New York Section.

Chairman: Alfred H. Mason.
Vice-Chairman: Arthur McGeorge.
Committee:
T. Lynton Briggs.
G. T. Bruckmann.
V. Coblentz.
H. Comor.
H. Endemann.
S. W. Fairchild.
Jas. Hartford.
E. G. Love.
T. Lungwitz.
John McKesson.
Thos. J. Parker.
J. H. Wainwright.
D. Wesson.
Hon. Treasurer: R. C. Woodcock.
Hon. Local Secretary:
Hugo Schweitzer, 159, Front Street, New York, U.S.A.

Meeting held on Monday, 11th November 1895.

MR. A. H. MASON IN THE CHAIR.

THE HISTORY OF MY PROCESS OF NICKEL EXTRACTION.

BY LUDWIG MOND, F.R.S.

Since I promised to your chairman, shortly after my arrival, to read a paper to you before leaving this country, I have considered what subject I could bring before you that would be of sufficient interest, considering that I am unprepared to illustrate it by experiments or diagrams.

I have decided to give you an account of the history of my process of extracting nickel from its ores, as an instance of an investigation undertaken in pursuit of pure science, which has led unexpectedly, in a few years, to an important industrial application.

I have often been asked by scientific men how I came to discover nickel carbonyl. I will tell you the story.

Soon after I had satisfied myself that the ammonia-soda process was far cheaper than the Leblanc process for producing carbonate of soda pure and simple, it became evident to me that a time would come when the Leblanc process would produce carbonate of soda as a by-product of the bleaching powder manufacture, which it would have to dispose of at any price it would fetch. I therefore undertook a series of experiments with the object of producing bleaching powder as a by-product of the ammonia-soda process. You all know that the usual form of this process consists in treating a solution of common salt in which caustic ammonia has been dissolved by carbonic acid, with the result that bicarbonate of soda is precipitated while a solution of ammonium chloride is formed. In the ordinary course of things this solution of chloride of ammonium is distilled with caustic lime, yielding gaseous ammonia, which returns to the process, and a solution of calcium chloride. Some investigators had endeavoured to produce chlorine from the chloride of calcium obtained by evaporating these solutions; others had proposed to substitute magnesia for the lime in distilling the solution of ammonium chloride, and to produce chlorine or hydrochloric acid from the $MgCl_2$ obtained by evaporating its solution.

I gave my attention to producing the chlorine direct from the ammonium chloride, separated from the solution, in which it is originally obtained, by refrigeration.

Ammonium chloride when vaporised is, as is well known, dissociated into ammonia and HCl; thus, if the vapour of NH_4Cl is passed over a metallic oxide this oxide is converted into a chloride, and the ammonia passes on together with the steam formed by the reaction.

I found that nearly all metallic oxides, with the exception of the alkalis and alkaline earths, and even a large number of metallic salts, were acted upon in this way by NH_4Cl vapour, and that a large number of the metallic chlorides so formed would give up their chlorine and be re-converted into oxides by submitting them to the action of air at a suitable temperature. I found that of all the substances investigated oxide of nickel yielded the best results, and that the next best were obtained by magnesia mixed with a certain amount of chloride of potassium. For obvious reasons I preferred the latter in working the process industrially, which has now been successfully at work for several years on a very considerable scale in our Winnington Alkali Works.

In developing this process I had to construct a plant for volatilising NH_4Cl, which I found an extremely difficult problem, as the vapour of this substance not only acts on oxides and salts, but also violently attacks the large majority of metals. I succeeded in lining iron vessels with glazed tiles in such a way that they would withstand this action, but I required valves for changing from the current of ammonium chloride vapour to hot air and *vice versâ*, which had to be very tight to prevent a large loss of ammonia.

I found that nickel was one of the few substances suitable for the construction of these valves, and that it was not at all attacked by ammonium chloride vapour. On the laboratory scale these nickel valves worked perfectly, but when I applied them on a manufacturing scale I found them to be acted upon and very soon to become leaky. The faces became covered with a black crust, which, on examination, was found to contain carbon.

The source of this carbon seemed mysterious, the only difference between the work on the small scale and that on the large scale being that on the small scale we swept the ammonia out of the apparatus before admitting the hot air by means of pure CO_2, while on the large scale we used the gases from a lime kiln, containing a few per cent. of CO. This led us to study the action of CO on nickel.

We found this metal to have the remarkable property of splitting off carbon from CO at a moderate heat, transforming it into CO_2.

About the same time I was engaged with my collaborator, Dr. Langer, in trying to find a method for eliminating the CO from hydrogenous gases, which we wanted for use in our gas battery. We tried to avail ourselves for this purpose of the remarkable property of nickel we had just discovered, and found to our satisfaction that by passing gases containing hydrogen, CO and a certain quantity of steam over finely-divided nickel at a temperature of 400° C. we could completely convert the CO into CO_2, obtaining its equivalent of hydrogen, which was just what we wanted.

This led to a more elaborate study of the action of CO upon nickel, with a view of determining whether a definite compound of nickel and carbon was formed. We found that a small quantity of nickel decomposed a very large quantity of CO, so that we could obtain a product containing only 15 per cent. of nickel and 85 per cent. of carbon, the nickel in which was only partially soluble in acids.

In the course of these experiments finely-divided nickel, formed by reducing nickel oxide at 400° C. by hydrogen, was treated with pure CO in a glass tube, at varying temperatures, for a number of days, and was then cooled down in a current of CO before it was removed from the tube. In order to keep the poisonous CO out of the atmosphere of the laboratory, we simply lit the gas escaping from the apparatus. To our surprise we found that, while the apparatus was cooling down, the flame of the escaping gas became luminous and increased in luminosity as the temperature got below 100° C. On a cold plate of porcelain put into this luminous flame, metallic spots were deposited similar to the spots of arsenic obtained with a Marsh apparatus; and on heating the tube through which the gas was escaping we obtained a metallic mirror, while the luminosity disappeared.

At the first moment we thought that there must be an unknown element in our nickel giving rise to the production of this effect, but when we examined the mirrors we found them to consist of pure nickel. As it seemed so very improbable that so heavy a metal as nickel should form a readily-volatile compound with CO, we purified our CO as perfectly as possible, but still obtained the same results.

We now endeavoured to isolate this curious and interesting substance by preparing the nickel with great care at the lowest possible temperature, and treating this nickel

Facsimile of L. Mond, The History of my Process of Nickel Extraction (*J. Soc. Chem. Industries*, 14(1895) 945 — 946).

pp. 9—10.

with CO at about 50° C., and thus we gradually increased the amount of the volatile nickel compound in the gases passing through the apparatus. We absorbed the excess of CO by cupreous chloride solution, and thus obtained a residue of several cubic centimetres, containing the volatile nickel compound mixed with a little nitrogen. By passing this gas through a heated tube we separated the nickel, obtaining an increased volume of gas, and found in this a quantity of CO corresponding to about four equivalents for one equivalent of nickel.

By further improving our method of preparing the finely-divided nickel and by passing the resulting gas through a refrigerator, cooled by snow and salt, we at last succeeded in liquefying this compound, and were able to produce it with ease and facility in any quantity we desired.

Thanks to the kindness of Dr. Torry, of Harvard University, I am able to show you a small quantity of this nickel carbonyl, which he prepared within a few days after he saw my first publication on the subject. It is a colourless liquid boiling at 43° C. and which solidifies at −25° C., forming needle-shaped crystals. It is soluble in alcohol, petroleum, and chloroform; it is not acted upon by dilute acids or alkalies, and can be readily distilled without decomposition. But on heating the gas to 150° C. it is completely dissociated into its components, pure CO being obtained and the nickel being deposited in a dense metallic film upon the sides of the vessel in which it is heated.

For a long time, while we were engaged in investigating the physical and chemical properties of this interesting substance—which was without parallel in the history of chemistry—and while we were endeavouring to obtain other similar compounds with other metals, I had myself no suspicion that this substance, which was until then only obtainable by very careful and elaborate laboratory manipulations, should ever become available for industrial purposes. But the longer we went on preparing it for our investigations, the more easy we found it to prepare it in quantity, after we once knew exactly the best conditions for so doing. After that I came to the conclusion that it ought to be possible to make use of the ease with which nickel is converted into a volatile gas by CO, while practically all other metals, and notably cobalt (which is so difficult to separate from nickel by other methods), was not acted upon by this gas, for separating nickel from cobalt and other metals on a manufacturing scale, and for obtaining it in a very pure state.

I erected a plant on a large scale near Birmingham, and after several years of hard work, during which the apparatus has had to be several times reconstructed so as to fulfil all the conditions of this rather delicate process, we have succeeded in our object, and now have for some time produced nickel at the rate of a ton and a half per week from the Canadian nickel copper matte imported into England. This matte, which contains about 40 per cent. of nickel, and an equal quantity of copper, is carefully roasted to drive out the sulphur as far as possible, and is then subjected to the action of hydrogenous gases, either water-gas or producer-gas, rich in hydrogen, in an apparatus which is called the "reducer," the temperature of which is under perfect control, so that 400° C. is never exceeded. From this apparatus the substance, which is now reduced to the metallic state, is taken through air-tight conveyors and elevators into another apparatus, called the "volatiliser," in which it is subjected, at a temperature not exceeding 80° C., to the action of CO gas.

This apparatus consists of an iron cylinder, divided into numerous compartments by shelves, and provided with a stirring device, which gradually moves the material from the top to the bottom, while the CO gas passes through in an opposite direction. The CO gas, which should be as rich as practicable, we prepare by passing pure CO_2 through incandescent coke; the pure CO_2 we make by passing the flue gas of a boiler or of a fire through a solution of carbonate of potash, and subsequently boiling the solution. The CO gas, charged with nickel carbonyl, leaving the volatiliser, is passed through a series of tubes or chambers, heated to about 180° C., in which the nickel is deposited in various forms, according to the speed of the gas current, the richness of the gas, and the existing temperature. The CO gas, thus almost completely freed from the nickel, is taken back by means of a blower into the volatiliser, where it takes up a fresh quantity of nickel and is constantly used over and over, so that the quantity consumed is limited to the very small amount of unavoidable loss through leakage of the plant.

The material under treatment is repeatedly taken from the volatiliser to the reducer and *vice versâ*, by means of air-tight conveyors and elevators, until the amount of nickel volatilised begins to fall off. It is then roasted again to remove the sulphur, which it still contains, and is treated by sulphuric acid to dissolve part of the copper. The residue, containing nickel, some copper, and the other impurities of the matte, is again subjected to the previously described treatment until the nickel has been extracted as far as practicable; and the ultimate residue, still containing a few per cent. of nickel, is melted up into matte again.

I have here a few samples of the various forms in which the nickel is obtained by this process. If the nickel is allowed to deposit slowly at a carefully regulated temperature, it can easily be obtained from the gas as a coherent metallic film, so that it is possible to coat any substance which can stand heating to 150° C. with a perfect covering of metallic nickel, and also to make articles of metallic nickel for direct use. I have here a knife-handle made in this way, and the finest delineaments of a mould can be perfectly reproduced in this manner.

I believe that the great facility with which hollow nickel goods can be made in this way, which at present either cannot be made at all, or only by the use of very powerful hydraulic machinery, will give a great impetus to the manufacture of nickel utensils for domestic purposes, the use of which is so very desirable from a sanitary point of view. The cost of the process, if carried out on a sufficiently large scale, is, as you will readily perceive, inconsiderable, as the consumption of material is very small, and the expenditure consists mainly in carefully superintending the various operations.

What gives me the greatest satisfaction in relation to this investigation is, that I believe I have succeeded in working out a purely chemical process for extracting nickel from its ores, which will be cheaper and simpler than any electrolytic process that can be used for the same purpose. Of late years, there has been a tendency to take chemical operations out of the hands of the chemist and to thrust them into those of the electrician, in the belief that the simplest way of obtaining a chemical change consists in the pulling apart a chemical compound by electrical energy, and subsequently putting its constituents together again in the forms that are desired. I know there are many chemical operations which will always be carried out to much greater advantage by the old chemical methods, and I have no doubt that newer methods will be found, of which nobody thinks at present, based upon purely chemical reactions, such as the process which I have brought before you to-night, which will effect the chemical changes we want to produce at a smaller expense of energy than can be done by electrolysis.

Discussion.

Prof. Peter P. Austen asked what other metals had been experimented upon with reference to the formation of carbonyls.

Mr. Mond stated that every metal at his disposal in England had been subjected to such experiments. Iron alone gave small quantities of a carbonyl. The infinitesimal quantities of this compound in water-gas cause the deposition of iron on the hoods of the Welsbach burner, thus reducing their effectiveness very considerably.

Messrs. C. F. Doremus and C. F. Chandler referred to experiences with similar iron deposits.