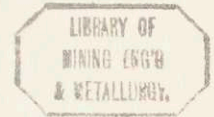


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THESIS

COMMERCIAL PRODUCTION OF  
CARBON FREE CHROMIUM OR FERROCHROME  
BY LEACHING FROM THE ORE AND ELECTROLYSIS

Respectfully submitted for the approval of the  
Faculty of Mining and Metallurgy of the Massachusetts  
Institute of Technology as partial fulfillment of the  
requirements for the Degree of Master of Science.

✓  
Signature redacted

Walter Crafts

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## INTRODUCTION

The purpose of this work was to find a commercial process for the preparation of chromium, free from carbon, for use in alloy steels. Chromium for such a use, should be either pure or alloyed only with iron. The usual metallurgical methods of removing carbon from ferro-chrome were considered, and, as the price indicates, the process is difficult and expensive. Electrolysis seemed to be the only feasible alternative.

The fused bath was considered, but given up for obvious reasons. Such a bath would have to be maintained at a very high temperature and would require a very pure source of chromium. Electrolysis of an aqueous solution also presented its difficulties. The only reasonably cheap source of chromium for such a purpose is sodium chromate. This could only be used in chromic acid solutions, which require about 15 Kw. hr. per pound of chromium. Sufficient work had not been done on the chromium sulphate and chloride solutions to know whether a continuous process could be used. If they could be used, the power cost would be about one-half that of the chromic acid bath. Chromium would have to be supplied to the chloride or sulphate solutions in its lower valence. Such a material would also be suitable for use with the chromic acid process.

The conclusion was, that to make chromium cheaply it was necessary to use the chloride or sulphate bath and to find a process for obtaining chromium in the lower valence from chromite. The problem then, divides itself naturally into two parts; (1) To get chromium from chromite by some roasting and leaching process, (2) To make possible the use of chloride or sulphate baths in a continuous process. The primary justification for the work was the matter of cost. Throughout the investigation this was considered the most important factor.

ROASTING AND LEACHING

Extraction of chromium from the ore is effected by: (1) Pyrometallurgical methods; (2) Alkaline oxidizing fusion. Neither of these methods gives a product suitable for making a low carbon chromium alloy cheaply. Some method of treatment, to be followed by acid leaching, seemed to be the best way to get the desired result.

A supply of finely ground South African chromite was obtained. The screen analysis follows.

|                                 |               |
|---------------------------------|---------------|
| On 65 mesh (opening 0.0082 in.) | 3.34 per cent |
| On 100 " ( " 0.0058 " )         | 4.14 " "      |
| On 200 " ( " 0.0029 " )         | 16.46 " "     |
| Thru 200 "                      | 76.06 " "     |

The chemical analysis of the ore follows:

|                                     |                |
|-------------------------------------|----------------|
| Cr <sub>2</sub> O <sub>3</sub>      | 46.02 per cent |
| FeO                                 | 13.24 " "      |
| Al <sub>2</sub> O <sub>3</sub>      | 14.07 " "      |
| SiO <sub>2</sub>                    | 7.37 " "       |
| MgO                                 | 15.30 " "      |
| Na <sub>2</sub> O(K <sub>2</sub> O) | 0.11 " "       |
| Loss on ignition                    | 3.66 " "       |
| Total                               | 99.77 " "      |

In order to find out what to expect from the untreated ore, it was treated with hot hydrochloric and sulphuric acids of varying strengths. The ore was stirred up with the acid in a beaker and kept at about 100°C. on a hot plate for two hours. This method of leaching was carried out through all subsequent work. The results (Table I) give a basis of comparison, but are not satisfactory as a means of obtaining soluble chromium. By

Table I.

## Leaching of Untreated Chromite

| H <sub>2</sub> SO <sub>4</sub> |                        | HCl                   |                        |
|--------------------------------|------------------------|-----------------------|------------------------|
| Concentration of Acid          | Extraction of Chromium | Concentration of Acid | Extraction of Chromium |
| 36 N                           | 19.2 %                 | 12 N                  | 7.4 %                  |
| 30                             | 16.8                   | 10                    | 10.4                   |
| 24                             | 14.0                   | 8                     | 8.3                    |
| 18                             | 13.8                   | 6                     | 6.3                    |
| 12                             | 11.7                   | 4                     | 8.1                    |
| 6                              | 13.1                   |                       |                        |

successive leachings with hot, concentrated sulphuric acid, a total of 35 per cent of the chromium in the ore was brought into solution. This was not considered to be satisfactory so that no more was done to the raw ore.

A few experiments were carried out to find the ef-

fect on the ore of sulphuric acid, when heated to 350°C. Very little increase in extraction was obtained. It was thought that a weak endothermic reaction occurred at 225°C., but control of the heat applied was very crude, so that it can not be stated positively. The results were so poor, that it was not investigated further. Attempts were made to form an alum, by the addition of potassium sulphate and sulphuric acid. These were heated to temperatures up to 500°C. without satisfactory results. The addition of sulphur in this temperature range was tried, but it also failed.

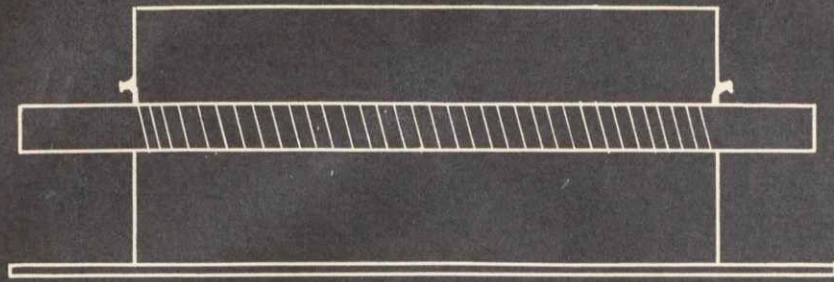
Roasting at higher temperatures was then tried. This was carried out in a tube resistance furnace (Fig. 1). The charges were thoroughly mixed and placed in sheet iron boats 8"x1"x1-1/2". Iron boats were used, since it was impossible to get refractory boats which were large enough to hold a charge of 10 grams of ore.

All the runs lasted for four hours. Temperature was indicated by a chrome-alumel thermocouple. The roasting may be classified as chloridizing, sulphatizing, and reducing.

Chloridizing was tried in order to obtain a soluble chromium salt. This would be suitable as a starting point for electrolysis. Common salt (NaCl) was used as a source of chlorine. To increase its activity, copper-free pyrite was added. A series of runs were also made with the addi-

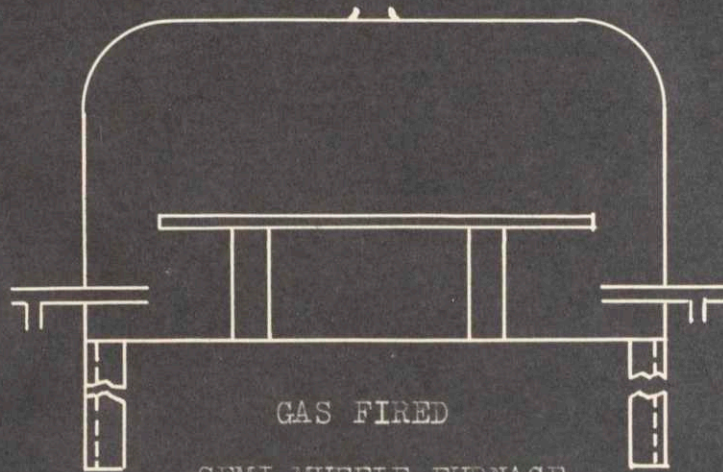


Figure 1.



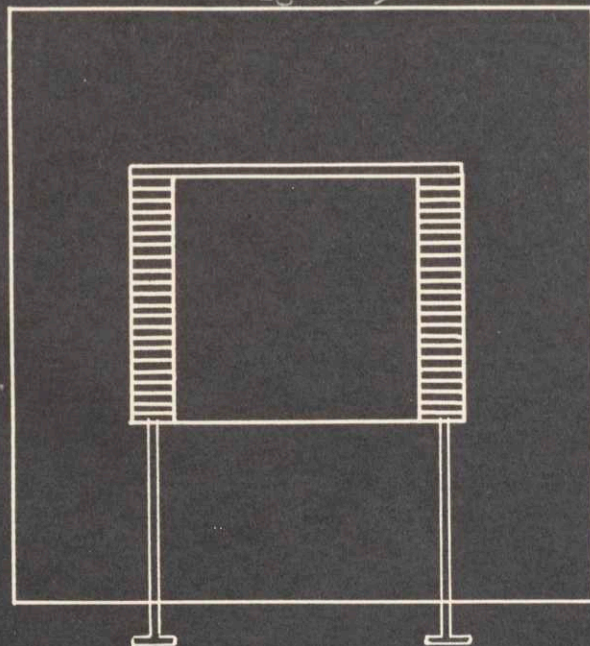
TUBE RESISTANCE FURNACE.

Figure 2.



GAS FIRED  
SEMI-MUFFLE FURNACE.

Figure 3.



CARB ON RESISTANCE FURNACE.

tion of charcoal. The temperatures used were from 500 to 1000°C. at intervals of 100°. On leaching with water there was no trace of any soluble chromium salt.

Sulphatizing under oxidizing conditions was tried with copper-free pyrite. Charges were made up of 10 grams of chromite and 10 grams of pyrite. These were treated to temperatures between 500 and 1000°C. This was no more successful than the chloridizing roasts.

Reducing roasts were then made with the intention of obtaining an acid soluble suboxide or metallic form of chromium. The charges consisted of equal amounts of chromite and charcoal. Illuminating gas was used to maintain a reducing atmosphere. They were heated to temperatures between 500 and 1000°C. and leached with 6 normal hydrochloric acid. The results (Table II) show a decided decrease from the extraction obtained on treating the raw ore.

Table II.

| Reducing Roasts 500°C.-1000°C. |  |
|--------------------------------|--|
| <u>Temperature</u>             | <u>Percentage Extraction<br/>of Chromium</u> |
| 500                            | 1.25   |
| 600                            | 2.75   |
| 700                            | 3.25   |
| 800                            | 2.10   |
| 1000                           | 1.50   |

The extraction seemed to become progressively smaller, over 700°C., the higher the temperature. Evidently there was no reduction, and the heat was serving only to make the chromium oxide more inactive. A charge of chromite and charcoal was then placed in a crucible and heated in a vertical tube furnace, with the intention of heating to 1200°C. At 1175°C. the furnace burned out. The thermocouple was also ruined, so that the temperature is not accurate. When leached, an extraction of about 40 per cent was obtained.

Reducing roasts at high temperatures were then carried out in a gas fired, semi-muffle furnace (Fig. 2). The atmosphere of the furnace was kept as reducing as possible by introducing pieces of charcoal and coke. Even then, some of the charges showed some oxidation at the top. The results show some unaccounted for variations which are attributed to this. The charges consisted of 50 grams of chromite and varying amounts of pulverized charcoal. The amount of charcoal used, was calculated, and is expressed in percentage by weight of the chromite. They were thoroughly mixed and lightly tamped into graphite crucibles. Granular charcoal was placed on top of the charge to a depth of one-half inch. The covering layer of charcoal was partially replaced by coke on the longer and hotter runs. The furnace was heated to temperature, and the crucibles put in. The time referred to in the table of results is the actual

time during which the crucible remained in the furnace. For the runs from 1150 to 1350°C., the above described furnace was used. Temperature control was obtained with a platinum-platinum rhodium thermocouple. For the run at 1400°C., the heating was done in a carbon resistance furnace (Fig. 3). Temperature was judged with an optical pyrometer. Due to the fumes it was difficult to control this accurately. As it was necessary to heat and cool the crucibles in the furnace, the time indicates only the interval during which the furnace was at 1400°C.

After the results of the runs at 1350°C. were obtained, it was plain that extraction was still increasing and that something was causing great irregularity in the results. It was thought that a reducing agent free from ash and in a finer state of division might give better results. The run at 1400°C. with charcoal was therefore duplicated with lampblack. There seems to be some benefit from its use.

After heating, the charge forms a friable cake. Leaching was done with 6 normal hot hydrochloric acid. The amount of chromium extraction is shown in Table III. By leaching the residue with concentrated sulphuric acid, an additional 5 to 8 per cent is obtained.

Table III.

## Reducing Roasts on Chromite (Charcoal)

Extraction of Chromium expressed in per cent

| 1100°C.              |              |      |       |      |      |      |
|----------------------|--------------|------|-------|------|------|------|
| Charcoal<br>% of ore | Time (hours) |      |       |      |      |      |
|                      | 1/2          | 1    | 1-1/2 | 2    | 3    | 4    |
| 15                   | 1.2          | 1.5  | 1.0   | 0.8  |      |      |
| 20                   | 1.8          | 1.6  | 0.8   | 0.9  |      |      |
| 25                   | 1.8          | 1.9  | 0.9   | 1.0  |      |      |
| 1150°C.              |              |      |       |      |      |      |
| 15                   | 1.4          | 1.2  | 1.2   | 1.5  |      |      |
| 20                   | 1.4          | 2.2  | 1.6   | 2.5  |      |      |
| 25                   | 1.3          | 2.8  | 2.2   | 3.2  |      |      |
| 1200°C.              |              |      |       |      |      |      |
| 15                   | 2.1          | 6.3  | 8.1   | 14.4 |      |      |
| 20                   | 1.9          | 10.0 | 15.7  | 21.2 |      |      |
| 25                   | 1.9          | 13.5 | 17.2  | 24.5 |      |      |
| 1250°C.              |              |      |       |      |      |      |
| 15                   | 1.7          | 19.0 | 26.7  | 29.7 |      |      |
| 20                   | 2.5          | 24.2 | 31.3  | 35.8 | 51.3 | 42.2 |
| 25                   | 5.1          | 28.5 | 35.8  | 39.6 | 50.7 | 43.8 |
| 30                   |              | 33.1 | 42.0  | 51.0 | 46.7 | 50.8 |
| 35                   |              | 34.3 | 49.2  | 50.7 | 44.5 | 41.3 |
| 1300°C.              |              |      |       |      |      |      |
| 15                   | 11.0         | 31.0 | 39.4  | 42.7 |      |      |
| 20                   | 11.2         | 36.8 | 45.3  | 52.7 |      |      |
| 25                   | 13.1         | 41.1 | 49.0  | 56.8 | 54.8 | 47.2 |
| 30                   |              | 30.5 | 46.6  | 54.5 | 61.3 | 43.7 |
| 35                   |              | 43.2 | 54.0  | --   | 46.3 | 50.2 |
| 1350°C.              |              |      |       |      |      |      |
| 20                   |              | 42.7 |       | 62.9 | 56.0 | 58.7 |
| 25                   |              | 51.3 |       | 59.3 | 64.0 | 66.1 |
| 30                   |              | 47.3 |       | 59.7 | 61.0 | 48.3 |
| 35                   |              | --   |       | 58.7 | 54.5 | 53.5 |
| 1400°C.              |              |      |       |      |      |      |
| 20                   |              |      |       | 39.2 |      |      |
| 25                   |              |      |       | 51.7 |      |      |
| 30                   |              |      |       | 57.3 |      |      |
| 1400°C. (Lampblack)  |              |      |       |      |      |      |
| 15                   |              |      |       | 55.0 |      |      |
| 20                   |              |      |       | 57.0 |      |      |
| 25                   |              |      |       | 64.2 |      |      |
| 30                   |              |      |       | 52.7 |      |      |

The conclusions concerning the reducing roasts at high temperatures are:

1. A yield of 70 per cent of the chromium in chromite can be obtained, as soluble chromium sulphate or chromium chloride.

2. The temperature should be close to 1350°C. Below that temperature maximum reduction is not obtained and above it, the ore frits and reduces the yield.

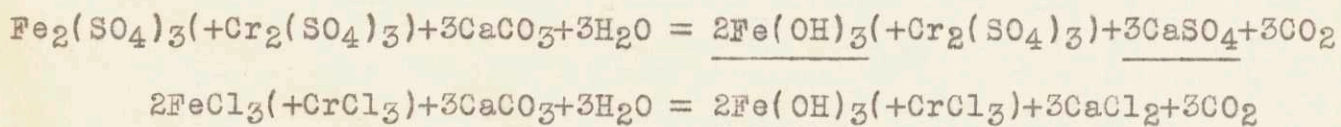
3. The time should be between two and three hours.

4. Lampblack is more efficient than charcoal as the reducing agent. For this ore, the amount of carbon should be 25 per cent of the amount of chromite.

CLEANING THE SOLUTION

The leaching solution, as it comes from the ore, is a mixture of iron and chromium chlorides or sulphates in the lowest valence. Aluminum was found in the solutions from the ore roasted between 500 and 1000°C., but was not found in the ore roasted at the higher temperatures. Since the practical temperature for roasting is about 1350°C., the solutions under consideration were practically free from aluminum. In the batch of solution on which the work was done there was 68 per cent chromium and 32 per cent iron as chlorides. At first a solution containing about 60gm.Cr/Liter was used, but the precipitate obtained was so voluminous that the solution was diluted to concentration of about 30 gm.Cr/Liter.

The method of cleaning was the differential precipitation of iron hydroxide with a base, such as limestone. The chemical reaction is



It was expected that with a limited amount of base, the chromium would not be precipitated. A series of runs were made in which the amount of limestone was gradually increased, by rolling on its side for eight hours a large bottle containing 50 c.c. of solution. Poor results were obtained as the iron was not com-

pletely oxidized to the ferric state. Another series of runs were made by agitating the solution in a tall narrow vessel by aerations for six hours. Thus both oxidation and agitation were obtained. In these runs, precipitated calcium carbonate was used, instead of limestone, as it reacted more quickly. The resultant solutions were very dark brown, indicating colloidal ferric hydroxide or basic chloride. There was a great deal of trouble experienced in precipitating the iron colloid. The solutions were heated with gelatin and with starch without coagulation. At the suggestion of Mr. O. C. Ralston, of the U.S. Bureau of Mines, egg albumen was tried. This was accompanied by more successful results. It was found that if precipitation is attempted before the colloidal solution has aged a week or two, incomplete coagulation is obtained. This was not understood until time was lacking to make a series of quantitative determinations.

From the results obtained, it was seen that six hours was not quite long enough for complete equilibrium to be obtained, but that there is a decided differential precipitation, the iron being precipitated first. The iron hydroxide or basic salt can be precipitated, after adequate aging, by albumen. Albumen is obtainable in commercial forms, so that the method is not too expensive.

If it is desired to precipitate chromium hydroxide, the remaining solution, if sulphate, could be converted to chloride by the addition of calcium chloride. Limestone can then be used without contaminating the product with calcium.



## ELECTROLYSIS

A review of the literature on chromium plating shows that up to 1905, equal attention was paid to the electrolysis of chromium salts and of chromic acid. Since that time chromic acid alone has been used. This is due to the fact that deposits from chromic acid are much better than those made from chromium chloride or sulphate. Since electrolysis of chromium is used only for plating, the nature of the deposit is of prime importance. For the present purpose, the nature of the deposit is not a matter of such great importance as is the cost of the power consumed in electrolysis. More attention therefore has been given to the work which has been done on chromium chloride and sulphate.

Bunsen<sup>1</sup> was the first to deposit chromium electrolytically. He used a boiling chromium chloride solution with a current density of 67 amp./sq.dec.

Placet and Bonnet took out several patents between 1890 and 1895 for the electrolysis of chromium salts. They were considerably discredited by the failure of Shick to get any chromium from their recipes. Later work seems to show that they could be used satisfactorily.

Moller and Street (English Patent 1898) used a

bath of sodium chrome alum and sodium sulphate. This was kept at 90°C. and electrolyzed with a current of 40 amp./sq.dec.

J. Ferec<sup>2</sup> secured results with a solution of 16% chromium chloride and 10% hydrochloric acid.

Cowper-Coles obtained good deposits with a solution containing 250 grams/Liter of chromium chloride. His current density was about 5 amp./sq.dec.

Glaser<sup>3</sup> electrolyzed chromium chloride and published the results of variations of the current density and of the concentration of the solution. The conditions were not stated very completely. Efficiency of deposition increased with the current density and concentration of the solution up to 158 gm. Cr/Liter.

Carveth and Curry<sup>4</sup> give a review of the work on chromic acid up to 1905, and show that a small amount of impurity, particularly sulphuric acid, aids the reduction of chromic acid.

Carveth and Mott<sup>5</sup> used a two-compartment cell with sulphuric acid (sp.gr. 1.12) as the anolyte. The best deposits were obtained between 10 and 40 amp./sq.dec. Stirring was found to reduce current efficiency. The nature of the anolyte was found to affect the efficiency. Ammonia gave the best results. The effect of varying the conditions was investigated carefully on the chloride and sulphate baths.

Efficiency was found to increase with higher temperature, current density and concentration of chromium in solution.

Le Blanc<sup>6</sup> working with a solution containing 89 grams of Cr/Liter and 2 grams  $H_3BO_3$ /Liter, decided that thick deposits could not be made from a sulphate solution. A current density of 10 to 20 amp./sq.dec. was used, at temperatures between 25 and 50°C. On adding chromium hydroxide a leafy deposit was obtained.

Of the three solutions which have been used, chromic acid is by far the most suitable. It can easily be kept up to the desired concentration, so that it is very well adapted to use in a continuous process. The theoretical amount deposited by one ampere hour is 0.3229 gram. Only about one-third of this is ever obtained, so that where power is a major consideration, the process is not practicable.

Chromium chloride solutions give a deposit which is not suitable for electroplating, but which is all right for refining. The theoretical yield is twice that of chromic acid (0.6458 gm./amp.-hr.) Current efficiency over 30 per cent is seldom attained.

Chromium sulphate solutions have the same advantages as the chloride solutions, with two exceptions. The current efficiency is a little higher. The condition of a sulphate bath can be controlled more easily than that of the chloride bath without introducing impurities. It was con-

sidered that the sulphate solution would be most satisfactory, so that practically all the work was done on it.

A few tests were made on chromic acid baths to which chromic hydroxide had been added. A solution of 16%  $\text{CrO}_3$  and 0.5%  $\text{Cr}_2(\text{SO}_4)_3$  was saturated with  $\text{Cr}(\text{OH})_3$ . The electrolyzing vessel was a 400 c.c. beaker. A cylindrical lead anode was used. The cathode was a mild steel bar 0.340 inches in diameter suspended from the top. Cooling was effected by placing the vessel in a larger beaker in which water was circulated. Excess  $\text{Cr}(\text{OH})_3$  was kept in the vessel. Cathodes were ground smooth, pickled in sulphuric acid, wiped dry and weighed. The results of these runs are shown in Table IV.

Table IV.

Electrolysis of Chromic Acid Saturated with  $\text{Cr}(\text{OH})_3$ 

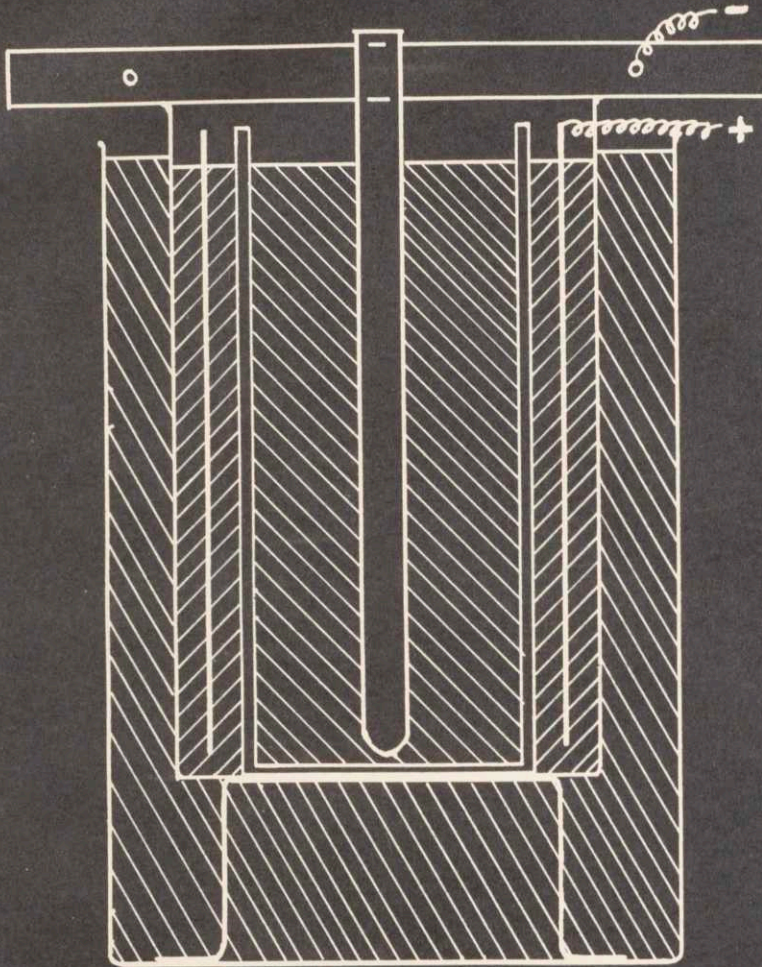
| C.D.<br>Amp/sq.dec. | Temperature | Yield<br>Gms/amp.hr. | Time<br>Hours | Remarks   |
|---------------------|-------------|----------------------|---------------|---|
| 8.5                 | 20          | .0865                | 7             | Smooth, good deposit                                  |
| 10                  | 20          | .0908                | 6             | " " "   |
| 12.5                | 20          | .0948                | 6             | " " "   |
| 12.5                | 25          | .0906                | 6             | " " "   |
| 15                  | 25          | .1000                | 6             | Rough   |
| 15                  | 30          | .0914                | 6             | Smooth  |
| 25                  | 30          | .1082                | 4             | Growths   |
| 35                  | 30          | .1190                | 3             | Smooth  |
| 45                  | 30          | .1173                | 2             | "   |
| 55                  | 30          | .1170                | 2             | Fairly smooth   |
| 40                  | 35          | .1128                | 2             | Rather rough  |
| 35                  | 30          | .1100                | 3             | 0.5 gm. $\text{V}_2\text{O}_5$ . Deposit cracked      |
| 35                  | 30          | --                   | 2             | 4c.c. 20% solution $\text{TiCl}_2$ .<br>Badly cracked |
| 35                  | 30          | .1027                | 3             | 0.5 gm. $\text{Fe}(\text{OH})_3$ . Good deposit       |
| 35                  | 30          | .1075                | 3             | 0.5 gm. $\text{Al}(\text{OH})_3$ . " "                |
| 35                  | 30          | --                   | -             | 0.5 gm. $\text{SnCl}_2$ . Badly cracked               |

No attempt was made to keep track of the previous history of the solutions for each run. The tests were made with the purpose of finding out the physical characteristics of the deposits, rather than to obtain the maximum efficiency. Additions of several metallic salts were tried to find their effect on efficiency and nature of the deposit. The most favorable addition was aluminum hydroxide. The deposit was more smooth and showed less tendency to growths. The lower current densities used with each temperature gave the better deposits. The most satisfactory deposits were obtained at the lower temperatures, 20 and 25°C. with current densities of 10 and 12.5 amp./sq.dec., respectively.

Electrolysis of chromium sulphate solutions was carried out in a two-compartment vessel. A porous clay cup which held about 170 c.c. held the cathode solution. Outside of this was a cylindrical lead anode. The cathodes were mild steel bars 0.340 inch in diameter. Sulphuric acid (sp.gr. 1.12) was used in the anode compartment. The whole cell was kept in a larger beaker which was filled with water and heated or cooled as required. Thermometers were kept in the cathode compartment and in the cooling water. A diagram of the cell is shown in Fig. 5. ?

Due to a temporary shortage of chromium sulphate, a solution was made up by neutralizing sulphuric acid with chromium hydroxide. This was concentrated to sp.gr. 1.45. Electrolysis with current densities up to 100 amp./sq.dec.

Figure 4.



TWO COMPARTMENT  
ELECTROLYSING VESSEL.

and temperatures from 20 to 90°C. failed to give any deposits.

A small supply of chromium sulphate manufactured by Merck and Company about fifteen years ago was obtained. It was dissolved to form a solution of sp.gr. 1.35. A few qualitative runs were made, in which it was found that satisfactory deposits could be obtained between 60 and 90°C. and up to 40 amp./sq.dec. A series of tests were begun, using a fresh solution each time. The change of efficiency on continued electrolysis was so great that it was impossible to use them more than once. Two of the runs were completed (Table V). It was impossible to duplicate this batch

Table V.

Chromium Sulphate (Merck sp.gr. 1.35)

30 amp./sq.dec. 80°C.

| Time    | Amp.hr. | Gm./amp.hr. | Efficiency | Remarks           |
|---------|---------|-------------|------------|-------------------|
| 1/2 hr. | 3.63    | --          | --         |                   |
| 1/2     | 3.63    | .1284       | 19.9       |                   |
| 1-1/2   | 11.17   | .1892       | 29.3       | Treeing           |
| 2/3     | 4.67    | .2800       | 43.4       | Good gray deposit |

30 amp./sq.dec. 90°C.

|       |       |       |      |                  |
|-------|-------|-------|------|------------------|
| 1/2   | 3.57  | --    | --   |                  |
| 1/2   | 3.57  | .0362 | 5.6  | Black deposit    |
| 1-1/2 | 10.85 | .0677 | 10.5 | Dark, with trees |
| 1/2   | 3.67  | .2370 | 36.7 | Good, gray       |

of chromium sulphate, so that the results are given only to show the difference between different lots. They also show

that 90°C. is too hot and reduces the efficiency.

A supply of chromium sulphate C.P. made by the J. T. Baker Co. was obtained. This was used during the remainder of the work. This was dissolved to form a solution of sp.gr. 1.35 containing 107 gm.Cr/Liter. After a few trials, it was obvious that the efficiencies obtained with this lot were not comparable to those obtained from the sulphate from Merck. Also that the change of efficiency during electrolysis was very great. Therefore, several long runs were made. The temperature was 80°C.  $\pm$  2° and the current density 40 amp./sq.dec. These runs checked fairly closely on the whole. A representative run is given in Table VI. As is seen in the accompanying graph, the efficiency is practically zero for a time, rises to a peak, falls off and again rises to

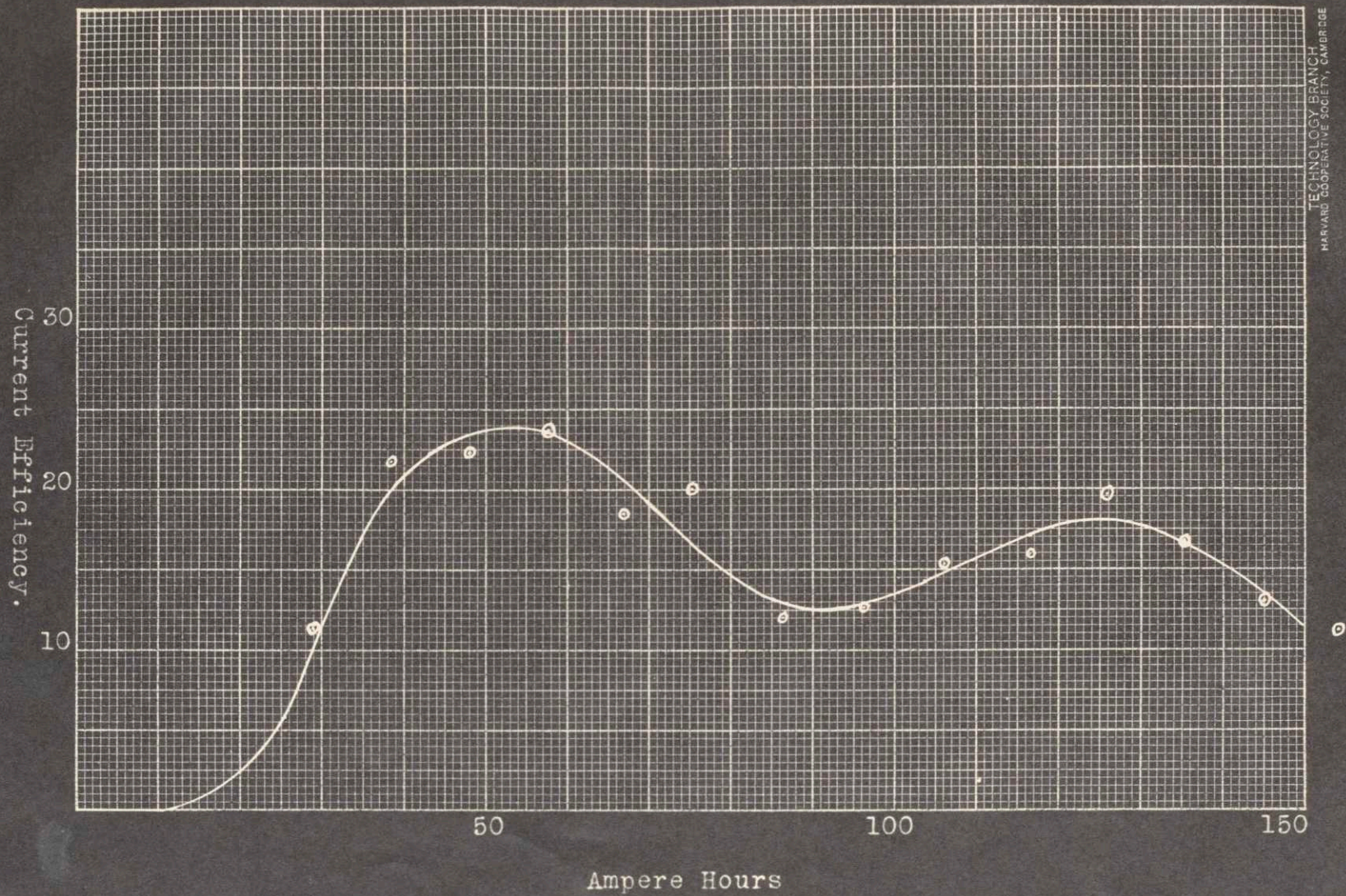
Table VI.

Chromium Sulphate/ $\frac{107}{\text{gm.}}/\text{L}$  40 amp./sq.dec. 80°C.

| No. | Time(hrs) | Amp.-hr. | Total<br>amp./hr. | Deposit<br>Grams | Efficiency | pH   |
|-----|-----------|----------|-------------------|------------------|------------|------|
| 1   | 1         | 9.7      | 9.7               | --               | --         | 4.58 |
| 2   | 2         | 19.36    | 28.36             | 1.3895           | 11.1       | 2.19 |
| 3   | 1         | 9.53     | 37.89             | 1.3482           | 21.8       | 2.67 |
| 4   | 1         | 9.52     | 47.41             | 1.3608           | 22.2       | 2.28 |
| 5   | 1         | 9.50     | 56.91             | 1.4604           | 23.7       | 2.55 |
| 6   | 1         | 9.50     | 66.41             | 1.1366           | 18.5       | 2.48 |
| 7   | 1         | 9.60     | 76.01             | 1.2418           | 20.0       | 2.43 |
| 8   | 1         | 9.90     | 85.91             | 0.7661           | 12.0       | 2.50 |
| 9   | 1         | 9.63     | 95.54             | 0.7900           | 12.7       |      |
| 10  | 1         | 9.80     | 105.34            | 0.9772           | 15.4       |      |
| 11  | 1         | 9.88     | 115.22            | 1.0004           | 15.75      |      |
| 12  | 1         | 9.70     | 124.92            | 1.2289           | 19.5       |      |
| 13  | 1         | 9.60     | 134.52            | 1.0243           | 16.5       |      |
| 14  | 1         | 9.60     | 144.12            | 0.8166           | 13.2       |      |
| 15  | 1         | 9.80     | 153.92            | 0.6985           | 11.0       |      |



EFFICIENCY CURVE FROM TABLE VI.



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Figure 5.

a second peak, somewhat lower than the first. The deposits which were obtained at the first peak were the best and were like the chromic acid deposits. Those obtained after the peak was passed, were fragile and cracked easily. Attempts were made to achieve the second peak while the bath was at a higher concentration of chromium. It was hoped that the efficiency would be higher. This was not achieved, as the deposits cracked too badly.

For a continuous process, it would be necessary to add chromium hydroxide or chromium sulphate. Addition of the latter is possible, but requires more attention to the condition of the bath than was possible in this investigation. Chromium hydroxide was thought to be a more simple solution. At first it was prepared by the precipitation by ammonia from chromium chloride. Later it was precipitated by calcium carbonate. Slightly better results were obtained with the latter. It was washed free of the mother liquor, but the amount of basic chloride was not determined. It was kept damp and weighed out wet, after the amount of chromium per unit was determined.

A solution of sulphate was electrolyzed to a point just beyond maximum efficiency. Enough chromium hydroxide was added, so that, apparently, the chromium content of the solution would be comparable to that which was present just before the maximum was reached. As it did not dissolve readily, the mixture was agitated, heated, allowed to stand 24 hours and filtered. The solution was then electrolyzed

Green oxide of chromium was deposited along with some metal. The metallic chromium cracked very badly and was black, without metallic luster. Boric acid was tried in the amount used by Le Blanc. It made matters worse. The chromium hydroxide was thought to be in the solution as a colloid, and some study was put on the subject from this point of view, but without result. Hydrogen ion concentration values were then obtained, which are inserted in Table VI. From these it was found that good efficiency is obtained at a hydrogen ion concentration of pH 2.5. This can vary between pH 2.3 and pH 2.7, but outside of this range there is a noticeable falling off in efficiency and character of the deposit. Chromium hydroxide was dissolved in the electrolyzed solutions until the hydrogen ion concentration was up to pH 2.5. Deposits from these solutions were a little better than from those in which chromium content was used as a basis of control.

A solution was then prepared as above described to which was added about 50 grams per Liter of  $MgSO_4 \cdot 7H_2O$  and 10 grams per Liter of NaF. Deposits were obtained which were not quite as good as those deposited from a pure chromium sulphate bath, but which were far better than any obtained from the solutions containing <sup>only</sup> chromium hydroxide. Time was lacking to make a thorough study of the bath or the conditions under which it should be electrolyzed. A few values were obtained, which are shown in Table VII. The physical character of the deposits was not all that might be desired, but show great

Table VII.

Chromium Sulphate with  $\text{Cr}(\text{OH})_3$ ,  $\text{MgSO}_4$ ,  $\text{NaF}$ 

| No. | Temp. | Current<br>Density<br>amp./sq.dec. | Gm/amp.hr. | Effici-<br>ency | Remarks                                     |
|-----|-------|------------------------------------|------------|-----------------|---|
| 1   | 50°   | 10                                 | .3138      | 48.7            | Not very good, some $\text{Cr}_2\text{O}_3$ |
| 2   | 50    | 16                                 | .3484      | 54.1            | Formed trees                                |
| 3   | 60    | 16                                 | .2256      | 34.5            | Good, ribbed                                |
| 4   | 80    | 16                                 | --         | --              | Poor, cracked badly                         |
| 5   | 50    | 22                                 | .3026      | 46.9            | Good, tendency to crack                     |
| 6   | 75    | 35                                 | --         | --              | No deposit                                  |

promise. The efficiencies obtained are very good and show that the cost of electrolysis for the purpose of refining, is not prohibitive. The voltage across the cell is about four volts. Assuming a yield of 0.25 grams of chromium per ampere hour, the power required for a pound of chromium would be less than eight kilowatt hours.

All the chromium which diffused into the anode compartment was oxidized to chromic acid. This suggests the possibility of a very desirable by-product, which would materially reduce the cost of electrolysis for chromium.

A few experiments were made with the solutions as they came from leaching the ore. As these solutions were chlorides, no great amount of time was spent on them, since the sulphate solutions would be used in any commercial process. The aim was to find out whether iron and chromium could be deposited together. The current density was about 20 amp./sq.dec. and the temperature 40°C. At first iron alone was deposited. This

cracked and had to be removed. When the solution was somewhat more lean in iron, a coherent deposit was obtained which was plated to a thickness of about one-sixteenth of an inch. It then became too rough for further deposition. This alloy contained about 40 per cent chromium. By careful control of the iron in the solution, it should be possible to make ferro-chrome with a higher chromium content. The yield of chromium was not accurately determined, but seemed to be about the same or a little less than in the straight chromium solutions. Since the cost of cleaning the solution is dispensed with, it should be cheaper to make ferro-chrome than pure chromium.

#### Conclusions.

1. That good deposits can be obtained from chromium sulphate solutions if the proper degree of acidity is maintained.
2. That chromium can be plated from chromium sulphate solutions containing magnesium sulphate and sodium fluoride when kept neutralized and concentrated with chromium hydroxide.
3. That the yield of chromium is at least 0.25 grams per ampere hour and that probably 0.50 grams or better can be obtained. The power used would amount to six to eight kilowatt hours per pound of chromium.
4. That ferro-chrome can be made electrolytically.

### GENERAL SUMMARY

In the work on this subject, it has been the aim to develop a complete process. Most of the results only indicate what can be expected, rather than determine actual conditions under which operations should be carried out. Due to a lack of time, many alternative methods have not been investigated, so that much work has yet to be done before the process could be undertaken commercially. However, it has been shown that there are commercial possibilities in the process which justify further work along this line. The results which have been found follow in their natural order.

1. Finely ground chromite is roasted with 25 per cent of its weight of lampblack or finely powdered charcoal (for this particular ore) at 1300 to 1350°C. for two to three hours, under reducing conditions.

2. The resultant sponge is leached with concentrated sulphuric acid at 100°C. It can reasonably be expected that the yield of soluble chromium will be about 70 per cent. With ores in which the gangue is less fusible, a greater extraction is to be expected.

3. The leaching solution, containing iron and chromium salts, is then cleaned of iron by precipitation with finely divided limestone, after agitation with air to oxidize the iron and chromium.

4. The remaining chromium sulphate liquor may be used as it is, after concentration, for the electrolysis, or the chromium may be precipitated as chromium hydroxide. The latter is produced by conversion of the sulphate to chloride with calcium chloride, and precipitation of the chromium hydroxide with limestone. Chromium hydroxide is then added to a chromium sulphate solution in the process of electrolysis.

5. Chromium is then plated out from a chromium sulphate solution in a two-compartment cell, to which has been added magnesium sulphate and sodium fluoride. This bath is kept up to strength with the product obtained from (4). The chromium concentration is kept high and the hydrogen ion concentration must not vary greatly from pH 2.5. The conditions of current density and temperature have not been determined closely, and the nature of the anode solution has not been investigated. The power cost is not more than eight kilowatt hours per pound and can probably be reduced to five or six kilowatt hours per pound.

6. If it is desired to make carbon-free ferrochromium, the cleaning and precipitation of the iron are eliminated. The only treatment required before electrolysis is concentration of the leaching solution. The conditions for deposition have not been accurately determined, but the work done indicates that an alloy of the same ratio of chromium to iron as in the leaching solution, namely

68% Cr and 32% Fe could be produced. The cost of electrolysis per unit of chromium is about the same as that for pure chromium. The alloy is absolutely free from carbon and should be very suitable for use in the production of alloy and special steels.

7. In the anode compartment, chromium can be oxidized to the chromate with high efficiency. No extra power is required for this, so that it can bear a part of the cost of electrolysis. Thus, by the production of a readily salable by-product, the cost of electrolytic deposition of chromium is lowered.



BIBLIOGRAPHY

1. Bunsen: Pogg. Ann., 91, 119, 1854.
2. J. Ferec: Electrometallurgy, p.366, 1897.
3. Glaser: Z.f.Elektrochemie, 7, 656, 1901.
4. Carveth and Curry: Trans. Am. Electrochemical Soc., 7, 115, 1905.
5. Carveth and Mott: J. Phys. Chem., 9, 231, 1905.
6. Le Blanc: Trans. Am. Elec. Soc., 9, 315, 1906.