the charge, it is usual to work with not more than 2·5 per cent. Some smelters stipulate for a reduction of the purchase price of the ore by a few shillings per unit percentage per ton if the lead present in the ore exceeds about 3 per cent. The amount of lead present in some smelting districts is so large that it is advantageous to use special means for intercepting lead passing over with the zinc vapour. This is particularly advantageous when galvanizers' waste of various kinds is added to the charges. One form of lead intercepter which has been used at the New Delaville Spelter Works, near Bloxwich, is shown in Fig. 22. Into the mouth of the retort *A* is fitted a fireclay condenser *B* having a partially closed inner end *C*, into which is fitted a fireclay cylinder *D* packed with anthracite or broken firebrick to intercept the lead. A passage *E* may be formed in a clay stopping *F*, inserted in the lower part of the inner end of the cylinder *D*, to allow intercepted lead to flow back into the retort. Each cylinder

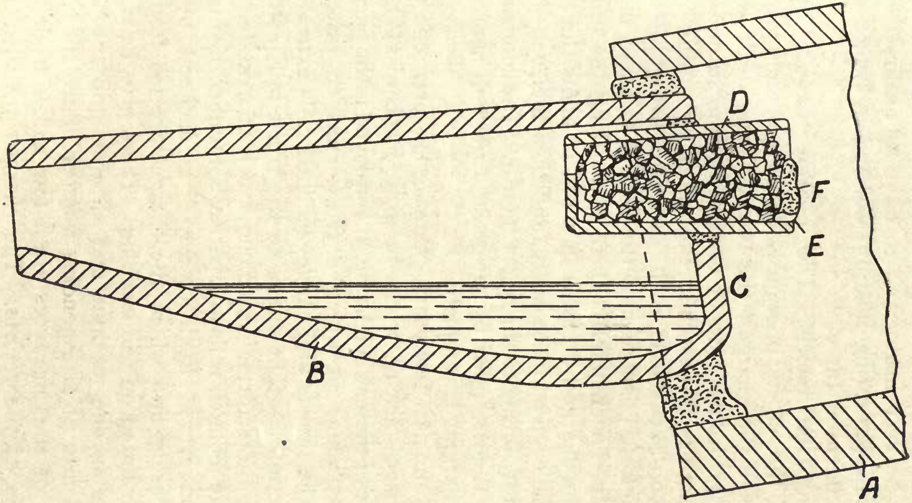

FIG. 22

LEAD INTERCEPTER

D served for several distillations, after which it was found to be very heavy and to have its anthracite or other lead-intercepting medium covered by white and yellow condensed fumes.

Charging the retorts. The charges having been prepared, the retorts, previously discharged and cleaned out, receive the charges, the retorts being dealt with either by horizontal rows or vertical rows in succession. Each charge is thrown into the retort by means of a small scoop-like shovel, each shovelful being pitched as far back as possible into the retort, so as to fill it completely. A channel is then made along the upper part of the charge by means of a rod to allow the first gases to be evolved more easily, and then the condenser is secured by luting to the retort mouth. The condenser mouth is then stopped by means of a piece of charcoal and the charging is complete.

During the past few years, charging has been effected at some zinc-smelting works by using mechanical chargers. One of these which has been employed is the Saeger charging-machine in which a truck runs on rails in front of the retorts and carries inclined rails extending in a direction at right angles to the truck rails and in line with the retorts. A second truck is mounted to run on the inclined rails and carries a number of rotary screw conveyors. Each conveyor is enclosed by a tubular casing into which the charges are fed from a hopper mounted on the machine. There may be eight conveyors on one machine and all are simultaneously traversed into a corresponding number of retorts until the ends of the conveyors are a few inches from the back ends of the retorts. The charges are then fed from the hopper and the conveyors rotated so as to deliver the charges first to the back ends of the retorts and then the conveyors are slowly withdrawn, feeding in and depositing the charges during the process.

Distilling the charges. When the charging of the retorts has been completed, the gas and air are turned on in the furnace, and the temperature increases rapidly, finally attaining a white heat. The stoppings of the condenser soon have to be pierced, such of them, that is, as have not already been blown out by the increasing pressure in the condensers, and flames issue from the condenser mouths. This flame is luminous at first, due to the burning of hydrocarbons from the reducing-agent. Later, the flame becomes non-luminous and shows the characteristics of burning carbonic oxide gas. A little later, the flame becomes luminous and of a bluish-white colour due to the presence of burning zinc vapour and then the prolongs are fitted to the condensers. After this stage, distillation of the zinc proceeds to its full extent.

During the earlier stages of the distillation, when the condensers are liable to be cool and the vapours of zinc are mixed with too much carbonic oxide and other gases, a great deal of blue powder and zinc oxide is produced. This blue powder and zinc oxide are collected at intervals from the prolongs and the condensers and set aside to be added to some of the later retort charges. The regulation of the temperature of the condensers so that it does not become too low, when blue powder would be formed, nor too high, when zinc vapour would pass on uncondensed, is a very important duty of the smelter superintending the operation. Any retort which breaks during the distilling process must be removed at once to prevent further loss of zinc, and deposits of blue powder and zinc oxide likely to block up the condensers and prolongs must also be removed. Molten zinc is withdrawn from the condensers about every six hours, and cast into slabs, after the surface of the molten metal has been skimmed.

The quantity of blue powder produced is about 4 per cent. of the weight of spelter obtained. This blue powder is only part of the loss of zinc during the distilling process, such loss being, on an average, about 15 per cent. of the total weight of zinc in the charge. This total loss is made up mainly of the zinc left in the exhausted charges, the zinc contained in the blue powder and zinc oxide produced, and the zinc vapour which is absorbed by or escapes through cracks in the retort walls. After the last cast of spelter has been made, the heat of the furnace is let down, and the retorts are allowed to cool prior to discharging.

Discharging and cleaning the retorts. The condensers are detached and the front part of the charge is removed separately, being richer in zinc than the rest, and suitable for adding to later charges. The rest of the charge is then withdrawn by means of rabbles, and the retorts cleaned from deposits of slag by means of scrapers or jets of steam or water. Defective retorts are removed, or patched with luting material.

During recent years, machines have been used at some smelting works for discharging the retorts. One of these machines, the Simmonds Retort Discharger, has been used at the works of the United States Zinc Company, at Sand Springs, Oklahoma, and at Pueblo, Colorado.

In this machine, a truck is mounted to run on rails along the zinc-smelting furnace, in front of the retorts, and comprises a framework the upper part of which supports a main carriage, on rails arranged at right angles to the truck rails. Beneath this upper or main carriage are five, six, or more superposed pairs of rails inclined upwards towards the retorts, each pair of rails

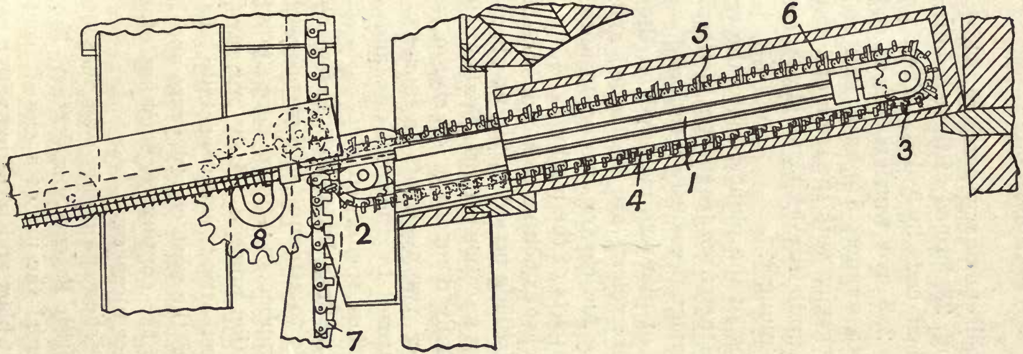

FIG. 23

SIMMONDS RETORT DISCHARGER

carrying a small auxiliary carriage which supports a plunger 1, Fig. 23, formed of three tubular members connected at their ends by yokes. These yokes carry sprocket wheels 2, 3, over which travels an endless chain 4, provided with scrapers 5. Each link of the chain has a finger 6 engaging with the teeth of a driving chain 7, which is held up to its work by an idler sprocket wheel 8 opposite each plunger.

The traversing of the plungers into the retorts and their withdrawal therefrom are effected by the movements of the main carriage previously mentioned. According to the number of plungers mounted on the machine, five, six, or more retorts are discharged and cleansed simultaneously. An electric motor mounted on the truck drives all parts of the machine.

The whole cycle of smelting operations occupies about 24 hours, the distilling period taking up about 19 hours of this time. For a section comprising about 100 retorts, the work is usually done by a supervisor, sometimes called a brigadier, two assistants or smelters, a stoker, and boys to attend to the prolongs and labourers to wheel coal, ashes, spelter, etc.

Continuous Smelting Processes. Reference has already been made to attempts to dispense with the use of the large number of retorts necessitated by the ordinary distillation process. Many processes, some of which have been tried experimentally, have been suggested during the past eighty years and have had for their object the continuous smelting of zinc ores in blast and other furnaces.

One of the earliest proposals was that of Duclos, described in British Patent Specification, No. 7662 of 1838. He proposed the use of a closed blast furnace supplied with hot blast and provided with a condensing apparatus. A later proposal of interest was made by

F. L. Clerc, in British Letters Patent, No. 2815 of 1876. He set out clearly the advantages sought to be obtained, viz., continuous working, economy of labour and fuel, and dispensing with the use of retorts. A mixture of calcined ore, carbonaceous material, and flux was to be charged into a blast furnace in such a way that the charge was always covered by heated carbonaceous fuel, which was hot enough to convert any ascending carbonic acid gas into carbonic oxide and prevent oxidation of the zinc vapour to oxide of zinc. The blast of air supplied to the furnace was to be preheated to a temperature above the melting-point of zinc. From the top of the furnace, the gases and zinc vapour were withdrawn and flowed slowly through a fireclay condenser, also maintained at a temperature above that of molten zinc. In the condenser, it was said, the zinc vapour cooled slowly and formed drops which ran together and formed molten metallic zinc. The gases and vapours leaving the condenser were cooled rapidly in iron pipes. The importance of keeping the zinc vapours diluted as little as possible with carbonic acid and other gases, in order to prevent formation of blue powder and oxide of zinc was clearly mentioned.

This full account of Clerc's process is given to show that the earlier inventors were acquainted with many of the difficulties to be overcome when attempting to smelt zinc ores in a blast furnace. It was appreciated that when the zinc vapour cooled below its boiling-point, condensation to the liquid form could be effected provided the vapour was not unduly diluted with carbonic acid and other gases, and that the cooling should not be so rapid as to cool the vapour below the melting-point of zinc, in which case blue powder would be formed. However, these earlier proposals met with no success.

Taking advantage of the well-known phenomenon of increase in the temperature of the boiling-point of a liquid with increase of the pressure under which it is vaporized, Dr. Lungwitz proposed, in United States Patent Specifications, Nos. 538785 and 555961, to smelt zinc ores in a blast furnace worked under a pressure of about 100 lbs. per square in., and thus prevent volatilization of the reduced zinc. Experiments were made on a commercial scale at Warren, New Hampshire, in the autumn of 1905. The blast furnace used was about 5 ft. in diameter and 30 ft. high, and stood successfully a pressure of about 120 lbs. per square inch. Difficulties in some of the details of working were met with and the experiments, not altogether unsuccessful, were postponed.

Another process which was tried experimentally, but with incomplete success, was that described in Nagel's United States Patent Specifications, Nos. 699969 and 766279, according to which zinc ore mixed with coal was smelted in a blast furnace maintained full of water gas supplied through the tuyères.

The want of full commercial success of processes of this kind was not due to failure to produce spelter, but to inability to avoid the production of too much zinc oxide and blue powder. There was obtained too much of that peculiar substance, blue powder, which is produced to some extent in the smelting of zinc ores in retorts. This blue powder is composed mainly of small particles of metallic zinc coated by a thin film of zinc oxide.

An electric smelting process which has been carried out commercially since about the year 1904, in Scandinavia, and has attracted a great deal of attention is that invented by C. G. P. de Laval of Stockholm. Furnaces to carry out the process were established about the year 1903, at Trolhattan, in Sweden, and Sarpsborg, in

Norway, and small quantities of spelter were put on the market in 1904. The heat nesessary to effect the smelting was obtained at first by means of an arc between electrodes passing through the furnace, but resistance furnaces were afterwards adopted at Trolhattan.

The spelter obtained has been produced by distilling zinc ores or some other zinciferous material, thus obtaining a spelter mixed with a great deal of zinc oxide, and then subjecting this impure spelter to a second and even a third treatment, in the electric furnace, until spelter of good quality was obtained. In so far as the process has been a commercial success, the result has been due mainly to the availability of a cheap source of power for producing the necessary electric current.

Experiments in electric smelting were carried out at Hartford, Connecticut, in 1912, and spelter is said to have been successfully produced, and in 1914, electric smelting was carried out experimentally at Nelson, British Columbia, in a furnace capable of producing one ton of spelter per day. The process was, however, discontinued.

An attempt, said to be successful, has also been made to smelt zinc ores continuously at Hamborn, Westphalia. Vertical, open-ended retorts are employed, the ores being charged in at the top and the residues withdrawn from the bottom. The zinc is condensed in clay condensers fitted at right angles to the sides of the retorts.

It may be concluded, from the evidence available, that smelting of zinc ores in a blast furnace has been commercially unsuccessful, but that electric smelting has been a success under favourable conditions.

CHAPTER VI

HYDROMETALLURGICAL PROCESSES

These include the electrolytic processes by which zinc is deposited from solutions of zinc salts obtained from the ores or other zinciferous materials and the so-called chemical processes by which the solutions of zinc salts are treated for the production of zinc oxide, which is then smelted by ordinary known processes. The electrolytic processes are essentially wet processes and the chemical processes are essentially combinations of wet and dry methods of zinc extraction. The chemical processes are for the most part in the experimental stage, but the electrolytic processes have passed that stage and are carried out with commercial success.

The zinc obtained by electrolytic processes is called electrolytic zinc or spelter and, generally speaking, its content of zinc, which is 99·95 per cent. or more, entitles it to be considered high grade. Its production has recently made rapid progress in Great Britain, Canada, Australasia, the United States, Japan, and several other countries. Electrolytic processes have been valuable in treating ores and other zinciferous materials which cannot be treated successfully by other processes of extraction, *e.g*, the complex zinc ores of the Rocky Mountains and of Western Tasmania in which the constituent minerals are so intimately associated that concentration by ordinary processes is very difficult or commercially impossible. A very practical proof of the success achieved is furnished by recent returns of the amount of electrolytic spelter produced. During the year 1916, the United States produced 10,963 tons, and in 1917, the production was 27,245 tons ; Canada produced 2,986 tons of electrolytic spelter in 1916, and about 10,000 tons in 1917 ; Great Britain and Japan also produced large quantities. The achievement of these results has not been effected without considerable effort and expense, and the history of such achievement is an interesting part of the annals of the zinc industry

The history of electrolytic processes for the extraction of zinc goes back about sixty years. In the year 1862, James Dickson described in very general terms a process for obtaining zinc from its ores by electrolysis. He proposed the deposition of zinc from aqueous, acid, or alkaline solutions, obtained by leaching roasted zinc ores, or by acting on the raw ores with acids. The only part of his description which shows that he understood the nature of the commercial difficulties of the process is a direction to use an electric current obtained at a low cost. Inability to obtain the necessary current at a sufficiently low cost was destined to prevent the commercial working of many processes, later in date than Dickson's and of a more practical nature. There does not appear to be any record of his processes having been tested on a commercial scale.

A later process of considerable interest was that of Létrange, described in British Patent Specification, No. 3211 of 1881. According to this process, blende ores were roasted at a low temperature to convert their zinc sulphide into sulphate. The roasted ore was treated with a weak solution of sulphuric acid to obtain a solution which was electrolyzed with liberation of sulphuric acid to be used again in the process. The solution was effected in four communicating vats of brick or stone lined with bitumen, the solvent being allowed to percolate through the roasted ore which was fed into the vats. Electrolysis was effected in cells of wood, lined with lead, or cells of glass or earthenware, or of brick or stone, lined with bitumen. Cathodes of zinc and anodes of lead, carbon, or other conductor insoluble in sulphuric acid were employed.

In consequence of the large amount of gelatinous silica produced in the process of dissolving the ores treated, Létrange's method of allowing the acid solvent to percolate through the ore was not satisfactory. Electrolytic spelter was, however, obtained by his process and exhibited at Chicago.

Experiments in producing electrolytic zinc were carried out by Prof. Dieffenbach, using blende-bearing pyrites, from Siegen, containing 8 per cent. or less of zinc. These experiments having been found satisfactory, a large plant was set up, in 1895, at Duisberg, where dense plates of zinc nearly half an inch thick were obtained. The metal was deposited from solutions obtained by subjecting the pyrites to a chloridizing roast and then leaching, but the details of the process employed at Duisberg were kept secret. Electrolytic zinc made at Duisberg appeared on the market, but only in small quantities.

An electrolytic spelter plant was also set up at Fuerfurth, where an important process, the Hoepfner, was worked for a time; revolving cathodes were used at Fuerfurth.

During the years 1896 and 1897, extensive experiments were made in the production of electrolytic zinc at Cockle Creek, New South Wales. The works erected there cost more than £200,000, but, after a series of carefully conducted trials, the process was a failure. The process was that known as the Ashcroft process by which Broken Hill ore was roasted and leached with sulphuric acid to obtain a solution which was separated from its bulky gelatinous-silica residue by means of filter presses.

The filter-press cakes were dried, briquetted, and smelted for recovery of lead, silver, and other metals, and the solution, after purification from lead, silver, antimony, and other elements, was electrolyzed in cells having anodes of pure lead and cathodes of zinc. The chief cause of failure of the process at Cockle Creek was the high cost of the electric current for effecting the deposition of the zinc.

In 1897, the Hoepfner process was introduced at the works of Messrs. Brunner, Mond & Co., Winnington, near Chester, and modifications of that process have been worked continuously since that time. In 1898, and for some years later, the works at Winnington was the only one in successful operation for producing electrolytic spelter. According to Hoepfner's process, the zinc ores are roasted, if necessary, to obtain zinc oxide and then mixed with water to form a pulp, which is treated with sulphurous acid to form zinc sulphite in solution; the free sulphurous acid present in this solution is then neutralized and the zinc sulphite decomposed by treatment with a solution of calcium chloride, magnesium chloride, or barium chloride. By this means, an insoluble sulphite is obtained, *e.g.*, calcium sulphite, and a solution of zinc chloride which, after purification, is electrolyzed. At the works at Winnington, a waste product, viz., calcium chloride solution, obtained in the Company's ammonia-soda works, is used in the production of the zinc chloride solution. The electrolysis is effected in cells having rotary iron cathodes and carbon anodes. Chlorine obtained in the anode reaction is used in the manufacture of bleaching-powder, while zinc of a high grade of purity, from 99·95 to 99·98 is obtained.

The working together, at Winnington, of more than one manufacturing process so that a waste product from one becomes a valuable reagent in another, has had a great deal to do in making the Winnington process successful, while many others have failed commercially.

The conditions brought about by the war led to further efforts to produce electrolytic spelter, and the results have been satisfactory. During the war, there has been a great demand for spelter of a high degree of purity, and, since good prices ruled in the spelter market, electrolytic spelter and re-distilled spelter have been supplied in large quantities.

An important plant for producing electrolytic spelter was put in operation in 1915 at Anaconda, Montana, by the Anaconda Copper Company with a proposed output of 5 tons of spelter per day. The process followed includes the roasting of the ores in Wedge furnaces, dissolving the roasted ores with air agitation, adding manganese dioxide and neutralizing free acid by adding limestone to the solution, and then agitating and aërating to set free ferric hydrate. The ore pulp is passed to a de-watering apparatus known as the Dorr thickener, which yields a clear solution containing most of the zinc of the ore as sulphate and a sediment which is transferred to an Oliver continuous filter. The cakes from the filter are treated in a blast furnace for the recovery of lead, silver, iron and other metals, and the expressed solution is added to the main solution from the Dorr thickener. Copper and cadmiun are eliminated from the solution by passing it through a tube mill filled with zinc balls, The solution, after clarification, is run to the electrolytic cells having anodes of pure lead and cathodes of aluminium. After 48 hours use, the cathodes acquire a weight of about 50 lb. and then the deposited zinc is stripped from them.

The results obtained were considered to be so satisfactory that the Anaconda Company commenced the erection at Great Falls, Montana, of a plant large enough to produce 35,000 tons of electrolytic spelter per year, and this plant commenced operations at the end of the year 1916.

An electrolytic spelter plant established at Trail, British Columbia, by the Consolidated Mining and Smelting Company of Canada, and, after completion in the following year, capable of producing about 70 tons of spelter per day, commenced operations in 1916. The process followed is of the kind adopted at Anaconda, the zinc being deposited from solutions of zinc sulphate obtained from the ores.

An electrolytic spelter plant producing 3 tons of spelter per day was put in operation at Park City, Utah, by the Judge Mining and Smelting Company, early in the year 1917. The electrolyte is zinc sulphate solution and rotary cathodes are employed.

About 10 tons of electrolytic spelter, obtained by treating Broken Hill ore, is being produced daily by the Electrolytic Zinc Company of Australia at their works at Risdon, near Hobart, Tasmania. These works commenced operations early in 1918.

These electrolytic processes and many others which have been employed or proposed have for their object the production of a solution of a zinc salt as free from impurities as possible, and the deposition of zinc from the solution by means of an electric current. Many other hydrometallurgical processes have been proposed for obtaining oxide of zinc, from which the zinc is recovered by a smelting process. Very few of these processes have been successful. One of the best known is the bisulphite process.

This process was developed at a works near Swansea about the year 1911 and was said to have been successful. The roasted ore was digested with water to form a pulp which was treated with sulphurous acid gas from the roasting furnaces. In this way, a solution of zinc bisulphite was obtained. This solution was withdrawn from the solid residues and treated to obtain zinc sulphite which was calcined to form zinc oxide for reduction in retorts in the usual way. The solid residues separated from the bisulphite solution were smelted for lead and other metals.

CHAPTER VII

ALLOYS OF ZINC

THE most important alloys of zinc used in the arts are those known under the generic name *brass*, the essential constituents of which are zinc and copper. That brass was made as early as the third century B.C. is suggested by a remarkable description of a copper-metal made by the Mossynoecians, who lived between Sinope and Trebizond. This description is in the Aristotelian treatise, *De Mirab. Auscult.*, *c.* 62, probably written by one of Aristotle's pupils. The metal is said to have been very bright and of a light colour and obtained, not by mixing tin with copper, but by melting copper with a kind of earth associated with it. According to report, the writer of the treatise adds, the one who discovered the mixture kept it secret, and the production of the copper-metal ceased.

Analyses of selected Roman coins of a yellowish colour, struck in the first century B.C. and the first century A.D. furnish strong evidence that the Romans understood the making of brass, and the references in the classics to *aurichalcum* or gold-copper and to *orichalcon* or mountain-copper, are generally consistent with this view.

The method adopted appears to have been a melting of copper with a kind of earth, viz., calamine or, more frequently, condensed furnace fumes obtained in smelting copper and other ores containing zinc. It was closely related to the process followed for many years for the manufacture of what was called *calamine brass*. This process, known as the *cementation process* and first clearly described by Theophilus, a monk of the eleventh century, consisted essentially in mixing calamine with coal and charging the mixture together with copper into melting-crucibles.

The early history of brass-making in this country is very imperfectly known. There are, however, a few well-ascertained facts which may be stated briefly. Brass, sometimes called *latten,* was employed, but probably not manufactured, from about the year 1272, when the monument of Henry III, in Westminster Abbey, was made by William Torrel. In 1565, William Humphrey, an assayer at the Mint, and Christopher Shutz obtained a patent giving the sole right to search for and mix calamine with metals. Calamine was found in Somersetshire in 1566, and the first true brass made by the new process was exhibited in 1568—(*Early History of the English Patent System,* E. Wyndham Hulme, 1896, p. 8).

Between the years 1580 and 1590, John Brode, a London goldsmith, set up works at Isleworth and claimed to be the first in England to use a mixture of copper and calamine and obtain a metal which could be hammered into sheets and raised into kettles and pans. After Brode's time, little seems to have been done until about the year 1650, when a brass works was set up in Surrey, probably at Wotton. In 1697, Houghton described the making of brass in England, and, by that date, the brass-making industry seems to have been firmly established. In that industry, Birmingham soon took a prominent part, the first brass-making works having been set up by Turner, in 1740, in Coleshill Street.

The modern method of making brass is to add gradually a quantity of spelter to molten copper contained in a crucible and covered by a layer of charcoal, the bath being stirred after each addition. To compensate for loss by volatilization, the amount of spelter added is greater than that in the resulting brass, but by keeping the temperature of the bath only about 100°C. to 150°C. above the point of solidification, the loss is minimized. The brass is usually ready for casting when a bluish-white flame plays over its surface.

The use of spelter for a part or the whole of the calamine used in the old cementation process was patented by Emerson of Bristol in 1781, but it was not until about the year 1870 that spelter brass, or that made by the direct melting of spelter with copper, completely took the place of calamine brass. The old process was considered to yield the best qualities of brass and a prejudice against the use of spelter brass had to be overcome.

Many kinds of brass, containing high percentages of copper, have long been used, mainly for the production of cheap jewellery. For this purpose they are well suited, being of a rich gold colour and easily worked by hammering and drawing cold. A few of these brasses will be described.

Tombac, a name of Malay derivation, is an alloy of very variable composition; it contains about 86 per cent. of copper and 14 of zinc, often with a little tin. Its colour ranges from copper-red to orange-yellow, according to the amount of zinc present. Pinchbeck, named after a London watchmaker of the eighteenth century, is of a dark gold colour and contains about 88 per cent. of copper and 12 of zinc. Mannheim gold is of a golden-yellow colour and contains about 80 per cent. of copper, 20 of zinc, and a little tin. Bristol metal contains about 75 per cent. of copper, and 25 of zinc, and Prince's metal, believed to have been first made by Prince Rupert, contains about 73 per cent. of copper and 27 of zinc.

There are also some brasses containing a large amount of copper which are used chiefly for imitation gilding. The best known of these is leaf gold or Dutch metal, which contains about 84 per cent. of copper and 16 of zinc. It is exceptionally malleable and is cast in small plates which are rolled into sheets and then hammered into thin leaves. Ormolu, sometimes called mosaic gold, may contain 67 per cent. of copper, nearly 33 of zinc, and a little tin, but, like many other brasses, its composition is very variable. It is used for making ornamental mounts for fancy articles of furniture.

There are also many so-called white brasses, used chiefly in imitation of silver, for spoons, tea-pots, buttons, and other articles. One of these alloys, nickel, or German silver, is of very variable composition; one of the best qualities contains 56 per cent. of copper, 16 of nickel, and 28 of zinc. Bath metal, for teapots, candlesticks, and buttons, contains 55 per cent. of copper and 45 of zinc. This brass is brittle, and so also is Birmingham platina, for casting into buttons, which contains about 75 per cent. of zinc and is almost as white as silver.

A highly important variety of brass is that used for engine and mill work, especially for the bearings of shafts. A brass suitable for such work is required to be homogeneous, compact, and tough but not too hard; it usually consists of copper 76 per cent., zinc 12 per cent., and tin 12 per cent. or, when used for very heavy bearing-pressures, less zinc and more tin.

Brass intended to be rolled into sheets or drawn into wire is as free from impurities as possible, and contains about 70 to 75 per cent. of copper and 30 to 25 of zinc, and a little tin. Cartridge-case brass is a high grade alloy, which can be readily rolled or drawn and contains 72 per cent. of copper and 28 of zinc as free as possible from cadmium to minimize any tendency to crack at the edges.

Most of the brasses described above are brittle at a red heat and this property is utilized for facilitating the stripping of a brass bush or other article from a rod or other part to which it has been fitted, all that is required being to heat the alloy to a low red heat and tap it with a hammer when it breaks up and falls away. There are, however, some varieties of brass malleable at a red heat, the best known being Muntz metal, also called yellow metal or patent brass. It was patented in 1832 by Muntz of Birmingham and has been used extensively for ships' sheathing and for bolts, pump barrels, and other parts exposed to the action of sea water. The validity of Muntz's patent was upheld, after long and costly litigation, on the grounds that the specification described the use of specific metals, viz., best selected copper and what was known as foreign zinc, in proportions of about 60 to 40, with the attainment of a useful result not previously obtained. Collins's yellow sheathing-metal, which could be rolled at a dull red heat and contained about 56 per cent. of copper and 44 of zinc was the alloy chiefly relied on to invalidate Muntz's patent. Another brass which can be worked hot or cold is naval brass for stanchions, bolts, etc., containing 62 per cent. of copper, 37 of zinc, and 1 of tin.

There are also many very useful alloys containing copper, zinc, and iron or manganese or iron and manganese, malleable but much harder and tougher than ordinary brass and of very great tensile strength. The chief of these are Gedge's or Aich's metal, containing 60 parts of copper, 38·2 of zinc, and 1·8 of iron; Sterro metal, very similar to Aich's metal and containing about 2 per cent. of iron; Delta metal, with 56 - 58 parts of copper, 40 - 42 of zinc, and small amounts of tin, lead, iron, and manganese; and Durana metal, with about 65 parts of copper, 30 of zinc, 1·75 of iron, 1·75 of aluminium, and a little tin and antimony. Gedge's or Aich's metal was invented in 1860 by Aich, of Venice, who claimed that, if the constituent metals were thoroughly incorporated with one another, the alloy would work hot or cold and could be rolled or stamped at a red heat, like wrought iron. Delta metal was introduced by Dick in 1883 and was called by the Greek equivalent of the letter *D*—the initial letter of the inventor's name.

There are also alloys of comparatively low melting points used for lining bearings ; some of these alloys, called anti-friction metals, contain a large amount of zinc, with antimony and copper.

Brasses containing aluminium have also been produced and are recommended for the manufacture of many parts of machinery. Their composition varies considerably, but an average composition is copper 60 parts, zinc 30 parts, and aluminium 2 parts, with a little tin, iron, and manganese.

Alloys containing zinc have been proposed for making the propeller blades of fast ocean liners. One of these, introduced by Parsons in 1910, contains 54·6 per cent. copper, 43·13 of zinc, and small amounts of iron, manganese, and tin. It is claimed for this alloy that it is very close-grained, being composed of minute, many angled crystals, which fit in and interlock one another, and that the alloy can, therefore, withstand the erosive action to which it is subjected during the rapid movement of the propeller as well as the corrosive action of the sea water.

During recent years, a series of light but strong alloys have been used in making parts of scientific instruments, automobiles, and aircraft. They are composed essentially of zinc and aluminium, the percentage of zinc ranging up to about 25. The angle brackets of Zeppelins have been made of an alloy of this kind containing about 90 parts of aluminium and 8 of zinc with small quantities of copper, iron, and manganese, and the channel sections have been made of an alloy containing the same metals, but the zinc amounted to 9 parts.

The alloys of zinc containing manganese, usually in small amounts, are of commercial importance and the manganese can be conveniently introduced into the alloy during its manufacture by using a previously formed alloy of zinc and manganese. An alloy of this kind, manufactured by Thermit, Limited, of London and Birmingham, contains 20 per cent. of manganese; it is a greyish-white alloy of very close texture.

Other alloys of zinc which may be mentioned are those used for soldering aluminium and containing large amounts of zinc and aluminium; vanadium brass containing 61 per cent. of copper, 38 of zinc, and 1 of tin, vanadium, and other elements; bismuth brass, an alloy of copper, zinc, nickel, and tin, with 0·1 per cent. of bismuth; and tungsten or wolfram brass containing about 60 per cent. of copper, 22 of zinc, 14 of nickel, and 4 of tungsten or wolfram.

The number of zinc alloys known in the arts is very great, and there are no fewer than 550 British Patent Specifications relating to alloys containing zinc, the compositions of many of which are stated specifically. The alloys described in this chapter are, therefore, only a few selected examples.

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THE END

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