# CHAPTER XII.

BIBLIOTECA

# TYPICAL METALLURGICAL PROCESSES.

Classification of Processes.—The methods that are adopted in extracting metals from their ores may conveniently be grouped in the following manner :---

The thick, black Roman numerals refer to the Thermal Equations, Chapter XI,

### A. DRY PROCESSES.

# I. a. By Simple Fusion with Suitable Fluxes.

| (a) In blast or rever-<br>beratory furnaces. | 1. Gold .<br>2. Silver<br>3. Platinum |   | This proce<br>plicable to<br>uncombined |
|--|---------------------------------------|---|---|
| (b) In tube-furnace.                         | 4. Copper<br>5. Bismuth               | • | .) uncombined<br>. By liquat            |

cess is only ap-metals in an d form. tion.

# β. By Simple Heating.

| (a) In kilns or rever-<br>beratories. | 1. Mercury (I.) | . From its sulphide, the presence of air being   |  |  |
|---------------------------------------|-----------------|--|--|--|
| (b) In retorts.                       | 2. Arsenic      | necessary.<br>From sulphides of<br>arsenic and iron, air ex-<br>cluded, always with appli-<br>ances for condensing the<br>volatilised metal. |  |  |

# II. By Reduction of Oxide by Carbon.

| <ul> <li>(a) In blast - furnaces</li> <li>r, more rarely, in hearths</li> <li>r crucibles.</li> <li>(b) Inreverberatory fur-<br/>ace.</li> </ul> | 4. Nickel | Usually after previous<br>roasting of sulphide or<br>arsenide;<br>Usually with simultane-<br>ous carburisation of the<br>liberated metal. |
|--|-----------|---|
|  | 8. Tin.   |   |

01 0

#### TYPICAL METALLURGICAL PROCESSES.

### AN INTRODUCTION TO METALLURGY. 406 (d) In furnaces heated 13. Aluminium (VII.) tion of the liberated metal. 14. Calcium, chro-mium, etc. electrically.

#### III. By Concentration as Sulphide;

# usually followed by reaction between sulphide and oxide, or between sulphide and sulphate.

furnaces. nace.

Usually after partial roasting; (a) In reverberatory 1. Copper (II.) urnaces.
(b) In liquation-fur3. Antimony .
(c) Starty arter partial reasting, sometimes, in the case of lead and antimony, the removal of the sulphur and precipitation of the metals is aided by a cheaper metal, iron.

(c) In Bessemer con- 4. Copper. verter.

IV. By Concentration in Sulphide, or Arsenide,

#### and subsequent smelting as in II. or III.

kel. alt.

| In reverberatory or | 1. | Gold |
|---------------------|----|------|
| blast-furnaces.     |    | Silv |
|                     | 3. | Cop  |
|                     | 4. | Niel |
|                     | 5  | Cob  |

# V. By Concentration in Other Metals, by Fusion.

Usually in blast-fur- 1. Gold. naces, but often in re-verberatory furnaces. 3. Platinum. The metal is subsequently con-centrated or extracted by (1) cupellation, (2) crystallisation (Pattinson process), (3) liquation, (4) recourse to wet methods, (5) (4) records to we method with the superior affinity of a third metal (zinc in Parkes' process), (6) electrolysis.

### VI. By Reduction of a Haloid Salt.

In reverberatory fur-naces or in crucibles. 2. Magnesium. { The halogen is removed by sodium.

#### B. PROCESSES INVOLVING THE USE OF MERCURY.

| .(a) In cradles, flumes, stamp<br>batteries, concentrators .<br>(b) In pans and appliances of<br>varied form | 1 0.12              | As part of the operation of dressing the ore.   |
|--|---------------------|---|
| (a) In heaps   | 2. Silver (VIII.) - | Patio process.<br>Old Freiberg process.<br>Cazo process.<br>Modern pan - amalga-<br>mation. |

# C. WET PROCESSES.

# a. Methods of Solution.

These processes are usually conducted in earthenware vessels, cast-iron pans, or vats, usually lined.

# I. a. Solution in Acids.

| 1. Gold In aqua regia.  |
|---|
| 2. Platinum   |
| 4. Bismuth In hydrochloric acid   |
| 5. Nickel.  |
| 6. Cobalt   |
| 8. Copper Chioric acid.   |
| 9. Lead.  |
| b. Solution in Alkaline Salts.  |
| 1. Gold In potassium cyanide.<br>2. Silver  |
| 3. ,, In hyposulphites.   |
| ·· ·  |
| II. Roasting to Sulphate, and extracting with Water.  |
| 1. Silver (X.) (Ziervogel process.)   |
| 2. Copper (II.) . The metal is precipitated by iron.  |
| III. Roasting with Salt, Soluble Chloride being formed.   |
|   |
| 1. Silver (IX.) . (Augustin and Von Patera processes.)<br>2. Copper . (Longmaid and other processes.) |
| 2. Copper (Longmaid and other processes.)   |
| IV. Formation of Soluble Chloride by Gaseous Chlorine.  |
| 1. Gold Plattner's process and its modifications.   |
| Or bromine may be used, a soluble bromide   |
| 2. Silver Any silver chloride, formed in the treat-   |
| ment of gold, may be dissolved out by   |
| sodium hyposulphite or brine.   |
| • 0 Will the the term   |
| $\beta$ . Methods of Precipitation.   |
| 1. Silver<br>2. Copper (XI.) .) Replacement by a cheaper metal.                                       |
| Gold Dy a precipitating agent.  |
| 2. Platinum   |
| Bismuth   |
| By precipitation, followed by reduction in  |

the dry way.

4. Zinc . 5. Lead

408

#### D. ELECTROLYTIC METHODS.

At the present time, electrolysis is mainly employed in the refining of copper,<sup>1</sup> less so in gold and silver refining,<sup>2</sup> in the precipitation of gold from dilute solutions,<sup>3</sup> and in the treatment of argentiferous lead. Numerous electrolytic methods of extracting and refining metals from their ores have been brought forward; few, however, have advanced beyond the experimental stage, of which the following are examples :-

| 1. | Copper   |     |   | From blister-copper or regulus.                |
|----|----------|-----|---|--|
|    | Lead .   |     |   | Bett's process.                                |
| 3. | Gold .   |     |   | By nascent chlorine produced electrolytically. |
| 4. | Aluminiu | m   |   | From aluminium in its fused salts.             |
| 5. | Antimony | 115 | 1 | Borchers' process. <sup>4</sup>                |
| 6. | Zinc .   |     |   | Electrolytic wet or dry methods.               |
| 7. | Steel .  | -   |   | Various methods, some already described.       |

Full descriptions of the methods adopted in extracting even the principal metals from their ores are not needed here, as the student has an abundant technical literature at his disposal. It is far more important for the student to become familiar with the nature of metallurgical operations generally, so that he may see how they differ from those conducted either in the laboratory or in purely chemical works. Hence a few typical metallurgical processes with considerable complexity of detail have been chosen for somewhat full treatment, since a knowledge of such groups of processes as those adopted at Swansea, Denver, and Freiberg gives the student a clearer insight into the practice of metallurgy than desultory reading affords.

Welsh Method of Copper-smelting.-This method, in modified forms, conducted in reverberatory furnaces, was until recently employed for a large proportion of the world's production of copper. In Germany a blast-furnace method is employed for the earlier stages. The one broad distinction between this method and the Welsh method consists in the fact that in the latter copper sulphide is the reducing agent, whilst in the German process it is carbonic oxide. Both processes depend essentially on the affinity which copper has for sulphur, which enables it to form a regulus while the associated metals are eliminated in an oxidised form.

In the Welsh method (fig. 183) comparatively poor ores, consisting of copper pyrites with a considerable proportion of iron pyrites, containing 5 to 15 per cent. of copper, richer ores of the same composition containing 15 to 25 per cent. of copper, and

TYPICAL METALLURGICAL PROCESSES.

copper pyrites with oxidised ores, are mixed so as to contain 9 to 15 per cent. of copper. The smelting method varies with the nature of the ore, but in

its original form comprised six distinct processes :--

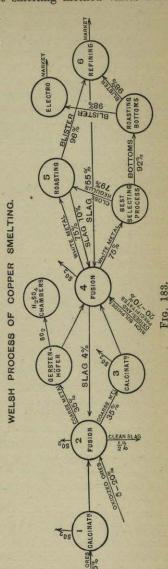
1. Calcination of Mixed Ores. -This consists in roasting the pyritic ores, whether rich or poor, containing iron pyrites, arsenic, and antimony. The roasting is always incomplete, and the extent to which it is carried depends on the proportion of sulphides available for the subsequent operations.

2. Fusion of the Roasted Ores for Regulus.—The ores are fused with slag rich in cuprous oxide, known as metal-slag, from the fourth operation. Fluorspar is useful as a flux, and is added with oxides and carbonates. The operation gives two productsa regulus, coarse-metal, in which it has been attempted to concentrate all the copper, and a slag, ore-furnace slag, which seldom contains more than 0.5 per cent. of copper and is mostly thrown away. The regulus contains 30 to 34 per cent. of copper and 23 per cent. of sulphur. It also contains a notable quantity of arsenic, antimony, and tin.

3. Calcination of Coarse-metal. -This calcination is always incomplete, but its degree of perfection depends on the quantity of oxidised ores which it is possible to reserve for the subsequent operation.

4. Fusion of Calcined Coarsemetal.-In this operation roasted regulus and sulphuretted ore rich in copper, and containing but

little sulphide of iron, are employed. Oxidised ores of copper. free from arsenic, antimony, and tin, are also added. Two products are obtained, regulus, containing 65 to 80 per cent. of



<sup>&</sup>lt;sup>1</sup> Peters, Copper Smelting, p. 576; Mineral Industries, vol. vii. (1899), p. 229. <sup>2</sup> Rose, Metallurgy of Gold.

<sup>3</sup> Ibid.

<sup>&</sup>lt;sup>4</sup> Dingler's Polytechnisches Journal, vol. cclxvi. (1887), p. 283. On electrolytic methods consult Balling, Die Electro-Metallurgie.

#### 411 TYPICAL METALLURGICAL PROCESSES.

#### AN INTRODUCTION TO METALLURGY.

copper, and 18 to 22 per cent. of sulphur, and metal-slag, which is a ferrous silicate, containing a little oxide of copper and shots of metallic copper, the total amount of copper it contains being 2 to 3 per cent. This slag is melted in operation 2.

5. Roasting the Regulus.-This operation is very complex, and comprises a series of roastings and fusion in an oxidising atmosphere. Its object is to purify the regulus and to scorify the iron, and to bring as much as possible of the copper to the metallic state. To operations of this character the Welsh smelter applies the term roasting, as distinguished from calcining. Two products are obtained, blister-copper, containing about 98 per cent. of copper, and a slag, roaster-slag, which always contains oxide of copper, shots of metallic copper, and often a small proportion of arsenic, antimony, and tin. This slag is usually added to the charge in operation 4.

6. Refining and Toughening .- The object of this operation is to purify the copper by oxidising the foreign bodies that it contains. The refining should bring the metal to the malleable state of marketable copper. The slag obtained, refinery-slag, is very rich in copper, about 55 per cent., and is added to the charge in operation 4.

In the original Welsh method of copper-smelting, reverberatory furnaces were exclusively employed, the area of the grate being generally about one-fifth of that of the hearth. The tendency, however, has been of late years to reduce the number of operations by judiciously mixing burnt pyritic ore with oxidised ores and slag, and running to a regulus in small cupolas or blast-furnaces. Subsequent enrichment of the regulus, reduction, and refining are still conducted in reverberatory furnaces. The ore is charged-in through a flat hopper, in which it is allowed to dry for some time before being introduced into the furnace. The internal dimensions of the calcining-furnaces are usually 30 feet by 12 feet, or 21 feet by 12 feet. The charge is 3 to 6 tons of ore, the calcination occupying twelve to twenty-four hours. The doors are then closed, and the temperature raised in order to decompose the sulphates. The gas evolved may consist of 10.6 per cent. of sulphurous and carbonic anhydrides, 9 per cent. of oxygen, and 80 per cent. of nitrogen.

The reverberatory furnaces, in which the fusion for regulus is effected, are so arranged as to give a high temperature, and the fireplace is consequently large in comparison with the laboratory portion. The bed consists of a series of layers of compressed sand cemented with metal-slag. It is about 15 to 20 inches in thickness, and slopes in all directions towards a tap-hole. There is a door in proximity to the flue, and through this door the slag is skimmed without allowing the air to pass over the regulus and oxidise it. In front of the tap-hole is a perforated receptacle, which can be lowered by a crane into a tank full of water. The bed is about 14 feet long, the distance between the top of the bridge and the roof being 23 inches. The charge is usually 2 tons of ore. Slags from subsequent operations are added, and fluorspar, if much earthy gangue is present. The materials used in the first fusion for regulus are chiefly oxides and sulphides of copper and iron, and the operation consists essentially in obtaining copper sulphide, thus :--

#### $2Cu_{2}O + 2FeS + 2SiO_{2} = 2Cu_{2}S + 2FeSiO_{3}$ Regulus. Slag.

The sulphides must be in excess, otherwise copper will be reduced and oxide of copper formed which will pass into the slag.

The calcination<sup>1</sup> of the regulus is effected in a furnace similar to that used for the first calcination. The charge is  $3\frac{1}{2}$  to  $6\frac{1}{2}$  tons of regulus. The reactions taking place are similar to those in the first calcination. The process occupies twenty to thirty-six hours, and 12 per cent. of the sulphur is eliminated.

The second fusion is conducted in a similar manner to the first fusion for coarse-metal. The charge is 2 tons of calcined coarsemetal and 12 cwt. of slag and oxidised ores. The regulus obtained consists of white-metal (75 per cent. of copper), or bluemetal (60 per cent. of copper), or pimple-metal (81 per cent. of copper). The slag is a silicate of iron, with about 4 per cent. of copper. The reactions are similar to those that obtain in the first fusion for regulus. Blue-metal contains some sulphide of iron, and pimple-metal contains an excess of the oxidised copper compounds. When very impure ores are dealt with, it is often found advisable to allow a little coarse copper to form as bottoms.

The roasting of these different varieties of regulus is conducted in a reverberatory furnace with a deep hearth. The process is prolonged as much as possible, and thus the arsenic and antimony may be caused to escape before the actual reducing action commences. When the pasty mass has collected at the bottom of the furnace the temperature is raised, and the reaction between the sulphide and the oxide takes place, metallic copper being formed. The chief reactions may be expressed thus :---

#### $Cu_{2}S + 2Cu_{2}O = 6Cu + SO_{2}$ $Cu_{o}S + 2CuO = 4Cu + SO_{o}$ .

This impure copper, blister-copper, is refined in furnaces similar to those used for fusion, except that the bed is deeper and the fireplace larger. The charge consists of about 10 tons of blister-copper in the form of pigs, which are loosely stacked, and an abundant supply of air is provided, so as to oxidise the metal as much as possible. The temperature is raised gently to the melting-point of copper; it is then moderated in order that the fusion

<sup>1</sup> Copper-smelters call these operations calcination, but roasting would be more accurate.

may be prolonged and oxidation occur. The melting occupies five to six hours, and the moderate heating is continued for five to six hours more, in order that the iron, antimony, arsenic, etc., may be completely oxidised. The temperature is then raised much higher for three to four hours more, when the oxidised products form a thin slag, containing a considerable quantity of copper oxide. This is raked off, and the surface covered with a layer of the purest anthracite or charcoal. A long pole of wood, green wood by preference, is pushed beneath the surface of the molten metal and held down by a suitable metal bar. The violent evolution of gas from the wood causes the metal to splash up amongst the carbonaceous covering, and this, with the gases from the wood, reduces, to the metallic state, the copper oxide that exists dissolved in the copper to the extent of 4 per cent. A small amount of the oxide must be left, and the workman judges, from a sample that he takes from time to time and tests by breaking in a vice, whether it is still "underpoled" or at "toughpitch," that is, ready for market, or "overpoled." If the last, he removes the carbon covering, and exposes the metal to the action of the air.<sup>1</sup>

In the so-called "direct" process, first successfully carried out at the Cape Copper Works, one portion of the rich regulus is carefully roasted in revolving cylinders or automatic rake calciners. This is then mixed with the unroasted portion and smelted in reverberatory furnaces, the above equations representing the changes. The feature of this method is that refined copper is produced in the one furnace and not the intermediate product, blister-copper. The original Welsh process has now undergone such modification that very little difference exists between it and the methods adopted in Germany at the wellequipped smelters of the Mansfeld Gewerkschaft, and also those of Freiberg and in the Harz mountains. In many of the modern works<sup>2</sup> in the United States the reverberatory furnace has been entirely dispensed with, and the process adopted consists in blastfurnace smelting for a regulus which is conveyed in the molten state to Bessemer converters. Here air is blown through the molten regulus, and copper is reduced to the metallic state, the reactions taking place being practically the same as those that

<sup>1</sup> Fuller information on the Welsh method of copper-smelting will be found in the following works :--

Percy, Metallurgy, vol. i. (London, 1861), p. 314.

Vivian, Copper Smelting: Its History and Processes, 1881. Howe, Copper Smelting, Washington, 1885.

Le Play, Procédés Métallurgiques employés dans le Pays de Galles, Paris, 1848.

Rivot, Principes généraux du Traitement des Minéraux métalliques, Paris, 1871.

Peters, Copper Smelting, and also The Principles of Copper Smelting. <sup>2</sup> Peters, Copper Smelting.

take place during reduction in reverberatory furnaces. The copper reduced in the converters is cast direct into anode plates and passed on to the electrolytic refineries.

Smelting of Gold and Silver Ores in Colorado.—The following is a short sketch, borrowed from Mr R. Pearce's Presidential Address, delivered at the meeting of the American Institute of Mining Engineers, in June 1889, of the methods formerly used at the Boston and Colorado Smelting Works. These methods, however, have now been replaced by more modern processes.

About 200 tons of ore are smelted per day, the ores including a great variety of copper, silver, and gold ores from Colorado, as well as from other Western States and Territories, and averaging 40 to 60 oz. of silver and  $\frac{1}{2}$  to 1 oz. of gold per ton, and 2 to 3 per cent. of copper. About 90 per cent. of the ore contains no copper, the other 10 per cent. furnishing that metal in sufficient quantity to make up the general average to 2 to 3 per cent. Half the ore, 100 tons per day, is roasted in furnaces or in kilns, but the operation is not complete in either case, as sulphur is always allowed to remain to the extent of 5 to 7 per cent. The other 100 tons are smelted without roasting. The roasted ore and siliceous ores are mixed so as to yield a slag containing 40 per cent. of silica and a regulus (ore metal) containing 40 per cent. of copper and 400 oz. of silver and 6 oz. of gold per ton. The capacity of each furnace is about 25 tons of ore per day, with 2 tons of rich slag added from other operations. In this smelting 13 tons charged yield 1 ton of ore-metal. This regulus always contains a certain amount of lead, but the proportion rarely exceeds 10 per cent.

In the next stage of the process, the charge consists of a mixture of two-thirds of roasted ore-metal and one-third of unroasted oremetal, together with the rich siliceous silver ore, in quantities sufficient to prevent corrosion of the furnace by the iron in the regulus. The concentration-furnace in which this operation is effected stands 3 feet above the level of the ore-furnace, so that the rich slag from the former may, when skimmed, flow directly into the latter, where it is reduced to the condition of ordinary ore-furnace slag. This effects a great saving in the cost of resmelting these rich slags. The regulus obtained contains 700 to 800 oz. of silver and 10 oz. of gold per ton, together with 60 per cent. of copper, each ton representing 20 to 21 tons of ore. This regulus is now ready for the extraction of the silver, which comprises the following operations :--

> Rough roasting. Fine grinding.

Fine roasting for silver sulphate.

Lixiviation, and the precipitation of the silver.

Refining and melting of the cement silver.

The regulus is crushed so as to pass through a screen of 6

meshes to the inch, and roasted for twenty-four hours. The bulk of the sulphur is driven off, and oxide of copper is formed, the mass still containing sufficient sulphur for the subsequent operation of roasting for silver sulphate. After cooling, the roasted material is ground finer under edge-rollers and passed through a 60-mesh screen. It is then ready for fine roasting or conversion of the sulphide into sulphate.

This operation, based on principles pointed out by Ziervogel, lasts about five hours. The first stage is conducted at a low temperature, and lasts about an hour and a half, copper sulphide being oxidised with evolution of heat. In the second stage, at a slightly increased temperature for an hour and a half, the material increases in volume, and assumes a porous appearance from the formation of copper sulphate. In the third stage, the temperature is further increased for an hour, or until the silver is completely changed into sulphate. If cuprous oxide is present at this stage, it will, during the operation of lixiviation with water, cause the reduction of the silver sulphate to metallic silver. The charge is consequently vigorously stirred, and turned over, in the fourth and last stage, in order completely to oxidise any cuprous oxide. The results of the operation are very materially affected by arsenic, by antimony, and, above all, by bismuth, metals which form insoluble silver compounds. The lixiviation of the roasted regulus is effected in tubs, and nothing but hot water is required. The solution, charged with silver sulphate, is allowed to flow over copper plates for the precipitation of the silver, a process requiring but little attention. The solution enters tank No. 1, charged with silver, and leaves tank No. 2, charged with copper, and without a trace of silver. It finally flows over scrap-iron for the precipitation of the copper. In the precipitated silver, some copper is found in the form of cuprous oxide or as metal. This is removed by prolonged boiling with water containing a small quantity of sulphuric acid, into which air is injected by a small steam-jet. The copper sulphate formed is carefully washed out of the silver, which is then dried and melted into bars of an average fineness of 999.

The residues from the silver extraction contain about 40 oz. of silver and 10 oz. of gold per ton, and 65 per cent. of copper as cupric oxide. They also contain lead and bismuth as sulphates, and iron as ferric oxide. They are mixed with pyritic ores containing gold, pyrites rich in sulphur, and siliceous gold ores, and are smelted direct for regulus with 65 per cent. of copper, and 10 to 15 oz. of gold and 80 oz. of silver per ton. The slag, which is similar in composition to that from the ore-furnace, is thrown away.

This regulus is treated so as to obtain a rich copper-gold alloy. This process involves two operations—(1) a combined roasting and smelting, and (2) a refining of the crude alloy. The aim of the

#### TYPICAL METALLURGICAL PROCESSES.

process is to concentrate the gold contained in the regulus into a rich gold- silver-copper alloy, containing also the bulk of the impurities existing in the regulus. This process is similar to the Swansea method of making "best selected copper." At Argo, about 12 tons of slabs of regulus, residue metal, are placed on the hearth of a large reverberatory furnace, and melted after partial oxidation. In the last stage of the melting, a reaction takes place between the oxide and sulphide, and a certain amount of metallic copper is liberated. This contains nearly all the gold, together with any foreign metals present in the regulus. The charge is tapped into sand-moulds, and the first few pigs nearest the tap-hole are found to have, under the enriched regulus, plates of this impure copper, commonly known as metallic bottoms. The proportion of these to the whole tap of regulus, or pimple-metal, is about 1 to 15. The bottoms contain 100 to 200 oz. of gold to the ton, and about 300 oz. of silver. They are subjected to processes of refining and separation, whereby the gold is recovered.

The pimple-metal, if the operation has been properly conducted, contains 0.1 to 0.2 oz. of gold per ton, 90 oz. of silver, and 77 per cent. of copper. It is crushed, roasted, ground fine, and again roasted to form silver sulphate. In fact, it is treated by the Ziervogel process in precisely the same manner as the rich silver regulus; but, as it contains little gold, a separate set of furnaces is used. The residue consists almost entirely of copper oxide with less than 10 oz. of silver per ton. It is dried, packed in barrels, and sold to the manufacturers of sulphate of copper, or is reduced to black copper by melting with small coal slack in a reverberatory furnace.

Thus it will be seen from the above brief sketch how intimately associated are the modern methods of metallurgy as applied to gold, silver, copper, and lead. For a full description of these methods the students should refer to the other volumes of this series.<sup>1</sup>

In these volumes detailed descriptions are given of the modern methods of treating complex ores containing the four abovementioned metals in quantities sufficient to render their extraction profitable. It will be seen to what a high state of efficiency the processes have been carried; how by judicious dressing the sulphides and oxidised material are carefully separated and subjected to special treatment, in the case of silver ores by the modifications of the original amalgamation processes and the newer "wet" processes. In these, stress is laid on the operation of roasting, this being regarded as the crucial point upon which the commercial success of the process may depend. Consequently the object of dressing methods is to limit the amount of material requiring this treatment, and to effect the operation by appliances which shall give a high efficiency.

<sup>1</sup> Collins, Metallurgy of Lead and Silver.

**Freiberg Process.**—The smelting works at Freiberg,<sup>1</sup> in Saxony, were originally established to treat the ores obtained from the mines of the district. At the present time, ores from all parts of the world are also smelted. There are also two works, of which the more important (the Halsbrüche Hütte) is situated about three miles from the town of Freiberg, the other (the Muldenhütte) being somewhat more distant.

The ores treated consist chiefly of the sulphides of lead; but silver and copper are always present in the mixture of ores which constitutes the furnace-charge. The plant also includes furnaces for the treatment of ores of zinc, arsenic and antimony fume. As an incidental process, sulphuric acid is made both by the ordinary lead-chamber method, and by a process in which the gases containing the sulphurous anhydride are stated to be passed over perforated clay slabs covered with platinised asbestos. Bismuth is also extracted from the portions of the cupellation-hearths in which is collected the greater part of the bismuth that was originally contained in the lead treated. Provision is also made for the extraction of copper, nickel, and cobalt present in the ores. The various departments of the work are kept distinct, and the treatment, as a whole, centres round the smelting of the lead ores, the various residues from the treatment of other ores, frequently rich in the precious metals, being added to the lead-smelting. charge. It is in this latter treatment that the distinctive features of the Freiberg smelting process are found, the lead ores being smelted in admixture with the copper ores and argentiferous and auriferous residues. For this purpose the Pilz water-jacketed furnaces are used. They were originally introduced about the year 1865 to replace the older types of blast-furnace which had long been employed. The extraction of silver by the classical Freiberg amalgamation process, conducted in barrels, was also abandoned about this period, and was replaced by the method still in use, by which the precious metals are collected in the smelted lead. The main features of this process are as follows :---In order to impart the necessary degree of strength and coherence to enable them to be treated in the blast-furnace, as well as to obtain them in pieces of a size adapted to such treatment, the ores are first roasted at a temperature sufficiently high to clot the mass. This is effected by subjecting a suitable mixture of ores to an oxidising roasting in a long-bedded reverberatory furnace. The sulphur of the ore is in this way oxidised, and the metals are left chiefly in the form of oxides. Towards the end of the roasting the temperature of the furnace is raised to a degree sufficient to partly fuse the oxidised charge then present; the roasted material can in this state be withdrawn from the furnace into sheet-iron wheel-barrows, in which it is allowed to solidify. The

<sup>1</sup> The description of this process has been left practically in its original form, as it includes several typical metallurgical operations.

# TYPICAL METALLURGICAL PROCESSES.

417

solidified material is afterwards broken up into pieces of the desired size, and classified according to the completeness with which the roasting has been effected, as indicated by the presence or absence of unroasted sulphide. It is then smelted down in the Pilz furnaces, in admixture with coke and brown coal. The products of this smelting are (1) lead; (2) a regulus, or mixture of fused sulphides of lead and copper; (3) a slag; and (4) a lead fume. A small quantity of speise, containing nickel and cobalt, is also occasionally obtained. The lead produced contains the greater part of the precious metals originally present in the charge, together with some copper and other impurities. Such lead has always to be subjected to a refining process before being desilverised by the method in use at the works, and, if very impure, a secondary refining process of liquation has also to be used. To avoid the necessity of this, the charge is usually maintained as free from impurities as possible, the percentage of the copper being at the same time kept low. The slag from the ore-smelting always contains lead in too large a quantity to admit of its being thrown away. It has therefore to be re-treated, and, as the lead obtained from this source is always very impure, any impure materials that it may be necessary to deal with are generally treated simultaneously with the slag, provided they are not too rich in the precious metals. The percentage of copper admissible in the furnace-charge for this slag-smelting is also greater than in that for the treatment of the ore. The ore-slag is treated in admixture with materials poor in silver and in lead, in a manner similar to the method adopted when smelting the ore. The products are the same as before-lead, speise, regulus, slag, and fume. The lead, however, is much less in relative quantity, and more impure than that obtained from the ore-smelting ; speise is a more frequent product, the regulus obtained is richer in copper, and the slag is so poor in silver and lead that it may be thrown away.

The further treatment of these various products is as follows :---Lead.-The slag-lead, and occasionally the ore-lead, is first submitted to a liquation process, which consists in melting the lead at as low a temperature as possible, on the sloping bed of an ordinary reverberatory furnace in a deoxidising atmosphere. By this means the lead melts and flows into a sump or hollow at the foot of the sloping bed of the furnace, leaving the greater portion of the copper it originally contained, together with iron and other impurities, the melting-points of which exceed that of lead, on the furnace-bed. Nearly all the silver present in the lead charged into the furnace, and with it the gold, passes into the liquated product, owing to the low melting-points of the silver-lead and gold-lead alloys there present. This liquated lead, together with the ore-lead, is then submitted to an oxidising fusion in a reverberatory furnace, the result being that the arsenic, antimony, tin,

416

and other impurities present, which had failed to be eliminated by the liquation process, are oxidised, and a portion of the lead being simultaneously oxidised and fused, they pass into this oxide scum, and can be removed with it. Owing to the varying degree of oxidisability of the several impurities, the fused litharge obtained at different stages of this process contains relatively larger or smaller quantities of the various impurities. These litharges, after removal from the furnace, are kept separate, and are known by the name of the more important impurity they contain. Each of them is afterwards reduced by itself in a small blast-furnace, the product being in each case a readily marketable hard lead, the impure litharge being first fused with a small percentage of carbon to reduce a portion of the lead, and in this way to collect any silver that may be present in the reduced lead formed. Any copper, too, that may have passed into the liquated lead is also oxidised, but the bismuth remains with the lead. Small quantities of the precious metals always pass into the fused oxide layer on the surface of the lead, but by far the larger proportion of that originally charged into the furnace remains with the purified lead. This lead is then treated by the ordinary Pattinson process, the lead being first melted at a low temperature and then allowed to cool gradually, the lead crystals poor in silver being separated from the richer molten portion. This treatment is repeated in the ordinary manner until the poor lead contains 0.1 per cent. of silver. Instead of continuing to treat this lead by the Pattinson process, the Parkes process of desilverisation by the aid of zinc is employed for the purpose of extracting the remaining silver and gold, the lead from this treatment being dezincified by an oxidising fusion, after which it is ladled into moulds and is ready for the market. The rich Pattinsonised lead is cupelled in cupellation-furnaces of the German type, with non-absorbent marl beds. The cupellation is so conducted that the lead, being charged into a hearth of large size, is oxidised until the residual material contains about 80 per cent. of the precious metals. This requires a higher temperature for its further treatment, and it is therefore removed from the large furnace to a similar but much smaller one, in which the remaining portion of the lead is eliminated, the fused gold and silver being granulated by pouring into water, the granules dried, and the gold and silver parted by the aid of sulphuric acid.

The litharge, if of a yellow colour, is reduced to the metallic state by a reducing-fusion in a small Pilz furnace, but any red litharge that is produced is sold as such. The beds of both the large and the small cupellation-furnaces show green spots at the places where the final products, rich in gold and silver, collected ; the bismuth, not being removed by oxidation until nearly all the lead has been oxidised, passes into these portions of the marl-beds, colouring them green. These green patches are carefully removed, dissolved in hydrochloric acid, and the bismuth oxychloride is precipitated by dilution with water. This is either sold as such after purification, or else is reduced to the metallic state by fusion in crucibles with iron. The other portions of the marl cupellation beds, being rich in lead, are on this account added to the various smelting charges.

Zinc.—The argentiferous zinc ores are roasted, the sulphurous anhydride evolved being collected and converted into sulphuric acid. The desulphurised ore is then mixed with carbon, and placed in the retorts, which are heated in a regenerative furnace by gaseous fuel. The zinc distils over, and is collected in fireclay receivers. The residues left in the retorts contain the precious metals, and are charged into the Pilz furnaces with the lead ores.

The zinc rich in silver and gold obtained by the Parkes process is distilled in an ordinary Morgan furnace, which consists of a hooded crucible contained in a wind-furnace. This completes the lead-smelting process proper, both the gold and silver present in the original materials treated having been collected, and the desilverised lead obtained in a form in which it is ready for the market.

The cupriferous regulus resulting from the ore-smelting contains usually but a few per cent. of copper, and consists chiefly of the sulphides of iron and lead. It may be mentioned that it is necessary to have considerable quantities of iron present in the furnace-charge, partly on account of the desulphurising action of the reduced metal, and partly because considerable quantities of zine are usually present, and the zinc-oxide, passing into the slag, would render it exceedingly pasty and difficult to fuse, were it not for the counteracting influence of large quantities of ferrous oxide.

This regulus, if its composition is such that this treatment is admissible, is roasted in kilns, the sulphurous anhydride produced being utilised in the manufacture of sulphuric acid. When roasted the regulus is added to the slag-smelting charge; the greater portion of the lead-oxide contained in the roasted regulus is then reduced to the metallic state, and a second regulus is produced, which is poorer in lead but richer in copper than was the one resulting from the ore-smelting. This regulus is too rich in copper to admit of its being roasted in kilns, the tendency of the pieces of regulus to clot together during the roasting being too great; it is therefore roasted in "stalls" which are built of brick, and much resemble ordinary cattle-stalls; they are rooffess, with low surrounding walls and a slightly sloping bed. On this bed wood is placed, the regulus to be roasted being piled up on it, and then covered over with a compact layer of finely divided roasted pyrites or regulus. The stalls are placed in rows side by side, and back to back, a tunnel being left between every two