436

It is allowed to settle, and run off into tubs C. Steam is conducted into the tubs, and when the liquid begins to boil, bleaching powder (chloride of lime) is added to peroxidise the iron, and the mass is allowed to boil for about three hours. The arsenic and iron come down together. If no iron be present in the solution some must be added. The liquid is then run off through filters D, to underground tanks E, whence it is pumped to tanks F, in which the mass is treated with sulphuretted hydrogen. Adjoining these tanks, of which there are six, there are also three lead retorts, in which sulphuretted hydrogen is produced. In these tanks the copper is precipitated, and the nickel and cobalt solution is strained through filters G, and drains into a second underground tank H. It is then pumped into a tank J, and there successively mixed with iron, chalk, chloride of lime, and water from tubs placed above the tank, with a view to precipitate, first, any copper that may have passed into solution during filtration, and then the iron which has taken the place of the copper. The charge is first boiled by the aid of steam pipes so as to expel the sulphuretted hydrogen. It is then run off to a tank L for stock. It is next pumped up into a dividing tank M, and heated with chloride of lime, the cobalt being precipitated as oxide at a temperature of 40°. The solution containing nickel is allowed to run off into another tank O, in which milk of lime is added, and the nickel precipitated as hydrated oxide. The liquid is allowed to run off as waste. The oxides are pumped into presses, and the water is drained off. The nickel oxide is dried on the roof of a muffle, heated, and crushed. It is then mixed with charcoal, and heated in a crucible in a reducing-furnace for eight or twelve hours. A rough powder is obtained, and in this form the metal is sold, or the nickel oxide is mixed into a paste with flour and water, which is heated and cut into cubes. These cubes are placed in crucibles with charcoal, and heated to a temperature above the meltingpoint of copper. The nickel oxide is reduced by the charcoal and by the carbonised flour. The metal does not melt, but preserves the form of cubes. The cobalt oxide is removed from the dividing tanks to stone jars, and treated by a process similar to that described, so as to remove the last trace of nickel. The cobalt is finally sent to market in the form of oxide.

The Extraction of Nickel from its Ores by the Mond Process.<sup>1</sup> —This interesting process marks an entirely new departure, in metallurgical practice, from the principles which have hitherto guided it. It depends on the remarkable property possessed by nickel of forming a volatile compound with carbon-monoxide. When this gaseous compound is heated to 180° C. nickel is released in the metallic form. The author was much impressed

<sup>4</sup> This description, taken from a paper communicated by the author to the Institution of Civil Engineers, in 1898, has been slightly modified, and kindly revised by Dr Langer. during a visit to Canada with the Imperial importance of the great nickeliferous district of Sudbury, Ontario, and the description of any new process which affords a hope of hastening the development of this remarkable district should prove to be interesting. The deposit itself presents many points of interest. According to Professor Coleman of Toronto, the nickel ores of Ontario resemble the gold ores of Rossland in British Columbia, as they consist of a mixture of pyrrhotite (magnetic pyrites) and copper pyrites. These sulphides form enormous masses near the margin of large areas of diorite, or weathered gabbro of Huronian age, the amount of nickel contained in the ore averaging between 21 per cent. and 10 per cent., the lower proportion being the more common. It is worthy of note that pyrrhotite from other parts of the country, found in association with Laurentian rocks, is almost barren of nickel. The importance of the nickel deposits of Ontario may be judged from the fact that, until the mines in the Sudbury region were worked, the world's supply of the metal was drawn chiefly from the mines of New Caledonia, an island in the Southern Pacific, supplemented by the Gap mine in Pennsylvania, and a few isolated mines in Norway and Hungary. The extent of the Sudbury deposits is greater than any of these, and New Caledonia, which belongs to France, is virtually the only rival of Ontario in the production of nickel.

The ore at Sudbury is smelted into a regulus, or matte, which contains between 12 per cent. and 20 per cent. of nickel, and about the same amount of copper. This matte may be enriched by suitable treatment, and is "Bessemerised" into a regulus which contains about 40 per cent. of nickel, and is specially free from iron, as the following analyses show :—

ANALYSES OF BESSEMER MATTE UNROASTED.

			I.	II.
			Per cent.	Per cent.
Nickel			40.938	31.35
Copper		-	45.714	48.86
Iron and (Al <sub>2</sub> O <sub>3</sub> )			0.405	0.81
Cobalt	100		0.136	
Sulphur .	44	14	11.960	

It is unnecessary to give a history of the metallurgy of nickel, but it may be well to state that Chronstet isolated the metal in the year 1751, and that Bergman confirmed his discovery in 1774. The methods hitherto employed for extracting the metal from its ores are very complicated; they have involved concentrating the nickel either as a sulphide (matte or regulus), or as arsenide (speise) followed by either "dry" or "wet" treatment. In the

439

case of certain ores, wet methods only have been employed. The metallic nickel has always to be subjected to a process of refining, mainly, as in the case of cast iron, with a view to separate it from associated carbon.

As regards the experiments from which this process was developed, a few brief historical details may be offered. In 1889 Dr Ludwig Mond, F.R.S., in collaboration with Dr Carl Langer, was engaged in working out a method for eliminating the carbonmonoxide from gases containing hydrogen<sup>1</sup> which they wanted for use in their gas battery.<sup>2</sup> In attempting to effect this, they were guided by the observation they had previously made that finely divided nickel has the remarkable property of removing carbon from carbon-monoxide at a temperature of 350° C., converting it into carbon-dioxide, while the dissociation of carbon-monoxide by heat alone, according to Victor Meyer and Carl Langer, remains incomplete at the high temperature of 1690° C. In the course of these experiments, which they carried out in conjunction with Dr Friedrich Quincke,<sup>3</sup> finely divided nickel, formed by reducing nickel oxide at 350° C. by hydrogen, was treated with pure carbon-monoxide in a glass tube at varying temperatures. In order to keep the poisonous carbon-monoxide out of the atmosphere of the laboratory, the gas escaping from the apparatus was ignited. They found to their surprise that while the tube containing the nickel was cooling, the flame of the escaping gas became luminous and increased in luminosity as the temperature sank below 100° C. Metallic spots were, moreover, deposited on a cold plate of porcelain held in this luminous flame, just as spots of arsenic are obtained in applying the Marsh test for that metal. It was also observed that on heating the tube through which the gas was escaping, a metallic mirror was obtained, while the luminosity of the flame disappeared. On examination these metallic deposits were found to be pure nickel. The next step was to endeavour to isolate this curious and interesting nickeliferous compound, by preparing nickel with great care at the lowest possible temperature, and treating it with carbon-monoxide at about 50° C. The amount of the volatile nickel compound in the gases passing through the apparatus was thus gradually increased. The gases issuing from the apparatus were treated with a solution of cuprous chloride to absorb the excess of carbonmonoxide, and in this way a residue of several cubic centimetres of a colourless gas was obtained, containing the volatile nickel compound. By passing this gas through a heated tube the nickel

p. 749.

and carbon-monoxide were again separated, and the volume of the carbon-monoxide thus set free was found to correspond to about four equivalents of carbon-monoxide to one equivalent of nickel. By further improving the method of preparing the finely divided nickel, and by passing the resulting gases through a refrigerator cooled by snow and salt, the investigators at last succeeded in obtaining the new compound in a liquid state, and were able to produce it with facility in any desired quantity.

Nickel carbonyl in its pure state is a colourless liquid, boiling at 43° C.; it has a specific gravity of 1.3185 at 17° C., and solidifies at -25° C. into needle-shaped crystals. It is soluble in alcohol, petroleum, and chloroform; and it is not acted upon by dilute acids or alkalies. It can be readily distilled without decomposition; but, on heating the vapour to 150° C., it is completely dissociated into its components, pure carbon-monoxide being obtained, while the nickel is deposited in a dense metallic film upon the sides of the vessel in which the compound is heated.

After the production of nickel carbonyl had become easy, Drs Mond, Langer, and Quincke directed their attention to the action of carbon-monoxide on other metals. A series of experiments was made with a view to obtain a similar compound with cobalt, which in its chemical and physical behaviour so much resembles nickel. The experiments gave, however, the unexpected result that, unlike nickel, cobalt will not combine with carbonmonoxide. Experiments were then made with iron, and indications were soon obtained of the existence of a volatile compound of iron and carbon-monoxide; a long time elapsed before this new compound was obtained in a pure state. It was finally isolated in a way similar to that by which the nickel carbonyl had been prepared, and proved to be a somewhat viscous liquid of pale vellow colour.<sup>1</sup> Its specific gravity at 18° C. is 1.4664; and it distils completely without decomposition at 102.8° C. under a pressure of 749 millimetres of mercury. When cooled to  $-21^{\circ}$  C. it solidifies into a mass of yellowish needle-shaped crystals. Its chemical composition is somewhat different from the nickel carbonyl, as it contains five equivalents of carbon-monoxide to one of iron. The liquid compound, to which the name of iron penta-carbonyl was given, undergoes no change when protected from the action of light; but exposure to daylight for several hours in a sealed tube is attended with the formation of goldcoloured, tabular crystals, and carbon-monoxide is evolved, so that the pressure in the tube rises considerably. The crystals have, when dried, a metallic lustre, and resemble flakes of gold; they contain two equivalents of iron to seven equivalents of carbonmonoxide. None of the other metals which were submitted to

<sup>1</sup> Ludwig Mond and Carl Langer on "Iron Carbonyls," Journ. Chem. Soc., vol. lix. p. 1090.

<sup>&</sup>lt;sup>1</sup> Ludwig Mond and C. Langer, "Improvements in obtaining Hydrogen." British Patent No. 12,608, 1888.

<sup>&</sup>lt;sup>2</sup> Ludwig Mond and C. Langer, "A New Form of Gas Battery," Proc. Roy. Soc., vol. xlvi. p. 296. <sup>3</sup> Ludwig Mond, C. Langer, and F. Quincke, Journ. Chem Soc., vol. lvii.

# AN INTRODUCTION TO METALLURGY.

440

investigation showed indications of combining directly with carbon-monoxide.

The discovery that in a mixture of metals only nickel and iron would form volatile compounds with carbon-monoxide, and that they could, therefore, be separated from the other metals, was sufficiently important to induce Dr Mond to arrange laboratory experiments with ores containing nickel, cobalt, iron, copper, etc., such as "kupfer-nickel" and "pyrrhotite." The experiments afforded such promising results that apparatus of considerable size, though still well within the limits of the resources of a laboratory, was set up, and in it several pounds of ore could be treated with carbon-monoxide.<sup>1</sup> A patent was also applied for on August 12, 1890, which describes the way in which such ores may be treated. It is pointed out that the principal nickel ores



which are metallurgically treated contain the nickel in combination with arsenic and sulphur besides other metals and gangue. These ores have first to be submitted to the process of calcination, in order that the nickel may be present in the form of oxide, and to drive off, as far as is practicable, the arsenic, sulphur, and other volatile bodies. The resulting oxide of nickel is treated with reducing gases, such as water-gas or producer-gas, in order to convert the oxide of nickel into finely divided metallic nickel; the material containing it is then cooled to about 50° C., and is treated with carbon-monoxide. In dealing with nickel ores which contain nickel oxide in chemical combination with silicic acid, arsenic acid, or other substances which cannot be removed by calcination, the ores are so treated as to convert the nickel into nickel speise or nickel matte, which is then subjected to calcination. The actual experiment upon which the beautiful process is based may be indicated by a diagram, fig. 188. The gasholder

<sup>1</sup> Ludwig Mond on "Metallic Carbonyls," Proc. Roy. Inst., vol. xiii. p. 668.



PLAN. FIG. 189.



Introduction to Metallurgy.]





# TYPICAL METALLURGICAL PROCESSES.

contains carbonic oxide, and a little of the gas is ignited to show that it burns with the characteristic flame of that gas. The gas then passes over finely divided metallic nickel at a temperature not necessarily exceeding 50° C., and the luminosity of the flame is materially increased. In a very few minutes the carbonic monoxide will take up its charge of nickel, and a luminous flame will deposit its nickel on any cold surface held over it. It can thus be shown within what a very small range of temperature the whole operation is conducted. By passing the gas into a tube, and by heating it, a brilliant deposit of metallic nickel is obtained on the inside, in the form of a mirror.

In 1892 an experimental plant on a large scale was erected at Smethwick, near Birmingham. After some years of patient work, during which the plant had several times to be reconstructed, in order to meet all the conditions of this somewhat delicate process, it gradually assumed the shape shown in fig. 189. Before describing it in detail, it will be well to give a brief account of the operations involved in the process, which are the outcome of many years' practical experience.

The process is more especially suitable for the extraction of nickel from ores which contain copper in addition to nickel and iron. These ores, which have on an average between 2 per cent. and 6 per cent. of nickel and about the same amount of copper, are first subjected to "heap roasting," to eliminate the greater part of the sulphur, and to convert the iron, which forms their chief constituent, into oxide. The roasting is necessary to enable the iron in the following operation of smelting to combine with the silica present in the ore to form a slag, and thus to effect the separation of the iron from the nickel and copper which unite with the remainder of the sulphur to form a regulus or matte. This matte contains the nickel and copper in a more concentrated form, the amount of each metal being usually 15 per cent. to 20 per cent., the residue consisting mainly of sulphur and iron. To concentrate the nickel and copper still further, the matte is "Bessemerised." A sample of such "Bessemerised" matte contained 31.37 per cent. of nickel, 48.62 per cent. of copper, and 0.70 per cent. of iron. It was prepared by the Canadian Copper Company, Sudbury, Ontario, from their ores, which contain an average of 4 per cent. of nickel and 4 per cent. of copper. This "Bessemerised" matte is crushed, ground, and subjected to a calcining operation so as to convert the sulphides into oxides, and it is then passed through a mill and dresser. This calcined Bessemer matte then consists practically of nickel oxide and copper oxide in varying quantities. It has been found in the practical working of the process to be advantageous to further concentrate the nickel by extracting part of the copper at this stage by treating the mixtures of oxides with dilute sulphuric

# AN INTRODUCTION TO METALLURGY.



furnace may be employed. After roasting, the matte contains

out taking up more than 1 per cent. to 2 per cent. of the nickel. The copper thus dissolved is in the form of copper sulphate and is obtained in a marketable form by crystallisa-The undissolved tion. residue from this operation contains between 45 per cent. and 60 per cent. of nickel, and, after drying, it is subjected to a carefully regulated reducing process by means of water-gas, after which it is treated with carbonmonoxide to extract part of the nickel present. In this first treatment with carbon-monoxide about twothirds of the nickel can be easily extracted; after this amount is volatilised the extraction becomes much slower, so that it has been found advantageous to recalcine the residues and repeat the copper extraction, the reduction, and the nickel extraction.

The five operations involvedarediagrammatically illustrated in fig. 190. The process begins, as will be seen, at one end with the material to be treated, "Bessemerised" matte; it ends with the market product, nickel. The "Bessemerised" matte proceeds, as the arrow indicates, to the first operation (1) of dead roasting, and for this purpose any suitable

TYPICAL METALLURGICAL PROCESSES.

35 per cent. of nickel, 42 per cent. of copper, and about 2 per cent. of iron.<sup>1</sup> It then passes to the second operation (2) for the extraction of part of the copper (about twothirds) by sulphuric acid, the copper being sold as crystallised sulphate of copper. The residue from this process contains about 51 per cent. of nickel and 21 per cent. of copper, and passes to the third operation (3) for reducing the nickel and incidentally the remaining copper, to the metallic state, care being taken to avoid reducing the iron. This is effected in a tower provided with shelves, over which mechanical rabbles pass, the reducing agent being the hydrogen contained in water-gas. The temperature does not exceed 300° C., and should be kept lower when much iron is present. From this tower the ore is conveyed continuously to the fourth operation (4) of volatilisation, in which part of the nickel is taken away by carbon-monoxide and forms the compound nickel carbonyl. The formation of this volatile compound is effected in a tower similar to the reducing tower, but the temperature is much lower, and does not exceed 100° C. From the volatiliser, the ore is returned to the reducer (3), and it continues to circulate between stages (3) and (4) for a period varying between seven days and fifteen days, until about 60 per cent. of the nickel has been removed as nickel carbonyl. The residue from this operation, amounting to about one-third of the original calcined matte, and not differing much from it in composition, is returned to the first operation and then naturally follows the same course as before. The nickel carbonyl produced in the fourth operation passes to the decomposer. This appliance is either a tower or a horizontal retort, which is heated to a temperature of 180° C., so as to decompose the nickel carbonyl and release the nickel in the metallic form, either on thin sheets of iron or, preferably, on granules of ordinary commercial nickel. Carbon-monoxide is also released, and is returned to the volatiliser to take up a fresh charge of nickel. It will be evident that when the operation is in progress, the gaseous carbon-monoxide and the partially reduced oxides of nickel and copper are continuously revolving in two separate circuits which join and cross each other in the volatiliser. The commercial product contains between 99.4 per cent. and 99.8 per cent. of nickel.

It will now be possible to proceed to a description of the working as the author saw it in full operation during a visit to Smethwick. The material under treatment during the author's visit was of Canadian origin, and had been received as calcined Bessemer matte containing 35.4 per cent. of nickel, 41.8 per cent. of copper, and about 2 per cent. of iron. This material was first passed through a ball mill and dresser with a 60-mesh riddle,

<sup>1</sup> Average results are given in the figure rather than the best which have been obtained.

442

445

#### AN INTRODUCTION TO METALLURGY.

444

and was then treated in quantities of 3 cwt. in a small lead-lined mixer with 200 lbs. of ordinary sulphuric acid, which had previously been diluted with about 20 cubic feet of mother liquor from previous operations. The temperature of the mixture soon rises by the action between the copper oxide and the sulphuric acid, and is kept, by means of a steam-jet, at a temperature of about 85° C. for half an hour. From this mixer, the charge is run out into a centrifugal hydro-extractor, provided with a filtering cloth, in which the solution of copper sulphate is separated from the solid residue containing the nickel. After the filtration of the charge is finished, the speed of the hydro-extractor is increased, and the residue is thus rendered sufficiently free from the liquor.

The solution containing the extracted copper runs from the hydro-extractor into a well, from which it is pumped into the crystallising vats. After a period of about eight days to ten days, the crystals of copper sulphate are taken out of the vats and the mother liquor is mixed with fresh acid and is again used for the extraction of copper. As already mentioned, a small amount of nickel and a little iron are also dissolved in the sulphuric acid during the copper extraction, so that the mother liquor from which the copper sulphate has crystallised becomes gradually contaminated with these two metals. It is therefore necessary to replace some of the mother liquor from time to time by fresh water, and to recover the nickel from the solution. The simplest method is to evaporate the solution to dryness and to roast the nickel and copper sulphates so obtained. The oxidised material is again introduced into the main process. The copper sulphate crystals from the crystallising vats are charged into a second hydro-extractor, where they are washed with a little clean water to remove all acidity; they are then dried and are ready for packing. The copper sulphate thus obtained is sufficiently pure for the market, as it contains only 0.05 per cent. of nickel and 0.048 per cent. of iron.

The residue from the copper extraction is taken from the hydro-extractor and stored in a bin until a sufficient quantity has been collected to make up a charge of 5 tons to 6 tons for the nickel-extracting plant. It now contains 52.5 per cent. of nickel, 20.6 per cent. of copper, and 2.6 per cent. of iron. The material is charged by hand at the rate of  $\frac{1}{2}$  ton per hour into a feeding-hopper, which communicates, through a rotary valve, with the conveyor, consisting of a tube enclosing a revolving spiral, which transports the material to an elevator. This lifts the material to the top of the reducing-tower, and discharges it through another rotary valve into this reducing-tower.

The reducer and the volatiliser in which the treatment with carbon-monoxide takes place, are fully described in Dr Mond's patent (No. 23,665 of December 10, 1895). The reducer consists of a vertical tower about 25 feet high, containing a series of shelves, which are hollow so as to admit of their being raised to a temperature of 350° C. by producer gas. The roasted matte falling on these shelves from above is stirred and made to descend from one shelf to that below it by rabbles actuated by a central vertical shaft. Water-gas passes up the tower to effect the reduction of the material. There are about fourteen of these shelves or trays in the tower. The five lower shelves are not heated by producer gas, but are cooled by a stream of water in order to reduce the temperature of the roasted and reduced matte to the temperature at which the volatiliser is worked.

The volatilising-tower resembles the reducer, but the shelves are not hollow, as there is no necessity to heat them. The reduced nickel requires a temperature of only 50° C. to enable it to combine with carbon-monoxide and form a volatile compound, and the material and gas are sufficiently hot to maintain this temperature. In the plant at Smethwick the volatiliser was made the same size as the reducer, but in the new plant it is somewhat smaller.

The decomposer has been devised with much care, and the nickel is deposited in it, from its gaseous compound with carbonmonoxide, on granules of ordinary commercial metal. The arrangements by which this is effected are very ingenious, and may be described almost in the words of Dr Mond's patent. The object is to obtain metallic nickel from nickel carbonyl in the form of pellets, which are specially suitable for the production of nickel alloys. For this purpose gases containing nickel carbonyl are passed through granulated nickel, which is kept at the temperature required for the decomposition of the carbonylabout 200° C. The nickel which thus separates from the carbonyl becomes deposited on the granulated nickel, which consequently increases in size. In order to prevent cohesion of the granulated nickel, it is kept in motion. When a number of the pellets have attained a convenient size, they are separated by sifting without interrupting the depositing operation, the smaller granules being returned to receive a further deposit from the nickel carbonyl. The appliance used for depositing the nickel originally consisted of a series of retorts lined with thin steel sheets, on which the nickel was deposited in layers. It was found, however, that the metal so obtained was very difficult to cut, and the apparatus above described was accordingly devised.

A magnified section of a granule of nickel, about  $\frac{3}{4}$  inch in diameter, shows a core of nickel which under higher magnification appears as a crystalline and convoluted structure, and this core is surrounded by concentric layers. The central core is ordinary commercial nickel, and the layers are nickel deposited from its carbonyl. In some cases granules of deposited nickel are found without any central core. These have grown from minute frag-

447

### AN INTRODUCTION TO METALLURGY.

ments of deposited nickel which have become detached during the course of deposition.

The water-gas used in the reducer is generated in gas-producers; anthracite is used to decompose the steam, and the water-gas is collected in a gas-holder, whence it is taken to the reducing-tower, to which reference has just been made. This gas contains, on entering the reducer, about 60 per cent. of hydrogen.

The reducing operation is so regulated that only a small quantity of hydrogen remains in the escaping gas, as a rule not more than 5 per cent. to 10 per cent. This waste gas is subjected to the action of a fine water-spray, which condenses the steam generated by the combustion of the hydrogen in the water-gas. Part of this waste gas is used for making the carbon-monoxide required in the volatiliser, by passing it through the CO retort charged with incandescent charcoal, which reduces the carbon-dioxide contained in the waste gas, and this increases the amount of carbon-monoxide in it. The gas issuing from this retort contains about 80 per cent. of carbon-monoxide, and is stored in another gasholder, which communicates with the main circuit of the carbonmonoxide gas. This main circuit of the carbon-monoxide passes through the volatiliser already referred to, where the nickel is taken up. The carbon-monoxide, now charged with nickel, passes through a filter to separate the fine particles of mattedust from the gases, then through an apparatus called the decomposer, and so described in the figure. In this decomposer the nickel taken up in the volatiliser is deposited. The gas, now deprived of its nickel, passes to the CO blower, which sends the carbon-monoxide to the volatiliser in order that it may take up a fresh charge of nickel.

The solid material from which the nickel is being extracted is kept circulating through the reducer and volatiliser for a period varying between seven days and fifteen days, during which time the oxides are gradually reduced to the metallic state and the nickel volatilised. When the material originally charged in has had the bulk of its nickel extracted it is run out through a rotary calciner, which converts the metals into oxides, so that they may be treated for the second time with sulphuric acid and carbonmonoxide. The ratio between the nickel and copper in the residues from the nickel extraction is practically the same as in the calcined Bessemer matte, with which the operations were started, but the amount of iron has increased by the removal of the copper and nickel, as the following figures show :- Original matte contains, nickel, 35.27 per cent., copper, 41.87 per cent., iron, 2.13 per cent. After the first treatment of copper and nickel extraction, the quantities are, nickel, 35.48 per cent., copper, 38.63 per cent., iron, 4.58 per cent.; and, after the second copper and nickel extraction, nickel, 35.83 per cent., copper, 35.56 per cent., and iron, 7.82 per cent. The amount of nickel extracted

in these two cases was, after the first treatment 61 per cent., and after the second treatment 80 per cent. of the nickel present in the original matte. It must be remembered, however, that in the second treatment only one-third of the original amount remains to be treated, while the final residue is only one-tenth. To avoid the formation of iron carbonyl, the temperature in the reducer has to be kept very low, and if this is done, the nickel extracted from a matte originally containing as much as between 6 per cent. and 10 per cent. of iron will not contain more than 0.5 per cent. of iron. If the amount of iron in the residues rises above this percentage, the extraction of the nickel is very much delayed, on account of the low temperature which must be maintained in the reducer. It is necessary, in such a case, to re-smelt the residues before proceeding with the extraction of the nickel and copper. The following are analyses of the deposited nickel :—

		I,	II.
a ga hard	-	Per cent.	Per cent.
Nickel		99.82	99.43
Iron and (Al <sub>2</sub> O <sub>2</sub> )	2.	0.10	0.43
Sulphur .		0.0068	0.0099
Carbon		0.07	0.087
Insoluble residue			0.026

By the kindness of Dr Mond, the author is able to indicate the nature of the plans required for a large manufacturing plant. This plant will, it is estimated, produce 1000 tons of nickel per year. The plant is so arranged that the matte is continuously charged into the first reducer and traverses the whole set of appliances. When the matte issues from the last volatiliser the nickel extraction is finished. The matte is re-roasted and submitted to the second copper and nickel extraction. There are ten appliances, consisting of one large reducer, eight combined reducers and volatilisers, and one large volatiliser. They are so arranged that the matte has first to pass through the large reducer, and is then lifted, by means of an elevator and conveyor, into a volatiliser (erected on the top of the next reducer). It passes through the volatiliser into the upper portion of the reducer, and in traversing this it is further reduced. It is then lifted again to the next volatiliser, and so on till it finally reaches the larger volatiliser at the end of the whole series, and, after passing through this, it is discharged into the roasting-furnace. The conveyor on the top of the volatilisers into which the elevators discharge, is common to the whole set of volatilisers and reducers. so that, in case any portion of the plant has to be disconnected, the rotary valve through which the material is discharged from

446

449

# 448 AN INTRODUCTION TO METALLURGY.

the conveyor into the volatiliser is stopped. The material then passes on through the conveyor into the next volatiliser. The two gases, carbon-monoxide in the volatilisers and water-gas in the reducers, are kept separate by rotary valves of the same construction as in the small plant. The water-gas connections are so arranged that each reducer receives fresh gas from the main, with the exception of the first large reducer, through which the waste gas of all the other reducers is passed, so as to burn completely all the hydrogen in the water-gas. The carbon-monoxide passes through the volatilisers from a common main, and is collected, after it has passed through the filters, in a main leading to the blower. From the blower the carbon-monoxide charged with nickel passes through a set of decomposers, and again into the main which feeds the volatilisers.

The Mond Nickel Company, Limited, of Clydach (Glamorgan), who have acquired Dr Mond's patents, have erected two large units as above described, which have now been in successful operation for about five years.

With regard to the application of steel containing between 1 per cent. and 7 per cent. of nickel in constructive work, it is not necessary to insist upon the importance of nickel steel not only for the manufacture of armour-plates but for all purposes where strength and lightness are essential. One manufacturer in the United States used in one year no less than 178 tons of nickel in the form of nickel steel, and it has been stated by a competent authority that "if propellor shafts were made of nickel steel the question of failures would seldom or never be raised." An attempt to deal adequately with the application of nickel would lead far beyond the scope of the present work, and the author only adds that the extraordinary properties of these alloys have formed the subject of elaborate investigations by the late Dr John Hopkinson<sup>1</sup> and by Mr Guillaume.<sup>2</sup>

Since the above description was written, the use of nickel for coinage (in some sixty countries), for cooking and other domestic utensils, and in nickel steel, has very largely augmented, especially the use of the latter in armour-plates, artillery, shafts and axles, steel rails, and bridge-building.

It will have been evident that the process possesses unusual interest as being the only one, in the whole range of metallurgy, in which a metal is obtained from its ores by causing it to combine with a gas to form a gaseous product from which it is subsequently released. Not the least remarkable feature of the process is presented by the fact that the temperature at which the whole operation is conducted never exceeds 350° C, which is far below dull redness. As a consequence, the plant is not, as is usually the case with metallurgical appliances, subjected to altera-

<sup>1</sup> Proc. Roy. Soc., vol. xlvii. p. 23; vol. xlvii. p. 138; vol. xlviii. p. 1. <sup>2</sup> Comptes Rendus, vol. exxiv. pp. 176, 752, and 1515, and vol. exxv. p. 235.

tions of temperature extending through a considerable range. The repairs needed are therefore inconsiderable, and the amount of fuel required is but small. The process works more or less automatically, and the amount of labour involved in conducting it can be reduced within very narrow limits. The main operation is, moreover, a regenerative one; the carbon-monoxide moves in a cycle and is the vehicle for continuously transferring the nickel from the ore or matte, and converting it into a marketable form. It follows that in the extraction of the nickel no new material except the reducing agent, water-gas, has to be introduced into the system. This is true even of the granules of commercial nickel which fill the decomposer and serve as a basis for the deposition of the nickel from the carbonyl. Their presence is essential in starting the process ; but their place is, as has already been pointed out, gradually taken by fragments of the deposited metal which become detached as the operation proceeds. The process will always occupy a prominent place in chemical history, and there would seem to be no reason why it should not play an important part in metallurgical practice.

Separation of Nickel and Copper by Means of Sodium Sulphide.—This process is applicable to the treatment of matte containing nickel, copper, and iron, and in it advantage is taken of the power which sodium sulphide possesses of dissolving sulphides of copper and iron, forming a solution of lower specific gravity than nickel sulphide.

In its original form the process consisted of mixing the matte with sodium sulphate and coke, running through a cupola, in which the sodium sulphate is reduced to sulphide, and allowing the molten product to flow into moulds, and separate, according to the specific gravity of the two portions. The different portions were then separated by fracture, and the tops, containing sulphides of copper, iron, and sodium, were charged into a smelting-furnace where the sodium sulphide was fluxed off in an iron slag and lost. The bottoms, containing nickel with some copper and iron, were re-treated with sodium sulphate and carbon, four or five treatments being necessary before the nickel was ready for reduction and purification.

In a modification of the process, the matte is so smelted that it will remain in a molten state subject to the high temperature of the furnace for a considerable time, during which the copper and iron sulphides are thoroughly dissolved by the sodium sulphide, and a good separation can be obtained in one melting. An openhearth reverberatory furnace is used, lined with magnesite brick, and the matte is charged either solid or molten with 60 per cent. of its weight of sodium sulphate, and 15 per cent. of coke.

A 50-ton charge is kept molten for four or five hours after fusion, during which time it is kept poled with poles of green wood. The charge may be run into moulds; but, in order to get

29

451

#### 450 AN INTRODUCTION TO METALLURGY.

the best results, the different strata in the furnace are tapped separately, the lower strata of nickel sulphide being tapped first. The nickel sulphide thus obtained is nearly pure, but when greater purity is required, it is recharged into the same furnace and re-treated.

The Electrolytic Refining of Base Bullion—Bett's Process.<sup>1</sup> —The refining of base bullion, argentiferous lead, etc., by means of Bett's process is becoming of considerable importance. The plant consists of wooden electrolysing vats coated with rubber paint, and has the general arrangement of a copper-refining plant.

The electrolyte consists of an acid aqueous solution of lead fluosilicide containing 8 per cent. of lead and 15 per cent. of free hydrofluoric acid. To this solution a certain addition of gelatine is added (about 0.1 gramme per litre), in order to make the deposit smooth and dense, for without this addition the cathode deposit is found to lack solidity and branches of the metal grow towards the anode and cause short-circuiting.

The electrolyte is made by diluting hydrofluoric acid (35 per cent.) with an equal volume of water, saturating with pulverised quartz, and then treating with white lead in the proper quantity, filtering, and adding the necessary gelatine or glue. In one plant the vats are  $86'' \times 30'' \times 42''$  deep; they hold 22 anodes weighing 3 tons.

The cathodes consist of thin sheets of pure lead suspended from copper bars. The electrodes are placed at a distance of  $1\frac{1}{2}$ to 2 inches. In a tank through which 4000 ampères are passing, 750 lbs, of refined lead are deposited per day.

During the process, Au, Ag, Cu, Sb, As, and Bi go into the anode mud, while Sn, Fe, Zn, Ni, and Co go into solution.

After the solution in the electrolysing vats has been in use some time it becomes contaminated with impurities and requires purification. For this purpose the lead present is first precipitated by means of sulphuric acid, and the hydrofluoric acid is precipitated by means of sodium chloride as sodium fluosilicate; from this compound the hydrofluoric acid is recovered with one-third the sulphuric acid required to decompose calcium fluoride.

The slimes may contain 8000 ounces of silver-gold per ton and are treated by the following process  $^2:$ —

1. The slime is agitated by means of steam and air in a leadlined tank with ferric sulphate solution; this sulphatises the copper, lead, and silver, dissolves all the copper and some silver, converts arsenic, antimony, and bismuth into oxides, and forms ferrous sulphate and free sulphuric acid.

2. The solution from No. 1 is treated with metallic copper in order to precipitate the silver.

<sup>1</sup> Mineral Industry, 1905, p. 421; Zeit. für Electrochemie, 1905, xi. p. 229; Mines and Minerals, 1905, xxv. p. 285.

<sup>2</sup> A. G. Bett's Electrochemical and Metallurgical Industry, 1905, iii. p. 272.

3. The residues from 1 and 2 are filter-pressed, washed, and then agitated with solution containing 12 to 15 per cent. hydrofluoric acid and 2 to 4 per cent. sulphuric acid to dissolve the antimony.

4. The residues from 3 are melted with soda and parted electrolytically, using an electrolyte containing 15 per cent. methylsulphuric acid, 7.5 per cent. of silver, and a gelatine addition equal to 1 part in 12,000. As a result of this electrolysis pure silver is obtained, any gold is retained in the linen bag in which the anode is placed, and copper and bismuth pass into solution. This solution is first treated with copper to precipitate any silver it contains, then the copper and bismuth are removed with lead. The bismuth and copper are separated by means of ferric sulphate, and the bismuth oxide thus obtained is reduced.

5. Copper oxide is added to the solution from 4, arsenic crystallised out, if necessary, then the solution is electrolysed, carbon anodes being used; ferric sulphate is thus regenerated and is returned for use in operation 1.

6. The antimony fluoride solution from 3 is electrolysed, regenerating hydrofluoric acid to be used again in 3.

BIBLIOTEC