

AN ABSTRACT OF THE THESIS OF

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The efficiency of the electrowinning of chromium from chromite ore was studied. Dissolution of the chromite was brought about by placing the finely ground ore at the anode in an electrolytic cell containing a solution of sodium bromate, and passing a current of electricity through the cell. Data were obtained to show the effect of current density, electrolyte concentration, temperature, alkalinity of electrolyte, and time of operation.

It was found that the concentration of sodium bromate is not particularly critical, but that a concentration of 200 to 350 grams per liter gives the best results. The electrolyte should be kept approximately neutral. Maximum efficiency was obtained at high temperature and low current density.

Two possible mechanisms of the reaction were considered. The first of these consists in the electrolytic production of perbromate at the anode and the oxidation of the ore by the perbromate. The second possibility, which appears to be the more satisfactory, is the dissolution of the ore by bromate in the acid layer near the anode, followed by regeneration of the bromate. By postulating this mechanism a satisfactory explanation can be given for the effect of the variables on the efficiency of the

A STUDY OF THE CHEMISTRY OF THE
DISSOLUTION OF CERTAIN REFRACTORY MINERALS

by

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A STUDY OF THE CHEMISTRY OF THE DISSOLUTION OF CERTAIN REFRACTORY MINERALS

INTRODUCTION

Chromium is found in nature in several different ores, the only one of commercial importance being chromite. The chemical formula usually given for chromite is $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, but the chromite found in nature is never of this exact composition. Some of the iron is replaced by magnesium and some of the chromium, by aluminum.

The chromite resources of Oregon consist of some hard rock minerals and the "black sands." The latter are found in many localities along the Pacific Coast in Southern Oregon. These black sands are derived from basic igneous rock of the ferro-magnesian type, the sands representing the more resistant minerals left from the erosion of these rocks. They consist of quartz, olivine, garnet, zircon, and other silicates together with chromite, ilmenite, hematite, magnetite, and frequently some gold and platinum.

The black sands have for many years been exploited for gold and platinum, little attention being given the chromite and other minerals. The chromium content and the ratio of chromium to iron are such that commercial exploitation for either metallurgical or chemical purposes is not possible by methods now in use.

For this reason research now in progress at Oregon

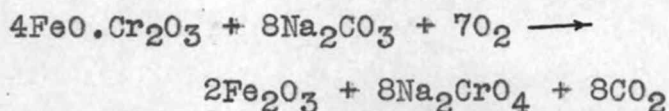
State College is directed toward the development of a process in which these and other non-metallurgical grade ores may be used. The process consists in the electrolytic dissolution of the ore. The experimental work has been directed toward the determination of the effect of certain variables on the efficiency of the process.

Approximately 70% of the chrome ore used in the United States is consumed by the steel industry in the production of alloy steels. The chromium is added in the form of ferrochromium, a metallic alloy of iron and chromium containing approximately 70% chromium (in the war emergency now reduced to 60%). Ferrochromium is produced in the electric furnace by reduction of the ore with carbon or silicon. The ore used must be lump containing 48 to 51 percent Cr_2O_3 and having a chromium to iron ratio of 2.8:1 to 3:1. These requirements preclude the use of many domestic ores.

The manufacture of refractory brick accounts for an additional 20 percent of the domestic consumption of chrome ore, while the remaining 10 percent goes to the chemical industries for the production of chromium salts used for tanning leather and other minor uses, and for the production of chromic acid used for chromium plating.

Compounds of chromium are prepared by fusing the finely ground ore (-130 mesh) with sodium carbonate in a reverberatory furnace. The iron in the ore is oxidized to

Fe_2O_3 and the chromium is converted to sodium chromate according to the reaction



The sodium chromate is extracted with water and the solution is then treated either to recover the sodium chromate or to convert it to other chromium compounds.

It is possible to produce chromates from some forms of chromite and from ferrochromium by several other methods, which depend on the digestion of the ore with sulfuric acid of specific gravity 1.54 and an oxidizing agent such as MnO_2 (9), PbO_2 (13), KMnO_4 (2), or HClO_4 (17). Other methods are described in the literature (4, 14, 15, 16) and have been discussed by Bailey (1) who attempted to use the described processes to dissolve chromite, but had little success. None of these methods are used in commercial production of chromates, and most of them would appear to be too expensive ever to become of economic importance.

EXPERIMENTAL PROCEDURE

APPARATUS. The cells used in this investigation consisted of glass tubes eight inches long and one inch in diameter, to one end of which a platinum electrode was sealed as shown in figure 1, page 5. In operation this electrode served as the anode. Electrical contact was made by setting the cell in a shallow trough filled with mercury, which was connected to the current source. The mercury trough was long enough to accommodate six cells. Figure 2, page 5, shows the wiring diagram for three cells. The cathodes consisted of sheet iron; the distance between the anode and cathode was approximately four inches.

ORE. It having been found, as reported by Bailey (1) that -60+80 mesh ore ground to -100 mesh gives satisfactory results, this material was used throughout that part of the investigation herein reported. The ore was that designated by Bailey as ore B and was taken from near North Bend, Oregon. The Cr_2O_3 content of the -60+80 fraction was 26.5%.

ELECTROLYTE. The electrolyte used in the earlier stages of this research was an aqueous solution of sodium chlorate. The results obtained were partially reported in a thesis by R. B. Bailey (1). Briefly, it was found that the best operating conditions were high temperature (70°C), high concentration of sodium chlorate, and anode current

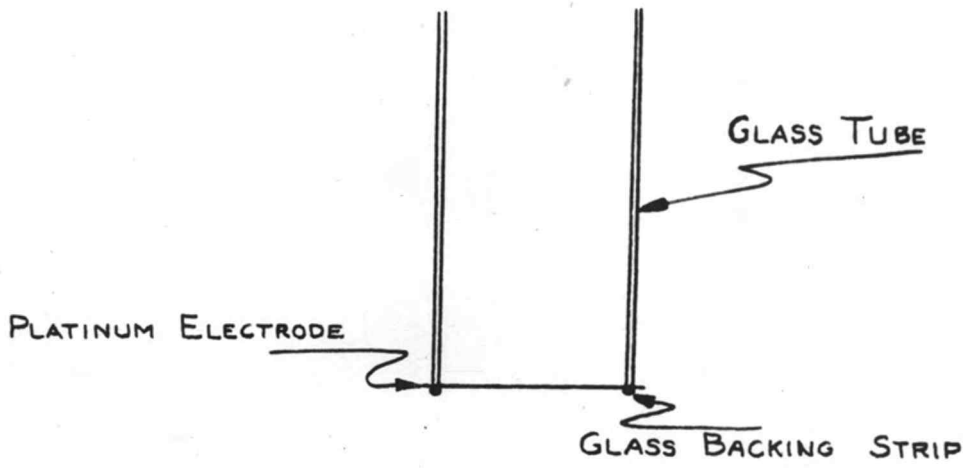


FIG. 1. CELL CONSTRUCTION

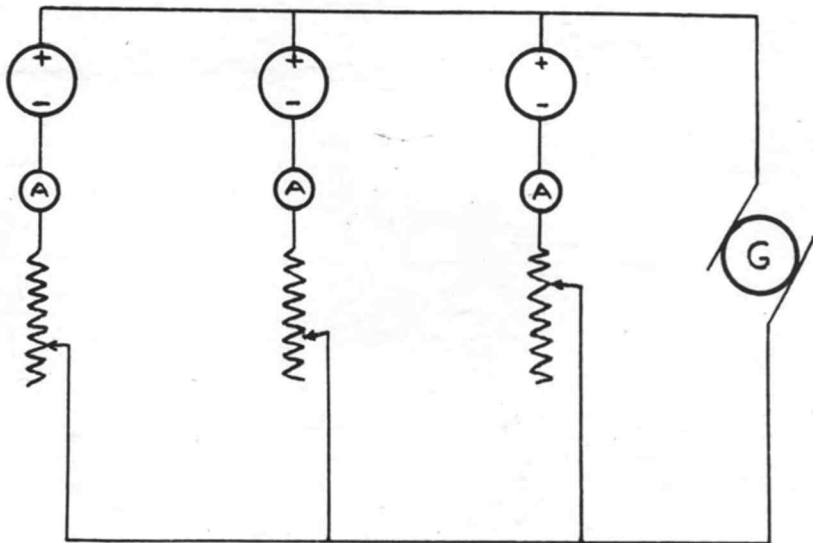


FIG. 2. WIRING DIAGRAM

density of about two amperes per square inch. It was also found that the efficiency decreased with increased time of operation.

Later it was found that higher efficiencies could be realized by using sodium bromate instead of sodium chlorate as the electrolyte. Consequently, the possibilities of bromate were investigated. Sodium bromate was used throughout that part of the investigation reported herein.

OPERATION. Fifty cc of the electrolyte and a weighed amount of ore were placed in the cells in a constant temperature bath. After the desired temperature was reached, a constant direct current of electricity was passed through the cells for the desired length of time, usually two hours. When the run was completed, the solution was filtered to remove the undissolved ore and ferric hydroxide. The amount of chromium dissolved was determined by reducing the hexavalent chromium to the trivalent state with sulfur dioxide (sodium sulfite plus sulfuric acid), and precipitating the trivalent chromium with ammonium hydroxide. The precipitate was then filtered from the solution, washed, and dissolved in dilute sulfuric acid. This solution was made basic with sodium hydroxide, and the chromium oxidized with sodium peroxide. After decomposition of the excess peroxide by boiling and carbonation, the solution was acidified with sulfuric acid and titrated with ferrous ammonium sulfate and potassium dichromate,

using the usual "titration mixture" of sulfuric acid and phosphoric acid, with sodium diphenylamine sulfonate as the indicator. The separation of the chromium was, of course, necessary because sodium bromate is a strong oxidizing agent in acid solution and would oxidize the ferrous ammonium sulfate in the titration. Various analytical methods were tried, but this was found to be the most satisfactory.

The variables considered were anode current density, temperature, concentration of electrolyte, alkalinity of electrolyte, time of operation, and anode material.

EFFECT OF VARIABLES

ANODE CURRENT DENSITY. The effect of anode current density at 20°, 40°, and 70° C is shown graphically in figure 3, where current density is plotted against ampere-hours per gram of chromium dissolved. It is found that at 20° C an increase in the anode current density results in increased efficiency, the increase being very marked between one ampere per square inch and 2.5 amperes per square inch, and much less marked as the current density is further increased.

At 40° C and one ampere per square inch anode current density the efficiency is much better than at 20°, but, whereas increasing the current density at 20° results in increased efficiency, at 40° the opposite effect is noted. At about 4 amperes per square inch the 20° and 40° curves intersect.

At 70° the effect of anode current density is approximately the same as at 40° over the range studied. In all cases the dissolution of the ore was accomplished more efficiently at 70° than at 40°.

These curves show the results obtained with a cell solution containing 350 grams of sodium bromate per liter and 3.5 grams of sodium hydroxide per liter. No data were obtained for extending these curves below one ampere per square inch. However, figure 4 shows the effect of further

decrease in current density at 70°, using a solution containing 300 grams of sodium bromate per liter and no caustic. This change in electrolyte composition was made because it was found that the efficiency of operation was somewhat better if no caustic were added to the solution at the beginning of the cell run, and that lower sodium bromate concentration also gave slightly better results. As shown in figure 4, the best results were obtained at an anode current density of 0.16 ampere per square inch, further decrease resulting in lower efficiency (more ampere-hours per gram of chromium).

All the points on these curves (figures 3 and 4) represent two-hour cell runs. Consequently, the quantity of electricity passed through the cells was not the same in all cases, but varied with the current density. It was thought that perhaps the decreased efficiency observed at higher current densities was due, at least in part, to the greater accumulation of chromate and other products of electrolysis. If any of these products have a detrimental effect, it might be expected that their effect would increase with increasing concentration, and consequently, with increasing quantity of electricity passed through the cell. Hence, it seemed best to operate the cells for the same number of ampere-hours rather than the same length of time. Figure 5 shows the results of a series of runs made at different current densities for different lengths of

time to give 0.6 ampere-hour of electricity in all cases. There is little difference between this curve and the one in figure 4 except that it is not quite so steep at the higher current densities. This seems to indicate that part of the effect shown in figure 4 must be attributed to the accumulation of products of electrolysis. Another difference between the two curves is that no minimum was reached in figure 5. The lowest point on this curve corresponds to a current density of 0.05 ampere per square inch. Lower current densities than this were not tried because it is improbable that any increase in efficiency likely to result from such low current densities would justify the added expense of larger anode areas.

ELECTROLYTE CONCENTRATION. The effect of concentration of sodium bromate was studied at different concentrations of sodium hydroxide as shown in figure 6. In all cases the current density was one ampere per square inch and the temperature was 70° C. It is seen that the concentration of sodium bromate is not particularly critical, but a solution containing 200 to 300 grams of sodium bromate per liter gives somewhat greater efficiency than either higher or lower concentrations.

ALKALINITY. As pointed out previously, the addition of sodium hydroxide to the solution at the beginning of the cell run causes the efficiency to drop, the decrease being about 30% with 5 grams per liter initial caustic.

It may be pointed out here that although the solution as a whole may be made alkaline at the beginning of a run, the solution in contact with the ore soon becomes acid, or at least less alkaline. This is due not only to the migration of bromate ions to the anode and the sodium ions to the cathode, but also to the formation of chromic acid by the oxidation of the ore. As a result of the latter the solution as a whole becomes more and more acid. Consequently, the cells to which no caustic had been added were slightly acid at the end of a two-hour run. However, while the cell was in operation the main body of the solution was basic enough to precipitate ferric hydroxide. Whenever a run of more than two hours' duration was made, sodium hydroxide was added as it became necessary.

TEMPERATURE. In figure 7, electrolyte concentrations are plotted against ampere-hours per gram of chromium dissolved, at 60°, 70°, and 80° C. The current density was one ampere per square inch. These curves show that the efficiency of the process increases as the temperature is increased to 70°. If the temperature is raised above 70°, little change in efficiency is noted at the lower concentrations of bromate. At 500 grams of bromate per liter, however, increasing the temperature from 70° to 80° decreases the efficiency by about 10%.

TIME OF OPERATION. To determine the effect of time of operation, a larger cell (1500 cc) was operated

continuously, and a sample was taken for analysis at intervals of about 75 ampere-hours. This cell was operated at one ampere per square inch and 70° C. The anode area was 7.1 square inches. Sodium hydroxide was added from time to time as required to maintain the main body of the solution slightly alkaline.

The results are shown graphically in figure 8, where grams of chromium are plotted against ampere-hours. If the efficiency of the process were constant, this would be a straight line. Actually, the efficiency drops off at a rate which increases with the time of operation. This is shown more clearly in figure 9 where ampere-hours per gram of chromium are plotted against ampere-hours consumed. Curve 2 shows the average ampere-hours required per gram of chromium dissolved in continuous runs for varying lengths of time. The slope of this curve is a measure of the decrease in efficiency of the process. Curve 1 is plotted from data derived from figure 8. Here the points on the curve show the ampere-hours required per gram of chromium dissolved when starting with a solution which has been operated for the number of ampere-hours corresponding to the abscissae of the points, and operating for 100 ampere-hours. Thus if a cell is operated with a fresh solution of sodium bromate for 100 ampere-hours, the average requirement per gram of chromium over this period is 7.5 ampere-hours. If the cell is operated for an additional

100 ampere-hours with this solution, the average requirement for the second 100 ampere-hours is 11.5 ampere hours per gram of chromium. This curve shows even more clearly than curve 2, the harmful effect of some product or products of electrolysis.

To determine the effect of accumulated chromium (which is dependent upon the time of operation) a solution was made up exactly like the original electrolyte except that it contained 38.1 grams of chromium (as determined by analysis of an aliquot part). This chromium concentration corresponds to a 510 ampere-hour run of the cell. After operating the cell for 100 ampere-hours with this solution, the amount of chromium dissolved was determined, and from this the number of ampere-hours required per gram. This point is shown in figure 9 (curve 3). It is seen that, although the accumulation of chromium has some detrimental effect, this is enough to account for only a small percentage of the drop in efficiency. This is being investigated further.

ANODE MATERIAL. While platinum anodes were used in all of the cell runs so far described, some other possible anode materials were considered. None of these showed any promise except, possibly, graphite. Figure 10 shows the results obtained using graphite anodes at different current densities. This curve is similar in shape to the one in figure 4 where platinum anodes were used, but the

efficiencies are somewhat lower. One difficulty encountered in making a quantitative study on graphite anodes is the fact that the current density is constantly decreasing because the anode area is increased by the abrasive action of the ore. No correction for this effect was made on the data plotted in figure 10. The "current densities" here are based upon the anode area calculated from the diameter, i.e., the "apparent" area.

FIGURE 3
EFFECT OF CURRENT DENSITY

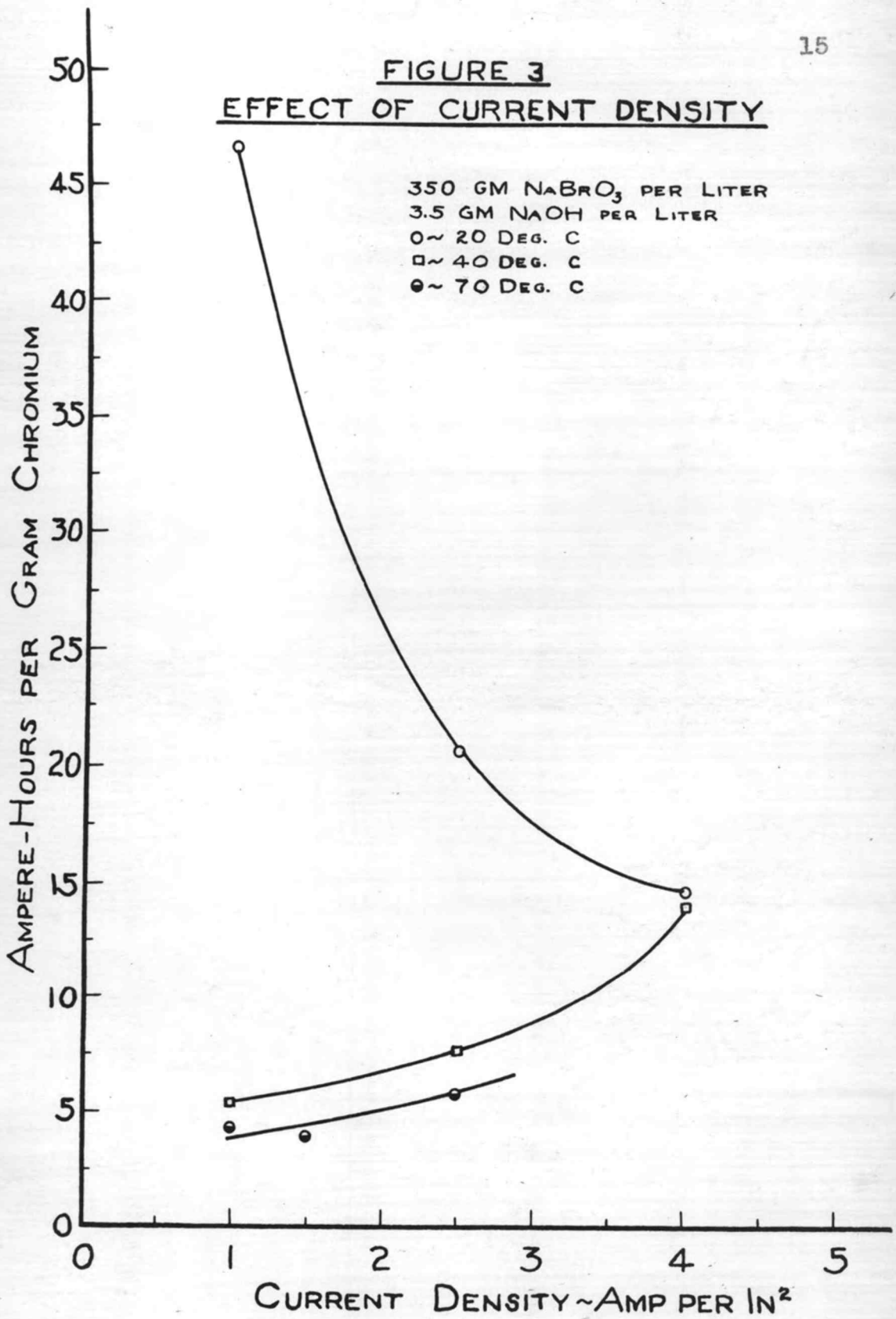


FIGURE 4
EFFECT OF CURRENT DENSITY

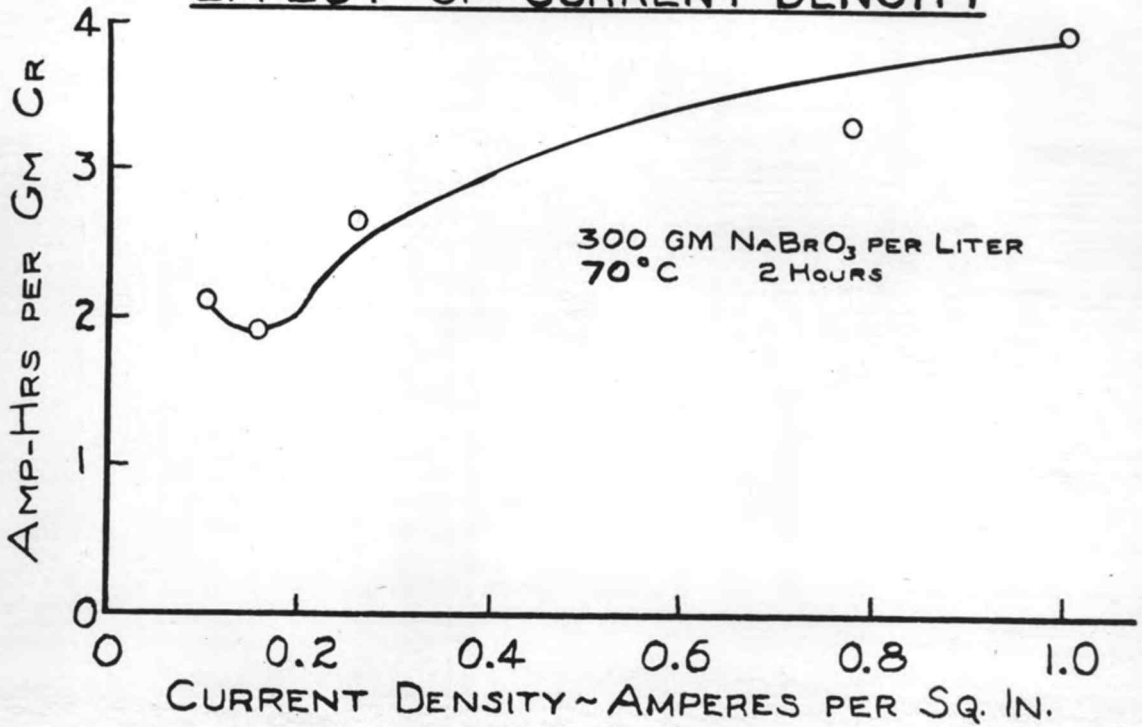


FIGURE 5
EFFECT OF CURRENT DENSITY

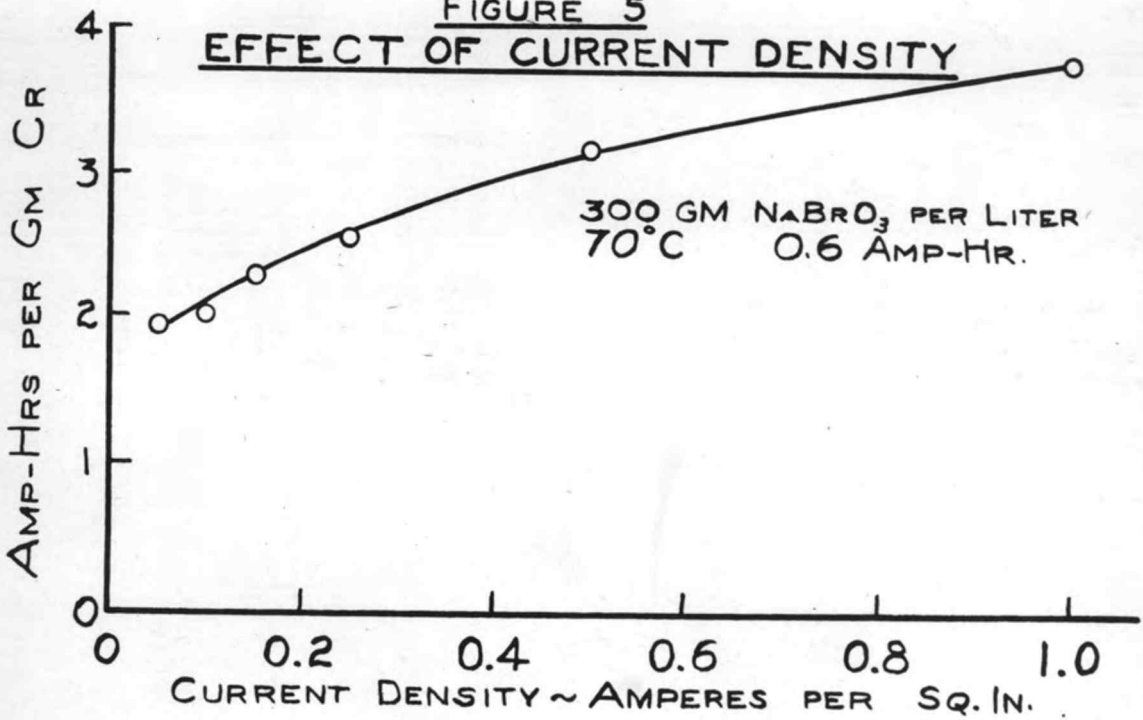


FIGURE 6
EFFECT OF ELECTROLYTE CONCENTRATION

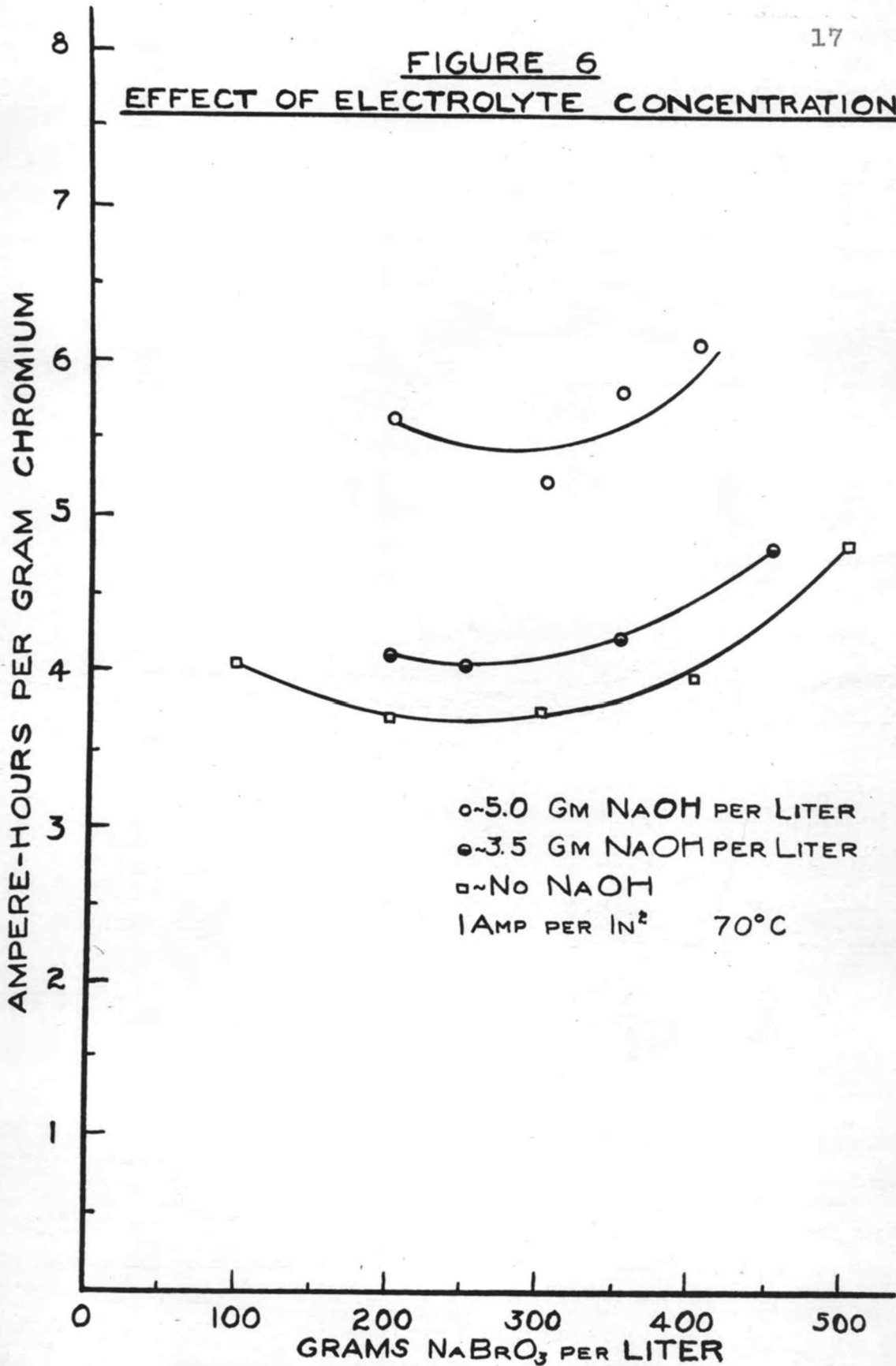


FIGURE 7
EFFECT OF ELECTROLYTE CONCENTRATION

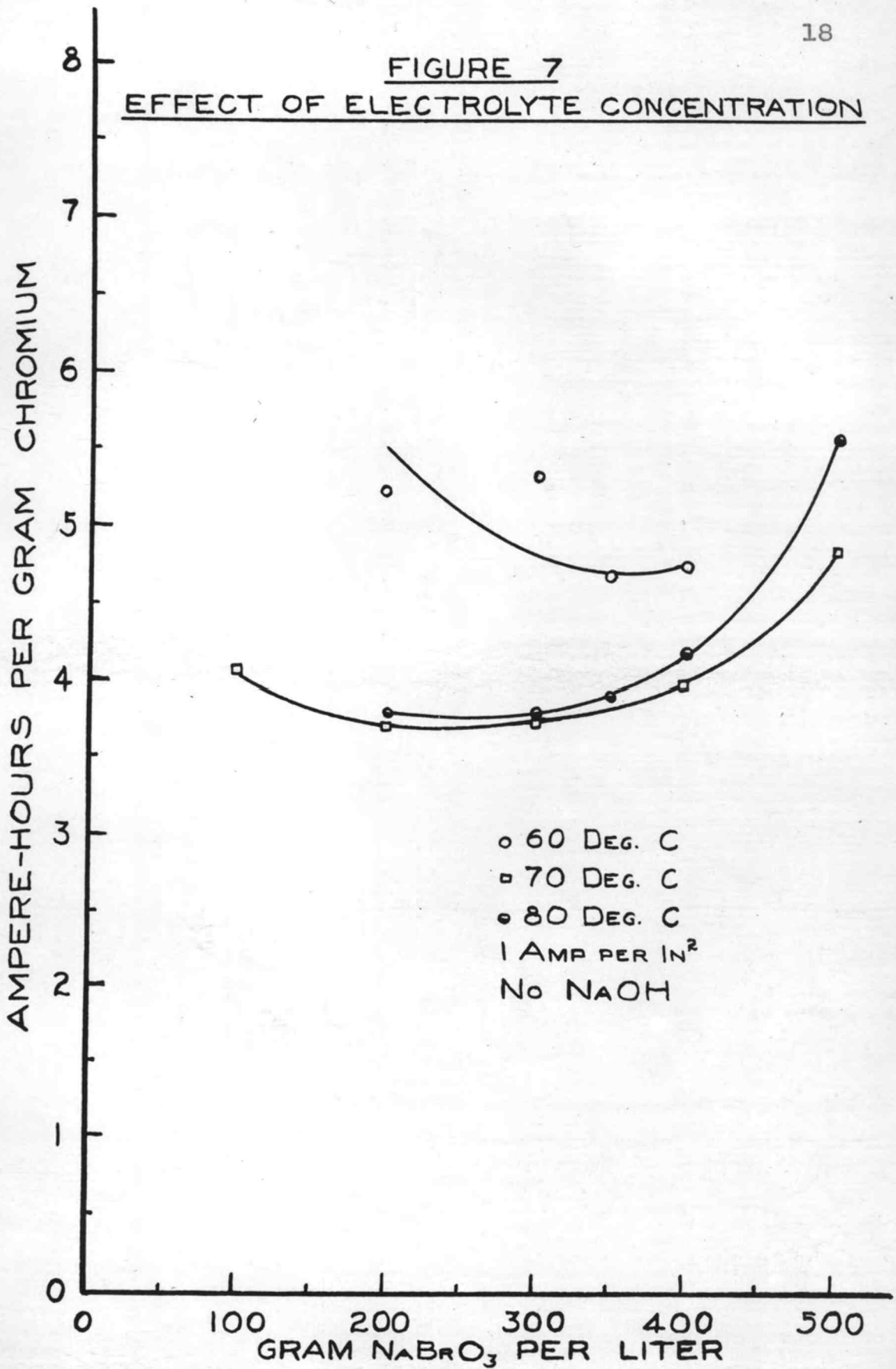


FIGURE 8
EFFECT OF TIME

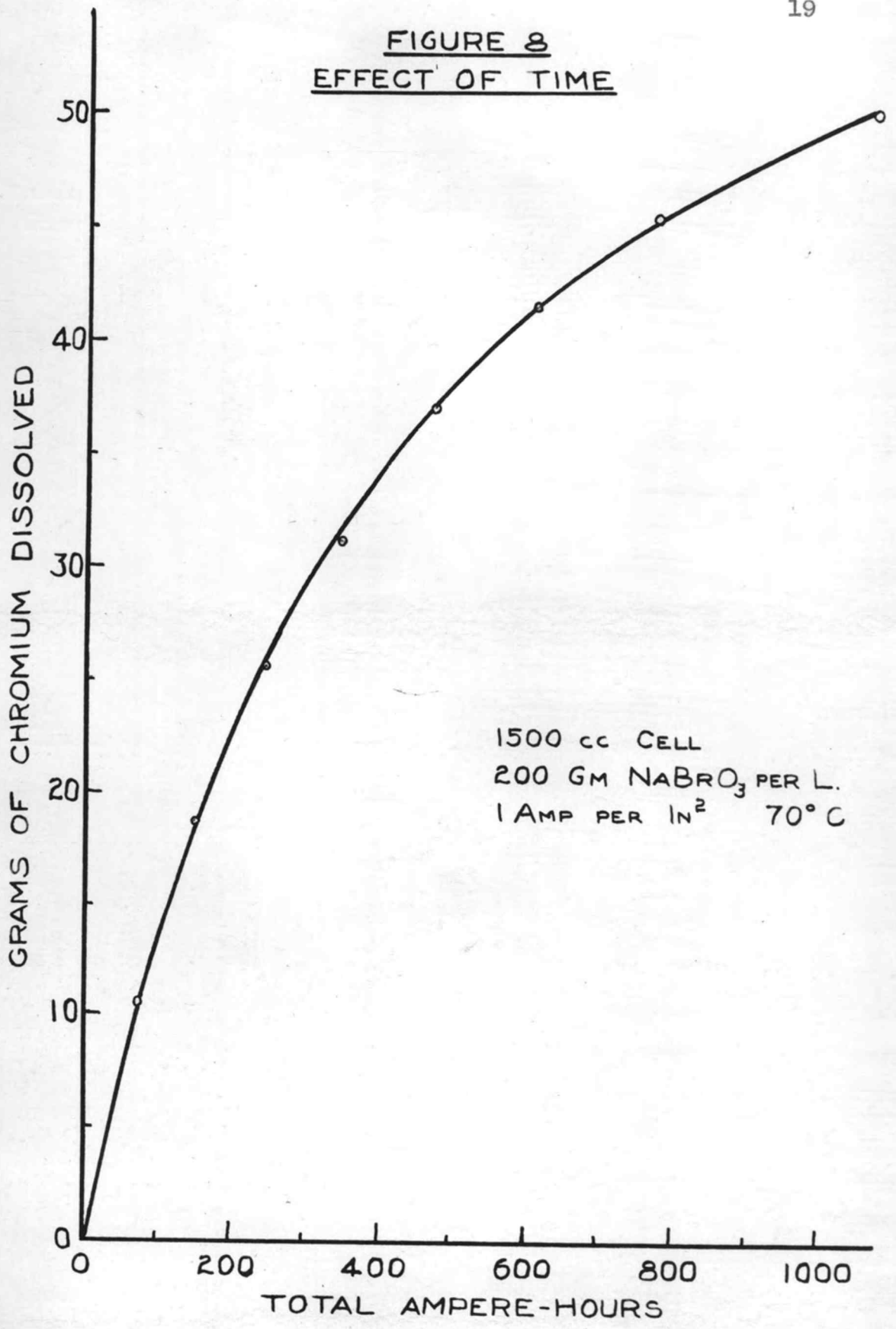
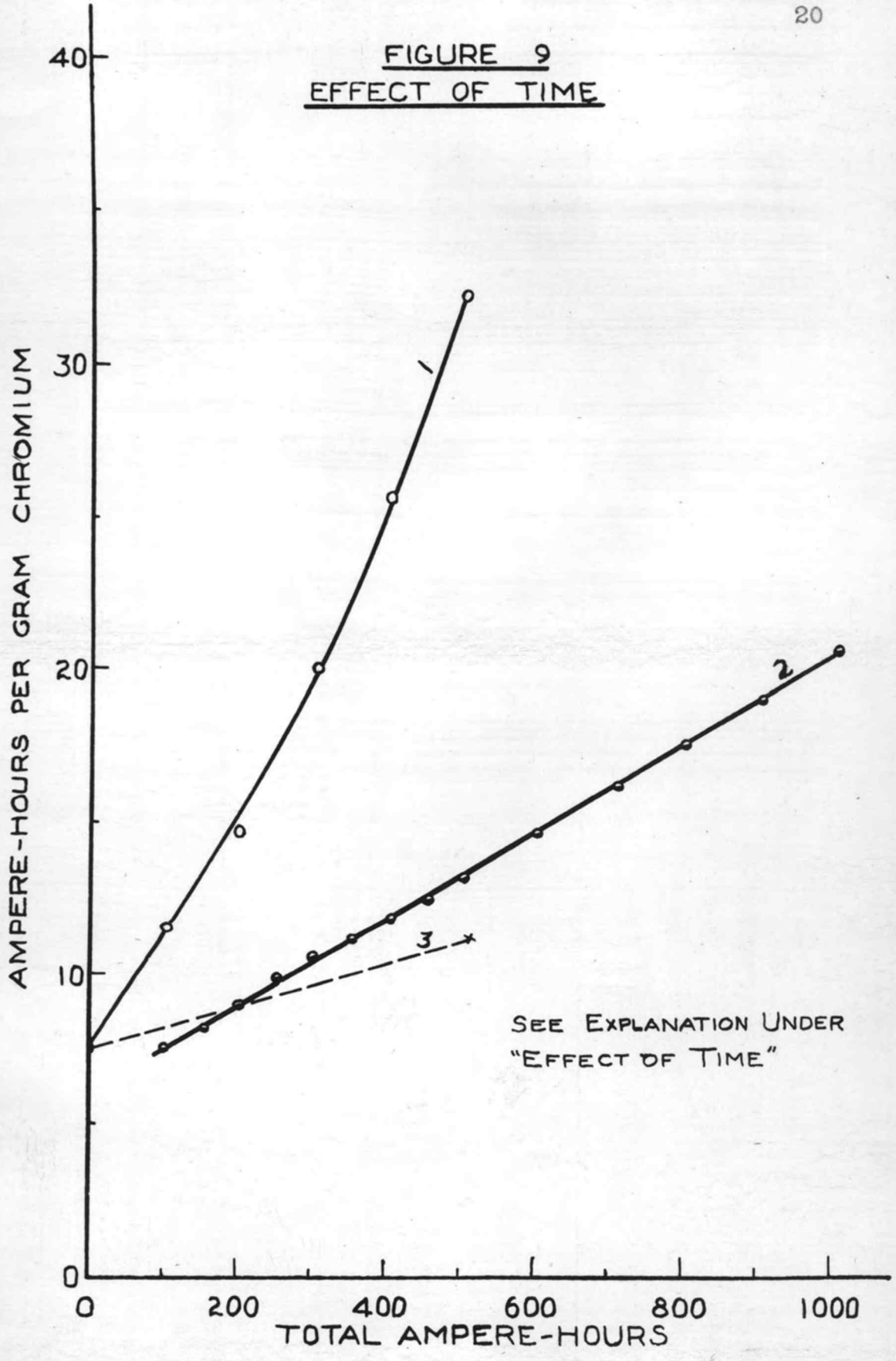
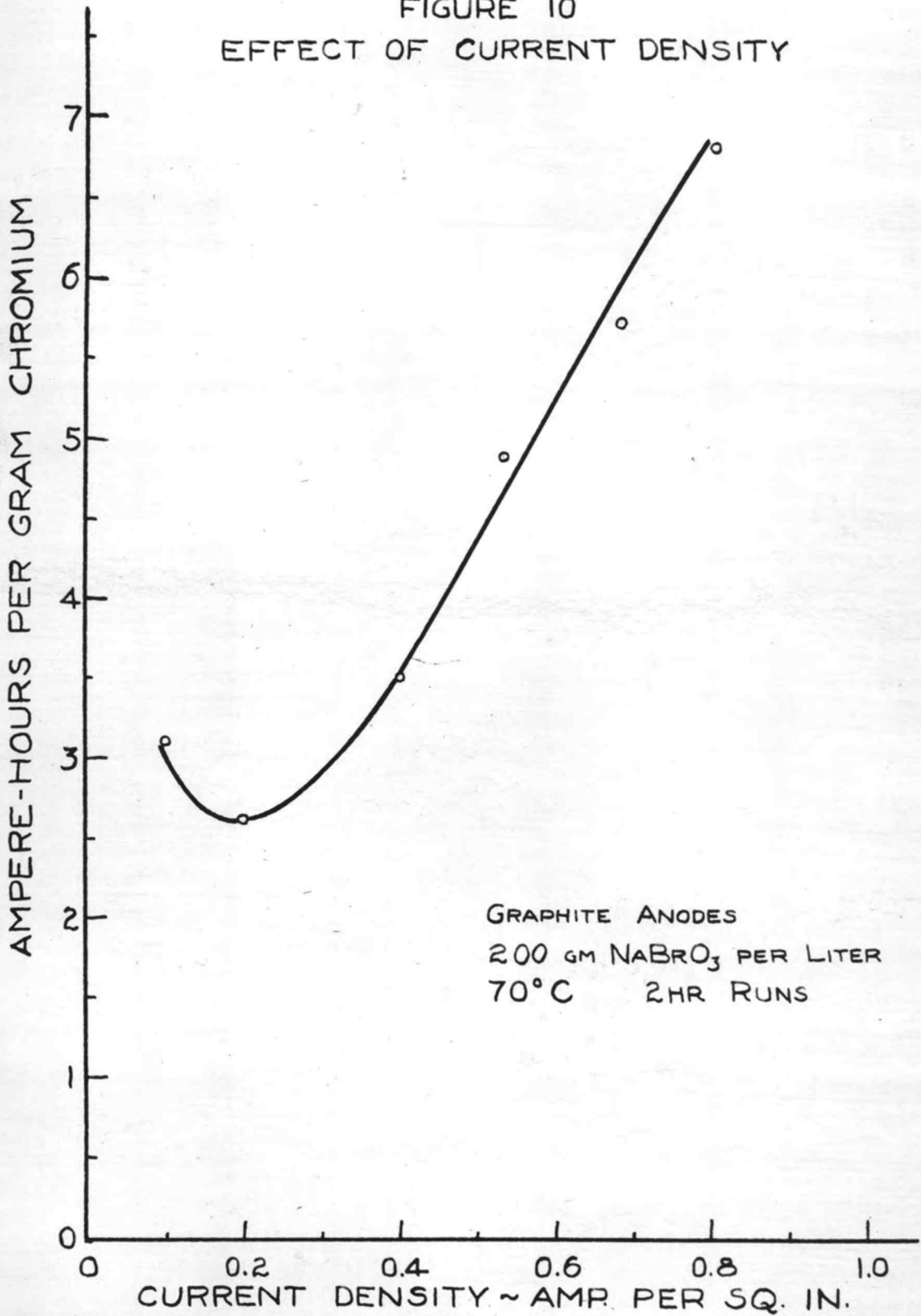


FIGURE 9
EFFECT OF TIME



SEE EXPLANATION UNDER
"EFFECT OF TIME"

FIGURE 10
EFFECT OF CURRENT DENSITY



Data

<u>Electrolyte Concentration</u>		<u>Current Density</u> Amp/□"	<u>Temperature</u> °C	<u>Gm Cr</u>	<u>Ampere-Hours</u> per Gm Cr
<u>GmNaBrO₃</u> per Liter	<u>GmNaOH</u> per Liter				
350	3.5	1.0	20	0.0238	46.7
		2.5		0.134	20.7
		4.0		0.300	14.8
350	3.5	1.0	40	0.180	5.55
		2.5		0.330	7.58
		4.0		0.281	14.2
300	3.5	1.0	70	0.247	4.54
				0.206	5.44
400	5.0	1.0	70	0.195	6.15
350				0.222	5.85
300				0.212	5.28
200				0.212	5.66
500	0.0	1.0	70	0.246	4.88
400				0.299	4.01
300				0.318	3.78
200				0.321	3.74
100				0.294	4.08
400	0.0	1.0	60	0.260	4.77
350				0.241	4.73
300				0.228	5.35
200				0.229	5.25
500	0.0	1.0	80	0.214	5.61
400				0.284	4.23
350				0.308	3.90
300				0.314	3.82
200				0.314	3.82
450	3.5	1.0	70	0.248	4.85
350				0.283	4.25
250				0.294	4.08
200				0.289	4.15
300	0.0	0.78	70	0.291	3.30
		1.00		0.314	3.95
		1.50		0.349	5.34
		1.97		0.355	6.76
		2.28		0.307	8.47

Electrolyte Concentration		Current Density Amp/□"	Temper- ature °C	Gm Cr	Ampere- Hours per Gm Cr
GmNaBrO ₃ per Liter	GmNaOH per Liter				
300	0.0	0.10	70	0.0587	2.11
		0.27		0.127	2.68
		0.16		0.105	1.90
200*	0.0	1.00	70	0.160	3.75
		0.75		0.196	3.07
		0.50		0.192	3.13
		0.25		0.236	2.54
		0.15		0.262	2.29
		0.125		0.283	2.17
		0.10		0.295	2.03
0.05	0.306	1.96			
200**	0.0	0.10	70		3.10
		0.53		4.85	
		0.80		6.80	

* Runs made for varying lengths of time to give 0.6 ampere-hours.

** Graphite anodes.

DISCUSSION

Earlier unpublished work by Mr. Joseph Schulein shows definitely that the dissolution of the ore is a secondary reaction. This fact was established by placing the ore in a Gooch crucible a fraction of an inch above the anode and passing current through the cell. After operating the cell for a short time, he found a considerable amount of chromium in solution. This indicates that the process consists either of the formation of an oxidizing agent at the anode, followed by the oxidation of the ore by this agent, or the oxidation of the ore by the bromate in the acid layer at the anode.

The mechanism first considered by the author was similar to that proposed by Bailey (1) to explain the action in a cell using sodium chlorate solution as the electrolyte. Briefly, this mechanism was as follows:

1. Perchloric acid is formed at the anode by the oxidation of the chlorate.
2. The ore is then oxidized by the perchloric acid.

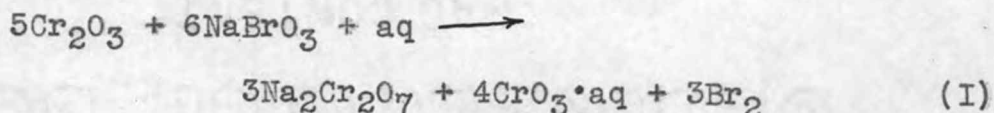
A search of the literature was made by the author in order to learn whether one might expect perbromic acid to be formed momentarily by the electrolysis of sodium bromate, in a manner analogous to the formation of perchloric acid from chlorates. Kämmerer (3) claimed to have prepared perbromic acid by the action of dry bromine vapor on

perchloric acid vapor, but the claim was denied by many investigators who attempted to reproduce Kämmerer's results (2, 10, 18). Muir (11) attempted to produce perbromic acid by electrolysis of bromic acid but did not succeed. Müller and Friedenberger (12) also attempted to prepare it by an electrolytic process, but they too were unsuccessful. According to Mellor (8), neither perbromic acid nor perbromates have found a place in the list of known chemical compounds. It should be kept in mind, however, that the failure to isolate and identify perbromic acid does not necessarily preclude the possibility of its existence for a very short time. Nevertheless, in the light of present knowledge, it does not seem necessary to postulate the electrolytic formation of perbromic acid in order to explain the process with which we are here concerned.

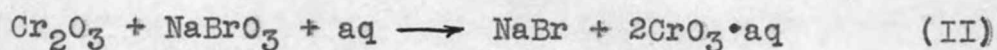
A more tenable theory seems to be the second mentioned at the beginning of this discussion, i.e., the oxidation of the ore by the bromic acid found near the anode, followed by regeneration of the bromic acid.

Lydén (6, 7), in a study of the behavior of chromic oxide, Cr_2O_3 , toward alkali halogenate solutions, found that the oxide could be dissolved by alkali chlorates and bromates in neutral solutions. In the case of bromates, bromine is liberated. By determining the amount of bromine liberated and the quantity of chromium dissolved, Lydén

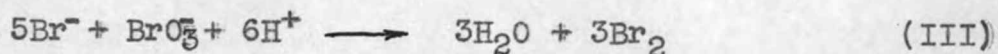
deduced that the reaction is



It is obvious that as the reaction proceeds, the solution becomes more and more acid because of the formation of chromic acid. This increased acidity, it was found, causes the reaction to proceed more rapidly. Thus the reaction is autocatalytic. In a later study (7), Lydén found that reaction (I) takes place in two steps, the primary reaction being



followed by the reaction



Reaction (III) tends to keep the hydrogen ion concentration from increasing, and consequently tends to check the increasing rate of reaction (II). As a result, a point is reached at which the rate of reaction begins to decrease. If any bromide is present at the beginning of the reaction, the rate does not begin to increase rapidly until practically all of the bromide has been oxidized to bromine.

Lydén (6) found that the oxidation of the Cr_2O_3 is favored by high temperature but also takes place at room temperature.

It would seem that this same mechanism could be applied to the process of dissolving chromite by electrolysis in a solution of sodium bromate. The mechanism would, of

course, be complicated by the presence of iron and other substances in the ore.

The passage of current through the cell has a two-fold effect. First, it produces an acid layer at the anode so that the reaction becomes very rapid in a short time; the period of induction is circumvented. Secondly, the bromide and bromine are reoxidized to bromate.

An attempt will now be made to explain the shapes of the curves in figures 3 to 10, on the basis of this mechanism. Referring to figure 3, at 20° C and 1 ampere per square inch, anode current density, the action is slow because of the low temperature and also because of the relatively low concentration of acid at the anode. Raising the current density increases the acidity of the solution in contact with the ore and therefore increases the rate of dissolution of the ore. The increase in the rate of attack of the ore is more than proportional to the increase in acidity and, consequently, more than proportional to the increase in current density. Thus, the operation is more efficient at high current densities (at 20°).

If the temperature is raised to 70° and the cell operated at 1 ampere per square inch, the reaction takes place much more rapidly than at 20°. This is due primarily to the higher temperature, but, since the chromium does dissolve more rapidly at the higher temperature, the acidity also increases more rapidly, producing a still more

favorable condition.

If now the current density is increased (the temperature being 70°) the action of the bromate on the ore takes place still more rapidly. However, since the acidity becomes quite high, the oxidation of bromide by bromate to form bromine becomes increasingly important. Also, thermal decomposition may take place at the higher concentration. The result is that the rate of oxidation of the ore does not increase as much, proportionately, as does the current passed, so that the process becomes less efficient with increasing current density. This same explanation applies to figures 4 and 5. It may be pointed out here that since the efficiency spoken of throughout this thesis is based upon the weight of chromium dissolved per unit quantity of electricity, it may not be, and probably is not, a true measure of the efficiency of the primary electrolytic process. For example, the electrolytic process, the exact nature of which is not known, may be just as efficient at low temperature and low current density as it is at high temperature and low current density, but, since the oxidation of the ore is accomplished more rapidly at high temperature, the efficiency based on dissolution of ore, is greater.

On the basis of the proposed theory, the effect of sodium hydroxide is as would be expected. (See figure 6). Initial alkalinity of the electrolyte results in a thinner

acid layer at the anode during electrolysis, so that the active solution is in contact with less ore. Consequently, less chromium would be dissolved per unit quantity of electricity. If the bromate concentration is very high, thermal decomposition takes place more rapidly. More bromate is then used up in accordance with reaction (III), page 26 and relatively less in reaction (II), page 26.

The shape of the curves in figure 7 can be explained in the same way. The fact that the process is less efficient at 80° than at 70° (when bromate concentration is high) is not unexpected, for if thermal decomposition takes place at 70° it should take place to a greater extent at 80°. It will be seen that at concentrations up to 350 grams per liter, thermal decomposition does not seem to be so important, since there is little difference between the efficiencies at 70° and 80°.

The reason for the decrease in efficiency with time, as shown in figures 8 and 9, is not definitely known. It seems, however, that it must be attributed to the increasing concentration of one or more of the products of electrolysis. As pointed out earlier, the effect of accumulated chromium has been studied and found to be relatively unimportant. The effect of other substances is being investigated, but as the work is not completed, none of the data obtained in these studies are included in this thesis. It will merely be mentioned that the bromate does not seem

to be regenerated as rapidly as it is decomposed (reactions II and III, page 26). This may prove to be the chief cause for the decreased efficiency with increased time of operation.

In closing this discussion, it should be said that the reason for the increased rate of oxidation of the ore in acid solution is not known. To say that it is due to hydrogen ion, or acid, catalysis is not an explanation unless the mechanism of this catalysis is given. It is known that an acid solution of a chlorate will give rise to perchlorate ions or perchloric acid. Despite the fact that perbromates have never been isolated, it does not seem unreasonable to assume that the same reaction takes place in an acid solution of a bromate, and that this higher oxyhalogen compound is the active constituent. This would explain why the reaction does not take place in a basic solution.

CONCLUSIONS

From the investigation thus far, the following conclusions have been reached:

1. The efficiency of the electrolytic dissolution of chromite ore increases with:
 - a. Increasing temperature to 70° C. at anode current densities below 4 amperes per square inch.
 - b. Decreasing anode current density at temperatures between 40° C. and 70° C., the efficiency at 70° C. continuing to increase with decreased current density to the lowest value of current density used, 0.05 amperes per square inch.
2. The efficiency of the electrolytic dissolution of chromite ore decreases with:
 - a. Increasing concentration of sodium bromate above 350 grams per liter or decreasing concentration below 200 grams per liter.
 - b. Increasing alkalinity of the electrolyte.
 - c. Increasing time of operation of the particular cell used.

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