

AN ABSTRACT OF THE THESIS OF

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Low-grade Oregon chromite has been electrolytically oxidized to sodium chromate, using a platinum anode and an iron cathode in an electrolyte of sodium chlorate. The ore is ground to -100 mesh and introduced into the electrolyte in direct contact with the anode. The following variables are considered: ore size, temperature, anode current density, concentration of electrolyte, initial pH of electrolyte, and duration of electrolysis. Each of these was studied over a limited range, emphasis being put on coming within commercial limits rather than on complete investigation. Results are reported in kilowatt hours per pound of chromium as chromate in solution, the lowest reported being 66 kilowatt hours per pound. No postulation is made as to the mechanism of the reaction.

Efficiency increases as concentration of the electrolyte is increased, except at 70° C. and anode current densities above 3.0 amperes per square inch, under which conditions there is a substantial decrease. Increasing the ore size and the duration of the electrolysis both cause a lowering of efficiency. An increase in current density at 70° C. lowers the efficiency, while below 40° C. the efficiency is increased by increasing the current density. Increasing the temperature at current densities below 2.5 amperes per square inch raises the efficiency; above 4.0 amperes per square inch the efficiency is lowered.

FACTORS AFFECTING THE EFFICIENCY  
OF THE ELECTROWINNING OF METALS  
FROM REFRACTORY ORES

by

RICHARD BURKE BAILEY

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APPROVED:

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# TABLE OF CONTENTS

|  | <u>Page No.</u> |
|--|-----------------|
| Introduction . . . . .                           | 1               |
| Experimental Procedure:                          |                 |
| Apparatus . . . . .                              | 6               |
| Ore . . . . .                                    | 8               |
| Variables . . . . .                              | 8               |
| Probable Limits of Error . . . . .               | 9               |
| Analytical Procedure . . . . .                   | 9               |
| Manipulation . . . . .                           | 11              |
| Results of Experimental Work:                    |                 |
| General Observations . . . . .                   | 13              |
| Effect of Concentration of Electrolyte . . . . . | 13              |
| Effect of Temperature . . . . .                  | 15              |
| Effect of Time . . . . .                         | 15              |
| Effect of Current Density . . . . .              | 15              |
| Effect of Initial pH . . . . .                   | 16              |
| Plate I - Effect of Temperature.                 |                 |
| Plate II - Effect of Time                        |                 |
| Plate III - Effect of Time                       |                 |
| Plate IV - Effect of Current Density             |                 |
| Plate V - Effect of Current Density              |                 |
| Plate VI - Effect of Current Density             |                 |
| Plate VII - Effect of Initial pH                 |                 |
| Plate VIII - Effect of Initial pH                |                 |
| Tabulation of Results . . . . .                  | 18              |
| Discussion . . . . .                             | 21              |
| Conclusions . . . . .                            | 25              |
| Bibliography                                     |                 |

FACTORS AFFECTING THE EFFICIENCY  
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INTRODUCTION

In many localities on the southern Oregon and northern California beaches are found the so-called "black sands", which are secondary mineral deposits containing, as a rule, an appreciable percentage of chromite, as well as any or all of the following: serpentine, garnet, quartz, olivine, ilmenite and magnetite.

As would be expected, these deposits vary considerably in  $\text{Cr}_2\text{O}_3$  content, the maximum being in the neighborhood of 40% and the minimum less than 10%. With a few exceptions, these sands cannot be concentrated by known methods to metallurgical or chemical grade and are therefore valueless as a present supply of chromium unless a method is developed for economically extracting their chromium content.

It is with this end in view that the Martin-Dennis Company of Newark, New Jersey, has financed the research being done at Oregon State College by Joseph Schulein, A. J. Classen and the author, with the help and advice of G. C. Ware.

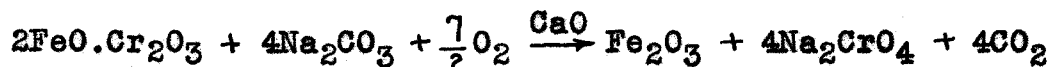
The purpose of the experimental work reported herein, therefore, is to determine the effect of certain variables upon the electrolytic oxidation of the low-grade domestic chromite ores.

While chromite ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) is theoretically 32%  $\text{FeO}$  and 68%  $\text{Cr}_2\text{O}_3$ , the ore used commercially for chromium production contains in the neighborhood of 50%  $\text{Cr}_2\text{O}_3$  and 15%  $\text{FeO}$ , stoichiometrical proportions being found only in meteorites. Commercial chrome ores are usually complex minerals of the spinel group ( $\text{MO} \cdot \text{M}_2\text{O}_3$ ), and although generally considered to have the formula  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ , the metals of the chromite crystal may be in part replaced by other metals. For example  $\text{FeO}$  may be replaced by  $\text{MgO}$  and  $\text{Cr}_2\text{O}_3$  by  $\text{Al}_2\text{O}_3$ .

Chromium produced today for the steel industry is made by reduction in the electric furnace using carbon or silicon as the reducing agent, carbon for high carbon ferrochrome and silicon for low carbon ferrochrome. This comprises approximately 70% of the total chrome ore used in the United States and requires a high grade ore - 47 to 51%  $\text{Cr}_2\text{O}_3$  with a chromium-iron ratio of 2.8:1 or 3:1. The product of this process is an alloy of iron and chromium, called ferrochrome, its analysis depending upon the proportions of iron and chromium in the furnace charge.

Approximately 20% of the chromite used in the United States goes into the manufacture of refractory brick. The remaining 10% is used in the chemical industry to produce various compounds of chromium. For this purpose also a high grade ore is required, which is treated as follows: The chromite is dried, crushed and then ball-milled down to

about -130 mesh, after which it is thoroughly mixed with soda ash and quick lime in the proper proportions and heated in a coal or gas fired furnace. The furnace reaction is



The lime acts as a bulking agent to keep the mass porous and prevent clogging the furnace. The calcine from the furnace is then leached with hot water, which dissolves the chromate and precipitates the iron as the hydroxide. The chromate is then filtered off and treated chemically to form the desired chromium compound.

Studies were made by Fischbeck and Einecke (1, 2) on the oxidation of both natural and artificially prepared chromite electrodes in dilute sulfuric acid solution. They showed that it is possible, by placing a piece of chromite in such a position that current passing from electrode to electrode must pass through it, to oxidize trivalent chromium to the hexavalent state. Their apparatus, as shown in the sketch, was basically two cells in series, the chromite acting as an anode for one and as a cathode for the other. The low conductivity of natural chromite caused a very large potential drop.

They reported that after three days' electrolysis with a current of 1 milliampere at 220 volts the catholyte contained 0.48 millimoles of  $\text{CrO}_3$ , or 0.013 grams of chromium. Current efficiency calculated from these figures



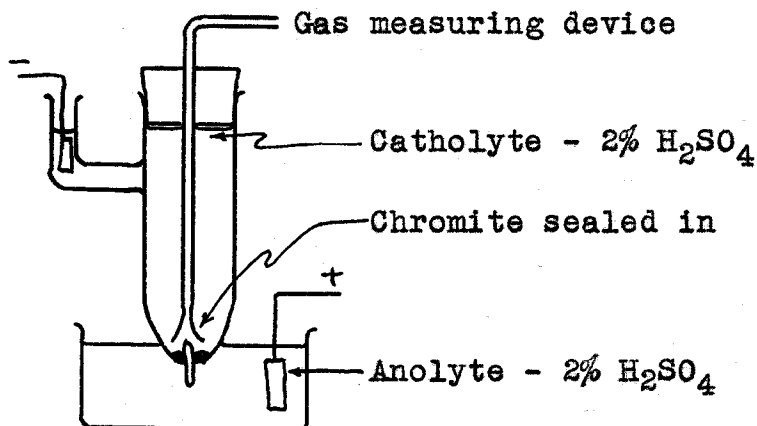


Fig. 1

is 5.54 ampere hours per gram of chromium, but the power efficiency is 554 kilowatt hours per pound of chromium due to the high voltage. What they designated as the catholyte was, of course, a complete cell with platinum cathode and chromite anode. The very low power efficiency, due to the high resistance of the chromite, eliminates this from practical consideration.

Loseva and Zolotuikli (5) extracted about one-half the chromium from Ural chromite in 8 to 10 minutes by heating to 150°-160° C. with sulfuric acid of specific gravity 1.83. They found the remainder unextractable by this method.

Pearson and Craig (7, 8, 9) describe a process for extracting metals of the chromium group from ores, waste or scrap metal, using an electrolyte in which the desired salt of the chromium group metal is soluble and in which any undesired salts, such as those of iron, are insoluble. The powdered ore is made into a paste and placed in a

porous anode compartment. An attempt was made by the writer to duplicate their work, using chromite as the raw material and an electrolyte of 25% NaOH in one case and 27%  $H_2SO_4$  in another. Neither of these electrolytes gave an appreciable amount of chromate in the two hour runs made on them.

Many patents have been obtained for production of chromates from ferrochrome, but these will not be considered here. The literature failed to reveal any other instances where chromium has been oxidized electrolytically from chromite.

## EXPERIMENTAL PROCEDURE

**APPARATUS.** The first cells used in this work were similar to that shown in figure 2, consisting of a glass tube approximately one inch in diameter closed at one end by a rubber stopper, over which was placed a 2-inch circle of heavy glass cloth to keep the products of electrolysis from attacking the stopper. The anode was a strip of platinum  $1/2$  inch wide bent into a U-shape so as to fit down over the end of the stopper, the current being conducted to it by a thin platinum strip extending out past the stopper.

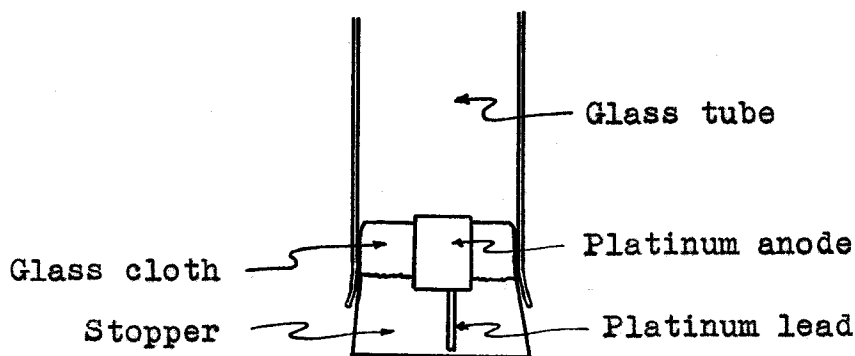


Fig. 2

In computing current densities only the top surface of the electrode was considered, since the under side and the portion between stopper and glass were not in effective contact with the electrolyte.

The cell design was later improved as shown in figure 3, the platinum in this cell being sealed to the

glass tube and forming the cell bottom. To form electrical contact the whole cell was set in a small beaker of mercury. The glass backing strip shown was to prevent the platinum from peeling away from the tube.

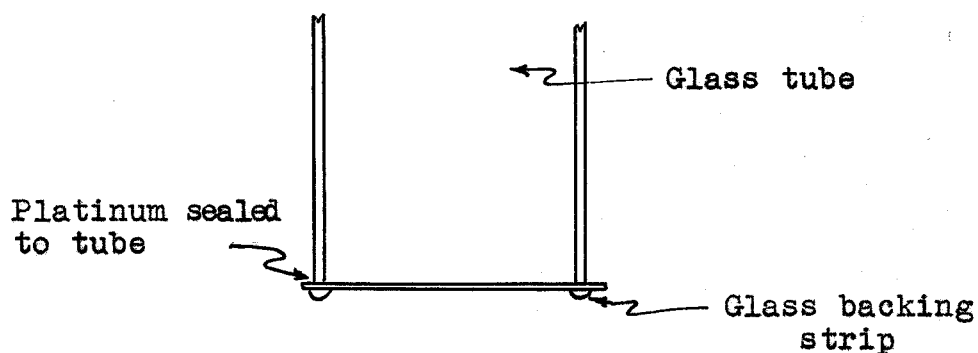


Fig. 3

Besides giving a definite anode area, this type of cell was found to be more easily cleaned and more convenient to use.

The cells were operated in groups of three as shown in the wiring diagram, figure 4, current being furnished by a 35-volt D.C. generator.

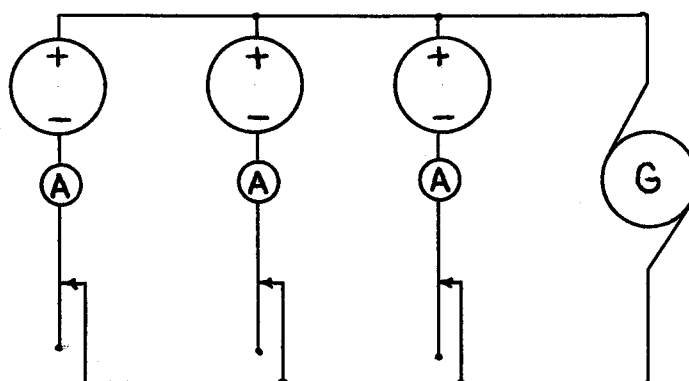


Fig. 4

ORE. The ore used in these experiments was taken from two locations on the beach near North Bend, Oregon. After a sieve analysis it was decided arbitrarily to use only the -60+80 fraction. A small pebble mill was used to break this ore from +80 down to the size desired. The designation of an ore as -100 mesh in this report means that it is -60+80 broken down to -100. A sieve analysis showed the following results:

| Fraction | Ore A | Ore B  |
|----------|-------|--------|
| -20+40   | 2.2%  | -      |
| -40+60   | 17.1  | 36.95% |
| -60+80   | 59.0  | 37.60  |
| -80+100  | 9.35  | 16.43  |
| -100+120 | 9.8   | 4.98   |
| -120+150 | 1.82  | 3.48   |
| -150     | 0.75  | 0.61   |

Analysis for chromium in the whole ores and in the -60+80 fractions showed the following results, on the basis of  $\text{Cr}_2\text{O}_3$ .

|       |           |        |                         |
|-------|-----------|--------|-------------------------|
| Ore A | Whole ore | 35.5%  | $\text{Cr}_2\text{O}_3$ |
|       | -60+80    | 36.0%  |                         |
| Ore B | Whole ore | 26.67% |                         |
|       | -60+80    | 26.5%  |                         |

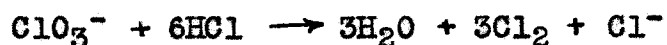
VARIABLES. The following variables were considered: ore size, temperature, anode current density, concentration of electrolyte, initial pH of electrolyte, and time of electrolysis. It will be understood that this is by no means a complete list, the time however being insufficient to cover more than those mentioned. Also the

investigation on none of the factors can be considered complete, since the main purpose of the work was to come within commercial operating limits on each and not to find the absolute optimum conditions for oxidation.

PROBABLE LIMITS OF ACCURACY. The factor most difficult to control was the total current passed during a run, this being due to the fact that evolved gas caused a marked fluctuation, the bubbles partially stopping the flow of current. In some cases this fluctuation was so great as to completely nullify the results obtained. It can be safely said, however, that for ore depths of one-half inch the current was controlled to  $\pm 0.05$  ampere, which would be 3.3% error for a current of 1.5 amperes. To obtain more accurate results a coulometer would be necessary. The temperature was controlled to within  $\pm 2^\circ$  C., although a higher temperature than the recorded one prevailed at the anode due to the heat generated by the current. In varying current density it was necessary to vary the total current rather than the anode area, since the latter was fixed by the cell design, but it is not known what error, if any, was caused thereby.

ANALYTICAL PROCEDURE. Several schemes of analysis were tried before one giving reproducible and speedy results was found. In a solution containing an easily reducible ion such as  $\text{ClO}_3^-$ , it is necessary to separate the chromium from the remainder of the solution to prevent

interference by the oxidizing agent. This can be accomplished in two ways - by reducing the  $\text{ClO}_3^-$  to  $\text{Cl}^-$  before analyzing, or by precipitating the chromium quantitatively from either the trivalent or hexavalent state. The first method tried involved breaking down the  $\text{ClO}_3^-$  by boiling with concentrated  $\text{HCl}$ , according to the equation

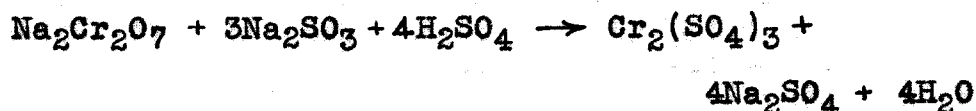


subsequently oxidizing the chromium with  $\text{Na}_2\text{O}_2$  in alkaline solution, acidifying and titrating with ferrous ammonium sulfate and potassium permanganate, according to the standard procedure. The high concentration of chloride ions in the final solution for titration, even though Zimmermann-Reinhardt solution was added to inhibit their effect, caused undependable results.

The next method considered was the gravimetric determination as  $\text{PbCrO}_4$  or  $\text{BaCrO}_4$ , both being tried and discarded as being too time-consuming.

The following procedure was finally determined to be the most accurate and speedy: The solution from the cell was washed into a beaker and made alkaline with  $\text{NaOH}$  to dissolve any  $\text{Cr}(\text{OH})_3$  which might have precipitated out in the cell, then the ore and  $\text{Fe}(\text{OH})_3$  were filtered off and washed thoroughly with weak alkali. The filtrate was then acidified with dilute  $\text{H}_2\text{SO}_4$  until the orange dichromate ion just replaced the yellow chromate ion, a change which is easily discernible. The addition of too much acid causes

incomplete reduction in the next step. The dichromate ion was then reduced to the chromic ion, using a saturated solution of  $\text{Na}_2\text{SO}_3$ . Complete reduction of the dichromate ion is shown by a brilliant emerald green solution, which turns blue green as excess reagent is added.



The reduced chromium was precipitated by a slight excess of  $\text{NH}_4\text{OH}$ , digested for 30 minutes and filtered on acid washed paper. If the filtrate was clear at that point and did not smell too strongly of ammonia, it was discarded - if colored it was acidified, reduced and reprecipitated - if too ammoniacal it was boiled to drive off the excess, and any precipitate filtered off. The precipitate was then dissolved in 1:3  $\text{H}_2\text{SO}_4$ , made slightly alkaline and oxidized with  $\text{Na}_2\text{O}_2$ , boiled to decompose excess oxidizing agent, acidified and titrated with ferrous ammonium sulfate and permanganate. The results obtained by this method were found to be reproducible.

**MANIPULATION.** As a result of extensive preliminary experiments by Joseph Schulein, the electrolyte used throughout this phase of the research was an aqueous solution of  $\text{NaClO}_3$ . The electrolyte was poured into the cell and the desired amount of finely ground ore introduced into the cell and allowed to settle into a layer directly on the platinum anode. After bringing the cell to the desired



temperature in a constant temperature bath, the current was passed for the desired time, usually two hours, and the cell solution analyzed for grams total chromium. The cathode was made of thin sheet iron and was suspended in the upper part of the electrolyte, approximately four inches from the anode. The results of each run were determined in kilowatt hours per pound of chromium, using an average potential drop across the cell of 20 volts in the power calculations.

## RESULTS OF EXPERIMENTAL WORK

**GENERAL OBSERVATIONS.** As soon as the current is turned on gas is given off at each electrode, the oxygen from the anode stirring the ore and causing some of it to be constantly in suspension in the electrolyte. After a few minutes a light precipitate appears in the electrolyte, gradually assuming the appearance of ferric hydroxide. Simultaneously the electrolyte starts to turn yellow, showing the presence of chromate. After some time, depending on the conditions of the run, a red layer appears next to the anode, probably  $\text{CrO}_3$ . As the chromate appears in the solution, a layer of chromic chromate is formed on the iron cathode, which is roughly proportional in amount to the chromate in solution. This layer of chromic chromate prevents the reduction of chlorate ions at the cathode. After the run has been made, the ore is found to be very slimy, no doubt because of ferric hydroxide and silicic acid mixed with it; and at the higher temperatures the smell of chlorine is usually noticeable when the cell is emptied.

**EFFECT OF CONCENTRATION OF ELECTROLYTE.** The maximum concentration of  $\text{NaClO}_3$  used was 500 grams per liter. The effect of this variable upon oxidation efficiency is apparently a function of current density, and to a lesser extent temperature. As would be expected, the normal effect of increasing the chlorate concentration is to

increase the efficiency of the process. Plate I shows three curves for each of two ore sizes at 2.5 amperes per square inch, each curve representing a definite chlorate concentration. From this plate it will be seen that at 70° the effect of concentration is not as critical for -100 mesh as for the unground -60+80 mesh ore. It will be noted also that at temperatures above 30° to 40°, an increasing chlorate content gives an increasing efficiency, while below this temperature range there is a slight deviation from this behavior, the 400 gram per liter curve going below the 500, indicating a better efficiency at 400 than at 500. However the curves representing 400 grams per liter are in each case based on only one point at 20°, therefore one cannot attach much importance to them at this temperature. Naturally our investigation was directed toward a minimum power expenditure per pound of chromium, so some of the upper reaches of the various curves were not investigated as fully as might be desired in a purely academic research project. Plate VI shows the effect of current density on the concentration-efficiency relation at 70°. It is apparent that at anode current densities above 3.0 amperes per square inch an increase in the chlorate concentration causes a decrease in efficiency, also that at current densities below 2.5 amperes per square inch, increasing the concentration causes an increase in efficiency.

**EFFECT OF TEMPERATURE.** As in the case of chlorate concentration, current density has a marked effect on the temperature-efficiency relation. A comparison of Plates IV and V discloses the fact that at current densities above 2.5 to 3.0 amperes per square inch, the efficiency of oxidation is greater at low temperatures than at 70°. Plate I shows, however, that at 2.5 amperes per square inch increasing the temperature causes increased efficiency, and the curves indicate that this holds true below that value of current density. The effect of raising the temperature is less critical at -100 mesh than at -60+80 mesh. From Plate I it also appears that the efficiency is a straight line function of temperature, at least at a current density of 2.5 amperes per square inch.

**EFFECT OF TIME.** This factor was considered first on the basis of comparatively small power input - comparing the results of 2- and 4-hour runs at 1.2 amperes. See Plate II. In each case efficiency decreased with time. Then a cell was run continuously and a sample analyzed at the end of each 100 ampere hours. See Plate III. The same results were found in this case for the early stages of electrolysis, but at 300 ampere hours the curve starts to level off to a constant efficiency.

**EFFECT OF CURRENT DENSITY.** The effect of anode current density appears to be largely tied in with the other variables already considered. The following generalizations

can be made regarding current density:

At 70° the efficiency decreases as current density is increased above 2.0 amperes per square inch - the effect being much more pronounced the higher the chlorate concentration. See plate VI.

At 40° the efficiency increases as current density is increased, at least up to 2.5 amperes per square inch. From 2.5 to 4.0 the efficiency apparently goes through a maximum. See plate IV.

EFFECT OF INITIAL pH. At 70° this variable, over a fairly wide range, has little effect. See Plates VII and VIII. Best results were obtained on the acid side, when the electrolyte was 3/4 normal with respect to sulfuric acid. Beyond this point on the acid side the efficiency falls off. Over the range from 3/4 normal sulfuric acid to 1/2 normal NaOH, the efficiency falls slowly but uniformly until at 1/2 normal NaOH the efficiency drops off sharply. At 40° no investigation was made on the acid side, but the effect of adding increasing amounts of NaOH was to increase the efficiency. At 20° no definite trend was noted, the points being too widely scattered to attempt correlation.

At this point it might be brought out that although the acidity or alkalinity can be fixed initially, there is no way of fixing the "working" acidity at the anode. Because of the diaphragm effect of the ore, the anolyte becomes acid as chromate ions are produced in its

vicinity. Considered as a whole the electrolyte becomes more and more acid as chromate ions are formed, so the question here is to maintain the proper overall pH by addition of NaOH from time to time.

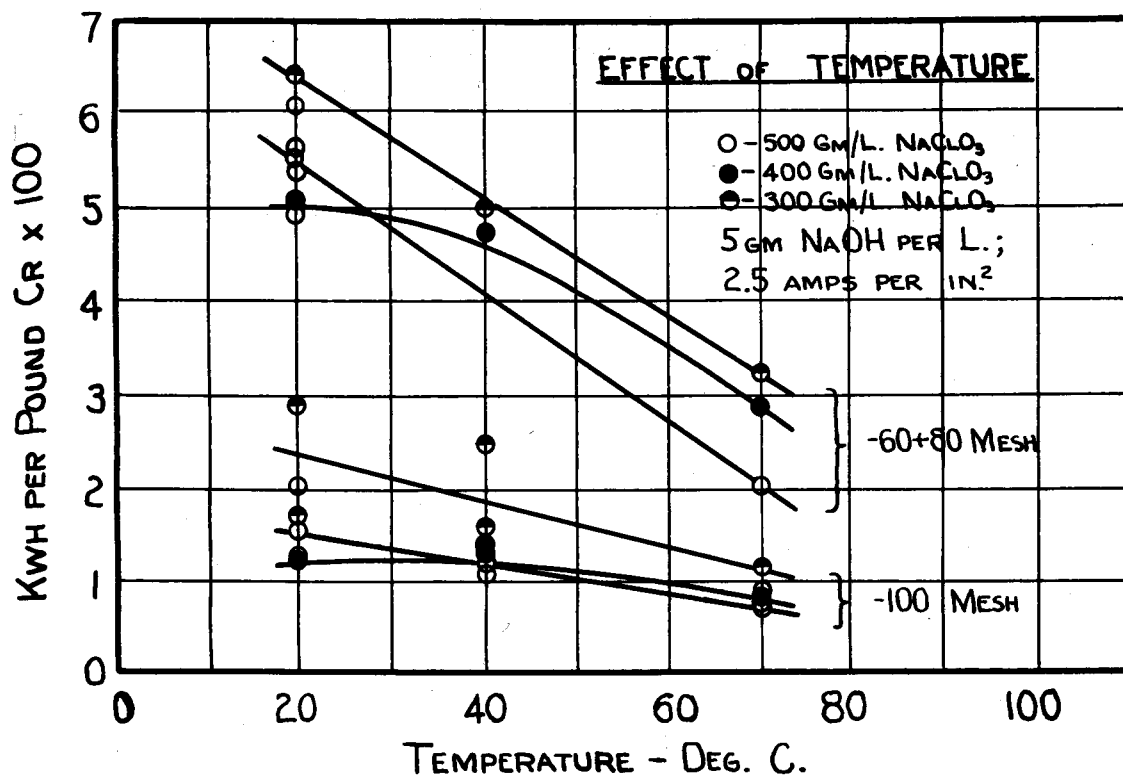


PLATE I

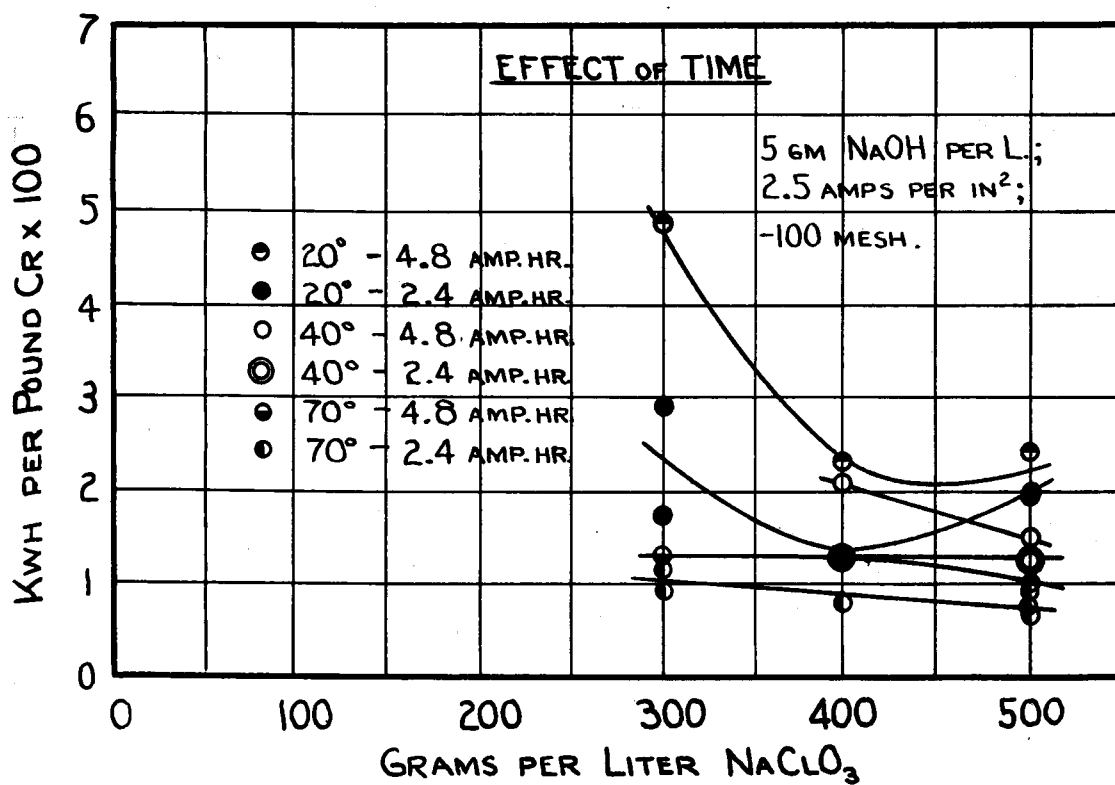


PLATE II

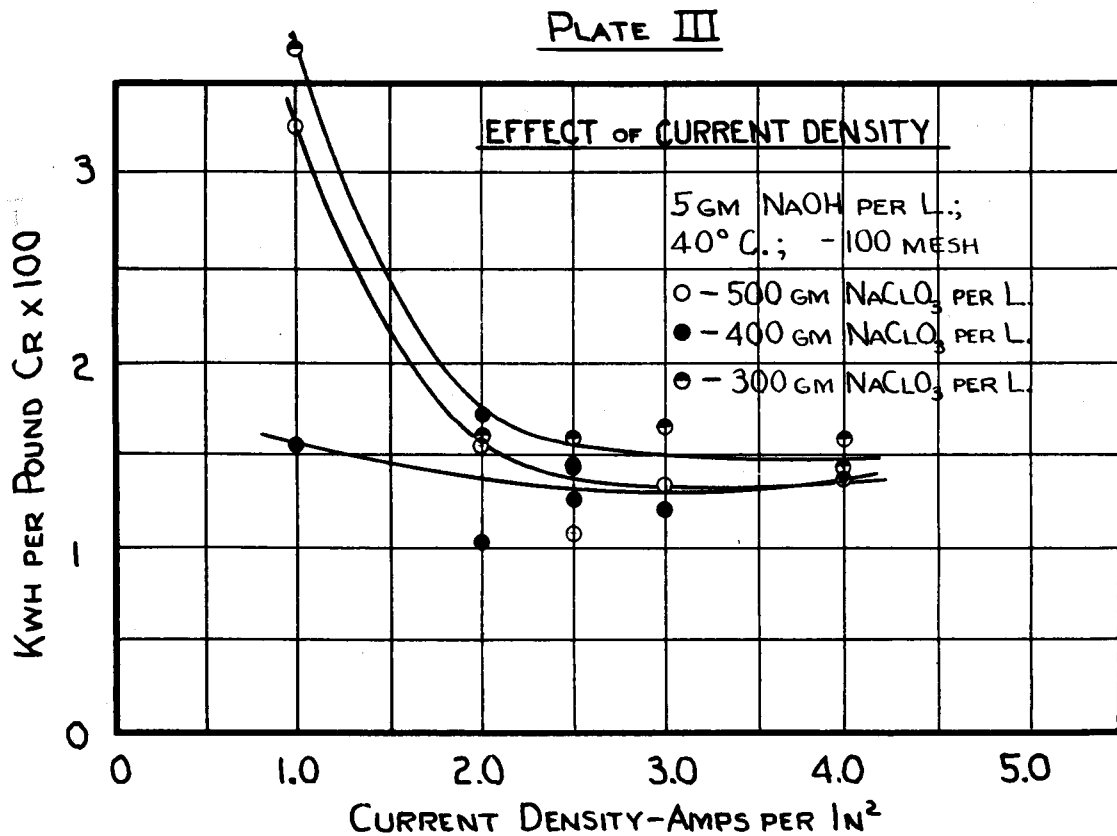
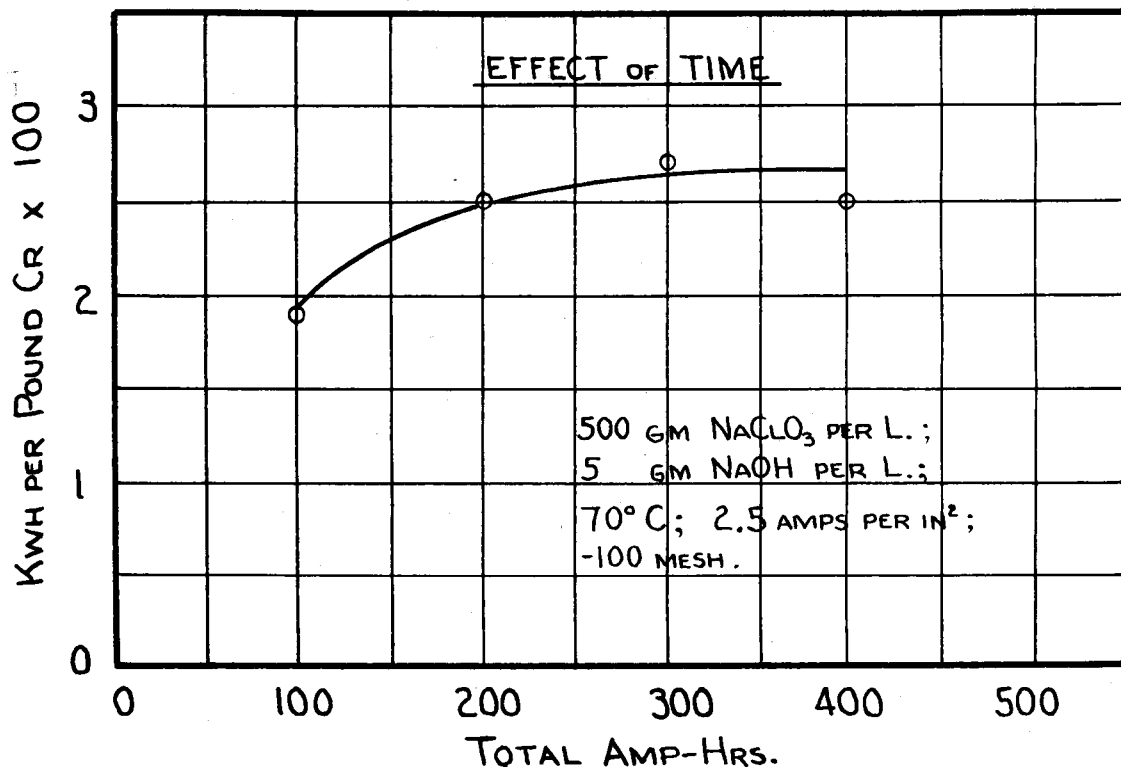


PLATE IV



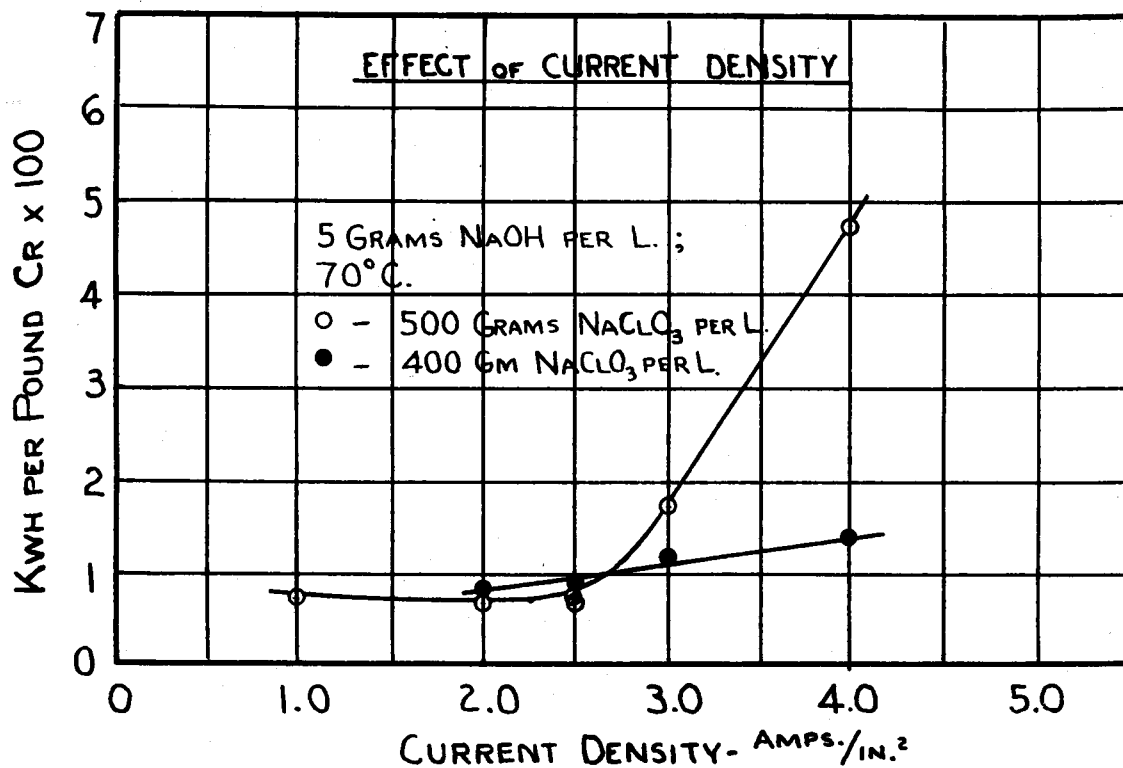


PLATE V

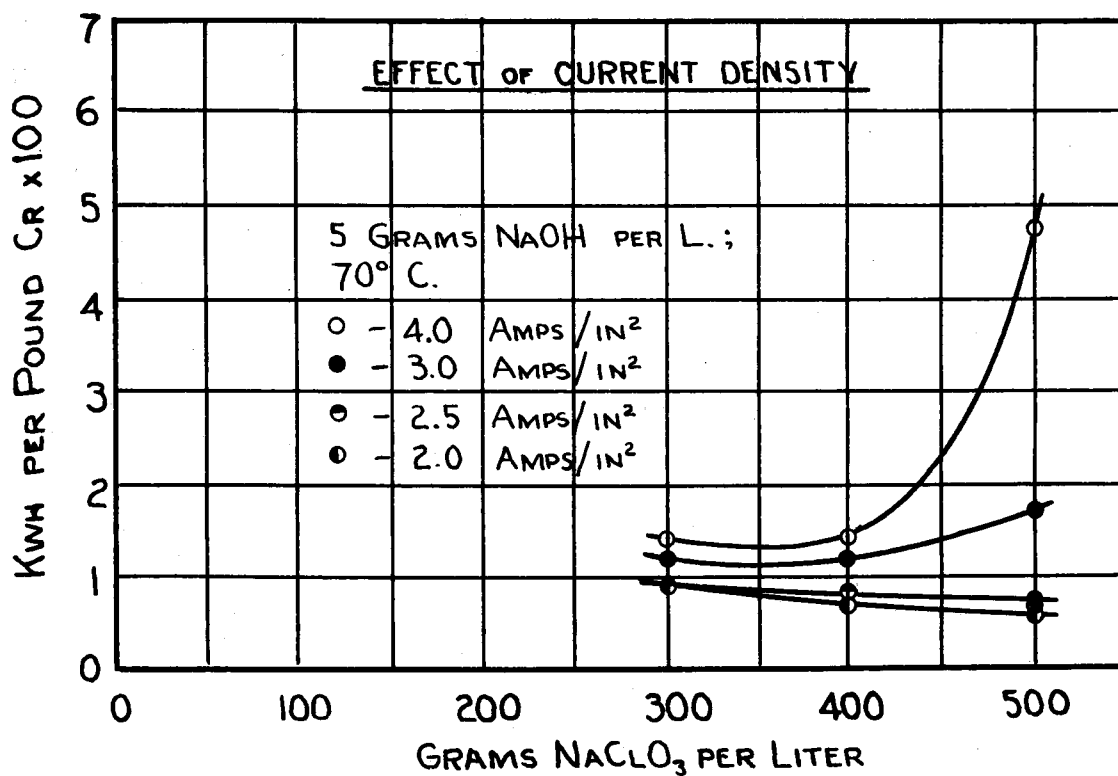
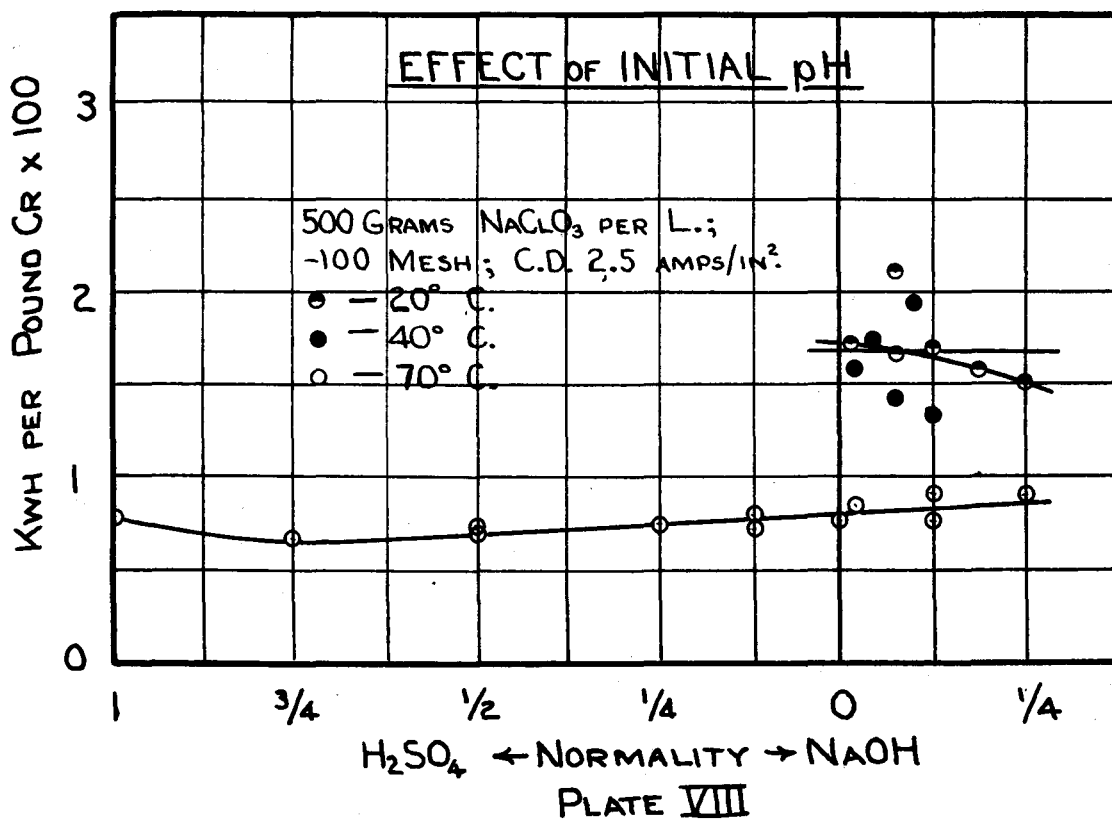
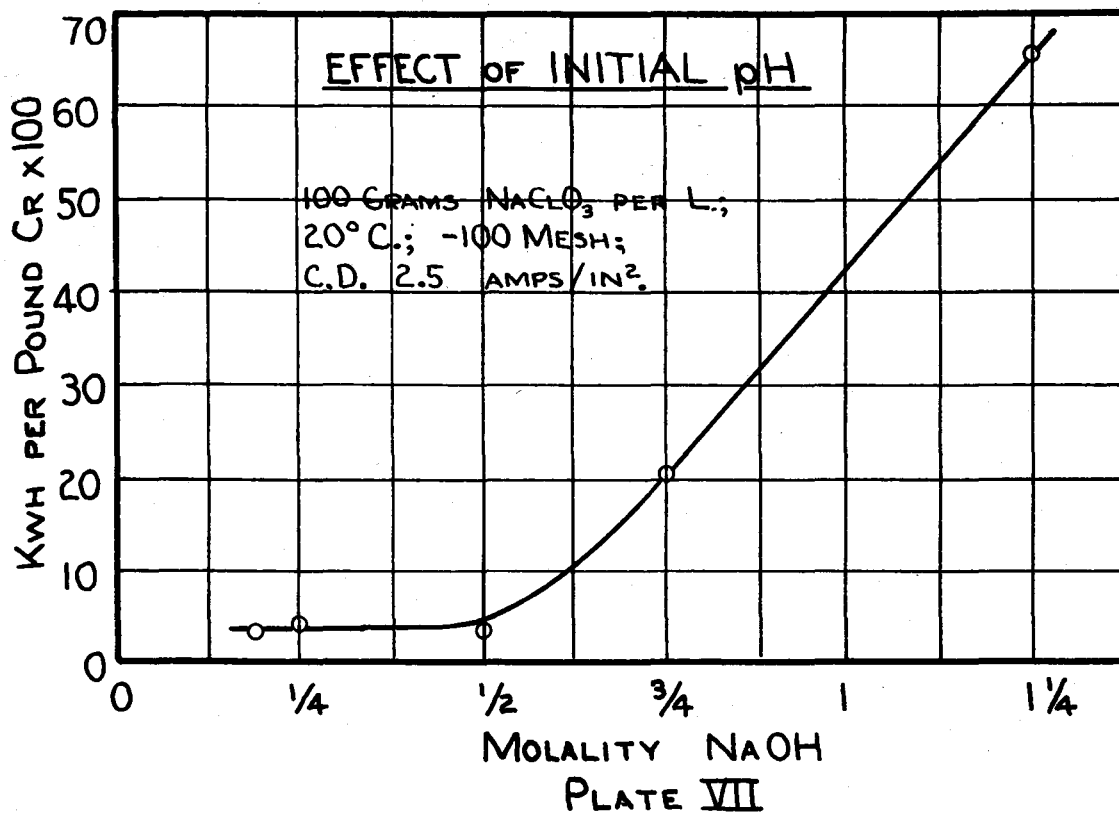


PLATE VI



## Tabulation of Results

| Plate | NaClO <sub>3</sub><br>gm/l | Temp.<br>°C | Time<br>hr | Current<br>amp | C.D.<br>amp/in <sup>2</sup> | NaOH<br>gm/l | Ore<br>Size | Chromium<br>kwh/lb |
|-------|----------------------------|-------------|------------|----------------|-----------------------------|--------------|-------------|--------------------|
| I     | 300                        | 20          | 2          | 1.2            | 2.5                         | 5            | -60+80      | 645                |
|       | "                          | 40          | "          | "              | "                           | "            | "           | 500                |
|       | "                          | 70          | "          | "              | "                           | "            | "           | 325                |
|       | 400                        | 20          | 2          | 1.2            | 2.5                         | 5            | -60+80      | 515                |
|       | "                          | 40          | "          | "              | "                           | "            | "           | 475                |
|       | "                          | 70          | "          | "              | "                           | "            | "           | 290                |
|       | 500                        | 20          | 2          | 1.2            | 2.5                         | 5            | -60+80      | 561,559            |
|       |                            |             |            |                |                             |              |             | 539,605            |
|       |                            |             |            |                |                             |              |             | 550,494            |
|       | "                          | 70          | "          | "              | "                           | "            | "           | 207                |
|       | 300                        | 20          | 2          | 1.2            | 2.5                         | 5            | -100        | 290,174            |
|       | "                          | 40          | "          | "              | "                           | "            | "           | 253,157            |
|       | "                          | 70          | "          | "              | "                           | "            | "           | 116, 92            |
|       | 400                        | 20          | 2          | 1.2            | 2.5                         | 5            | -100        | 135                |
|       | "                          | 40          | "          | "              | "                           | "            | "           | 144,123            |
|       | "                          | 70          | "          | "              | "                           | "            | "           | 86                 |
|       | 500                        | 20          | 2          | 1.2            | 2.5                         | 5            | -100        | 171,207            |
|       |                            |             |            |                |                             |              |             | 170                |
|       | "                          | 40          | "          | "              | "                           | "            | "           | 146,110            |
|       |                            |             |            |                |                             |              |             | 133                |
|       | "                          | 70          | "          | "              | "                           | "            | "           | 78,91,73           |
| II    | 300                        | 20          | 4          | 1.2            | 2.5                         | 5            | -100        | 492                |
|       | 400                        | "           | "          | "              | "                           | "            | "           | 236                |
|       | 500                        | "           | "          | "              | "                           | "            | "           | 243,196            |
|       | 300                        | 20          | 2          | 1.2            | 2.5                         | 5            | -100        | 290,174            |
|       | 400                        | "           | "          | "              | "                           | "            | "           | 135                |
|       | 500                        | "           | "          | "              | "                           | "            | "           | 199                |
|       | 400                        | 40          | 4          | 1.2            | 2.5                         | 5            | -100        | 210                |
|       | 500                        | "           | "          | "              | "                           | "            | "           | 160                |
|       | 400                        | 40          | 2          | 1.2            | 2.5                         | 5            | -100        | 144,123            |
|       | 500                        | "           | "          | "              | "                           | "            | "           | 146,133            |
|       | 300                        | 70          | 4          | 1.2            | 2.5                         | 5            | -100        | 129                |
|       | 400                        | "           | "          | "              | "                           | "            | "           | 129                |
|       | 500                        | "           | "          | "              | "                           | "            | "           | 100                |
|       | 300                        | 70          | 2          | 1.2            | 2.5                         | 5            | -100        | 92,116             |
|       | 400                        | "           | "          | "              | "                           | "            | "           | 86                 |
|       | 500                        | "           | "          | "              | "                           | "            | "           | 78,73,92           |
| III   | 500                        | 70          | 5.5        | 18             | 2.5                         | 5            | -100        | 190                |
|       | "                          | "           | 11.1       | 18             | "                           | "            | "           | 250                |
|       | "                          | "           | 16.6       | "              | "                           | "            | "           | 270                |
|       | "                          | "           | 22.2       | "              | "                           | "            | "           | 250                |

| Plate  | NaClO <sub>3</sub><br>gm/l | Temp.<br>°C | Time<br>hr | Current<br>amp | C.D.<br>amp/in <sup>2</sup> | NaOH<br>gm/l | Ore<br>Size | Chromium<br>kwh/lb |
|--------|----------------------------|-------------|------------|----------------|-----------------------------|--------------|-------------|--------------------|
| IV     | 300                        | 40          | 2          | 0.5            | 1.0                         | 5            | -100        | 378                |
|        | "                          | "           | "          | 1.0            | 2.0                         | "            | "           | 169,159            |
|        | "                          | "           | "          | 1.2            | 2.5                         | "            | "           | 157                |
|        | "                          | "           | "          | 1.5            | 3.0                         | "            | "           | 166                |
|        | "                          | "           | "          | 2.0            | 4.0                         | "            | "           | 141,161            |
|        | 400                        | 40          | 2          | 0.5            | 1.0                         | 5            | -100        | 156                |
|        | "                          | "           | "          | 1.0            | 2.0                         | "            | "           | 169,105            |
|        | "                          | "           | "          | 1.2            | 2.5                         | "            | "           | 144,123            |
|        | "                          | "           | "          | 1.5            | 3.0                         | "            | "           | 121                |
|        | "                          | "           | "          | 2.0            | 4.0                         | "            | "           | 136,137            |
|        | 500                        | 40          | 2          | 0.5            | 1.0                         | 5            | -100        | 324                |
|        | "                          | "           | "          | 1.0            | 2.0                         | "            | "           | 154                |
|        | "                          | "           | "          | 1.2            | 2.5                         | "            | "           | 146,110            |
|        | "                          | "           | "          | 1.5            | 3.0                         | "            | "           | 134                |
|        | "                          | "           | "          | 2.0            | 4.0                         | "            | "           | 136                |
| V & VI | 300                        | 70          | 2          | 1.0            | 2.0                         | 5            | -100        | 93                 |
|        | "                          | "           | "          | 1.2            | 2.5                         | "            | "           | 93                 |
|        | "                          | "           | "          | 1.5            | 3.0                         | "            | "           | 122                |
|        | "                          | "           | "          | 2.0            | 4.0                         | "            | "           | 141                |
|        | 400                        | 70          | 2          | 1.0            | 2.0                         | 5            | -100        | 80                 |
|        | "                          | "           | "          | 1.2            | 2.5                         | "            | "           | 86                 |
|        | "                          | "           | "          | 1.5            | 3.0                         | "            | "           | 121                |
|        | "                          | "           | "          | 2.0            | 4.0                         | "            | "           | 143                |
|        | 500                        | 70          | 2          | 0.5            | 1.0                         | 5            | -100        | 78                 |
|        | "                          | "           | "          | 1.0            | 2.0                         | "            | "           | 71                 |
|        | "                          | "           | "          | 1.2            | 2.5                         | "            | "           | 73,78              |
|        | "                          | "           | "          | 1.5            | 3.0                         | "            | "           | 174                |
|        | "                          | "           | "          | 2.0            | 4.0                         | "            | "           | 477                |
| VII    | 100                        | 20          | 2          | 1.2            | 2.5                         | 7.5          | -100        | 363                |
|        | "                          | "           | "          | "              | "                           | 10           | "           | 413                |
|        | "                          | "           | "          | "              | "                           | 20           | "           | 369                |
|        | "                          | "           | "          | "              | "                           | 30           | "           | 2090               |
|        | "                          | "           | "          | "              | "                           | 50           | "           | 6650               |
|        | "                          | "           | "          | "              | "                           | "            | "           | "                  |
| VIII   | 500                        | 20          | 2          | 1.2            | 2.5                         | 1            | -100        | 171                |
|        | "                          | "           | "          | "              | "                           | 3            | "           | 212,169            |
|        | "                          | "           | "          | "              | "                           | 5            | "           | 171                |
|        | "                          | "           | "          | "              | "                           | 7.5          | "           | 157                |
|        | "                          | "           | "          | "              | "                           | 10           | "           | 152                |
|        | 500                        | 40          | 2          | 1.2            | 2.5                         | 1            | -100        | 161                |
|        | "                          | "           | "          | "              | "                           | 2            | "           | 174                |
|        | "                          | "           | "          | "              | "                           | 3            | "           | 144                |
|        | "                          | "           | "          | "              | "                           | 4            | "           | 197                |
|        | "                          | "           | "          | "              | "                           | 5            | "           | 133                |
|        | "                          | "           | "          | "              | "                           | "            | "           | "                  |
|        | "                          | "           | "          | "              | "                           | "            | "           | "                  |
|        | "                          | "           | "          | "              | "                           | "            | "           | "                  |
|        | "                          | "           | "          | "              | "                           | "            | "           | "                  |



## DISCUSSION

In considering the experimental results, it is felt that not enough is known of the reaction to be able to state with accuracy the mechanism involved. Previous unpublished work by Schulein shows, however, that the reaction is a secondary one. To establish this fact he supported the ore in a gooch crucible a fraction of an inch above the electrode and passed current for a suitable length of time. He found an appreciable amount of chromium in the solution, though no quantitative results are available. This might be compared with the work of Fischbeck and Einecke (see page 3), but it will be recalled that their potential drop was extremely high (220 volts) while the drop in Schulein's apparatus was of the order of 20 volts. Their chromite presumably acted as an electrode, the high voltage being due to the high resistivity of chromite, while this could not have been the case in Schulein's cell because of the low voltage required. This fact shows that the ore does not need to be in contact with the anode in order for oxidation to take place, so it is probable that some product of the electrolysis is the oxidizing agent and is merely regenerated at the anode.

In attempting to determine the active agent in breaking up the ore, several possibilities were considered. The hydrogen peroxide theory of Glasstone and Hickling (3)

was considered as a possible explanation since sodium peroxide is a common flux for chromite. This theory is, in brief, that hydroxyl ions discharging at the anode form free hydroxyl radicals which combine to form  $H_2O_2$ . However,  $H_2O_2$ , if formed at all, would be formed as readily in other electrolytes as long as they do not contain catalysts for its decomposition, and the results in an electrolyte of NaOH with no chlorate present were almost negligible. Also the ferric ion is a catalyst for hydrogen peroxide decomposition, so its presence at the anode, and the high temperature at that point would cause the peroxide to decompose rapidly. For these reasons the hydrogen peroxide theory is believed not to apply to this reaction.

A more tenable theory is that the chlorate ions are oxidized to perchlorates, either by nascent oxygen as postulated by Bennett and Mack (8), or by the discharge of chlorate ions proposed in Oechsli's chloric acid theory, and in the more recent mechanism of Knibbs and Palfreeman (4) where two chlorate radicals combine after discharging and react with water, forming perchloric and chloric acids. The perchloric acid, if formed, would be in a concentrated layer close to the anode, and at an elevated temperature due to the current. G. Frederick Smith (10) says in regard to the chemical solution of chromite, "The nearest approach to a suitable single acid is concentrated perchloric acid, but it would be desirable to be able to increase the

temperature at which it could be used and simultaneously to increase the solubility of chromic acid, which forms an insoluble protective coating on the surface of the undissolved ore." In support of this contention can be offered the fact that increasing the temperature normally increases the efficiency of the process under consideration. The fact that high current density and high temperature combined decrease efficiency can be explained by excessive disruption of the ore layer and mixing of anolyte and catholyte by the gas evolved. However, the fact that increasing the chlorate concentration at high current density and temperature causes lowered efficiency cannot be explained by this theory or any other so far considered.

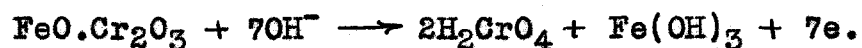
Another possibility is that the nascent chlorate, after discharging, is the active agent in oxidizing the chromite. Yet another is that chloric acid or nascent chlorine are formed at the anode and attack the ore. According to Oechsli's theory the discharged chlorate radicals combine with water to form chloric acid and oxygen, the chloric acid breaking down into perchloric and chlorous acids by auto-oxidation. The chlorous acid is oxidized to chloric acid by nascent oxygen. In support of this mechanism is the formation of chlorine gas at the anode.

All of these mechanisms are possible, with modifications, but none has enough evidence in its favor for a postulation. For instance none explains the fact that



increasing the chlorate ion concentration causes a decrease in efficiency at high temperature and current density. Before a workable theory can be proposed, more work must be done on the effect of current density on the other variables.

Whatever the nature of the intermediate mechanism involved in bringing the iron and the chromium into solution, the sum of all the reactions may be written



## CONCLUSIONS

Within the range investigated, the following conclusions are reached:

1. The efficiency of electrowinning of chromium from chromite is increased by:
  - a. Increasing the  $\text{NaClO}_3$  concentration of the electrolyte, at anode current densities below 2.5 amperes per square inch.
  - b. Increasing the temperature, at anode current densities below 2.5 amperes per square inch.
  - c. Increasing the current density, below  $40^\circ \text{C}$ ., an approximately constant efficiency prevailing from 2.5 to 4.0 amperes per square inch.
2. The efficiency of electrowinning of chromium from chromite is decreased by:
  - a. Increasing the  $\text{NaClO}_3$  concentration of the electrolyte, at anode current densities above 3.0 amperes per square inch.
  - b. For a given current, increasing the time, a constant value being reached in the neighborhood of 300 ampere hours per 1500 cc electrolyte.
  - c. Increasing the temperature, at anode current densities above 4.0 amperes per square inch.
  - d. Increasing the current density at  $70^\circ \text{C}$ .
  - e. Increasing the ore size.

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