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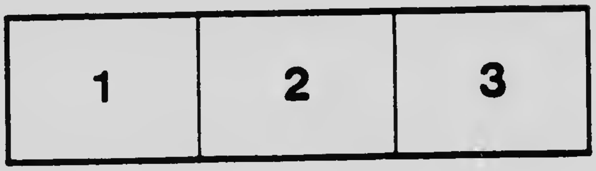
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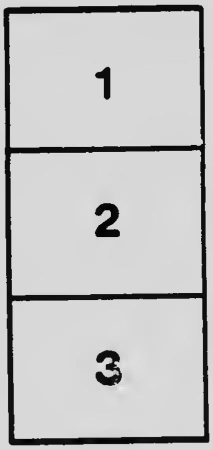
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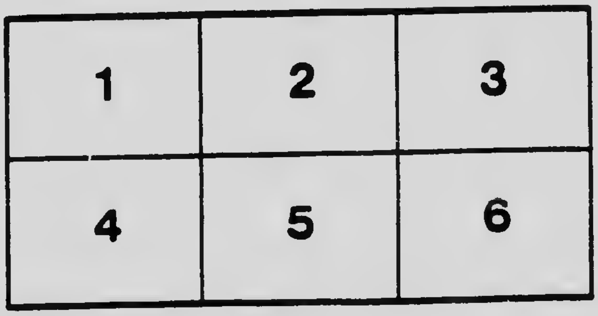
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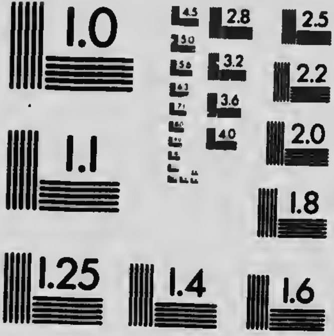

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MINES BRANCH

Eugene Haanel, Ph.D., Director

RESEARCHES ON COBALT AND COBALT ALLOYS, CONDUCTED AT QUEENS UNIVERSITY, KINGSTON, ONTARIO, FOR THE MINES BRANCH OF THE DEPARTMENT OF MINES

PART I.

PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE

BY

H. T. KALMUS, B.Sc., Ph.D.

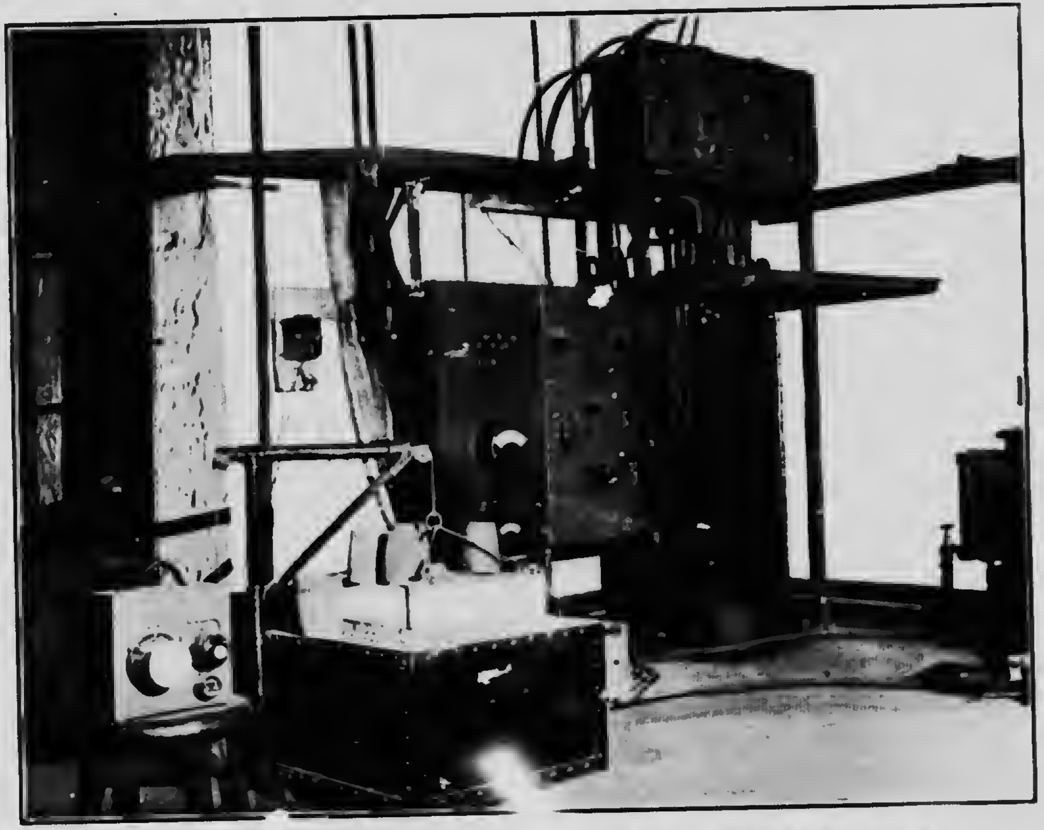
ASSISTED BY

C. W. Day, M.A., C. Harper, B.A., W. L. Savell, B.Sc., and R. Wilcox

OTTAWA
GOVERNMENT PRINTING BUREAU
1913

No. 259

Frontispiece PLATE I.



Back of electric furnace used for reduction of [illegible]$_3O_4$ with C: showing leads, bus-bars, switchboard, and transformer.

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No. 259

LETTER OF TRANSMITTAL

Dr. Eugene Haanel,
Director of Mines Branch,
Department of Mines,
Ottawa, Ont.

Sir,—

I beg herewith to submit a report on "The Preparation of Metallic Cobalt by Reduction of the Oxide," the same being the first part of the series of investigations on cobalt and cobalt alloys, for the purpose of increasing their economic importance, conducted at Queens University, Kingston, Ontario, for the Mines Branch of the Department of Mines, Ottawa.

I have the honour to be, Sir,
Your obedient servant,
(Signed) **H. T. Kalmus.**

Kingston, Aug. 19, 1913.

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RESEARCHES ON COBALT AND COBALT ALLOYS, CONDUCTED AT QUEENS UNIVERSITY, KINGSTON, ONT., FOR THE MINES BRANCH OF THE DEPARTMENT OF MINES

PART I.

THE PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE

BY

H. T. Kalmus, B.Sc., Ph.D.

THE PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE

INTRODUCTORY

The general investigation of the metal cobalt and its alloys, for the purpose of finding increased commercial uses for them, has been, and is being conducted along the following general lines:—

I. THE PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE.
II. A STUDY OF THE PHYSICAL PROPERTIES OF THE METAL COBALT.
III. ELECTRO-PLATING WITH COBALT AND ITS ALLOYS.
IV. COBALT ALLOYS OF EXTREME HARDNESS.
V. COBALT ALLOYS WITH NON-CORROSIVE PROPERTIES.
VI. COBALT STEELS.

This paper is Part I of the above series, and is a report of researches conducted at the School of Mining, Queens University, Kingston, Ontario, for the Mines Branch of the Department of Mines.

In connexion with all of this work it has been necessary to prepare considerable quantities of the metal in as pure a state as possible. The process for the preparation of fairly pure cobalt oxide has been very completely worked out, and has been practised on a large scale at several Canadian smelters. For this reason, the oxide was chosen as a raw material from which to prepare the metal.

As the work progressed, it became more and more apparent that some of the uses for the metal, which were being demonstrated at these laboratories and elsewhere, would probably lead to the preparation of the metal in large quantities at some of the Canadian smelters. Hence, it became of increasing importance that the metallurgy of the preparation of the metal from the oxide be studied. This has been done with greater care than was necessary merely for the production of the quantities required for experimental purposes.

There are four methods of reducing commercial cobalt oxide, in order to obtain metallic cobalt in reasonably pure form:—

I. BY REDUCTION WITH CARBON.
II. BY REDUCTION WITH HYDROGEN GAS.
III. BY REDUCTION WITH CARBON MONOXIDE GAS.
IV. BY REDUCTION WITH ALUMINIUM.

Each of these methods has been studied at considerable length, and this paper is a report of the results. It should serve as a guide to those who will subsequently be interested in the preparation of metallic cobalt in large quantities.

PREPARATION OF COBALT OXIDE FOR REDUCTION EXPERIMENTS

The Co_3O_4[1] used for these experiments was made from cobalt hydrate, precipitated by bleach from a cobalt chloride solution. This hydrate in contact with the atmosphere is greenish-black in colour. It was calcined at 750° C. yielding a black oxide of approximately the composition Co_3O_4. This is shown by the following analyses, made at widely different times, which are typical of a large number:—

Analysis of purified cobalt oxide, June, 1912.

Co	
Fe	71·99%
Ni	0·11%
S	0·040%
Ca	0·020%
SiO_2	0·030%
	0·19%

Analysis of purified cobalt oxide, November, 1912.

Co	71·52%
Fe	0·27%
Ni	0·020%
SiO_2	0·18%
S	trace

Analysis of purified cobalt oxide, April, 1913.

Co	
Fe	72·30%
Ni	0·10%
Ca	trace
S	0·15%
SiO_2	0·052%
	0·39%

The oxides corresponding with the theoretical formulae would have cobalt contents as follows:—

Co_2O_3	
Co_3O_4	Co = 71·1%
Co_4O_7	Co = 73·4%
CoO	Co = 76·0%
	Co = 78·8%

It is obvious then when we take into account the portion of the sample which is not cobalt oxide, that the oxide itself is largely Co_3O_4. It is not necessary for the purpose of our calculations to assume that this oxide alone is present, for we shall base our computations upon the actual analyses as we have found them. However, in writing the reactions throughout this paper, we snall, for simplicity, consider the oxide to be Co_3O_4.

---

[1] For a consideration of the various oxides of cobalt, including the proof that the black oxide used for these reductions was largely Co_3O_4, see pages 33—36.

Purification of Cobalt Oxide

Cobalt oxide as we obtained it from the smelters, and as sold on the market, analysed approximately as follows:—

Barrel No. 1	
Co	70·36%
Ni	1·12%
Fe	0·82%
S	0·45%
As	0·10%
SiO_2	0·20%
CaO	0·50%

Barrels No. 3 and No. 4	
Co	69·2%
Ni	1·4%
Fe	0·50%
CaO	0·37%
S	0·54%
Insoluble	1·46%
Ag	trace

Analyses, of course, vary widely from one shipment to another; the above samples are high in Fe, S, and Ca, and would be considered by most smelters as No. 2 grade.

Metal produced from oxide analysing as above, is of sufficient purity for most purposes. This is especially true if lime be added to the melt to slag off the sulphur. However, for other purposes metal is required in which the impurities nickel, iron, sulphur, arsenic, and silica are reduced to very small percentages. Starting with a crude cobalt oxide, these impurities may be reduced as far as is desired by the following procedure.

Silica.—Dissolve the crude oxide in hydrochloric acid according to the reaction,

$$Co_3O_4+8\ HCl=3\ CoCl_2+4\ H_2O+Cl_2.$$

This may best be done by heating and agitating with steam. If silica is present it will not dissolve, and may be removed by filtration or decantation. The same is true of silicates which are not decomposed by this treatment. Decomposable silicates would send a certain amount of silica into solution, which would be thrown out again during the next step, and be filtered off with the arsenic and iron.

Iron and Arsenic.—To the cobalt chloride solution formed by dissolving the oxide in hydrochloric acid as above, gradually add finely divided $CaCO_3$ or pure marble, until no further precipitate is formed. This calcium carbonate addition will precipitate a heavy brown mud, which contains the iron and arsenic content of the original oxide.

Nickel.—For most purposes it will not be necessary to separate the small amount of nickel from the cobalt, but if this is desirable it may be done as follows. The cobalt chloride solution, containing a certain amount of nickel chloride, is of an intense red or claret colour. Add a solution of bleach to this mixed chloride solution until it has almost completely lost its colour. The bleach solution differentially precipitates hydrates of nickel and cobalt, so that the nickel is not appreciably brought down until the cobalt has been almost entirely precipitated.

The bleach will precipitate a black hydrated oxide of cobalt, and the diminishing redness of the solution will indicate the end point. If all of the steps above outlined have been applied to the original oxide, this final black precipitate may be calcined at about 750° C., to yield black Co_3O_4.

Sulphur.—Any sulphur which was present in the original oxide and which has been carried through to the final product, or which may have been introduced with the bleach, may readily be removed by boiling the final dried oxide with sodium carbonate and dilute hydrochloric acid as follows.

The Na_2CO_3 reacts with the sulphur, in the form of sulphate after the calc ation, according to the reaction,

$$CaSO_4+Na_2CO_3=Na_2SO_4+CaCO_3.$$

The soluble sodium sulphate formed is washed out with water. A furtl washing is given with dilute hydrochloric acid, which decomposes the calciu carbonate into soluble calcium chloride and CO_2 gas. The $CaCl_2$ is wash out with water. This method is, of course, only applicable for the remov of small percentages of Ca and S, as they are found in the oxides in questio

A shipment of oxide from the smelter analysing

Co	70·36%
Ni	1·12%
Fe	0·82%
S	0·45%
As	0·10%
Ca	0·50%
SiO_2	0·20%

was treated by the above method, and the impurities thereby reduced to tl following very small amounts:—

Co	71·99%
Ni	0·041%
Fe	0·11%
S	0·020%
Ca	0·021%
As	none
SiO_2	none

There are other methods of purifying the Co_3O_4. For example, the bleac solution may be freed of its SO_4 content with $BaCl_2$, and the Ca and exces a precipitated with Na_2CO_3, thus yielding a fairly pure solution of sod bleach. The SO_4 content of the $CoCl_2$ solution may be precipitated wit BaCl—and the differential precipitation of cobalt and nickel accomplishe with the purified solution of soda bleach.

PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE WITH CARBON

Method of Experiment.—These experiments all consisted in intimatel mixing definite amounts of finely divided carbon in various forms, with Co_3O_4, and heating the mixture to constant temperature for a measure time. The charges employed varied in size from a few grams to 10 pounds and were heated in lined graphite crucibles, unlined graphite crucibles, and in clay crucibles.

Furnaces—The reduction took place either in an oil fired Steele-Harvey furnace of 60 pounds metal capacity, No. 20 crucible, which could be controlled at any temperature up to 1550° C., or, in a modified Hoskins electric resistor furnace. This latter has a heating chamber, 8″ cube, which can be maintained at constant temperature to within about 10-20° C., at any temperature up to 1650° C. Some of the small charges were run in clay crucibles placed within the electric tube furnace described under, "Reduction of Co_3O_4 with Hydrogen Gas," and shown in Fig. 3.

The furnaces with connexions are shown in Plates I, II, III, IV, and Fig. 1.

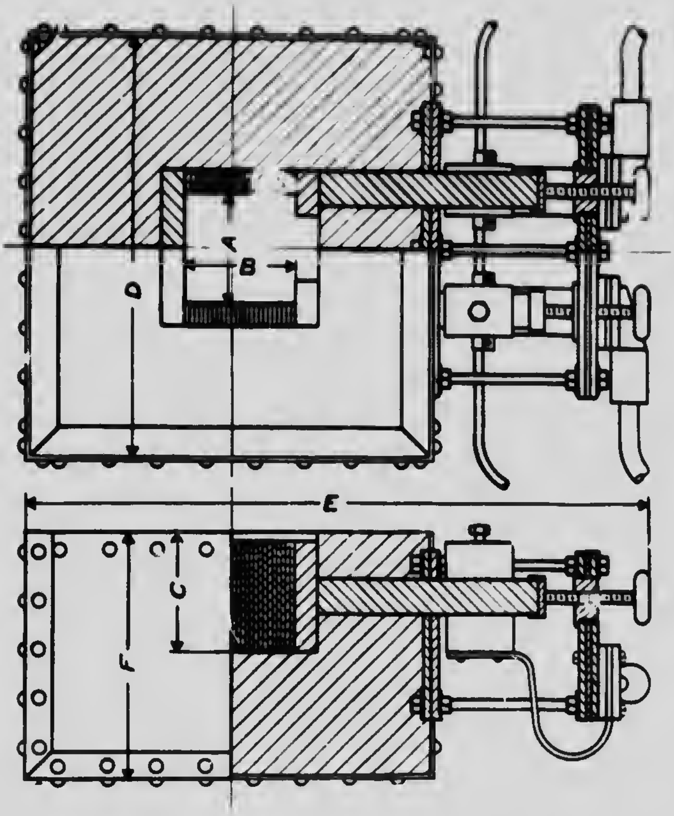

FIG. 1. Detail drawings of electric furnace used for reduction of Co_3O_4 with C.

The reactions for the reduction of cobalt oxide with carbon are:—

(1) $Co_3O_4+4C=3Co+4CO$.
(2) $Co_3O_4+4CO=3Co+4CO_2$ or, combining (1) and (2),
(3) $2Co_3O_4+4C=6Co+4CO_2$.

If all the oxygen for the oxidation of the carbon be supplied by the cobalt oxide, and if all the carbon be burned to CO_2, none of it escaping as CO, then the reaction goes according to equation (3).

In practice neither of these conditions is strictly obtained, but with proper design of furnace they may be closely approximated.

The data for a series of experiments on the direct reduction of cobalt oxide with carbon follow.

The Run.—In each case the charge was made up by intimately mixing a weighed amount of finely divided oxide with a weighed amount of finely ground carbon. This charge was placed in a carbon or clay crucible, which with its charge was placed either in the Steele-Harvey oil furnace or in the electric furnace. The mixture was frequently stirred with an iron rod during the reduction.

Carbon.—The form of carbon chosen for the reduction, whether powdered charcoal, coke, coal, etc., depends somewhat upon the impurities from which it is desirable to keep the resulting metal free, but also the choice greatly influences the speed of the reduction.

Three sets of experiments, Runs A—H, R I—R VIII, and H I—H III were made with powdered anthracite coal, such as is used for the manufacture of carbon electrodes, while further experiments, Runs H IV—H XIX, were made with powdered charcoal or lampblack. The carbon was in all cases powdered to an extremely fine flour.

Temperature Measurements. Temperature readings were made at frequent intervals with a platinum platinum-rhodium thermo-element, with a Wanner optical pyrometer, or with a Fery radiation pyrometer, and adjustments of the furnace made to keep the temperature constant to within about 20° during the run.

The charge was put into the crucible which was within the furnace, both crucible and furnace being at a temperature somewhat higher than the intended temperature of the run. It was learned by experience, for the different sizes of charge and qualities of crucible, at about what temperature to maintain the furnace prior to inserting the charge, in order that the charge might come to the desired equilibrium temperature, with proper furnace adjustment, in about ten minutes. There is, therefore, a period of about ten minutes, at the beginning of each run, during which the average temperature of the charge is not as high as that noted with the Wanner optical pyrometer, which observes the surface of the charge. We satisfied ourselves that the centre of the charge was at the same temperature as the surface, within 20 or 30° C., after the first ten minutes, by exploring the centre with a thermo-element, and noting simultaneously its readings and those of another thermo-element, and of the Wanner optical pyrometer.

In the following runs we have not attempted to make a correction for the lag in coming to temperature during these first ten minutes. This lag would be considerably less than ten minutes for the smallest crucibles which we used, would be about ten minutes for the four pound charges, and possibly as long as twenty minutes in the worst cases, with the ten pound charges.

Reduction of Co_2O_3 with Carbon

The oxide used for runs A—H, analysed as follows:

Co	71·36%
Ni	1·12%
Fe	0·82%
S	0·45%
As	0·10%
SiO_2	0·20%
Ca	0·50%

In runs A—H, No 12 unlined carbon crucibles were used, and the charge was stirred every ten minutes during reduction. In these runs no attempt was made to show the progress of the reduction, but at the close of the run the charge was raised as rapidly as possible to the melting point and the melt poured into an iron mould to be weighed. Considerable reduction must take place during the interval of melting the charge after the close of

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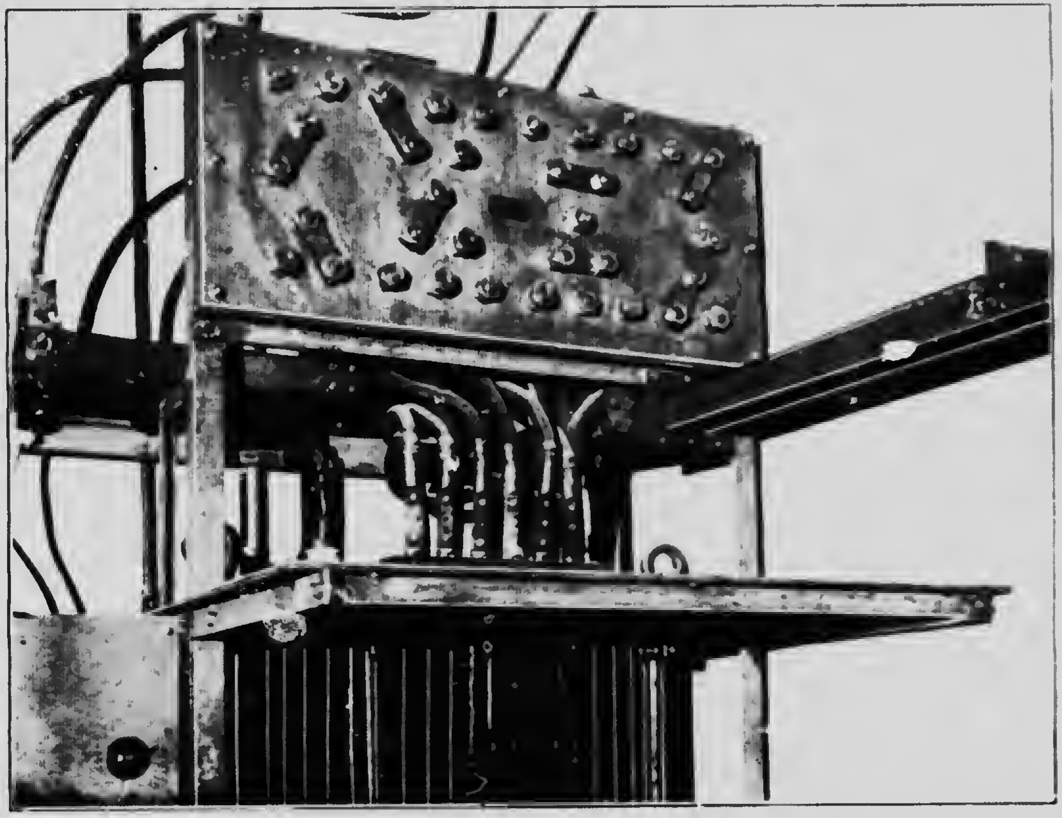
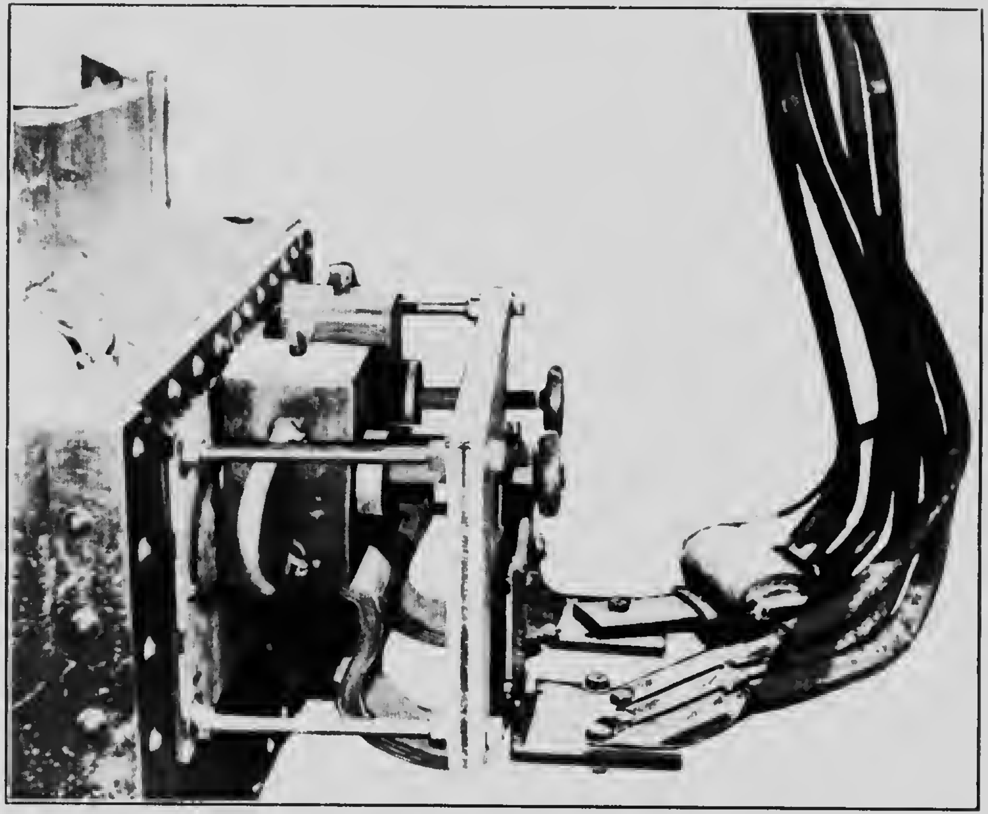
[1] Some of the smallest charges were inserted with containing crucible.

PLATE II.



Near view of the switchboard and secondary terminals of the transformer.

PLATE III



Details of front of furnace.

the run. The purpose of these particular runs was to study the yields under somewhat the same conditions which must necessarily pertain in practice.

Reduction of Co_3O_4 with Powdered Anthracite Coal (A)

These runs are typical of a large number showing similar results.

HARVEY-STEELE OIL FURNACE

Number of run	Charge	Average temperature	Time of reduction	Yield of Co in lbs. and % of theoretical amount	Carbon present in resulting metal	Remarks
Run A, Jan. 18 1913	Co_3O_4, 5 lbs. Powdered coal, 8·3 oz.	1200° C.	1 hr. 30 min.	3 lbs. 1·5 oz. =87%	— —	Considerable unreduced oxide slag. C is approximately theoretical amount according to equation 3.
Run C, Jan. 20, 1913	Co_3O_4, 4 lbs. Powdered coal, 6·9 oz.	1200° C.	30 min.	2 lbs. 12·5 oz. =98%	0·18% C.	Melt free from unreducible oxide slag. C is 10% in excess of theoretical amount.
Run H, Nov. 19, 1912	Co_3O_4, 10 lbs. Powdered coal, 1 lb	1200° C.	1 hr. 45 min.	6 lbs. 9 oz. =92%	0·086% C.	3 oz. lime added shortly before pouring. C is only theoretical amount.

ELECTRIC CRUCIBLE FURNACE

Number of run	Charge	Average temperature	Time of reduction	Yield of Co in lbs. and % of theoretical amount	Carbon present in resulting metal	Remarks
Run G. Jan. 20, 1913	Co_3O_4, 4 lbs. Powdered coal, 6·6 oz.	900° C.	2 hr. 30 min.	2 lbs. [illegible] oz. =9[illegible]%	0·21% C.	At end of 2 hrs. 30 min. charge not completely reduced, but completed during subsequent raising to melting point.
Run B, Jan. 18 1913	Co_3O_4, 4 lbs. Powdered coal, 6·51 oz.	1200° C.	1 hr. 0 min.	2 lbs. 13 oz. =99%	0·29% C.	
Run D, Jan. 20 1913	Co_3O_4, 4 lbs. Powdered coal, 6·9 oz.	1200° C.	2 hr. 0 min.	2 lbs. 13·5 oz. =100%	0·20% C.	
Run E. Jan. 13, 1913	Co_3O_4, 4 lbs. Powdered coal, 6·9 oz.	1500° C.	1 hr. 0 min.	2 lbs. 11·75 oz. =96%	0·22% C.	
Run F, Jan. 20, 1913	Co_3O_4, 4 lbs. Powdered coal, 6·6 oz.	1500° C.	1 hr. 30 min.	2 lbs. 12·7 oz. =98%	0·23% C	

The oxide used for the runs shown in the following table, R I—R VIII, analysed as follows:—

Co	69·2%
Ni	1·4%
Fe	0·50%
CaO	0·37%
S	0·54%
Insoluble	1·46%
Ag	trace

In the following runs, R I to R VIII, No. 20 unlined carbon crucibles were used, except where it is specifically noted that they were lined. No attempt was made to obtain a yield, but they are intended to show the progress of the reduction. Very finely powdered anthracite coal was used just as in the runs A—H

Reduction of Co_3O_4 with Powdered Anthracite Coal (B)

HARVEY-STEELE OIL FURNACE

Number of run	Charge	Average temperature of run	Sample number and time of reduction in minutes up to removal of samples	Analysis of samples[1,2]	Remarks and reduction (when 100% is complete reduction)
Run R I. May 16, 1913	Co_3O_4, 10 lbs. Powdered coal, 17·5 oz.	601° C.	R2 = 1 hr. 22 min.	73·6%	Very slightly reduced.
Run R II. May 19, 1913	Co_3O_4, 10 lbs. Powdered coal, 16·5 oz.	753° C.	R3b = 1 hr. 31 min.	74·1%	Very slightly reduced.
Run R III. May 20, 1913	Co_3O_4, 10 lbs. Powdered coal, 16·5 oz.	888° C.	R4b = 1 hr. 30 min.	73·8%	Very slightly reduced.
Run R IV. May 21, 1913	Co_3O_4, 10 lbs. Powdered coal, 16·5 oz.	1057° C.	R5b = 1 hr. 35 min.	83·8%	28% reduction.
Run R VI. May 22, 1913	Co_3O_4, 10 lbs. Powdered coal, 16·5 oz.	1203° C.	R6a = 30 min. R6b = 49 min.	81·3% 93·0%	30% reduction. 74% reduction.
Run R VII. May 23, 1913	Co_3O_4, 10 lbs. Powdered coal, 16·5 oz.	1283° C.	R7a = 31 min. R7b = 47 min.	91·1% 93·9%	70% reduction. 77% reduction.
Run R VIII. May 28, 1913	Co_3O_4, 10 lbs. Powdered coal, 1 lb. 1·4 oz.	1592° C.	1 = 11 min. 2 = 16 min. 3 = 21 min. 4 = 26 min. 5 = 31 min. 6 = 36 min.	76·7% 81·8% 91·0% 93·9% 93·9% 91·8%	12% reduction. 32% reduction. 66% reduction. 77% reduction. There was apparently some oxidation.

It will be noticed in the above runs with powdered anthracite coal that the reductions are extremely low. It was, therefore, thought advisable to check these runs with experiments on a very small scale in porcelain crucibles, in such a manner that there could be no doubt as to the time during which the charge was maintained at the temperature in question.

A number of these runs were made with a thermo-element near the centre and at the outside of the charge. In the small furnace used for these runs the crucible with its charge came to temperature in a very few minutes so that the outside and inside thermo-elements agreed to within 20° C. Approximately this condition was maintained throughout the run, and the time recorded is the time from which the charge reached the desired temperature to the time of removal of the sample.

The results of the previous runs with powdered anthracite coal were confirmed by these small scale runs, and a satisfactory complete reduction could not be obtained at temperatures much below 1200° C

Reduction of Co_3O_4 with Powdered Charcoal

Further experiments were tried on the reduction of Co_3O_4 with very finely powdered charcoal. A large number of these gave fairly concordant results, which showed a greater reduction at all temperatures than the corresponding powdered anthracite coal runs.

Without giving the details of about twenty-five runs, it may be said that complete reduction was obtained with from 20-30% excess of powdered charcoal, at 900° C. or over, and with the size of charge and furnaces employed by us, complete reduction was brought about in less than an hour. At 1000—1100° C., the reduction with powdered charcoal was very much more rapid than at 900° C., often completing itself in less than 10 minutes.

---

[1] These analyses are for cobalt, nickel, and iron combined, of which about 97% was cobalt, as may be seen from the analysis of the original oxide.

[2] Carbon analyses were, of course, made, and the percentage of cobalt given in this column takes into account the residual carbon.

Reduction of Co_3O_4 with Lampblack

Experiments on the reduction of Co_3O_4 with lampblack were tried with results identical with those on the reduction of Co_3O_4 with powdered charcoal.

Briquets—Experiments on the reduction of Co_3O_4 with powdered charcoal were tried forming the charge into briquets. A small percentage[1] of molasses was used as a binder. These experiments were made under the same furnace and temperature conditions as those on the reduction of Co_3O_4 with powdered charcoal in bulk. Seven such runs showed throughout, that the reduction was not very different in its velocity from the corresponding runs with powdered charcoal, although the difference was uniformly in favour of the briquetted charges. A satisfactory reduction could probably not be made at temperatures below 800—850° C., even briquetting the charges, as compared with 900° C. for the charges in bulk.

Reduction in the form of briquets yields a sintered mass which can be handled commercially without fusing the reduced metal. This is a distinct advantage of this method.

The Metal—The metal produced by reduction of cobalt oxide with carbon is sufficiently pure for most purposes; it need not contain more than a few tenths of a per cent of carbon. The following characteristic analyses are taken at random from a large number to show the nature of the metal:—

Analyses of Metallic Cobalt Produced by Reduction of Commercial Cobalt Oxide with Carbon

July, 1912.

Co	97·05%
Ni	1·50%
Fe	1·00%
S	0·22%
C	0·20%
Ca	0·25%
SiO_2	0·12%

August 15, 1912.

Co	98·50%
Ni	0·65%
Fe	0·58%
C	0·22%
S	0·47%
Ca	0·60%
SiO_2	0·13%

October 10, 1912.

Co	98·84%
Ni	0·61%
Fe	0·56%
C	0·24%
Mn	0·06%
Ca	0·24%
S	0·21%
SiO_2	0·14%

---

[1] The mo' [illegible] would correspond to the addition of about 1% of carbon.

October 11, 1912.

Co	98·62%
Ni	0·50%
Fe	0·15%
C	0·13%
Ca	0·27%
S	0·22%
SiO_2	0·11%

June 11, 1913.

Co	98·30%
Fe	1·39%
Ni	trace
S	0·46%
As	0·11%
SiO_2	0·12%
Ca	0·58%

It is obvious from these analyses that the oxides taken for reductio with carbon were those directly from the smelter, which had not been treate by the method outlined on pages 3 and 4 to remove the impurities. It obvious that the iron, nickel, sulphur, and silica contents could have bee reduced to mere traces by purifying the oxide before reduction in accordanc with the method given. We have done this repeatedly, where a pure meta was required for experimental purposes.

It is, however, of importance to note that metal with very low carbo content may be made by direct reduction of the oxide with carbon.

Conclusions

I. Reduction of Co_3O_4 with powdered anthracite coal does not tak place rapidly so as to make it commercially interesting, either in the o fired crucible type of furnace or in the electric crucible type of furnace, until temperature in the neighbourhood of 1200° C. is reached.

II. In either the oil fired crucible type of furnace or in the electri crucible type of furnace, substantially complete yields of metallic cobal may be obtained by reduction of Co_3O_4 with powdered anthracite coa in the neighbourhood of 1200° C., for not more than 1 hour, with subsequen rapid melting and pouring.

III. With the oil fired crucible furnace, using unlined graphite crucible complete yields are only obtained with powdered anthracite coal when ther is an excess of approximately 10% of this latter.

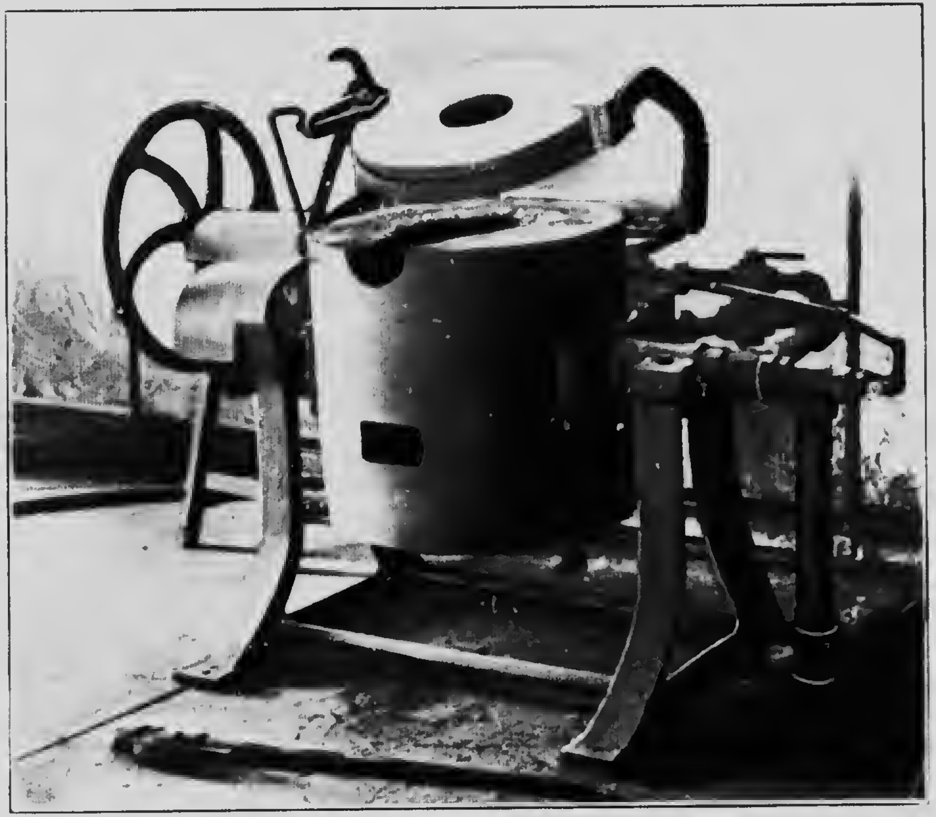
IV. With the electric crucible type of furnace, used by us, complet reduction may be obtained using only the theoretical quantity of powdere anthracite coal. In this furnace there is a considerable reduction due to th carbon monoxide atmosphere caused by the carbon resistor plates.

V. Both in the oil fired and in the electric crucible type of furnac greater reductions of Co_3O_4 are obtained using powdered charcoal, than wit powdered anthracite coal, at the corresponding temperature.

VI. With the oil fired or electric crucible type of furnace, complet reduction may be obtained with powdered charcoal at 900° C. or highe For this reduction a considerable excess of charcoal was required, under on conditions from 20–30%.

VII. Powdered lampblack shows results in accordance with those fo powdered charcoal.

PLATE IV.



Harvey-Steele oil furnace, used for Co_3O_4 reduction with carbon.

VIII. Briquetting the charges with an organic binder tends to increase the rate of reduction at all temperatures. A minimum of about 800° C. may be employed for the reduction of Co_3O_4 with charcoal in the form of briquets as against 900° C. for the same charge in bulk.

IX. The briquetted charges yield a metal which for many purposes is mechanically better in that it is in the form to be handled without fusing.

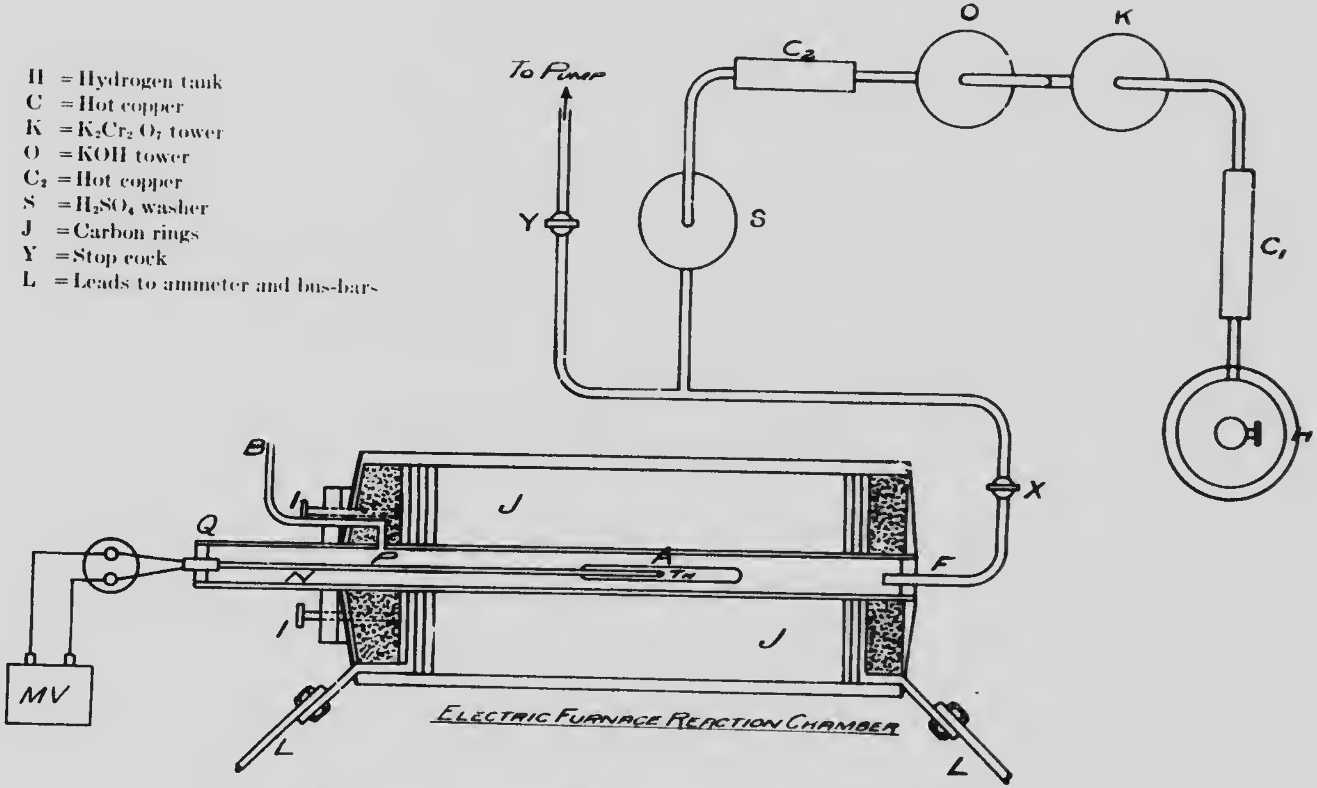
X. With sufficient carbon to get a complete yield of metal, the final product need only contain about 0·20% of carbon.

XI. At this laboratory, in electric furnaces not especially designed for this work, we reduce enough oxide to make 56 pounds of the metal in an eight hour day, with the furnace absorbing 12 K.W. Thus, on a commercial basis, the power charge for this reduction would be small.

PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE WITH HYDROGEN GAS

Method and Apparatus

These experiments consisted in placing an alundum boat, containing a weighed amount of dried cobalt oxide, in a horizontal tube electric resistor furnace, maintaining its temperature therein constant for a definite length of time, during which a stream of hydrogen gas was passed through the furnace. A schematic sketch of the apparatus is shown in Fig. 2, and photographs in Plates V and VI.

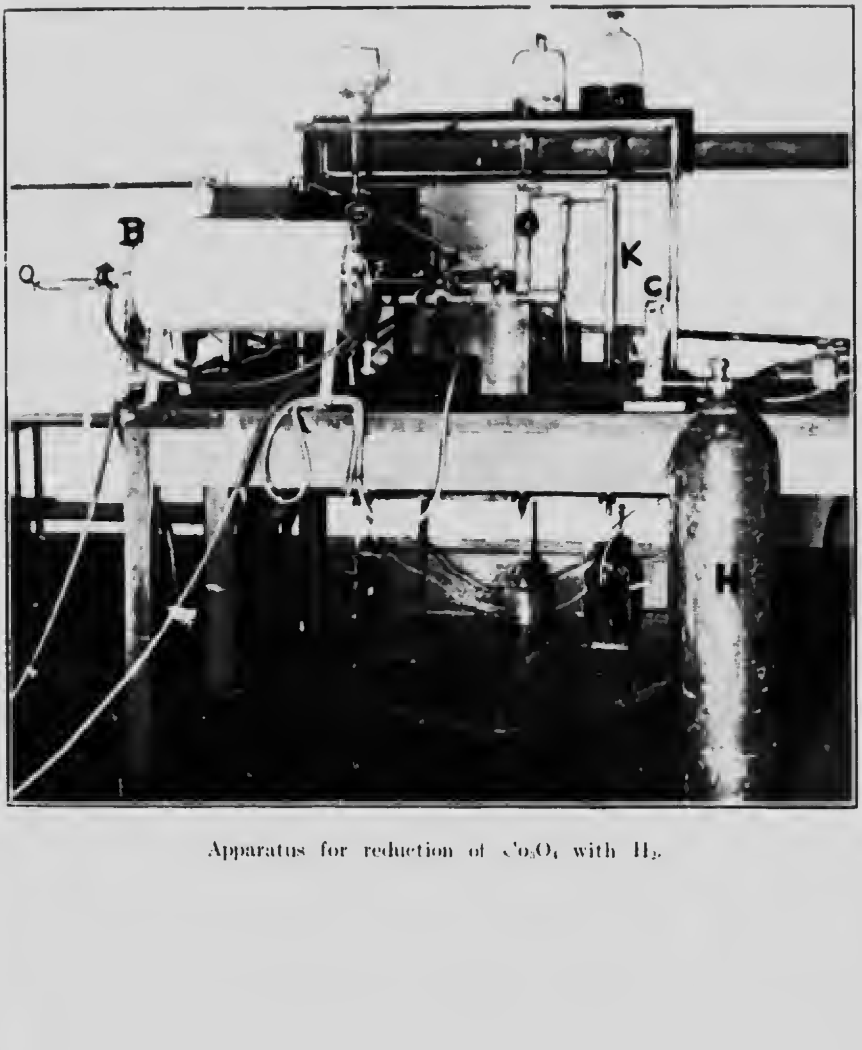


H = Hydrogen tank
C = Hot copper
K = $K_2Cr_2O_7$ tower
O = KOH tower
C_2 = Hot copper
S = H_2SO_4 washer
J = Carbon rings
Y = Stop cock
L = Leads to ammeter and bus-bars

FIG. 2. Arrangement of apparatus for reduction of Co_3O_4 by hydrogen gas.

FIG. 2. Arrangement of apparatus for reduction of Co_3O_4 by hydrogen gas.

PLATE V



Apparatus for reduction of Co_3O_4 with H_2.

The hydrogen supplied from a tank H, was purified by passing over hot copper C_1, through successively a potassium bichromate tower K, a potassium hydroxide tower O, hot copper a second time at C_2, and finally a sulphuric acid tower S.

After this purification it entered the furnace at the point F, passed over the alundum boat situated at A, and the excess of hydrogen was burned at the further end of the furnace at B. During the run the exit for the gas was through the by-pass PB, the exit Q being sealed.

The heating element of the furnace itself is a series of coaxial carbon ring plates J, which could be pressed together more or less tightly by suitable screws I. The furnace was supplied with alternating current at 25 volts from a transformer, and could be controlled at any temperature up to 1350° C.

The details of the furnace are shown in the drawing, Fig. 3.

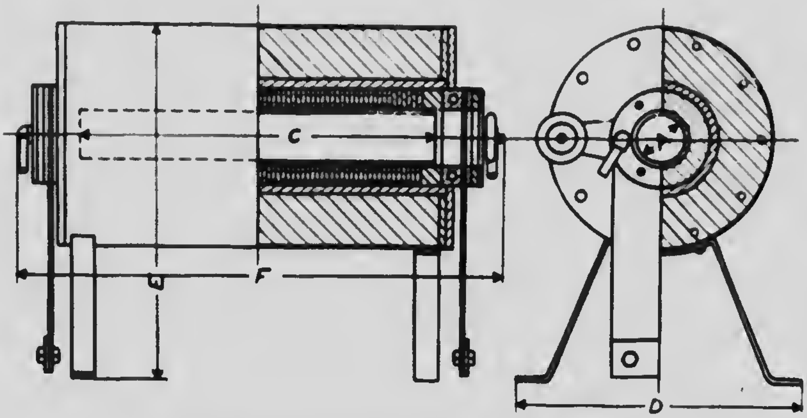


FIG. 3. Details of electric furnace for reduction of Co_3O_4 with H_2.

The temperature measurements were made by a platinum platinum-rhodium thermo-element Th and readings were taken at frequent intervals on a very sensitive millivoltmeter Mv. In this way the temperature was maintained substantially constant by hand regulation of the screws I.

All temperature measurements were made with thermo-elements which were calibrated at frequent intervals, in the usual way, against known melting points.

The power absorbed by the furnace was from 2 to 12 K.W., according to the temperature that was desired to be maintained.

Method of Conducting a Run

After having heated the furnace to the desired temperature, by a suitable current through the carbon rings J, runs were made as follows:—

(a) After closing the cock X, which separates the purifying system from the furnace, the air was exhausted from the hydrogen system by opening cock Y, and operating a pump.

(b) Gas burners were lighted to heat copper filings in tubes C_1 and C_2, through which the hydrogen is to pass.

(c) Solutions of potassium bichromate, potassium hydrate, and sulphuric acid, were started flowing through the purifying towers K, O, and S, which were partially filled with glass beads.

(d) Cock Y was closed and cock at outlet of hydrogen tank H was partially opened to allow a flow of hydrogen into the purifying system, until the pressure inside the system was a little greater than atmospheric pressure.

(e) Cock X was now opened to allow hydrogen to flow into the hot furnace.

(f) Flow of hydrogen was adjusted by cock at outlet of hydrogen tank H, until hydrogen burned freely at outlet end of furnace B. During the run the end Q was closed, and the gas escaped through the by-pass P B.

(g) When adjustment (f) was satisfactory, assuring an excess of hydrogen within the furnace, the weighed dried alundum boat, containing the charge of cobalt oxide, was placed in the hot furnace at the position A, and the time noted.

(h) The run proper had now commenced, during which observations of time, temperature, and power were made, and the furnace adjusted to keep the temperature constant.

(i) After a definite time the boat with its contents was withdrawn from the centre of the furnace, to the overhanging cool end of the furnace core N, in which it was allowed to cool, but through which, during the cooling, hydrogen was passed.

(j) When cool the boat was removed to a dessicator and weighed.

COBALT OXIDE REDUCTION WITH HYDROGEN COOLING IN AN ATMOSPHERE OF HYDROGEN

The cobalt oxide used for the following runs I to IX, analysed as follows:

Co_3O_4 used for Runs I to IX.

Co	72·3%
Ni	trace
Fe	0·10%
Ca	0·15%
S	0·052%
SiO_2	0·39%

It will be noticed that this oxide contained 72·1% of the metals cobalt, nickel, and iron, in the form of oxides which may be computed without appreciable error to be cobalt oxide. Any sample contains, therefore, 0·75% of unreducible calcium sulphate, calcium oxide, and silica, 99·2% of cobalt oxide running $\frac{72\cdot1}{99\cdot2} = 72\cdot9\%$ in cobalt. This oxide, therefore, corresponds very closely to Co_3O_4. The oxygen content of the substance which could be reduced by hydrogen is equal to 27·1% of 99·2% = 27·0%. This figure is accurate to within the experimental error of the runs, and is used as the basis of the following computations. That is to say, in the column headed "Percentage loss in weight," 27·0% would represent complete reduction, and the last column headed "Reduction where 100% is complete reduction," is computed in terms of 27·0% actual reduction as total.

Following are the data and the reductions computed therefrom:—

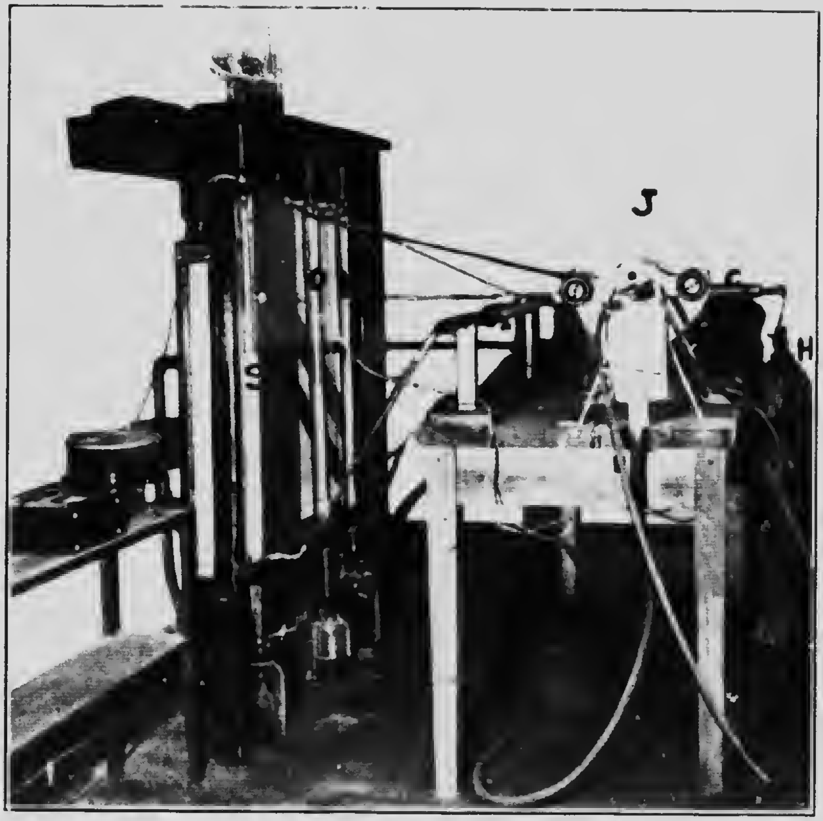
Reduction of Cobalt Oxide with Hydrogen at 585° C.

Run 1—July 15, 1913.

Mean temperature during run . . . . 585° C.

Average deviation of single temperature observation from the mean 1·3°C.

PLATE VI.



Apparatus for reduction of Co_3O_4 with H_2.

BOAT I.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	8·5888 grams.			
5 min.	8·0944 grams.	0·4944 grams.	24·6%	91·0%

Boat empty = 6·5853 grams.
Boat + Co_3O_4 = 8·5888 grams.
Initial weight of Co_3O_4 = 2·0035 grams.

After this weighing an accident occurred to boat, so it was recharged with dried cobalt oxide as follows:

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	8·7632 grams.			
5 min.	8·2088 grams.	0·5544 grams.	25·5%	94·2%
15 min.	8·2158 grams.	0·5516 grams.	25·4%	94·0%

Boat empty = 6·5844 grams.
Boat + Co_3O_4 = 8·7632 grams.
Initial weight of Co_3O_4 = 2·1788 grams.

BOAT II.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	7·4025 grams.			
5 min.	6·8432 grams.	0·5593 grams.	25·8%	95·6%
15 min.	6·8932 grams.	0·5093 grams.	23·4%	86·7%

Boat e[illegible] 2330 grams.
Boat + [illegible] ·4025 grams.
Initial we[illegible] Co_3O_4 = 2·1695 grams.

It was noted at the close of this run that there was a slight oxidation at one point in the boat.

Run II—July 16, 1913.
Mean temperature during run .... 584° C.
Average deviation of single temperature observation from the mean .. 1·0° C.

BOAT I.

Time of reduction	We [illegible] f bo [illegible] O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	8·1251 grams.			
15 min.	7·6024 grams.	0·5227 grams.	26·0%	96·2%
30 min.	7·5988 grams.	0·5263 grams.	26·6%	98·3%
60 min.	7·5966 grams.	0·5255 grams.	26·2%	97·0%

Boat empty = 6·1156 grams.
Boat + Co_3O_4 = 8·1251 grams.
Initial weight of Co_3O_4 = 2·0095 grams.

BOAT II.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	7·2476 grams.			
15 min.	6·7210 grams.	0·5266 grams.	26·1%	96·8%
30 min.	6·7200 grams.	0·5276 grams.	26·2%	97·0%
60 min.	6·7210 grams.	0·5266 grams.	26·1%	96·8%

Boat empty = 5·2307 grams.
Boat + Co_3O_4 = 7·2476 grams.
Initial weight of Co_3O_4 = 2·0169 grams.
All the reduced samples were steel grey.

Reduction of Cobalt Oxide with Hydrogen at 600° C.

Run III—April 16, 1913.
Mean temperature during run.................................... 609° C.
Average deviation of single temperature observation from the mean 4·2° C.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	8·5976 grams.			
7 min.	8·2630 grams.	0·3346 grams.	16·8%	62·2%
15 min.	8·1556 grams.	0·4420 grams.	22·1%	81·8%
30 min.	8·1504 grams.	0·4472 grams.	22·4%	83·0%
60 min.	8·0950 grams	0·5026 grams.	25·2%	93·0%

Boat empty = 6·6005 grams.
Boat + Co_3O_4 = 8·5976 grams.
Initial weight of Co_3O_4 = 1·9971 grams.

Run IV—April 17, 1913.
Mean temperature during run.................................... 597° C.
Average deviation of single temperature observation from the mean.. 2·0° C.

BOAT I.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	8·1296 grams.			
7 min.	7·6200 grams.	0·5096 grams.	25·3%	94·0%
15 min.	7·6190 grams.	0·5106 grams.	25·4%	94·2%
30 min.	7·6290 grams.	reoxidized during removal from furnace		

Boat empty = 6·1174 grams.
Boat + Co_3O_4 = 8·1296 grams.
Initial weight of Co_3O_4 = 2·0122 grams.

BOAT II.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	7·2714 grams.			
7 min.	6·7586 grams.	0·5128 grams.	25·4%	94·2%
15 min.	6·7652 grams.	0·5062 grams.	25·2%	94·1%
70 min.	6·7666 grams.	reoxidized during removal from furnace		

Boat empty = 5·2503 grams.
Boat + Co_3O_4 = 7·2714 grams.
Initial weight of Co_3O_4 = 2·0211 grams.

Run V—April 21, 1913.
Mean temperature during run.................................. 598° C.
Average deviation of single temperature observation from the mean.. 1·7° C.

BOAT IV.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	7·2452 grams.			
15 min.	6·7358 grams.	0·5094 grams.	25·5%	94·3%
60 min.	6·7358 grams.	0·5091 grams.	25·5%	94·3%

Boat empty = 5·2452 grams.
Boat + Co_3O_4 = 7·2452 grams.
Initial weight of Co_3O_4 = 2·0000 grams.
Boat showed slight reoxidation at one end when removed from furnace.

April 22, 1913.

BOAT I.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction.
0 min.	8·1182 grams.			
60 min.	7·6026 grams.	0·5156 grams.	25·8%	95·7%
120 min.	7·6032 grams.	0·5150 grams.	25·7%	95·3%

Boat empty = 6·1182 grams.
Boat + Co_3O_4 = 8·1182 grams.
Initial weight of Co_3O_4 = 2·0000 grams.
This material, 25·7% loss in weight, analysed for cobalt as follows:—

Analysis I.......................... Co = 97·25%
Analysis II.......................... Co = 97·30%

The material resulting from this run contained the 0·75% of unreducible $CaSO_4$, CaO and SiO_2, and 1·4% of oxygen presumably in the form of Co_3O_4[1], and 0·10% of nickel and iron. It should, therefore, contain 100 − 2·3 = 97·7% of cobalt. This checks with the analytical value 97·3%, to within the accumulative error in the analyses.

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[1] Co_3O_4 is the stable oxide at 598° C, see pages 33-35.

Reduction of Cobalt Oxide with Hydrogen at 725° C.

Run VI—July 17, 1913.
Mean temperature during run .... 727° C.
Average deviation of single temperature observation from the mean . 1·5° C.

Boat I.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	8·1296 grams.			
5 min.	7·5952 grams	0·5344 grams.	26·5%	98·1%
10 min.	7·5952 grams.	0·5344 grams.	26·5%	98·1%
30 min.	7·5938 grams.	0·5358 grams.	26·6%	98·5%
60 min.	7·5926 grams.	0·5370 grams.	26·6%	98·5%

Boat empty = 6·1114 grams.
Boat + Co_3O_4 = 8·1296 grams.
Initial weight of Co_3O_4 = 2·0182.

Boat II.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	7·2964 grams.			
5 min.	6·7470 grams.	0·5494 grams.	26·6%	98·5%
10 min.	6·7482 grams.	0·5482 grams.	26·5%	98·1%
30 min.	6·7470 grams.	0·5494 grams.	26·6%	98·5%

Boat empty = 5·2286 grams.
Boat + Co_3O_4 = 7·2964 grams.
Initial weight of Co_3O_4 = 2·0678 grams.

Reduction of Cobalt Oxide with Hydrogen at 825° C.

Run VII—July 18, 1913.
Mean temperature during run.................................. 824° C.
Average deviation of single temperature observation from the mean.. 4·3° C.

Boat I.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	8·1098 grams.			
2½ min.	7·5766 grams.	0·5332 grams.	26·6%	98·5%
5 min.	7·5766 grams.	0·5332 grams.	26·6%	98·5%
15 min.	7·5760 grams.	0·5338 grams.	26·7%	98·8%
30 min.	7·5744 grams.	0·5354 grams.	26·75%	99·0%
60 min.	7·5744 grams.	0·5354 grams.	26·75%	99·0%
150 min.	7·5726 grams.	0·5372 grams.	26·80%	99·2%

Boat empty = 6·1082 grams.
Boat + Co_3O_4 = 8·1098 grams.
Initial weight of Co_3O_4 = 2·0016 grams.

BOAT II.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	7·2804 grams.			
2½ min.	6·7311 grams.	0·5463 grams.	26·61%	98·5%
5 min.	6·7320 grams.	0·5484 grams.	26·71%	98·8%
15 min.	6·7310 grams.	0·5494 grams.	26·75%	99·0%
30 min.	6·7312 grams.	0·5492 grams.	26·75%	99·0%
60 min.	6·7300 grams.	0·5504 grams.	26·80%	99·2%

Boat empty = 5·2242 grams.
Boat + Co_3O_4 = 7·2804 grams.
Initial weight of Co_3O_4 = 2·0562 grams.

The product from this run seemed to be of a slightly lighter gray shade than that from the runs at lower temperatures.

Reduction of Cobalt Oxide with Hydrogen at 965° C.

Run VIII—July 18, 1913.
Mean temperature during run.......................... 965° C.
Average deviation of single temperature observation from the mean.. 1·0° C.

BOAT I.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	7·2642 grams.			
1 min.	6·7106 grams.	0·5236 grams.	25·6%	94·8%
5 min.	6·7144 grams.	0·5198 grams.	26·9%	99·4%
30 min.	6·7150 grams.	0·5512 grams.	27·1%	100%
60 min.	6·7132 grams.	0·5510 grams.	27·1%	100%

Boat empty = 5·2230 grams.
Boat + Co_3O_4 = 7·2642 grams.
Initial weight of Co_3O_4 = 2·0412 grams.

BOAT II

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	8·6074 grams.			
1 min.	8·0627 grams.	0·5447 grams.	26·8%	99·1%
5 min.	8·0616 grams.	0·5458 grams.	26·9%	99·4%
30 min.	8·0610 grams.	0·5464 grams.	26·9%	99·4%
60 min.	8·0588 grams.	0·5486 grams.	27·0%	99·7%

Boat empty = 6·5718 grams.
Boat + Co_3O_4 = 8·6074 grams.
Initial weight of Co_3O_4 = 2·0326 grams.

Reduction of Cobalt Oxide with Hydrogen at 1070° C.

Run IX.—July 19, 1913.
Mean temperature during run . . . . 1073° C.
Average deviation of single temperature observation from the mean . . 2·1° C.

BOAT I

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	7·3213 grams.			
2 min.	6·7689 grams.	0·5524 grams.	26·28%	96·8%
5 min.	6·7558 grams.	0·5655 grams.	26·90%	99·4%
30 min.	6·7538 grams.	0·5675 grams.	27·00%	99·7%
60 min.	6·7533 grams.	0·5680 grams.	27·05%	99·9%

Boat empty = 5·2202 grams.
Boat + Co_3O_4 = 7·3213 grams.
Initial weight of Co_3O_4 = 2·1011 grams.

BOAT II.

Time of reduction	Weight of boat + Co_3O_4	Loss in weight	Per cent loss in weight	Reduction where 100% is complete reduction
0 min.	8·5955 grams.			
1 min.	8·1031 grams.	0·4921 grams.	21·38%	90·0%
5 min.	8·0516 grams.	0·5439 grams.	26·90%	99·4%
30 min.	8·0488 grams.	0·5467 grams.	27·00%	99·8%
60 min.	8·0472 grams.	0·5483 grams.	27·10%	100·0%

Boat empty = 6·5740 grams.
Boat + Co_3O_4 = 8·5955 grams.
Initial weight of Co_3O_4 = 2·0215 grams.

The check between the composition of the oxide used for these hydrogen reduction experiments, as determined by analysis (page 14) and as determined by the reduction experiments, is entirely satisfactory. For a further discussion see pages 33–35.

A number of the early experiments to reduce Co_3O_4 with hydrogen were made allowing the reduced product to cool in the atmosphere. In every case reoxidation took place. These runs were made at various temperatures from 500°C. to 1000° C., and curiously enough the reoxidation at the higher temperatures was progressively less than at the lower temperatures.

Conclusions

(a) The reduction of Co_3O_4 to metallic cobalt by hydrogen gas takes place very rapidly at all temperatures above 500° C.

(b) At temperatures between 500° C. and 700° C., over 90% of the reduction of Co_3O_4 to Co takes place in a few minutes, but a further reduction takes place very slowly if at all.

(c) Between 700° C. and 1100° C., the amount of reduction of Co_3O_4 to Co which takes place during the first few minutes increases very rapidly with rising temperature, and at the higher temperatures it is complete.

(d) The hydrogen reduction method is to be especially recommended for the production of moderate quantities of very pure carbon-free cobalt for special purposes, just as it has been used for the production of metallic tungsten.

(e) For the production of cobalt from Co_3O_4 by hydrogen, the charge must be completely cooled in an atmosphere of hydrogen.

PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE WITH CARBON MONOXIDE GAS

Method and Apparatus

These experiments were performed by placing an alundum boat, containing a weighed amount of dried cobalt oxide, in a horizontal tube electric resistor furnace, maintaining its temperature therein constant for a definite length of time, during which a stream of carbon monoxide gas was passed through the furnace. A schematic sketch of the apparatus is shown in Fig. 4, and a photograph in Plate VII.

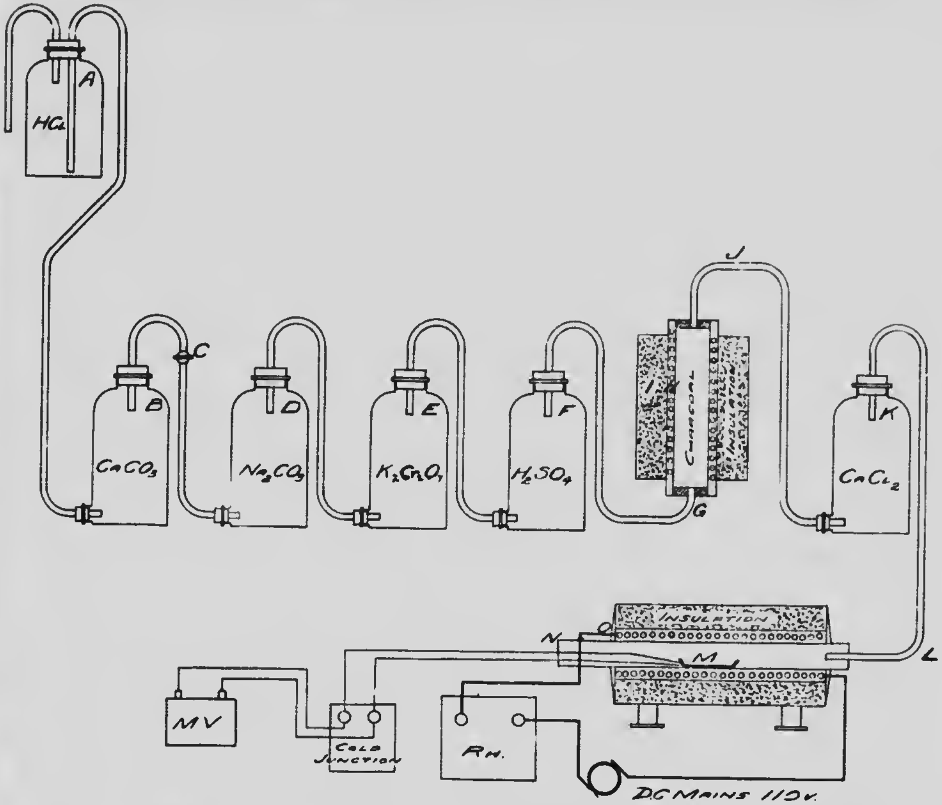


Fig. 4. Arrangement of apparatus for reduction of cobalt oxide by carbon monoxide gas.

Carbon-Monoxide Generator

The carbon monoxide gas was supplied by passing carbon dioxide gas over hot wood charcoal, which reduced it according to the reaction

$$CO_2 + C = 2CO.$$

A hydrochloric acid container A was mounted so as to discharge into a large bottle B, containing calcium carbonate, the two together forming the usual carbonic acid gas generator. The gas discharged through the cock C, and after passing successively through wash bottles D, E, and F, containing respectively sodium carbonate, potassium bichromate, and sulphuric acid, entered the lower end of the carbon monoxide generating furnace at G.

This generating furnace was of the electric resistance type, and was made by winding nichrome wire over an alundum cylinder, the two being embedded in magnesite cement, and insulated within a cylindrical iron container. The wire is shown in section at H and the iron container at I.

The entire core of the furnace was filled with wood charcoal, which was maintained at about 1000° C. by an appropriate current through the heating element. As a result, carbon monoxide gas left the generator at J, with a certain amount of moisture which was absorbed by passing through calcium chloride at K.

Finally, substantially pure carbon monoxide gas entered the reaction furnace proper at L, passed over the alundum boat M, with its cobalt content, and the excess burned off at N.

The Reaction Furnace

The reaction furnace proper is shown in Plate VII at R. It consisted of a central silica tube LN, 2 feet in length, and 1 inch in internal diameter. This was wound with calorite or nichrome wire, of such resistance that it could be controlled by a suitable rheostat Rh on 110 volt direct current mains, to maintain the temperature constant to within less than 10 degrees during a run, at any temperature up to 1000° C.

Temperature Measurements

The temperature measurements were made by a platinum platinum-rhodium thermo-element Th, and readings were taken at frequent intervals on a very sensitive millivoltmeter Mv.

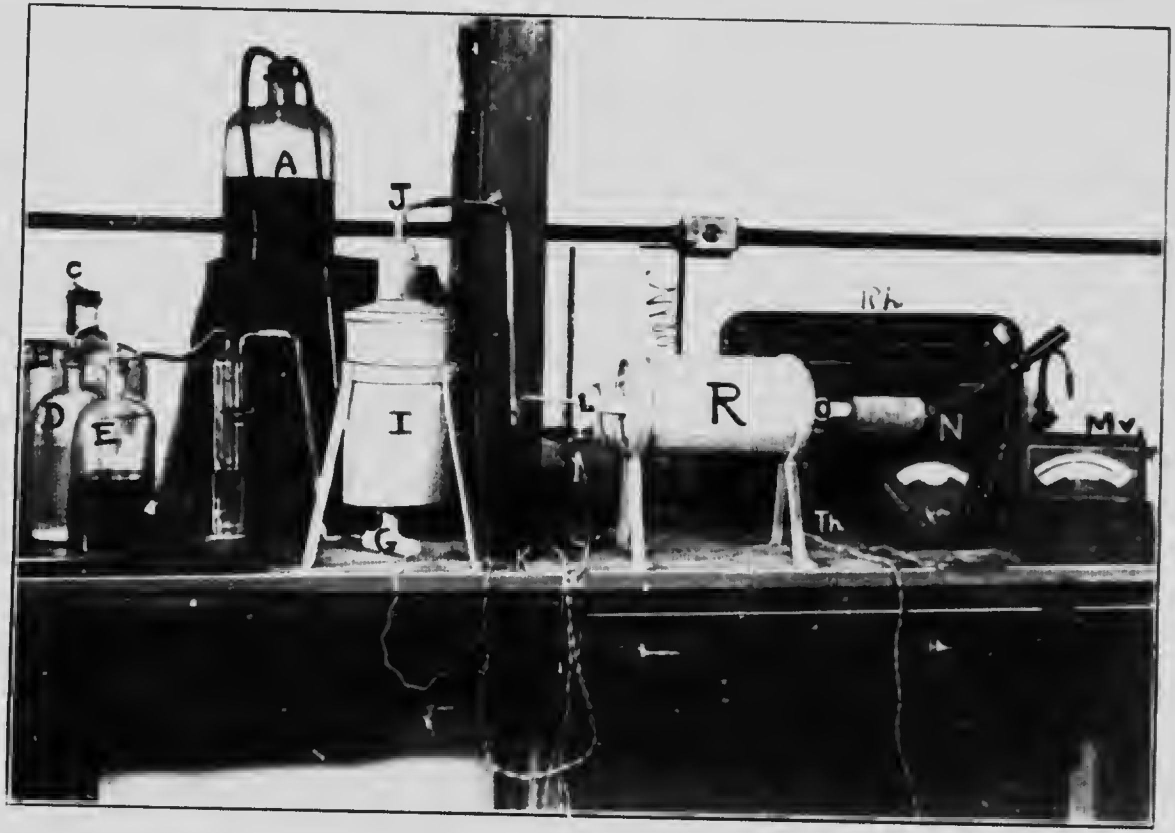
The thermo-elements used for the temperature measurements were calibrated at frequent intervals in the usual way against known melting points.

Cooling Charge in Carbon-Monoxide Atmosphere

The tube NL was of sufficient length that it extended beyond the end of the furnace proper from O to N. The portion O—N was 1 foot in length and was kept cool by a circulation of water, so that at the close of a run the boat was removed from the centre of the furnace to O—N, where it cooled while the stream of CO gas was still passing over it. Thus, the oxide was brought to room temperature in an atmosphere of carbon monoxide.

Method of Conducting a Run

After having heated the reaction furnace, and the CO producer furnace, by suitable currents, to the desired temperatures, runs were made as follows:—



Apparatus f[illegible]he reduction of Co_3O_4 with carbon-monoxide.

(a) The cock C was opened to allow CO_2 gas to pass through the purifying system DEF into the producer furnace at G.

(b) The CO gas generated in the producer furnace GJ passed through the reaction furnace LN and was lighted at N.

(c) The weighed dried boat with its charge was introduced into the exterior of the reaction furnace, that is, into the cold projecting end of the silica tube ON.

(d) Temperature and time observations were begun, and when the desired temperature had been reached, the boat was moved to the interior of the furnace at M.

(e) The run proper had now commenced, during which observations of time and temperature were made and the rheostat Rh adjusted to keep the temperature constant.

(f) After a definite time the boat with its contents was withdrawn from the centre of the furnace to the cooling chamber ON, in which it was allowed to cool, but through which, during the cooling, carbon monoxide gas was flowing.

(g) When the boat was cool, the current of carbon monoxide was gradually diminished by closing the cock C, until it was finally entirely cut off.

(h) When the boat was cooled to the atmospheric temperature, it was removed to a dessicator and weighed.

The earlier observations on the reduction of cobalt oxide with carbon monoxide were made without the precaution to cool in an atmosphere of CO gas, part (f) of the run. In this early work the boat was removed from the furnace and immediately placed within the dessicator.

As a result of the cooling in the atmosphere, reoxidation took place to a very decided extent. A number of runs of this sort were made, the degree of reoxidation being, of course, more or less accidental. A single pair of these runs given below in full, Runs I–II, are typical of them all.

COBALT OXIDE FOR CARBON MONOXIDE REDUCTION EXPERIMENTS

The cobalt oxide for the CO reduction experiments was purified by the method outlined on pages 3 and 4. It analysed as follows:

Co_3O_4 used for Runs I–XVIII.

Co	72·3%
Ni	trace
Fe	0·10%
Ca	0·15%
S	0·052%
SiO_2	0·39%

It will be noticed that this oxide contained 72·4% of the metals cobalt, nickel, and iron, in the form of oxides which may be computed without error to be cobalt oxide. Any sample contains, therefore, 0·75% of unreducible calcium sulphate, calcium oxide, and silica. 99·2% of cobalt oxide running $\frac{72\cdot4}{99\cdot2} = 72\cdot9\%$ in cobalt. This oxide, therefore, corresponds very closely to Co_3O_4. The oxygen content of the substance which could be reduced by carbon monoxide is equal to 27·1% of 99·2% = 27·0%. This figure is accurate to within the experimental error of the runs, and is used as the basis of the following computations. That is to say, in the column headed "Percentage loss in weight," 27·0% would represent complete reduction, and the last column headed, "Reduction where 100% is complete reduction," is computed in terms of 27·0% actual reduction as total.

The following are the data and the reductions computed therefrom:—

Reduction of Co_3O_4 with CO—Cooling in the Atmosphere

A number of the first runs were made reducing Co_3O_4 with CO and allowing the reduced product to cool in the atmosphere before weighing. As will be seen below, under these conditions reoxidation took place rapidly, so that but a single pair of runs, Runs I and II, are given, which are typical of them all.

Run I—December 16, 1912.

BOAT I.

Average temperature 602° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
11 15		596° C.	0	10·5655 grams			
	11 30	599° C.	15	10·3520 grams.	0·2135	10·6	39·3%
11 45		597° C.					
	12 00	580° C.	30	10·3440 grams.	0·2215	11·1	41·1%
12 07½		600° C.					
	12.22½	590° C.	45	10·3500 grams.	0·2155	10·8	39·9%
3 30		580° C.					
	3 45	620° C.	60	10·3080 grams.	0·2575	12·9	47·8%
3 52		610° C.					
	4 07	615° C.	75	10·3070 grams.	0·2585	12·9	47·8%
4 15		610° C.					
	4 22	605° C.	82	10·3300 grams.	0·2355	11·8	43·6%
4 30		610° C.					
	4 40	600° C.	92	10·3400 grams.	0·2255	11·3	41·8%
4 47		610° C.					
	5 02	605° C.	107	10·4110 grams.	0·1545	7·8	39·6%

Initial weight of boat + dried oxide = 10·5655 grams.
Initial weight of Co_3O_4 = 1·9996 grams.

Run II—December 16, 1912.

BOAT II.

Average temperature 594° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
11 27½		585° C.	0	13·3049 grams.			
	11 52½	— —	30	13·0570 grams.	0·2479	12·4	46·0%
12 00		575° C.					
	12.15	575° C.	45	13·0700 grams.	0·2349	11·7	43·3%
3 30		575° C.					
	4.00	600° C.	75	13·0412 grams.	0·2639	13·2	48·8%
4 07		610° C.					
	4 30	600° C.	97	13·0600 grams.	0·2449	12·3	45·5%
4 40		600° C.					
	4 55	600° C.	112	13·0860 grams.	0·2189	11·9	44·0%
5 02		605° C.					
	5 32	605° C.	142	13·1000 grams.	0·2049	10·3	38·2%

Initial weight of boat + dried oxide = 13·3049 grams.
Initial weight of Co_3O_4 = 1·9344 grams.

The reoxidation of cobalt oxide after reduction with carbon monoxide takes place with great vigour. If the boat be withdrawn from the hot furnace directly into the atmosphere, it may be seen to glow with great brilliancy. If the content of the boat, while still warm, be snapped out on the floor, it will reoxidize with such vigour that a cracking sound, as of a mild explosion, is heard to attend the reaction. That is, the reoxidation taking place according to the reaction

$$6\ CoO+O_2=2\ Co_3O_4$$

is extremely exothermic.

In the runs I and II, December 16, during the first part of the run, and up to the time that it began to gain in weight, the Co_3O_4 in both boats gradually changed to a grey colour. At the end of the run it was black again. This grey material is CoO.

On account of the irregularities of reoxidation, the furnace reaction chamber was lengthened by substituting a silica tube of length LN for the one of length LO as shown in Plates V, VI, and VII. The overhanging tube ON, about 1 foot in length, was cooled by water, and served as a cooling chamber for the boat while CO gas was still passed through it.

The following runs, representative of a large number, show the rate of the reduction of cobalt oxide by CO gas when the cooling was controlled so that no reoxidation could take place.

Reduction of Cobalt Oxide by Carbon Monoxide Gas—Cooling in CO Gas.

Reduction of Co_3O_4 with CO at 350° C.

Run III—April 24, 1913.

Average temperature 347° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
5 10		338° C.	0	8·0410 grams.			
	5 15	349° C.	5	7·6770 grams.	0·3640	18·2	67·3%
11 45		359° C.					
	11 55	348° C.	15	7·5370 grams.	0·5040	25·2	93·2%
1.40		350° C.					
	2 10	345° C.	45	7·9130 grams.	0·1289	deposit of carbon	
3 32		359° C.					
	3 47	347° C.	60	7·9202 grams.	0·1208	deposit of carbon	

Initial weight of boat+dried oxide = 8·0410 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

The oxide became a greenish grey colour at the end of the first five minutes, and a uniform steel grey colour at the end of fifteen minutes. From then on it began to gain in weight, due to a deposit of carbon.

At the close of many runs at this temperature, there was an extremely heavy deposit of carbon in the boat.

This run was typical of a number, which showed a reduction from the original black oxide to the green, followed by a change from the green to the grey, and then a gain in weight, due to a deposit of carbon. The only possible source of carbon was from the carbon monoxide gas, so that the finely divided metallic cobalt, which was formed during the first stages of the reduction of the grey oxide, probably acted catalytically to decompose carbon monoxide gas at this temperature. This is an extremely interesting decomposition which might well be studied with considerable care.

Reduction of Co_3O_4 with CO at 450° C.

Run IV—April 15, 1913.

BOAT I.

Average temperature 451° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
3 51		450° C.	0	8·0574 grams.			
	3 56	447° C.	5	7·6152 grams.	0·4422	22·1	81·8%
4 15		455° C.					
	4 25	453° C.	15	7·7902 grams.	0·2672	13·4	49·5%

Initial weight of boat + dried oxide = 8·0574 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

A strong odour of hydrocyanic acid was noticed throughout this run. After five minutes or so, a deposit of carbon began to form in the boat. due to the decomposition of carbon monoxide by finely divided cobalt, as in the runs at 350° C.

Run V—April 16, 1913.

BOAT I.

Average temperature 453° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
2 21		455° C.	0	8·0576 grams.			
	2 26	455° C.	5	7·6390 grams.	0·4276	21·4	79·2%
2 55		456° C.					
	3 05	456° C.	15	7·7932 grams.	0·2644	13·2	48·4%
3 .35		447° C.					
	4 05	455° C.	45	8·0730 grams.	gain		
4 36		451° C.					
	4 51	452° C.	60	8·1372 grams.	gain		

Initial weight of boat + dried oxide = 8·0576 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

Throughout this run a strong odour of HCN was noticed, as in the run above. This is true of all the reductions of cobalt oxide with carbon monoxide in the neighbourhood of 450° C.

These two runs are typical of a large number of similar ones. Our observations seem to show that the decomposition of CO by Co takes place only through a temperature interval in the neighbourhood of from 300—450° C

Reduction of CoO_x, with CO at 600° C.

Run VI—February 18, 1913.

BOAT I.

Average temperature 583° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
11 36		580° C.	0	7·3060 grams.			
	11 40	574° C.	5	6·9810 grams.	0·3250	16·2	60·0%
2 52		582° C.					
	[illegible] 02	581° C.	15	6·7790 grams.	0·5270	26·4	97·8%
4 48		590° C.					
	[illegible]	589° C.	35	6·7700 grams.	0·5360	26·8	98·0%
Feb. 20 4 09		[illegible]° C.					
	[illegible]	[illegible]8° C.	50	6·7680 grams.	0·5380	26·9	99·6%
5 11		[illegible]2° C.					
	5 26	575° C.	65	6·7650 grams.	0·5410	27·0	100·0%

Initial weight of boat + dried oxide = 7·3060 grams.
Initial weight of Co_3O_4 = 2·0020 grams.

Run VII—February 18, 1913.

BOAT II.

Average temperature 596° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
Feb. 21 3.41		598° C.	0	8·0610 grams.			
	4 01	590° C.	[illegible]	7·5300 grams.	0·5310	26·5	98·1%
4 44							
	5 54	595° C.	30	7·5280 grams.	0·5330	26·6	98·4%

Initial weight of boat + dried oxide = 8·0610 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

Run VIII—April 3, 1913.

BOAT I.

Average temperature 600° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
11 14		595° C.	0	8·133 grams.			
	4 24	605° C.	10	7·713 grams.	0·420	21·0	77·9%

Initial weight of boat + dried oxide = 8·133 grams.
Initial weight of Co_3O_4 = 2·000 grams.

Run IX—April 3, 1913.

BOAT II.

Average temperature 597° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
4.36		600° C.	0	8·6266 grams.			
	4.41	592° C.	5	8·2025 grams.	0·4241	21·2	78·3%
5.02		590° C.					
	5 12	606° C.	15	8·1315 grams.	0·4951	24·7	91·0%

Initial weight of boat+dried oxide = 8·6266 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

Run X—April 9, 1913.

Average temperature 611° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
5.21		603° C.	0	8·6280 grams.			
	5.41	630° C.	20	8·0988 grams.	0·5282	26·4	97·8%
Apl. 10 11.04		609° C.					
	11 21	603° C.	37	8·0986 grams.	0·5294	26·5	98·1%
11.45		603° C.					
	12.00	611° C.	52	Reoxidized on taking from cooling tube. Run continued with new sample.			

Initial weight of boat+dried oxide = 8·6280 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
Apl. 11 2.18		611° C.	0	8·6283 grams.			
	3 07	625° C.	49	8·1016 grams	0·5267	26·3	97·7%
4.05		625° C.					
	4 25	611° C.	69	8·0970 grmms.	0·5313	26·7	98·8%
5 13		603° C.					
	5.30	613° C.	86	8·0840 grams.	0·5443	27·2	100·0%
Apl. 12 11.07		602° C.					
	12.07	613° C.	146	8·0864 grams.	0·5419	27·1	100·0%

Initial weight of boat+dried oxide = 8·6283 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

Run XI—April 23, 1913.

BOAT I.

Average temperature 594° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
2 42		598° C.	0	8·0500 grams.			
	2.47	582° C.	5	7·5370 grams.	0·5130	25·7	95·0%
3 37		600° C.					
	3 47	590° C.	15	7·5248 grams.	0·5262	26·3	97·2%
4.15		590° C.					
	4 45	602° C.	45	7·5172 grams.	0·5328	26·7	99·0%
5.15		600° C.					
	5 30	588° C.	60	7·5172 grams.	0·5328	26·7	99·0%

Initial weight of boat + dried oxide = 8·0500 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

Run XII—April 23, 1913.

BOAT II.

Average temperature 601° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
11.24		601°	0	8·6320 grams.			
	11 29	602° C.	5	8·1192 grams.	0·5128	25·6	94·9%
11 55		600° C.					
	12.05	600° C.	15	8·1018 grams.	0·5320	26·5	98·0%
2 24		598° C.					
	2 51	604° C.	45	8·1012 grams.	0·5308	26·5	98·0%
3 09		601° C.					
	3 24	598° C.	60	8·1002 grams	0·5318	26·6	98·4%

Initial weight of boat + dried oxide = 8·6320 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

Reduction of Co_3O_4 with CO at 750° C.

Run XIII—April 26, 1913.

Average temperature 754° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
2 43		757° C.	0	8·6306 grams.			
	2.48	755° C.	5	8·0972 grams.	0·5334	26·7	99·0%
3.21		752° C.					
	3.31	748° C.	15	8·0940 grams.	0·5366	26·8	99·3%
4.10		756° C.					
	4.40	748° C.	45	8·0934 grams.	0·5372	26·9	99·8%
5 20		758° C.					
	5 35	758° C.	60	8·0928 grams.	0·5378	26·9	99·8%

Initial weight of boat + dried oxide = 8·6306 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

Run XIV—June 27, 1913.

Average temperature 752° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
2 03		753° C.	0	8·6306 grams.			
	2 08	756° C.	5	8·0952 grams.	0·5354	26·8	99·6%
2 43		753° C.					
	2 53	756° C.	15	8·0940 grams.	0·5366	26·8	99·6%
3 35		748° C.					
	4 05	752° C.	45	8·0930 grams.	0·5376	26·9	99·8%
4 35		748° C.					
	4 50	751° C.	60	8·0928 grams.	0·5378	26·9	99·8%

Initial weight of boat + dried oxide = 8·6306 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

Run XV—July 29, 1913.

Average temperature 749° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
3 59		750° C.	0	8·1366 grams.			
	4 04	748° C.	5	7·6160 grams.	0·5206	24·9	92·3%
4 22		735° C.					
	4 32	748° C.	15	7·5769 grams.	0·5597	26·7	99·1%
4 46		750° C.					
	5 16	756° C.	45	7·5761 grams.	0·5605	26·8	99·6%
5.32		754° C.					
	5 47	750° C.	60	7·5759 grams.	0·5607	26·8	99·6%
10.58		750° C.					
	12 21	750° C.	150	7·5761 grams.	0·5605	26·8	99·6%

Initial weight of boat + dried oxide = 8·1366 grams.
Initial weight of Co_3O_4 = 2·0903 grams.

Run XVI—July 25, 1913.

Average temperature 751° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
2 30		748° C.	0	8·0458 grams.			
	2 35	753° C.	5	7·5250 grams.	0·5208	26·0	96·2%
2 50		750° C.					
	3 00	748° C.	15	7·5132 grams.	0·5326	26·6	98·8%
3 47		748° C.					
	4 17	758° C.	45	7·5121 grams	0·5334	26·7	99·1%
4 40		748° C.					
	4 55	753° C.	60	7·5116 grams.	0·5342	26·7	99·1%

Initial weight of boat + dried oxide = 8·0458 grams.
Initial weight of Co_3O_4 = 2·0000 grams

Reduction of Co_3O_4 with CO at 900° C.

Run XVII—July 27, 1913.

Average temperature 900° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
4 11		902° C.	0	8·0430 grams.			
	4 16	907° C.	5	7·5136 grams.	0·5294	26·5	98·2%
4 41		902° C.					
	4 51	892° C.	15	7·5052 grams.	0·5378	26·9	99·8%
5 20		902° C.					
	5 50	902° C.	45	7·5040 grams.	0·5390	27·0	100·0%
11 03		902° C.					
	11 18	893° C.	60	7·5040 grams.	0·5390	27·0	100·0%

Initial weight of boat + dried oxide = 8·0430 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

Run XVIII—July 23, 1913.

Average temperature 900° C.

Time of placing boat in furnace	Time of removal of boat	Temperature	Time of reduction in mins.	Weight of boat + Co_3O_4	Loss in weight in grams.	Loss in weight in per cent.	Reduction where 100% is complete reduction
2 53		902° C.	0	8·0430 grams.			
	2 58	892° C.	5	7·5118 grams.	0·5312	26·6	98·8%
2.22		900° C.					
	2 32	900° C.	15	7·5062 grams.	0·5368	26·8	99·7%
2 52		902° C.					
	3 22	890° C.	45	7·5048 grams.	0·5382	26·9	99·8%
3 51		902° C.					
	4 06	910° C.	60	7·5048 grams.	0·5382	26·9	99·8%

Initial weight of boat + dried oxide = 8·0430 grams.
Initial weight of Co_3O_4 = 2·0000 grams.

The check between the composition of the oxide used for these CO reduction experiments, as determined by analysis (page 23), and as determined by the reduction experiments themselves, is entirely satisfactory. For a further discussion see pages 3 -35.

Conclusions

(a) The reduction of Co_3O_4 to metallic cobalt by carbon monoxide gas takes place very rapidly at all temperatures above 600° C.

(b) Between 350° C. and 450° C., carbon monoxide at first reduces Co_3O_4 to cobalt, but after a time the finely divided cobalt decomposes the CO gas, depositing carbon.

(c) At temperatures between 500° C. and 750° C., over 90% of the reduction of Co_3O_4 to Co takes place in a few minutes, but a further reduction to completion takes place very slowly.

(d) Between 750° C. and 900° C., the amount of reduction of Co_3O_4 to Co, which takes place during the first few minutes, increases very rapidly, and at the higher temperatures it is complete.

(e) Where producer gas is available it should offer a cheap and efficient means of producing large quantities of pure metallic cobalt from the oxide.

(f) For the production of cobalt from Co_3O_4 by CO, the charge must be completely cooled in an atmosphere of CO.

REDUCTION OF COBALT OXIDE WITH ALUMINIUM

The molecular heat of formation of aluminium oxide (Al_2O_3) is 392,600 kilogram calories, and is greater than that of any other metallic oxide. The molecular heat of formation of ferric oxide (Fe_2O_3) is correspondingly 195,600 kilogram calories. It is, therefore, obvious, that if finely divided aluminium be intimately mixed with ferric oxide (Fe_2O_3), the latter possibly in the form of rolling mill scale, that the reaction

$$Fe_2O_3+2\ Al=Al_2O_3+2\ Fe$$

will take place, provided the temperature be raised at some point in the mixture sufficient to start the reaction. This principle has been used by the Goldschmidt Thermit Co. to produce molten iron for welding purposes.

It is obvious that for every 160 kilograms of ferric oxide and 54 kilograms of metallic aluminium that are mixed together and fired in this way, there are developed $392{,}600-195{,}600=197{,}000$ kilogram calories of heat. This is sufficient to raise the entire mass to a white heat, so that the molten iron readily settles to the bottom from where it may be tapped.

In a similar manner, metallic cobalt may be prepared by reduction of cobalt oxide with aluminium according to the reaction

$$3\ Co_3O_4+8\ Al=4\ Al_2O_3+9\ Co.$$

The molecular heats of formation of FeO, Fe_2O_3, and Fe_3O_4, and of CoO, Co_2O_3, and Co_2O_4, are given in the following table:—

Molecular Heats of Formation

FeO	65,700[1]	CoO	50,500[2]
Fe_2O_3	195,600[1]	Co_2O_3	146,000[3]
Fe_3O_4	270,800[1]	Co_3O_4	193,400[2]

It is, therefore, obvious that for every 723 kilograms Co_3O_4 and 216 kilograms of aluminium that are mixed together and fired, there are developed $4\times392{,}600-3\times193{,}400=990{,}200$ kilogram calories of heat. We would, therefore, expect a reaction quite as vigorous, if not more vigorous, than the corresponding one with ferric oxide.

Experiments on the Reduction of Co_3O_4 with Metallic Aluminium

Experiments were tried, October 1912, using a standard Goldschmidt Thermit conical welding furnace, as shown in Plate VIII. Into this was charged 5–10 pounds of finely divided Co_3O_4 with the theoretical amount of aluminium, according to the equation

$$3\ Co_3O_4+8\ Al=4\ Al_2O_3+9\ Co.$$

The reaction was started by lighting a fuse of finely divided aluminium and potassium chlorate, rolled in a piece of tissue paper. The furnace fired with extreme violence, often blowing off the cover of the furnace, and in every case becoming an intense white heat.

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[1] Metallurgical Calculations, J. W. Richards, Part I, 1908, page 16.
[2] Tables Annuelles, Internationalles des Constantes, Vol. I, 1910, page 428.
[3] Computed.

PLATE VIII.

Crucible for the reduction of Co_3O_4 with Al: in position over mould.

The vigour of the reaction was so great that the lining of the furnace, although the best alundum-magnesite-cement mixture, would stand up only for two or three charges.

The Metal

The metal produced in this manner was readily tapped from the bottom of the furnace into iron or sand moulds. It frequently contained less than 0·1% of aluminium, and, of course, was carbon free.

The various metals, chromium, molybdenum, etc., made by the Goldschmidt Co. by this method, as they have come to us, run about 0·5% in aluminium and are carbon free.

Conclusions

This aluminium reduction method can obviously be used with considerable satisfaction where absolutely carbon free metal is required, and where a considerable cost is not prohibitive. Moreover, it affords a method of preparing cobalt-aluminium alloys at once by adding an excess of metallic aluminium.

The price of crude aluminium such as might be used for this purpose is in the neighbourhood of 17 cents per pound. One pound of aluminium will reduce and melt in this way a little over two pounds of metallic cobalt. Therefore, there is a charge of 17 cents in the form of 1 pound of metallic aluminium, for the power for reducing and melting two pounds of metallic cobalt. There might, of course, be some return for the fused aluminium oxide which resulted from the process, but even allowing liberally for this, the costs are very high as compared with the carbon and CO method of reduction described elsewhere in this paper.

It is obvious that the heating costs must be high by the aluminium method, for heat is being supplied at a temperature greater than 2100° C., that is at a temperature far in excess of what is required for the reduction of the oxide and the melting of the metal, and with consequent attendant increased losses, due to conduction and radiation.

OXIDES OF COBALT

The following oxides of cobalt have been described in various places throughout the literature: Co_2O, CoO, Co_8O_9, Co_6O_7, Co_4O_5, Co_3O_4, Co_7O_{10}, Co_2O_3, $Co_{12}O_{19}$, Co_3O_5, CoO_2, and considerable disagreement is to be found among the statements concerning them.

The existence of many of these compounds is doubtful, and there are but three of them which particularly concern the commercial manufacturer of cobalt oxide—Co_3O_4 ,Co_6O_7, and CoO. These concern us in the production of metallic cobalt. We shall, therefore, describe these three oxides as we have observed them in the course of our experiments.

Cobalto-Cobaltic Oxide (Co_3O_4)

The ordinary black commercial cobalt oxide which has been prepared from the hydrate by calcining in the neighbourhood of 750° C., is a mixture of Co_3O_4 and Co_6O_7, but largely the former.

There is an abundance of proof throughout this paper that this black oxide is largely Co_3O_4, of which the following may be particularly noted:—

(a) The purified cobalt oxide used for hydrogen reduction experiments, making allowance for the impurities according to the analyses, was computed to contain 72·9% cobalt. The hydrogen reduction experiments, using this same oxide, showed wherever the reduction was complete, a loss of oxygen amounting to 27·0%. As was shown on pages 14 and 20, this checks with the 72·9% of cobalt with allowance made for the slight impurities. Hence, this black oxide must be largely Co_3O_4, as may be seen from the following theoretical percentages:—

Co_2O_3	71·1%	cobalt
Co_3O_4	73·4%	"
Co_6O_7	75·9%	"
CoO	78·8%	"

(b) The purified cobalt oxide used for the carbon monoxide experiments, making allowance for the impurities according to the analysis, was computed to contain 72·9% cobalt. The CO reduction experiments, using this same oxide showed wherever reduction was complete, a loss of oxygen amounting to 27·0%. As was shown on pages 23 and 31, this checks with 72·9% cobalt, with allowance made for the slight impurities. Hence, this black oxide must be largely Co_3O_4 according to the table under (a).

(c) As a further proof that black oxide calcined at a good red heat is Co_3O_4, the following experiment was tried:—

A pure black hydroxide of cobalt was made from electrolytic cobalt by the potassium-cobalti-nitrite method. This was calcined to constant weight at 105° C., yielding a chocolate brown powder, which was uniform under the microscope.

Several samples of this brown powder were calcined to constant weight at 640° C., and in each instance showed a loss of weight between 11·5% and 11·8%. Therefore, the brown powder corresponds very closely to $Co_2O_3.H_2O$.

The material resulting from these calcinations was a black powder identical in appearance under the microscope with the black cobalt oxide of commerce. A sample of this previously calcined black oxide was calcined at a red heat to a constant weight of 0·8300 grams. The same sample was then completely reduced with a mixture of hydrogen and carbon monoxide gas at 900° C., which brought it to a constant weight of 0·6063 grams. Thus, the loss in weight was 27·2%.

Except for traces, this material was free from non-reducible substances, so that the oxide contained 72·8% cobalt, against 73·4%, corresponding theoretically with Co_3O_4.

This was checked several times, which substantiates the statement that black cobalt oxide is Co_3O_4.

(d) A further experiment was performed as follows: black oxide was brought to constant weight at 640° C., and immediately thereafter brought to constant weight by heating to 1020° C. This experiment was tried several times and in every instance the percentage loss in weight was found to be very close to 7·1%. The resulting grey oxide at 1020° C. analysed 79·3% Co, corresponding very well with CoO (78·8% Co).

The theoretical loss in passing from Co_3O_4 to CoO is 6·6%. As against this, the theoretical loss passing from Co_3O_4 to Co_6O_7 would be 3·3%, and correspondingly, passing from Co_6O_7 to CoO the loss would be 3·3%. Thus, there is very little doubt but that our reduction of the black oxide formed at red heat, to the grey at 1020° C., corresponds with the transition from Co_3O_4 to CoO.

(e) Two independent samples of brown $Co_2O_3.H_2O$, calcined to constant weight at 640° C., analysed for cobalt[1] respectively 74·7% and 73·8%. This analysis is between Co_3O_4=73·4% Co and Co_6O_7=75·9% Co. This black oxide is, therefore, largely Co_3O_4 with some Co_6O_7.

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[1] Including very small amounts of Ni and Fe.

The black hydrated cobalt oxide, as formed commercially by precipitation from a chloride or sulphate solution with bleach[1], or the brown $Co_2O_3 \cdot H_2O$, may be calcined at any temperature between 385° C. and 910° C., to yield substantially the same product, but in practice it is better to calcine at a good red temperature, in order that the calcination may take place with reasonable speed.

That there is a range between 385° C. and 910° C., through which very little oxidation or reduction of the black Co_3O_4 takes place, is shown by the following figures:—

Starting with Co_3O_4, heated to constant weight at 385° C. the

loss in weight heating it to constant weight at	640° C.	0·7%
loss " " " " " " " "	770° C.	1·2%
loss " " " " " " " "	860° C.	2·1%
loss " " " " " " " "	910° C.	2·5%

Just above 910° C., however, the reduction begins to take place very rapidly, and the black Co_3O_4 reacts to become grey CoO. Continuing the experiment for which the figures above are given, we have:

Loss in weight heating it to constant weight at	980° C.	7·0%

Co_3O_4 shows no trace of being magnetic.

The Oxide (Co_6O_7)

Co_6O_7 is not to be distinguished from Co_3O_4 either in appearance or in method of preparation; in fact, we have not succeeded in forming a pure oxide of cobalt which analysed very close to 75·9%. On the other hand, as will be noticed in many places throughout this paper, the analyses of the material obtained by calcining at a red heat are frequently something in excess of 73·4% after making allowance for impurities. We, therefore, assume that a certain amount of Co_6O_7 accompanies the Co_3O_4.

Cobalt Monoxide (CoO)

Cobalt monoxide is the stable oxide of cobalt when calcination takes place at a high temperature, that is, in the neighbourhood of 1000° C.

It is a grey powder and may be reduced to the metal by heating with carbon monoxide gas at any temperature above 450° C., or with hydrogen gas at any temperature above 250° C.

Cobalt monoxide also exists in an allotropic form which is a yellow-green powder. Either the yellow-green or the grey cobalt monoxide oxidizes to Co_3O_4, or to a mixture of Co_3O_4 and Co_6O_7 when heated to any temperature between 385° C. and 910° C. The yellow-green variety is readily formed by heating Co_3O_4 with 2 to 3% by weight of C at temperatures in the neighbourhood of 900° C.

Numerous analyses of the purified grey oxide have been made, which range around the theoretical value 78·8%. The following experiment was tried to prove that yellow-green oxide is an allotropic form of the grey CoO.

Black Co_3O_4 calcined at 640° C. to constant weight was then calcined to constant weight at 1020° C. It lost thereby 7·1% in weight, and the product was grey CoO. Yellow-green CoO, produced by the reduction of black Co_3O_4 with hydrogen at 300° C., was calcined to constant weight in air at 640° C., gaining thereby 6·5% in weight and becoming black. This experiment, like the others, indicates that the grey and the yellow-green

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[1] See page 3

oxides are identical to within such limits that if the yellow-green be CoO, the grey cannot depart from it by more than the formula $Co_{19}O_{20}$. Such differences as there are, however, seem uniformly to show that the grey has slightly the greater oxygen content of the two.

A further experiment was performed with the yellow-green oxide as follows: freshly prepared yellow-green oxide was reduced to metal with hydrogen and carbon monoxide gas, and brought to constant weight. During the reduction the loss in weight was 21·5% in one case and 21·3% in another, corresponding very well with the reduction of CoO to metallic cobalt which would be 21·3%.

Both the grey and the green CoO are non-magnetic, and the samples of grey prepared by us, as well as those obtained from commercial sources, are homogeneous powders under 100 diameters magnification.

Nearly 1,000 pounds of commercial black cobalt oxide have been given to this laboratory for these experiments, and the parts to follow, by The Deloro Mining and Reduction Co., Deloro, Ontario, to whom we take this opportunity of expressing our thanks. We particularly thank Prof. S. F. Kirkpatrick in this connexion, and as well for many valuable suggestions during the progress of these researches.

The properties of the metal, as prepared by the different methods discussed in this paper, are not considered here, as a discussion of them will form part of the publication of another part of these researches soon to follow under the title, "A Study of the Physical Properties of the Metal Cobalt."

CANADA
DEPARTMENT OF MINES
HON. LOUIS CODERRE, MINISTER; R. W. BROCK, DEPUTY MINISTER;

MINES BRANCH
EUGENE HAANEL, PH.D., DIRECTOR.

REPORTS AND MAPS OF ECONOMIC INTEREST

PUBLISHED BY THE

MINES BRANCH.

REPORTS.

1. Mining Conditions in the Klondike, Yukon. Report on—by Eugene Haanel, Ph.D., 1902.

†2. Great Landslide at Frank, Alta. Report on—by R. G. McConnell and R. W. Brock, M.A., 1903.

†3. Investigation of the different electro-thermic processes for the smelting of iron ores, and the making of steel, in operation in Europe. Report of Special Commission—by Dr. Haanel, 1904.

†4. Rapport de la Commission nommée pour étudier les divers procédés électro-thermiques pour la réduction des minerais de fer et la fabrication de l'acier employés en Europe—by Dr. Haanel. (French Edition), 1905.

5. On the location and examination of magnetic ore deposits by magnetometric measurements—by Dr. Haanel, 1904.

†7. Limestones, and the Lime Industry of Manitoba. Preliminary Report on—by J. W. Wells, 1905.

†8. Clays and Shales of Manitoba: Their Industrial Value. Preliminary Report on—by J. W. Wells, 1905.

†9. Hydraulic Cements (Raw Materials) in Manitoba: Manufacture and Uses of. Preliminary Report on—by J. W. Wells, 1905.

†10. Mica: Its Occurrence, Exploitation, and Uses—by Fritz Cirkel, M.E., 1905. (See No. 118.)

†11. Asbestos: Its Occurrence, Exploitation, and Uses—by Fritz Cirkel, 1905. (See No. 69.)

†12. Zinc Resources of British Columbia and the Conditions affecting their Exploitation. Report of the Commission appointed to investigate—by W. R. Ingalls, 1905.

†16. *Experiments made at Sault Ste. Marie, under Government auspices, in the smelting of Canadian iron ores by the electro-thermic process. Final Report on—by Dr. Haanel, 1907.

†17. Mines of the Silver-Cobalt Ores of the Cobalt district: Their Present and Prospective Output. Report on—by Dr. Haanel, 1907.

†18. Graphite: Its Properties, Occurrence, Refining, and Uses—by Fritz Cirkel, 1907.

†19. Peat and Lignite: Their Manufacture and Uses in Europe—by Erik Nystrom, M.E., 1908.

†20. Iron Ore Deposits of Nova Scotia. Report on (Part I)—by Dr. J. E. Woodman.

†21. Summary Report of Mines Branch, 1907-8.

22. Iron Ore Deposits of Thunder Bay and Rainy River districts. Report on—by F. Hille, M.E.

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*A few copies of the Preliminary Report, 1906, are still available.
†Publications marked thus † are out of print.

†23. Iron Ore Deposits, along the Ottawa (Quebec side) and Gatineau rivers. Report on—by Fritz Cirkel.

24. General Report on the Mining and Metallurgical Industries of Canada, 1907-8.

25. The Tungsten Ores of Canada. Report on—by Dr. T. L. Walker.

26. The Mineral Production of Canada, 1906. Annual Report on—by John McLeish, B.A.

26a. French translation: The Mineral Production of Canada, 1906. Annual Report on—by John McLeish.

27. The Mineral Production of Canada, 1907. Preliminary Report on—by John McLeish.

†27a. The Mineral Production of Canada, 1908. Preliminary Report on—by John McLeish.

†28. Summary Report of Mines Branch, 1908.

†28a. French translation: Summary Report of Mines Branch, 1908.

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30. Investigation of the Peat Bogs and Peat Fuel Industry of Canada, 1908. Bulletin No. 1—by Erik Nystrom and A. Anrep, Peat Expert.

32. Investigation of Electric Shaft Furnace, Sweden. Report on—by Dr. Haanel.

47. Iron Ore Deposits of Vancouver and Texada islands. Report on—by Einar Lindeman, M.E.

†55. Report on the Bituminous, or Oil-shales of New Brunswick and Nova Scotia; also on the Oil-shale industry of Scotland—by Dr. R. W. Ells.

58. The Mineral Production of Canada, 1907 and 1908. Annual Report on—by John McLeish.

NOTE.—*The following preliminary bulletins were published prior to the issuance of the Annual Report for 1907-8.*

†31. Production of Cement in Canada, 1908.

42. Production of Iron and Steel in Canada during the Calendar Years 1907 and 1908.

43. Production of Chromite in Canada during the Calendar Years 1907 and 1908.

44. Production of Asbestos in Canada during the Calendar Years 1907 and 1908.

†45. Production of Coal, Coke, and Peat in Canada during the Calendar Years 1907 and 1908.

46. Production of Natural Gas and Petroleum in Canada during the Calendar Years 1907 and 1908.

59. Chemical Analyses of Special Economic Importance made in the Laboratories of the Department of Mines, 1906-7-8. Report on—by F. G. Wait, M.A., F.C.S. (With Appendix on the Commercial Methods and Apparatus for the Analysis of Oil-shales—by H. A. Leverin, Ch. E.)

Schedule of Charges for Chemical Analyses and Assays.

†62. Mineral Production of Canada, 1909. Preliminary Report on—by John McLeish

63. Summary Report of Mines Branch, 1909.

67. Iron Ore Deposits of the Bristol Mine, Pontiac county, Quebec. Bulletin No. 2—by Einar Lindeman and Geo. C. Mackenzie, B.Sc.

†68. Recent Advances in the Construction of Electric Furnaces for the Production of Pig Iron, Steel, and Zinc. Bulletin No. 3—by Dr. Haanel.

69. Chrysotile-Asbestos: Its Occurrence, Exploitation, Milling, and Uses. Report on—by Fritz Cirkel. (Second Edition, enlarged.)

†71. Investigation of the Peat Bogs and Peat Industry of Canada, 1909-10; to which is appended Mr. Alf. Larson's Paper on Dr. M. Ekenberg's Wet-Carbonizing Process; from Teknisk Tidskrift, No. 12, December 26, 1908—translation by Mr. A. v. Anrep, Jr.; also a translation of Lieut. Ekelund's Pamphlet entitled 'A Solution of the Peat Problem,' 1909, describing the Ekelund Process for the Manufacture of Peat Powder, by Harold A. Leverin, Ch.E. Bulletin No. 4—by A. v. Anrep (Second Edition, enlarged).

81. French Translation: Chrysotile-Asbestos: Its Occurrence, Exploitation, Milling, and Uses. Report on by Fritz Cirkel.

82. Magnetic Concentration Experiments. Bulletin No. 5—by Geo. C. Mackenzie.

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†Publications marked thus † are out of print.

83. An investigation of the Coals of Canada with reference to their Economic Qualities: as conducted at McGill University under the authority of the Dominion Government. Report on—by J. B. Porter, E.M., D.Sc., R. J. Durley, Ma.E., and others—
    Vol. I—Coal Washing and Coking Tests.
    Vol. II—Boiler and Gas Producer Tests.
    Vol. III—
      Appendix I
        Coal Washing Tests and Diagrams.
    Vol. IV—
      Appendix II
        Boiler Tests and Diagrams.
    Vol. V—
      Appendix III
        Producer Tests and Diagrams.
    Vol. VI—
      Appendix IV
        Coking Tests.
      Appendix V
        Chemical Tests.

†84. Gypsum Deposits of the Maritime Provinces of Canada—including the Magdalen Islands. Report on—by W. F. Jennison, M.E. (See No. 245.)

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Note.—*The following preliminary bulletins were published prior to the issuance of the Annual Report for 1909.*

†79. Production of Iron and Steel in Canada during the Calendar Year 1909.

†80. Production of Coal and Coke in Canada during the Calendar Year 1909.

85. Production of Cement, Lime, Clay Products, Stone, and other Structural Materials during the Calendar Year 1909.

89. Reprint of Presidential address delivered before the American Peat Society of Ottawa, July 25, 1910. By Dr. Haanel.

90. Proceedings of Conference on Explosives.

92. Investigation of the Explosives Industry in the Dominion of Canada, 1910. Report on—by Capt. Arthur Desborough. (Second Edition.)

93. Molybdenum Ores of Canada. Report on—by Professor T. L. Walker, Ph.D.

100. The Building and Ornamental Stones of Canada, Vol. I. Report on—by Professor W. A. Parks, Ph.D.

100a. French translation: The Building and Ornamental Stones of Canada, Vol. I. Report on—by W. A. Parks.

102. Mineral Production of Canada, 1910. Preliminary Report on—by John McLeish.

†103. Summary Report of Mines Branch, 1910.

104. Catalogue of Publications of Mines Branch, from 1902 to 1911; containing Tables of Contents and List of Maps, etc.

105. Austin Brook Iron-bearing district. Report on—by E. Lindeman.

110. Western Portion of Torbrook Iron Ore Deposits, Annapolis county, N.S. Bulletin No. 7—by Howells Fréchette, M.Sc.

111. Diamond Drilling at Point Mamainse, Ont. Bulletin No. 6—by A. C. Lane, Ph. D., with Introductory by A. W. G. Wilson, Ph.D.

118. Mica: Its Occurrence, Exploitation, and Uses. Report on—by Hugh S. de Schmid, M.E.

142. Summary Report of Mines Branch, 1911.

143. The Mineral Production of Canada, 1910. Annual Report on—by John McLeish.

Note.—*The following preliminary Bulletins were published prior to the issuance of the Annual Report for 1910.*

†114. Production of Cement, Lime, Clay Products, Stone, and other Structural Materials in Canada, 1910.

†115. Production of Iron and Steel in Canada during the Calendar Year 1910.

†116. Production of Coal and Coke in Canada during the Calendar Year 1910.

†117. General Summary of the Mineral Production of Canada during the Calendar Year 1910.

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†Publications marked thus † are out of print.

145. Magnetic Iron Sands of Natashkwan, Saguenay county, Que. Report on—by Geo. C. Mackenzie.

†150. The Mineral Production of Canada, 1911. Preliminary Report on—by John McLeish.

151. Investigation of the Peat Bogs and Peat Industry of Canada, 1910-11. Bulletin No. 8—by A. v. Anrep.

154. The Utilization of Peat Fuel for the Production of Power, being a record of experiments conducted at the Fuel Testing Station, Ottawa, 1910-11. Report on—by B. F. Haanel, B.Sc.

155. French translation: The Utilization of Peat Fuel for the Production of Power, being a Record of Experiments conducted at the Fuel Testing Station, Ottawa, 1910-11. Report on—by B. F. Haanel.

156. French translation: The Tungsten Ores of Canada. Report on—by Dr. T. L. Walker.

167. Pyrites in Canada: Its Occurrence, Exploitation, Dressing, and Uses. Report on—by A. W. G. Wilson.

170. The Nickel Industry: with Special Reference to the Sudbury region, Ont. Report on—by Professor A. P. Coleman, Ph.D.

184. Magnetite Occurrences along the Central Ontario Railway. Report on—by E. Lindeman.

196. French translation: Investigation of the Peat Bogs and Peat Industry of Canada, 1909-10; to which is appended Mr. Alf. Larson's paper on Dr. M. Ekenburg's Wet-Carbonizing Process: from Teknisk Tidskrift, No. 12, December 26, 1908—translation by Mr. A. v. Anrep; also a translation of Lieut. Ekelund's Pamphlet entitled "A Solution of the Peat Problem," 1909, describing the Ekelund Process for the Manufacture of Peat Powder, by Harold A. Leverin Ch. E. Bulletin No. 4—by A. v. Anrep. (Second Edition, enlarged.)

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> NOTE.—*The following preliminary Bulletins were published prior to the issuance of the Annual Report for 1911.*
>
> 181. Production of Cement, Lime, Clay Products, Stone, and other Structural Materials in Canada during the Calendar Year 1911. Bulletin on—by John McLeish.
>
> †182. Production of Iron and Steel in Canada during the Calendar Year 1911. Bulletin on—by John McLeish.
>
> 183. General Summary of the Mineral Production in Canada during the Calendar Year 1911. Bulletin on—by John McLeish.
>
> 199. Production of Copper, Gold, Lead, Nickel, Silver, Zinc, and other Metals of Canada, during the Calendar Year 1911. Bulletin on—by John McLeish.
>
> 200. The Production of Coal and Coke in Canada during the Calendar Year 1911. Bulletin on—by John McLeish.

202. French translation: Graphite: Its Properties, Occurrence, Refining, and Uses—by Fritz Cirkel, 1907.

216. Mineral Production of Canada, 1912. Preliminary Report on—by John McLeish.

224. Summary Report of the Mines Branch, 1912.

226. French translation: Chrome Iron Ore Deposits of the Eastern Townships. Monograph on—by Fritz Cirkel. (Supplementary Section: Experiments with Chromite at McGill University—by Dr. J. B. Porter.)

227. Sections of the Sydney Coal Fields—by J. G. S. Hudson.

†229. Summary Report of the Petroleum and Natural Gas Resources of Canada, 1912—by F. G. Clapp. (See No. 224.)

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233. French translation: Gypsum Deposits of the Maritime Provinces of Canada—including the Magdalen Islands Report on—by W. F. Jennison.

262. The Mineral Production of Canada during the Calendar Year 1912. Annual Report on—by John McLeish.

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>
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†**Publications marked thus † are out of print.**

247. Production of Iron and Steel in Canada during the Calendar Year 1912. Bulletin on—by John McLeish.

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257. Production of Cement, Lime, Clay Products, Stone, and other Structural Materials during the Calendar Year 1912. Report on—by John McLeish.

258. Production of Coal and Coke in Canada, during the Calendar Year 1912. Bulletin on—by John McLeish.

259. Preparation of Metallic Cobalt by Reduction of the Oxide. Report on—by H. T. Kalmus B.Sc., Ph.D.

NOTE.—*Lists of manufacturers of clay products, stone quarry operators, and operators of lime-kilns, are prepared annually by the Division of Mineral Resources and Statistics, and copies may be had on application.*

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56. French translation: Bituminous or Oil-shales of New Brunswick and Nova Scotia, also on the Oil-shale Industry of Scotland—by R. W. Ells

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203. Building Stones of Canada—Vol. II: Building and Ornamental Stones of the Maritime Provinces. Report on—by W. A. Parks.

209. The Copper Smelting Industry of Canada. Report on—by A. W. G. Wilson.

222. Lode Mining in Yukon: An Investigation of the Quartz Deposits of the Klondike Division. Report on—by T. A. MacLean, B.A.Sc.

245. Gypsum in Canada: Its Occurrence, Exploitation, and Technology. Report on—by L. H. Cole.

254. Calabogie Iron-Bearing District. Report on—by E. Lindeman.

263. French translation: Recent Advances in the Construction of Electric Furnaces for the Production of Pig Iron, Steel, and Zinc. Bulletin No. 3—by Dr. Haanel.

264. French translation: Mica: Its Occurrences, Exploitation, and Uses. Report on—by Hugh S. de Schmid.

265. French translation: Annual Mineral Production of Canada, 1911. Report on—by John McLeish.

MAPS

†6. Magnetometric Survey, Vertical Intensity: Calabogie Mine, Bagot township, Renfrew county, Ontario—by E. Nystrom, 1904. Scale 60 feet = 1 inch. Summary report, 1905. (See Map No. 249.)

†13. Magnetometric Survey of the Belmont Iron Mines, Belmont township, Peterborough county, Ontario—B. F. Haanel, 1905. Scale 60 feet = 1 inch. Summary report, 1905. (See Map No. 186.)

†14. Magnetometric Survey of the Wilbur Mine, Lavant township, Lanark county, Ontario—by B. F. Haanel, 1905. Scale 60 feet = 1 inch. Summary report, 1905.

†33. Magnetometric Survey, Vertical Intensity: Lot 1, Concession VI, Mayo township, Hastings county, Ontario—by Howells Fréchette, 1909. Scale 60 feet = 1 inch.

†34. Magnetometric Survey, Vertical Intensity: Lots 2 and 3, Concession VI, Mayo township, Hastings county Ontario—by Howells Fréchette, 1909. Scale 60 feet = 1 inch.

†35. Magnetometric Survey, Vertical Intensity: Lots 10, 11, and 12, Concession IX, and Lots 11 and 12, Concession VIII, Mayo township, Hastings county, Ontario—by Howells Fréchette, 1909. Scale 60 feet = 1 inch.

NOTE.—1. Maps marked thus * are to be found only in reports.
2. Maps marked thus † have been printed independently of reports, hence can be procured separately by applicants.

*36. Survey of Mer Bleue Peat Bog, Gloucester township, Carleton county, and Cumberland township, Russell county, Ontario—by Erik Nystrom, and A. v. Anrep. (Accompanying report No. 30.)

*37. Survey of Alfred Peat Bog, Alfred and Caledonia townships, Prescott county, Ontario—by Erik Nystrom, and A. v. Anrep. (Accompanying report No. 30.)

*38. Survey of Welland Peat Bog, Wainfleet and Humberstone townships, Welland county, Ontario—by Erik Nystrom and A. v. Anrep. (Accompanying report No. 30.)

*39. Survey of Newington Peat Bog, Osnabruck, Roxborough, and Cornwall townships, Stormont county, Ontario—by Erik Nystrom and A. v. Anrep. (Accompanying report No. 30.)

*40. Survey of Perth Peat Bog, Drummond township, Lanark county, Ontario—by Erik Nystrom and A. v. Anrep. (Accompanying report No. 30.)

*41. Survey of Victoria Road Peat Bog, Bexley and Carden townships, Victoria county, Ontario—by Erik Nystrom and A. v. Anrep. (Accompanying report No. 30.)

*48. Magnetometric Survey of Iron Crown claim at Klaanch river, Vancouver island, B.C.—by E. Lindeman. Scale 60 feet = 1 inch. (Accompanying report No. 47.)

*49. Magnetometric Survey of Western Steel Iron claim, at Sechart, Vancouver island, B.C.—by E. Lindeman. Scale 60 feet = 1 inch. (Accompanying report No. 47.)

*53. Iron Ore Occurrences, Ottawa and Pontiac counties, Quebec, 1908—by J. White and Fritz Cirkel. (Accompanying report No. 23.)

*54. Iron Ore Occurrences, Argenteuil county, Quebec, 1908—by Fritz Cirkel. (Accompanying report No. 23.)

†57. The Productive Chrome Iron Ore District of Quebec—by Fritz Cirkel. (Accompanying report No. 29.)

†60. Magnetometric Survey of the Bristol Mine, Pontiac county, Quebec—by E. Lindeman. Scale 200 feet = 1 inch. (Accompanying report No. 67.)

*61. Topographical Map of Bristol Mine, Pontiac county, Quebec—by E. Lindeman. Scale 200 feet = 1 inch. (Accompanying report No. 67.)

†64. Index Map of Nova Scotia: Gypsum—by W. F. Jennison.
†65. Index Map of New Brunswick: Gypsum—by W. F. Jennison. } (Accompanying report No. 84.)
†66. Map of Magdalen Islands: Gypsum—by W. F. Jennison.

†70. Magnetometric Survey of Northwest Arm Iron Range, Lake Timagami, Nipissing district, Ontario—by E. Lindeman. Scale 200 feet = 1 inch. (Accompanying report No. 63.)

†72. Brunner Peat Bog, Ontario—by A. v. Anrep.
†73. Komoka Peat Bog, Ontario—by A. v. Anrep. } (Accompanying report No. 71.)
†74. Brockville Peat Bog, Ontario—by A. v. Anrep.

†75. Rondeau Peat Bog, Ontario—by A. v. Anrep.
†76. Alfred Peat Bog, Ontario—by A. v. Anrep. } (Accompanying report No. 71.)
†77. Alfred Peat Bog, Ontario: Main Ditch profile—by A. v. Anrep.

†78. Map of Asbestos Region, Province of Quebec, 1910—by Fritz Cirkel. Scale 1 mile = 1 inch. (Accompanying report No. 69.)

†94. Map showing Cobalt, Gowganda, Shiningtree, and Porcupine districts—by L. H. Cole, B.Sc. (Accompanying Summary report, 1910.)

*95. General Map of Canada, showing Coal Fields. (Accompanying report No. 83—by Dr. J. B. Porter.)

*96. General Map of Coal Fields of Nova Scotia and New Brunswick. (Accompanying report No. 83—by Dr. J. B. Porter.)

*97. General Map showing Coal Fields in Alberta, Saskatchewan, and Manitoba. (Accompanying report No. 83—by Dr. J. B. Porter.)

*98. General Map of Coal Fields in British Columbia. (Accompanying report No. 83—by Dr. J. B. Porter.)

*99. General Map of Coal Field in Yukon Territory. (Accompanying report No. 83—by Dr. J. B. Porter.)

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†106. Austin Brook Iron Bearing district, Bathurst township, Gloucester county, N.B.—by E. Lindeman. Scale 400 feet = 1 inch. (Accompanying report No. 105.)

†107 Magnetometric Survey, Vertical Intensity: Austin Brook Iron Bearing District—by E. Lindeman. Scale 400 feet = 1 inch. (Accompanying report No. 105.)

*108. Index Map showing Iron Bearing Area at Austin Brook—by E. Lindeman. (Accompanying report No. 105.)

*112. Sketch plan showing Geology of Point Mamainse, Ont.—by Professor A. C. Lane. Scale, 4,000 feet = 1 inch. (Accompanying report No. 111.)

†113. Holland Peat Bog, Ontario—by A. v. Anrep. (Accompanying report No. 151.)

*119-137. Mica: Township maps, Ontario and Quebec—by Hugh S. de Schmid. (Accompanying report No. 118.)

†138. Mica: Showing Location of Principal Mines and Occurrences in the Quebec Mica Area—by Hugh S. de Schmid. Scale 3·95 miles = 1 inch. (Accompanying report No. 118.)

†139. Mica. Showing Location of Principal Mines and Occurrences in the Ontario Mica Area—by Hugh S. de Schmid. Scale 3·95 miles = 1 inch. (Accompanying report No. 118.)

†140. Mica: Showing Distribution of the Principal Mica Occurrences in the Dominion of Canada—by Hugh S. de Schmid. Scale 3·95 miles = 1 inch. (Accompanying report No. 118.)

†141. Torbrook Iron Bearing District, Annapolis county, N.S.—by Howells Fréchette. Scale 400 feet = 1 inch. (Accompanying report No. 110.)

†146. Distribution of Iron Ore Sands of the Iron Ore Deposits on the North Shore of the River and Gulf of St. Lawrence, Canada—by Geo. C. Mackenzie. Scale 100 miles = 1 inch. (Accompanying report No. 145.)

†147. Magnetic Iron Sand Deposits in Relation to Natashkwan harbour and Great Natashkwan river, Que. (Index Map)—by Geo. C. Mackenzie. Scale 10 chains = 1 inch. (Accompanying report No. 145.)

†148. Natashkwan Magnetic Iron Sand Deposits, Saguenay county, Que.—by Geo. C. Mackenzie. Scale 1,000 feet = 1 inch. (Accompanying report No. 145.)

†152. Map showing the Location of Peat Bogs investigated in Ontario—by A. v. Anrep.

†153. Map Showing the Location of Peat Bogs investigated in Manitoba—by A. v. Anrep.

†157. Lac du Bonnet Peat Bog, Manitoba—by A. v. Anrep.

†158. Transmission Peat Bog, Manitoba—by A. v. Anrep.

†159. Corduroy Peat Bog, Manitoba—by A. v. Anrep.

†160. Boggy Creek Peat Bog, Manitoba—by A. v. Anrep.

†161. Rice Lake Peat Bog, Manitoba—by A. v. Anrep

†162. Mud Lake Peat Bog, Manitoba—by A. v. Anrep.

†163. Litter Peat Bog, Manitoba—by A. v. Anrep.

(Accompanying report No. 151.)

†164. Julius Peat Litter Bog, Manitoba—by A. v. Anrep.

†165. Fort Frances Peat Bog, Ontario—by A. v. Anrep.

(Accompanying report No. 151.)

*166. Magnetometric Map of No. 3 Mine, Lot 7, Concessions V and VI, McKim township, Sudbury district, Ont.—by E. Lindeman. (Accompanying Summary report, 1911.)

†168. Map showing Pyrites Mines and Prospects in Eastern Canada, and Their Relation to the United States Market—by A. W. G. Wilson. Scale 125 miles = 1 inch. (Accompanying report No. 167.)

†171. Geological Map of Sudbury Nickel region, Ont.—by Prof. A. P. Coleman. Scale 1 mile = 1 inch. (Accompanying report No. 170.)

†172. Geological Map of Victoria Mine—by Prof. A. P. Coleman.

†173. " " Crean Hill Mine—by Prof. A. P. Coleman.

†174. " " Creighton Mine—by Prof. A. P. Coleman.

(Accompanying report No. 170.)

†175. " " showing Contact of Norite and Laurentian in vicinity of Creighton mine—by Prof. A. P. Coleman. (Accompanying report No. 170.)

NOTE.—1. Maps marked thus * are to be found only in reports.

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†176. Geological Map of Copper Cliff offset—by Prof. A. P. Coleman. (Accompanying report No. 170.)

†177. " " No. 3 Mine—by Prof. A. P. Coleman. (Accompanying report No. 170.)

†178. " " showing vicinity of Stobie and No. 3 mines—by Prof. A. P. Coleman. (Accompanying report No. 170.)

†185. Magnetometric Survey, Vertical Intensity: Blairton iron mine, Belmont township, Peterborough county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†185a. Geological Map, Blairton iron mine, Belmont township, Peterborough county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†186. Magnetometric Survey, Belmont iron mine, Belmont township, Peterborough county, Ont.—by E. Lindeman 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†186a. Geological Map, Belmont iron mine, Belmont township, Peterborough county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†187. Magnetometric Survey, Vertical Intensity: St. Charles mine, Tudor township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†187a. Geological Map, St. Charles mine, Tudor township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.

†188. Magnetometric Survey, Vertical Intensity: Baker mine, Tudor township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†188a. Geological Map, Baker Mine, Tudor township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. Accompanying report No. 184.)

†189. Magnetometric Survey, Vertical Intensity: Ridge iron ore deposits, Wollaston township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†190. Magnetometric Survey, Vertical Intensity: Coehill and Jenkins mines, Wollaston township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†190a. Geological Map, Coehill and Jenkins mines, Wollaston township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†191. Magnetometric Survey, Vertical Intensity: Bessemer iron ore deposits, Mayo township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†191a. Geological Map, Bessemer iron ore deposits, Mayo township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†192. Magnetometric Survey, Vertical Intensity: Rankin, Childs, and Stevens mines, Mayo township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†192a. Geological Map, Rankin, Childs, and Stevens mines, Mayo township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†193. Magnetometric Survey, Vertical Intensity: Kennedy property, Carlow township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†193a. Geological Map, Kennedy property, Carlow township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†194. Magnetometric Survey, Vertical Intensity: Bow Lake iron ore occurrences, Faraday township, Hastings county, Ontario—by E. Lindeman, 1911. Scale 200 feet = 1 inch. (Accompanying report No. 184.)

†204. Index Map, Magnetite occurrences along the Central Ontario Railway—by E. Lindeman, 1911. (Accompanying report No. 184.)

†205. Magnetometric Map, Moose Mountain iron-bearing district, Sudbury district, Ontario: Deposits Nos. 1, 2, 3, 4, 5, 6, and 7—by E. Lindeman, 1912. (Accompanying report No. 266.)

†205a. Geological Map, Moose Mountain iron-bearing district, Sudbury district, Ontario. Deposits Nos. 1, 2, 3, 4, 5, 6, and 7—by E. Lindeman. (Accompanying report No. 266.)

†206. Magnetometric Survey of Moose Mountain iron-bearing district, Sudbury district, Ontario: S[illegible]ern part of Deposit No. 2—by E. Lindeman, 1912. Scale, 200 feet = 1 inch. (Accompanying report N[illegible])

†207. Magnetometric Survey of Moose Mountain iron-bearing district, Sudbury district, Ontario: [illegible]sits Nos. 9, and 9A—by E. Lindeman, 1912. Scale 200 feet = 1 inch. (Accompanying report No. 266.)

†208. Magnetometric Survey of Moose Mountain iron bearing district, Sudbury district, Ontario: Deposit No. 10—by E. Lindeman, 1912. Scale 200 feet = 1 inch. (Accompanying report No. 266.)

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†208a. Magnetometric Survey, Moose Mountain iron-bearing district, Sudbury district, Ontario: Eastern portion of Deposit No. 11—by E. Lindeman, 1912. Scale, 200 feet = 1 inch. (Accompanying report No. 266.)

†208b. Magnetometric Survey, Moose Mountain iron-bearing district, Sudbury district, Ontario: Western portion of Deposit No. 11—by E. Lindeman, 1912. Scale, 200 feet = 1 inch. (Accompanying report No. 266.)

†208c General Geological Map, Moose Mountain iron-bearing district, Sudbury district, Ontario—by E. Lindeman, 1912. Scale, 800 feet = 1 inch. (Accompanying report No. 266.)

†210. Location of Copper Smelters in Canada—by A. W. G. Wilson, Ph. D. Scale, 197·3 miles = 1 inch. (Accompanying report No. 209.

†220. Mining Districts, Yukon—by T. A. MacLean. Scale 35 miles = 1 inch. (Accompanying report No. 222.)

†221. Dawson Mining District, Yukon—by T. A. MacLean. Scale 2 miles = 1 inch. (Accompanying report No. 222.)

†232. Mineral Map of Canada. Scale 100 miles = 1 inch. (Accompanying report No. 230.)

†249. Magnetometric Survey, Caldwell and Campbell mines, Calabogie district, Renfrew county, Ontario—by E. Lindeman, 1911. Scale, 200 feet = 1 inch. (Accompanying report No. 254.)

†250. Magnetometric Survey, Black Bay or Williams Mine, Calabogie district, Renfrew county, Ontario—by E. Lindeman, 1911. Scale, 200 feet = 1 inch. (Accompanying report No. 254.)

†251. Magnetometric Survey, Bluff Point iron mine, Calabogie district, Renfrew county, Ontario—by E. Lindeman, 1911. Scale, 200 feet = 1 inch. (Accompanying report No. 254.)

†252. Magnetometric Survey, Culhane mine, Calabogie district, Renfrew county, Ontario—by E. Lindeman, 1911. Scale, 200 feet = 1 inch. (Accompanying report No. 254.)

†253. Magnetometric Survey, Martel or Wilson iron mine, Calabogie district, Renfrew county, Ontario—by E. Lindeman, 1911. Scale, 200 feet = 1 inch. (Accompanying report No. 254.)

†261. Magnetometric Survey, Northeast Arm iron range, Lot 339 E. T. W. Lake Timagami, Nipissing district, Ontario—by E. Nystrom, 1903. Scale, 200 feet = 1 inch.

IN THE PRESS.

268. Map of Peat Bogs Investigated in Quebec—by A. v. Anrep, 1912.
269. Large Tea Field Peat Bog, Quebec " "
270. Small Tea Field Peat Bog, Quebec " "
271. Lanorie Peat Bog, Quebec " "
272. St. Hyacinthe Peat Bog, Quebec " "
273. Rivière du Loup Peat Bog " "
274. Cacouna Peat Bog " "
275. Le Parc Peat Bog, Quebec " "
276. St. Denis Peat Bog, Quebec " "
277. Rivière Ouelle Peat Bog, Quebec " "
278. Moose Mountain Peat Bog, Quebec " "

Address all communications to—

Director Mines Branch,
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