

phys.
Thesis
1927
Electrochem.

SEP 31 1928
LIBRARY

THE CORROSION OF DURIRON ANODES

BY

W. H. H.
CHARLES W. DINAN

COURSE XIV -1927

✓

Cambridge, Mass.

October 15, 1927

Prof. A.L. Merrill,
Secretary of the Faculty,
Massachusetts Institute of Technology,
Cambridge, Mass.

Dear Sir:-

In partial fulfillment of the requirements
for the degree of Bachelor of Science in Electrochemical
Engineering, I submit the accompanying thesis.

Respectfully submitted,

Charles W. Dinan

Phog

160219

ACKNOWLEDGMENT

The writer wishes to acknowledge the advice and other helpful suggestions of Prof. M. deKay Thompson.

TABLE OF CONTENTS

	<u>PAGE</u>
Object	1
Introduction	1
Method - Apparatus - Procedure	7
Discussion	15
Conclusion	17
Results	19
Bibliography	24
Appendix	25

INTRODUCTION

OBJECT: The object of this investigation is to determine the advisability of using durion anodes in certain electrolytic oxidations.

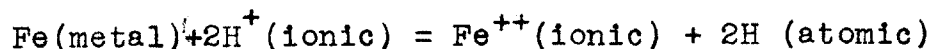
THEORY: The use of platinum electrodes has been very extensive and completely satisfactory, from the scientific viewpoint, when unattackable electrodes are required. However, from the economic viewpoint, the use of platinum is objectionable because of its excessive cost, and the resulting value of goods tied up. Therefore, from the start of industrial electrochemistry, research workers have been trying to discover a substitute for platinum that will be both cheap and practically unattackable. Various metals or alloys have been found satisfactory under certain conditions but none have been found that may be used for as many different purposes as platinum. Since the problem is primarily one of corrosion, an explanation of the theory of corrosion brings to view the various factors which play a part in this investigation.

The electrochemical theory is now generally accepted as the one which best explains the mechanism of corrosion.

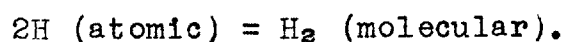
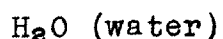
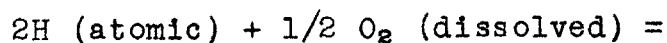
Since the test is being made on an alloy of silicon and iron, the theory may be specifically applied to the metal.

According to the explanation by Speller in "Corrosion", "Iron, like all other elements, has a definite, inherent tendency to go into solution when placed in contact with water. Iron can enter solution only by displacing some other element already in the solution. Hydrogen is the element usually plated out. This hydrogen gathers on the surface of the iron in the form of a thin, invisible film. The presence of this film obstructs the progress of the reaction by insulating the metal from the solution. In order that corrosion may proceed, the film must be removed. This may be removed by depolarization, combination with oxygen to form water, or it may pass off as gaseous hydrogen."

Corrosion reactions:



Removal of hydrogen:



In all electrolytic cells, an oxidation takes place at the anode. Since the primary corrosion reaction is the oxidation of the metal, the anode is the more severely attacked. Therefore, the formation of an unattackable anode is the object of men working in this field of research.

The effect of alloying various quantities of silicon with iron was first studied systematically by Jouve, in France, in the year 1900. The possibilities of this combination were borne out owing to the fact that when conducting analyses of steel-silicon alloys, considerable difficulty was experienced in the attack of acid upon these metals. After having prepared a series of silicon steel alloys for the purpose of acid resisting, progress in this investigation was held up because of the unsatisfactory physical nature of the metal. However, in 1907, Jouve stated that he had been successful in overcoming to a very great extent the difficulties inherent in the preparation of these alloys. Numerous castings and vessels were produced with considerable satisfaction although the greater part of these pieces were of comparatively small size.

Later, in Germany, "Neutrалеisen" was produced for the purpose of making castings to withstand nitric or sulphuric acid. The production of "Neutrалеisen" met with many disappointments, finally resulting in the abandonment of its manufacture. The development of the electric furnace has proved a valuable aid to the satisfactory commercial production of alloys of ferro-silicon and consequently these alloys are now produced in good quality and in good quantities. In the year 1917, Kowalke, in America, ^{did} ~~made~~ considerable research to determine the resistance to corrosion of alloys of iron and silicon. He found that when silicon is present in a lesser quantity than 12%, it does not promote a satisfactory resistance to corrosion. Also, when the silicon content of the alloy reaches 16% or upwards the acid resisting quality again falls. Consequently, in producing these high silicon irons for acid resisting, one is compelled to work between fairly narrow limits. The most suitable alloys have been found to be those containing between 13% and 15% of silicon. The metal is extremely hard and melts at about 1250° C. Owing to its hardness it is impossible to machine it in any other way

than by grinding with high-speed abrasive wheels.

There are several recognized manufacturers of high silicon irons for resisting acids both, in this country and in Europe, and each has its separate trade brand. In this country, the best brands are "Duriron" made by the Duriron Company, Dayton, Ohio, and "Corrosiron", produced by the Bethlehem Foundry & Machine Co., Bethlehem, Pa. In Europe, the most important alloys go under the names of "Ironac", "Tantiron", and "Narki" metal.

Since high silicon iron was developed primarily as an acid-resisting alloy, there is no reason to assume that this alloy is adaptable to other conditions of corrosion. On the contrary, when the alloy is placed in contact with strong alkaline solutions, it is appreciably attacked and is very unsatisfactory as a base-resisting metal. The base attacks the silicon forming silicates, thus ruining the structure of the alloy. However, it is an interesting problem to study the corrosion of high silicon iron in certain electrolytic oxidations, and to determine the inhibiting effect of the silicon under conditions widely divergent from those for which the alloy was intended. Therefore, a study was made of the

electrolysis of various solutions using duriron anodes.

REVIEW OF LITERATURE

Some work has been done relative to the corrosion of duriron in acid solutions but very little work has been published concerning the behavior of duriron anodes. Kowalke made an extensive study of the acid corrosion of iron silicon alloys, the results of which he presented to the American Electro-Chemical Society in 1917. Fink and Eldridge, in a paper presented to the American Electro-Chemical Society in 1921, mentioned the use of duriron anodes by the Chili Exploration Company at its Chuquicamata copper refining plant. More information about the results obtained by this company are lacking due to its failure to publish any work which was carried out in this field. In 1922, J.M. Cosgrove and J.S. Sarros performed a thesis at the Massachusetts Institute of Technology on the corrosion of duriron anodes in NaOH solutions of various concentrations. They arrived at the conclusion that the rate of corrosion increases considerably with an increase in temperature. Their results also show that there is an increase in the rate of corrosion as the concentration of the NaOH is increased.

However, they did not complete any work on electrolytic oxidations using duriron anodes. Therefore, any commercial application of their work is lacking. Since 1922, no work in this field has been published.

METHOD - APPARATUS - PROCEDURE

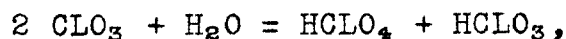
The apparatus used in this investigation consisted of a source of electromotive force, 115V D.C., a 15^a ammeter, voltmeter, 3V-15^V-150V, rheostats, and a series of four cells. The four cells were placed in a zinc-lined tank about six feet long, and a cross-section about ten inches square and open at the top. The cells consisted of one or two liter beakers, a cylinder of sheet lead as cathode and an anode of duriron supplied by the Duriron Company of Dayton, Ohio. The series of four cells were placed across the 115 volt D.C. supply with the ammeter and rheostats in series. The voltmeter was fitted with long leads to obtain the voltage drop across each cell. The tank was filled with water to maintain a fairly constant temperature. In the case of low temperatures, cold water was circulated through the tank and in the case of higher temperatures the warm bath was kept stationary, the heat

given off by the passage of the current compensating for the heat lost to the atmosphere.

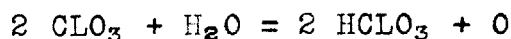
In this investigation, three different oxidations were tried. First, a solution of potassium chlorate was subjected to electrolysis for the purpose of producing potassium perchlorate. Next, a solution of chrome alum in sulphuric acid was electrolyzed to form chromic acid. Lastly, a basic solution of potassium manganate was oxidized for the production of potassium permanganate.

In the first case the procedure according to Elbs was followed with slight variations. The electrolyte consisted of a saturated solution of $KClO_3$ at room temperature. In order to keep the solution saturated, a cloth bag filled with solid $KClO_3$ was suspended in the solution. A duriron anode and lead sheet cathode were used instead of the platinum electrodes recommended by Elbs. The cells used were one liter glass beakers. No diaphragm is necessary in this run. The four cells were placed in series in a bath of circulating cold water.

The electrolytic oxidation of chlorates to perchlorates depends on the reaction,



whereby 2 discharged chloric acid ions unite with water to give one molecule of perchloric acid and one molecule of chloric acid, which form salts with the alkali produced at the cathode. This reaction is confined to low temperature. At warmer temperatures, the transformation of the acid radicals occurs,



and the evolution of oxygen replaces the oxidation of the chlorates.

In the first run, the current was adjusted to about 8 amperes and the electrolysis was allowed to continue over-night. According to Elbs, when the experiment has been in progress some time, the electrolytic becomes saturated with KClO_4 and fine crystals of perchlorate fall from the anode to the bottom of the vessel. Actually, however, the electrolyte soon became badly contaminated with iron rust and no crystals of perchlorate appeared. Oxygen was evolved continuously during the run. After the run the solution was treated with H_2SO_4 in just sufficient quantities to dissolve

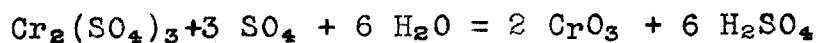
the precipitate of ferrous and ferric hydroxide. When this was done nothing else remained in the liquid as solid matter giving further proof of the absence of KClO_4 . A second test was made with the same solution having a current density about double that of the first test. This increase in current density raises the anode potential and presents a possibility of obtaining a yield of KClO_4 . In this case, it was impossible, with the means available, to keep the temperature below 25°C ., as recommended, owing to the heat evolved by the I^2R losses in the cells. However, this procedure met with no more success than the first. Therefore, it was decided to leave the chlorate solution and turn to the chrome alum electrolysis.

The oxidation of chromiumpulphate to chromic acid is carried on in an electrolyte consisting of 200 grams chrome alum, $\text{KCr}(\text{SO}_4)_2 + 12 \text{H}_2\text{O}$, dissolved in hot water, 150 cc concentrated sulphuric acid and the solution is made up to 1000 cc. The cells were two liter beakers having a lead sheet cylinder as cathode, duriron anodes, and a porous pot containing the anode and anode solution. The porous pot is used to prevent the mixing of the anode and cathode solutions. The electrolysis

was carried out in the first test with a current density at the anode of about 2 amperes per 100 sq. cm. at a temperature of around 50° C.

The cells were surrounded by a hot bath and the heat developed in the cells was enough to maintain a fairly high temperature although it varied considerably during the tests. During the run, SO₂ was evolved continuously from the anode, its presence being readily detected because of its pungent odor. The process of oxidation is expressed by the equation.

*must
have been
to D. +
chromium
alt.*



At the cathode hydrogen is evolved almost quantitatively. The yield is determined by titrating samples of the anode solution with ferrous ammonium sulphate and potassium permanganate. This titration proved to be most difficult because of the various color changes which occur as the end point is approached. The anode solution, even after dilution, imparts a strong green color to the liquid. The green color persists after adding the excess ferrous ammonium sulphate but on titrating back with the potassium permanganate, the green first slowly changes to blue, then to purple, and when excess permanganate has been added, the solution turns dark red. After titrating a number of samples from the same anode solution

the one which appeared to be the most representative was chosen. This, however, showed no yield.

Another run was made with this solution having a current density about four times as great as in the first case. This run showed no better results and there was considerable increase in the corrosion of the duriron anodes. After each of these runs, the anodes were covered with a soft gray coating which was removed by rubbing lightly with emery paper before drying and weighing the anodes. Pitting was observed in only a few places on the metal pieces. For the most part, corrosion was fairly uniform over the entire surface. However, the anodes soon lost the smoothness that they possessed at first and became quite rough wherever they were in contact with the solutions.

The next electrolysis tried was the oxidation of potassium manganate to permanganate. There was very little information available concerning this process but a fair idea of the procedure was obtained from a thesis by Schabacker in 1916 on the electrolytic production of potassium permanganate.

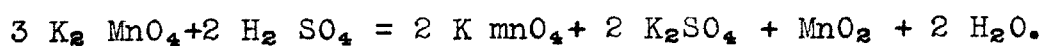
The procedure was varied with the view of determining the adaptability of duriron anodes rather than producing permanganate commercially.

Three electrolytes were made up, the first being about one normal in sodium hydroxide, the second, one-half normal, and the third, one-sixth normal. Forty grams of potassium manganate were then added for each liter of solution. The cells consisted of sheet lead cathodes, duriron anodes, porous pots, and two-liter beakers as vessels.

The three cells were then placed in series across 115 volts, the current being regulated by series resistances. The cells were placed in a tank of circulating cold water during the electrolysis to prevent excess heating. A current density of about 2 amperes per 100 sq.cm. was used and the oxidation was carried out for two and one-half hours. A slight evolution of oxygen was perceptible at the anode during the electrolysis. After the run the anodes were covered with a soft brown coating which was rubbed off before weighing.

Schabacker, in his investigation determined the current efficiency by means of the deficiency in oxygen evolved at the anode. This, however, was deemed inadvisable because of the great possibility of error. Therefore, an analysis of the solution was made. First, the insoluble matter in the potassium manganate was determined by taking a weighed sample, dissolving, filtering, and igniting the residue. From the weight of the

residue, the percentage of insoluble matter in the manganate may be found. Direct titration of the anode solution after electrolysis was impossible since the reduction with ferrous sulphate, must be carried on in an acid solution to prevent the formation of MnO_2 . Moreover, the direct addition of sulphuric acid would result in the conversion of the manganate to permanganate and manganese dioxide according to the reaction.



Therefore, the analysis was carried out as follows:

The OH concentration of a sample of the anode solution was determined by adding an excess of $Cd SO_4$ solution. This precipitated cadmium hydroxide which came down first as a brown solid, showed the presence of impurities. After filtering, the residue was redissolved in dilute sulphuric acid and reprecipitated with sodium hydroxide. This time the cadmium hydroxide came down as a white solid. The solution was again filtered and the residue dried and weighed. From the weight of the cadmium hydroxide and the volume of the sample taken, the OH concentration was calculated.

Another sample of the anode solution was treated with excess sulphuric acid. The resulting solution is treated with excess ferrous ammonium sulphate and titrated back to the end point with a solution of $K MnO_4$ of known strength. Lastly, the acid concentration of the final solution is found by neutralizing with a solution of sodium hydroxide. From the acid concentration at the end, the OH concentration of the initial sample, and the amount of acid added to the solution, the acid disappearance may be determined. The acid thus lost is the acid used to convert the potassium manganate to permanganate according to the preceding reaction. Therefore, from the total permanganate present, and the permanganate formed by the acid reaction, it is possible to determine the amount of $K MnO_4$ formed during the electrolysis and thereby, the current efficiency may be calculated. Because of the lack of time it was impossible to run checks on the potassium manganate oxidations.

The anodic potentials of duriron was then measured in each of the solutions investigated. One of the anodes was covered with pitch leaving a rectangular opening of a definite area on one side. The various cells

used were again set up and the variation of anode potential with current density was measured.

The current through the cells was varied by means of rheostats in series. The anode potentials were measured by the usual slide wire method except that a potentiometer was substituted for the slide wire. The temperature of the solutions were kept as nearly alike as possible to the temperatures under which the tests were made.

DISCUSSION:

The electrolytic oxidation of $KClO_3$ proved unsuccessful under the conditions of this investigation but better results should be obtained if the conditions were altered. The oxidation should be carried out in a cold solution instead of at room temperature. Therefore, if a cooling coil were immersed in the cell solution it might be possible to obtain a yield of $KClO_4$. However, some provision must be made for keeping the iron rust out of the solution since this greatly decreases the current efficiency and contaminates the product. The solution could be made slightly acid to prevent the formation of ferrous and ferric hydroxide but the acid addition would increase the corrosion of the anodes. Also, the increased quantity of iron in the solution would materially affect the current efficiency. In view of these facts it is not considered feasible to use duriron anodes for the electrolytic production of $KClO_4$.

The attempt to produce chromic acid electrolytically using duriron anodes met with still less success than the first oxidation tried.

Not only was there no yield of chromic acid, but the corrosion rate of the anodes was so large that it would be impractical to carry out such an oxidation even if the acid were produced quantitatively.

The electrolytic production of $KMnO_4$ was successful to a limited extent with the duriron anodes. However, the current efficiency was found to be extremely low. This value could be increased by altering conditions. For example, an excess supply of K_2MnO_4 should be in contact with the anode solution to replace that portion that is oxidized to $KMnO_4$. The continued formation of potassium permanganate will soon saturate the solution and crystals of the solid will separate out. The procedure followed in the analysis of the anode solutions became much more involved than was at first expected and considerable experimental error was consequently introduced in the result. In fact, the last part of the work became a complicated problem in quantitative analysis rather than in electrochemistry. A simpler procedure should be mapped out and followed if more work is to be done in this field.

The measurements of the anode potentials are likely to be somewhat in error due to a slight difference in potential between one terminal of the 115 volt supply which was used to electrolyze the cells, and a terminal of the 20 volt battery which was used to send the current through the potentiometer.

CONCLUSIONS:

In view of the results of this investigation, the use of duriron anodes is found to be entirely unsatisfactory in ~~acid~~ ^{the} solutions, ^{tested.} In neutral solutions, the rate of corrosion is considerably lower but, unless a high enough current efficiency can be realized, the use of duriron anodes cannot be recommended. In basic solutions, the corrosion is very much lower than in neutral solutions. Therefore, duriron anodes may be used satisfactorily provided the current efficiency in the process is high enough to make it commercially successful.

The loss due to corrosion in alkaline solutions decreased appreciably as the OH ion concentration was increased. This decrease will probably meet a limiting value when the solution gets so strongly basic that it attacks the silicon of the alloy forming silicates. It would be

interesting to perform some experiments along this line to see if such a limiting value is approached, and if so, where. It was also found that the rate of corrosion increases considerably with an increase in the current density, and also with an increase in temperature. Therefore, in order to carry out an electrolysis with duriron electrodes, the conditions favorable for a small loss of the anode consist of a high OH ion concentration in the solution, low current density and low temperature.

RESULTS

Run #1 KClO₃ solution

Current density = 4.7 amperes per 100 sq.cm.

Average temperature = 22.5° C.

Rate of corrosion of anodes per faraday.

#1	#2	#3	#4
.257 g	.225 g	.260 g	.251 g

Current efficiency = 0

Run #2 KClO₃ solution

Current density = 8.25 amperes per 100 sq.cm.

Average temperature = 28° C.

Rate of corrosion of anodes per faraday.

#1	#2	#3	#4
.480 g	.452 g	.477 g	.484 g

Current efficiency = 0

Run #3 Chrome alum solution

Current density = 4.88 amperes per 100 sq.cm.

Average temperature = 55° C.

Rate of corrosion of anodes per faraday.

#1	#2	#3	#4
2.49 g	2.63 g	2.81 g	2.57 g

Current efficiency = 0

Run #4 Chrome alum solution

Current density = 17.6 amperes per 100 sq.cm.

Average temperature = 60.5° C.

Rate of corrosion of anodes per faraday.

#1	#2	#3	#4
3.38 g	3.06 g.	3.45 g	3.22 g.

Current efficiency = 0.

Run #5 Potassium manganate solution

Current density = 2 amperes per 100 sq.cm.

Average temperature = 25.5° C.

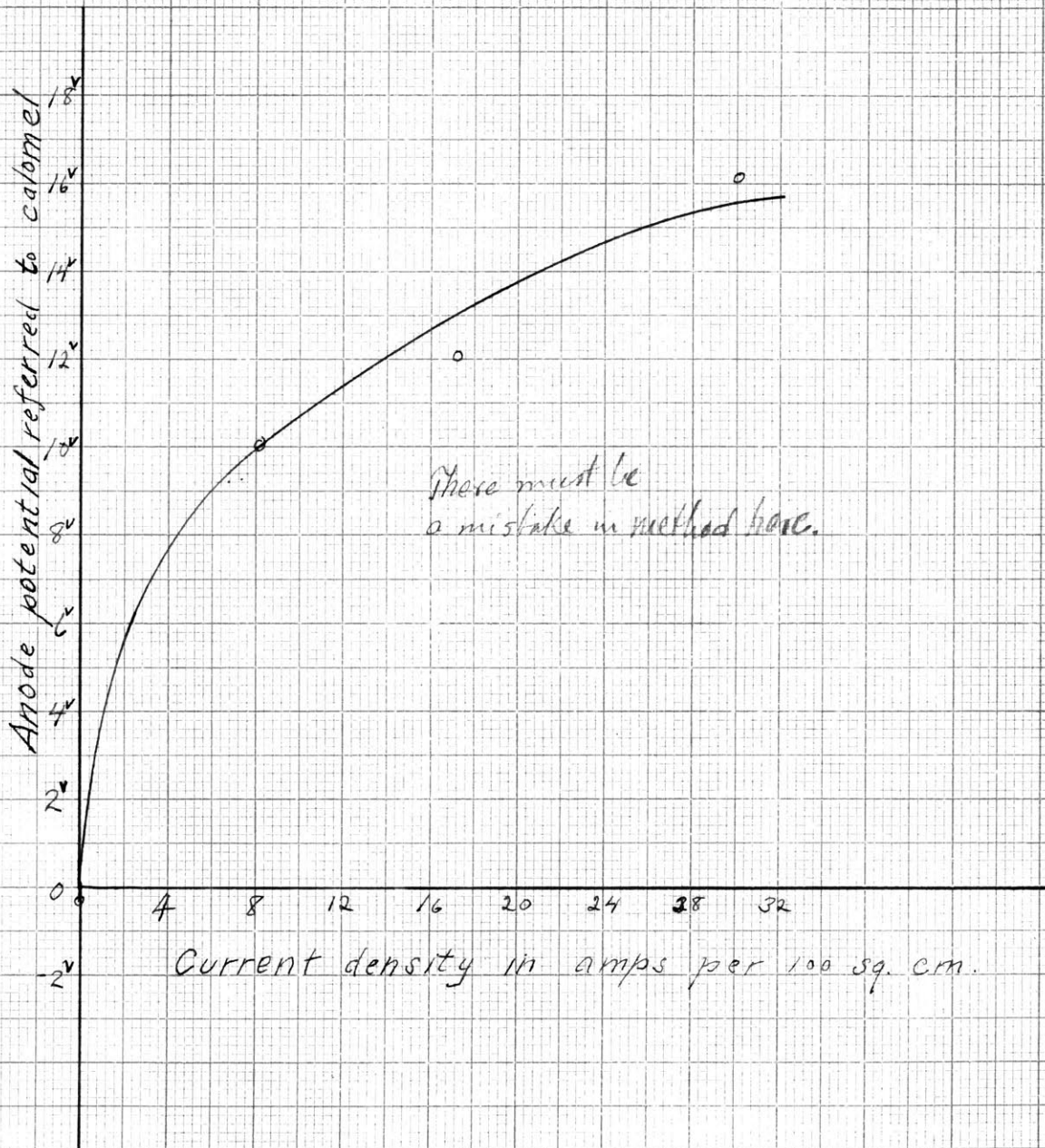
Rate of corrosion of anodes per faraday.

#1	#2	#3
1 Normal NaOH sol	1/2 normal NaOH sol.	1/6 normal NaOH sol.
.027 g.	.160 g.	.267 g.

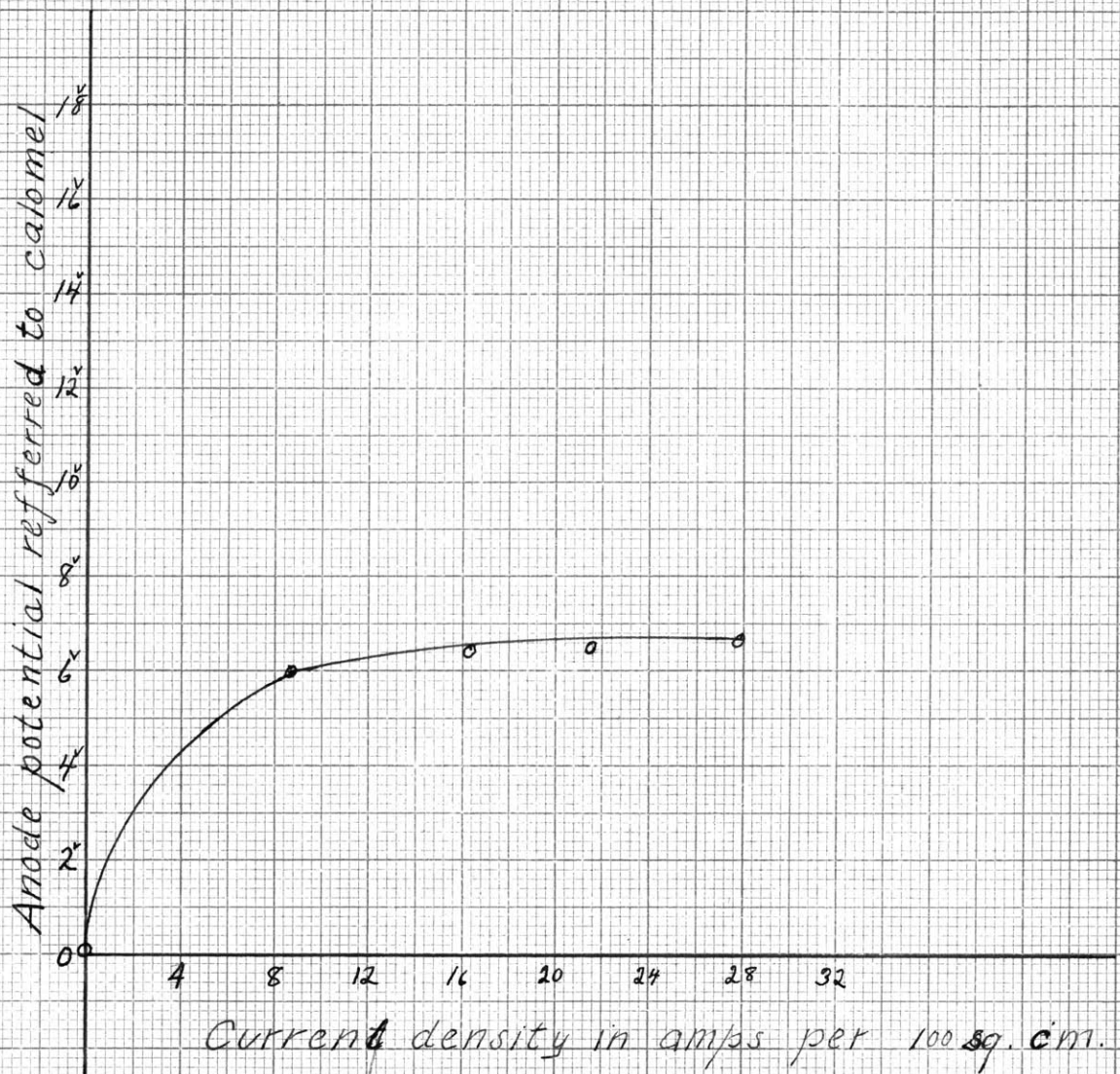
Current efficiency

#1	#2	#3
1.65%	1.01%	.75%

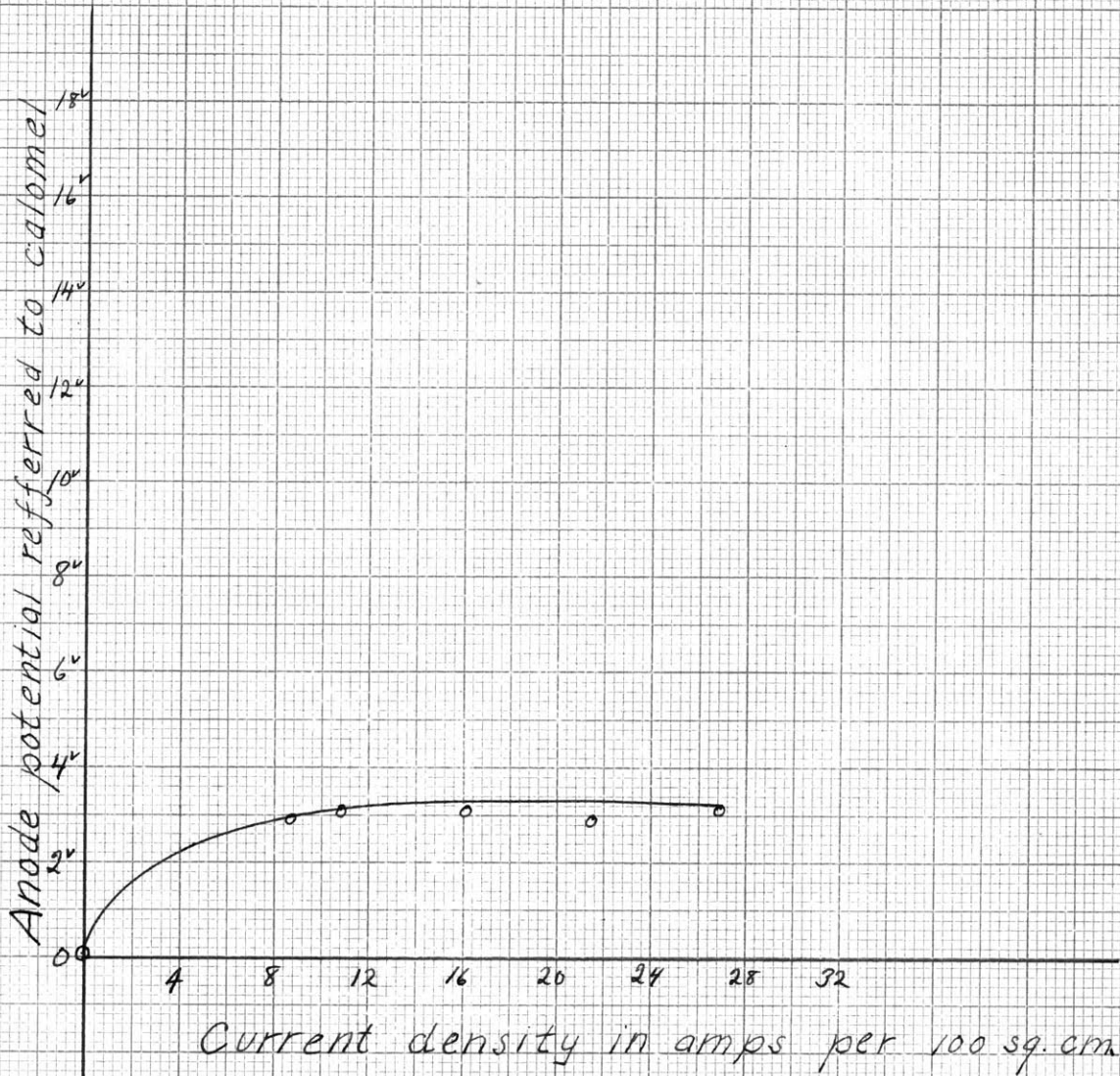
Duriron Anode Potential in Saturated $KClO_3$ Solution referred to Calomel. $20^\circ C.$



Duriron Anode Potential in Chrome Alum Solution
referred to Calomel. 45° C.



Duriron Anode Potential in one normal
NaOH solution of K_2MnO_4 at $20^\circ C$.



BIBLIOGRAPHY

1. Dr. Karl Elbs, Electrolytic Preparations, p. 17-19, 33-35.
2. Thorp: "Outlines of Industrial Chemistry," p. 299.
3. Kowalko; American Electrochemical Society, 1917, p. 206.
4. The Effect of Silicon on the Electrical Properties of Iron. Chem.Abs. 4.1972.
5. S.J. Tungay; Acid-Resisting Metals, p. 21.
6. H.P. Talbot; "Quantitative Analysis", p. 68.
7. Cosgrove and Sarros; "The Corrosion of Duriron Anodes", M. I. T. Thesis, 1922.
8. Schabacker; "The Electrolytic Preparation of Potassium Permanganate", M. I. T. Thesis, 1916.
9. F.N. Speller "Corrosion", p. 9.

APPENDIX

CALCULATIONS

Run #1

Total coulombs = $23.75 \times 3600 \times 8 = 684,000$ coulombs

$$\frac{684,000}{96,500} = 7.1 \text{ faradays.}$$

$$\text{Current density} = \frac{8}{170} \times 100 = 4.7 \text{ amperes per } 100 \text{ sq. cm.}$$

Loss per faraday

1. $\frac{1.822}{7.1} = .257 \text{ g}$	2. $\frac{1.599}{7.1} = .225 \text{ g}$	3. $\frac{1.844}{7.1} = .260 \text{ g}$
4. $\frac{1.786}{7.1} = .251 \text{ g.}$		

Run #2

Total coulombs

$5 \times 3600 \times 14 = 252,000$ coulombs

$$\frac{252,000}{96,500} = 2.61 \text{ faradays}$$

$$\text{Current density} = \frac{14}{170} \times 100 = 8.25 \text{ amperes per } 100 \text{ sq. cm.}$$

Loss per faraday

1. $\frac{1.255}{2.61} = .480 \text{ g.}$	2. $\frac{1.179}{2.61} = .452 \text{ g.}$	3. $\frac{1.244}{2.61} = .477 \text{ g.}$
4. $\frac{1.263}{2.61} = .484 \text{ g.}$		

Run #3

Total coulombs

$$2\text{-}2/3 \times 3600 \times 8.3 = 79600 \text{ coulombs}$$

$$\begin{array}{r} 79,600 \\ \hline 96,500 \end{array} = .826 \text{ faradays}$$

$$\text{Current density} = \frac{8.3}{170} \times 100 = 4.88 \text{ amperes per } 100 \text{ sq. cm.}$$

Loss per faraday.

1.	2.	3.
2.058	2.172	2.319
$\frac{\quad}{.826} = 2.49 \text{ g.}$	$\frac{\quad}{.826} = .263 \text{ g.}$	$\frac{\quad}{.826} = 2.81 \text{ j}$
	4. $\frac{2.123}{.826} = 2.57 \text{ g.}$	

Run #4

Total coulombs

$$1.5 \times 3600 \times 15 = 80200 \text{ coulombs}$$

$$\begin{array}{r} 80,250 \\ \hline 96,500 \end{array} = .83 \text{ faradays}$$

$$\text{Current density} = \frac{15}{85} \times 100 = 17.5 \text{ amperes per } 100 \text{ sq. cm.}$$

Loss per faraday

1.	2.	3.
2.807	2.538	2.874
$\frac{\quad}{.83} = 3.38 \text{ g.}$	$\frac{\quad}{.83} = 3.06 \text{ g.}$	$\frac{\quad}{.83} = 3.45 \text{ g.}$
	4. $\frac{2.670}{.83} = 3.22 \text{ g.}$	

Run #5

Total coulombs

$$2.5 \times 3600 \times 2 = 18,000 \text{ coulombs}$$

$$\frac{18,000}{96,500} = .187 \text{ faradays}$$

$$\text{Current density} = \frac{2}{100} \times 100 = 2.0 \text{ amperes per } 100 \text{ sq. cm.}$$

Loss per faraday

1.	2.	3.
$\frac{.005}{.187} = .027 \text{ g.}$	$\frac{.030}{.187} = .160 \text{ g.}$	$\frac{.050}{.187} = .267 \text{ g.}$

Analysis of $K_2 MnO_4$ anode solutions.

Sample of 100 cc anode solution taken

Excess $CdSO_4$ added

Weight of $Cd(OH)_2$ precipitate

1 N.	1/2 N	1/6 N
13.596 g.	7.450 g.	2.487 g.

Normalities of solutions

13.596	7.450	2.487
----- 10 = .931	----- 10 = .510	----- 10 = .170
146	146	146

Sample of 100 cc anode solution taken.

100 cc 4.9 N H_2SO_4 added

Titrated with $FeSO_4$

1 N	1/2 N	1/6 N
174 cc $Fe SO_4$	180 cc $FeSO_4$	194 cc $FeSO_4$

Equivalent of .0988 N $KMnO_4$

181 cc	187 cc	201 cc
--------	--------	--------

Grams of $KMnO_4$

.566 g	.585 g	.628 g
--------	--------	--------

H_2SO_4 disappearance

.21 cc	.74 cc	1.05 cc
--------	--------	---------

Mols $K MnO_4$ from acid

.000514	.00181	.00257
---------	--------	--------

Grams $KMnO_4$ from acid

.081 g.	.286 g.	.406 g.
---------	---------	---------

$KMnO_4$ produced by electrolysis

.485 g	.299 g.	.222 g.
--------	---------	---------

Current efficiency in KMnO_4 production

Time = 2.5 hours Current = 2 amps.

Coulombs = $2.5 \times 3600 \times 2 = 18000$

$$\text{Faradays} = \frac{18000}{96500} = .187 \text{ F}$$

Theoretical production = $.187 \times 158 = 29.5$ grams KMnO_4

Current efficiency

1 N.	1/2 N.	1/6 N.
$\frac{.485}{29.5} \times 100 = 1.65\%$	$\frac{.299}{29.5} \times 100 = 1.01\%$	$\frac{.222}{29.5} \times 100 = .75\%$

Dimensions of anodes

6" x 2" x 1/2"

Run #1

Depth of anodes submerged = 5.5# inches

Electrolyte: Saturated solution of $KClO_3$

Time	V ₁	V ₂	V ₃	V ₄	Current	Temp.
11:15 AM	7.40	7.40	7.55	7.93	7.50	20.0° C
1:00 PM	7.38	7.40	7.53	7.92	7.60	21.0
3:00 PM	7.38	7.38	7.52	7.90	7.60	22.0
5:00 PM	7.38	7.38	7.52	7.90	7.60	22.0
6:00 PM	7.37	7/38	7.52	7.90	7.65	22.5
9:00 PM	7.33	7.34	7.47	7.85	8.45	24.0
11:00 AM	7.33	7.34	7.47	7.85	8.60	24.0

Weight of anodes

	1	2	3	4
Before	370.892 g.	388.639	372.216	383.714
After	<u>369.070</u>	<u>387.040</u>	<u>370.372</u>	<u>381.928</u>
Loss	1.822	1.599	1.844	1.786

Average temperature = 22.5° C.

Run #2

Depth of anodes submerged = 5.5 inches

Electrolyte: Saturated solution of $KClO_3$

Time	V ₁	V ₂	V ₃	V ₄	Current	Temp.
10:00 AM	11.25	11.10	12.20	11.70	14.00	25° C
11:00 AM	11.30	11.18	12.30	11.75	14.00	28
12:00 M	11.32	11.20	12.34	11.80	14.00	30
1:00 PM	11.34	11.25	12.35	11.82	14.00	31
2:00 PM	11.35	11.27	12.35	11.84	14.00	31.5
3:00 PM	11.35	11.27	12.36	11.84	14.00	31.6

Weight of anodes

	1.	2.	3.	4.
Before	369.070	387.040	370.372	381.928
After	<u>368.815</u>	<u>385.861</u>	<u>369.128</u>	<u>380.665</u>
Loss	1.255	1.179	1.244	1.263

Average temperature = 28° C.

Run #3

Depth of anodes submerged = 5.5 inches

Electrolyte: 200 grams chrome alum, 150 cc concentrated

H₂SO₄ per 1000 cc. of hot aqueous solution.

Time	V ₁	V ₂	V ₃	V ₄	Current	Temp.
6:20 PM	3.80	3.70	4.10	3.95	8.30	47° C
6:50 PM	3.65	3.60	4.00	3.90	8.30	66
7:20 PM	3.70	3.65	4.05	3.90	8.30	59
7:50 PM	3.80	3.75	4.10	3.95	8.30	52
9:00 PM	3.95	3.90	4.20	4.05	8.30	47

Weight of Anodes.

	1.	2.	3.	4.
Before	369.070	387.040	370.376	381.928
After	<u>367.012</u>	<u>384.868</u>	<u>368.057</u>	<u>379.795</u>
Loss	2.058	2.172	2.319	2.123

Average temperature = 55° C.

Titration of 20 cc sample of anode solution to determine yield.

Fe NH ₄ (SO ₄) ₂ .0542 N.	KMNO ₄ .0988 N
36.63 cc	26.48 cc
<u>18.72 cc</u>	<u>16.95 cc</u>
17.91 cc	9.53 cc

$$17.91 \times \frac{.0542}{.0988} = 9.45$$

Yield = 0

Run #4

Depth of anodes submerged = 3.75 inches

Electrolyte: 200 grams chrome alum. 150 cc concentrated
H₂SO₄ per 1000 cc of hot aqueous solution.

Time	V ₁	V ₂	V ₃	V ₄	Current	Temp.
12:25	5.05	4.50	4.70	5.25	15.00	53
12:55	4.85	4.50	4.65	5.15	15.00	58
1:15	4.90	4.45	4.65	5.15	15.00	62
1:30	4.85	4.40	4.60	5.10	15.00	63
1:53	4.80	4.30	4.50	5.00	15.00	64

Weight of Anodes.

	1.	2.	3.	4.
Before	367.012	384.868	368.057	379.795
After	<u>364.205</u>	<u>382.330</u>	<u>365.183</u>	<u>377.125</u>
Loss	3.807	2.538	2.874	2.670

Average temperature = 60.5° C.

Titration of 20 cc sample of anode solution to
determine yield.

Fe (NH ₄)(SO ₄) ₂ (.0542 N)	KMNO ₄ (0988N)
24.48 cc	20.95
<u>9.25</u>	<u>28.42</u>
15.23 cc	8.53

$$15.23 \times \frac{.0542}{.0988} = 5.40 \text{ cc}$$

Yield = 0

Run #5

Depth of anodes submerged = 3.5 inches

Electrolyte: 40 grams K_2MnO_4 per liter in one normal,
one-half normal and one-sixth normal NaOH.

Anode solution of 500 cc.

	1N	1/2 N	1/6 N		
Time	V_1	V_2	V_3	Current	Temp.
1:10	4.00	5.40	4.40	2	24° C
1:40	4.05	6.20	3.85	2	25
2:10	4.05	6.15	3.85	2	26
2:40	3.95	5.91	3.83	2	26
3:40	3.90	5.70	3.80	2	28

Weight of Anodes.

	1.	2.	3.
Before	364.207 g.	382.330	365.183
After	<u>364.202</u>	<u>382.300</u>	<u>365.133</u>
Loss	.005 g.	.030	.050 g.

Average temperature = 25.5° C.

Anode area in contact with the solutions = 100 sq. cm.

Insoluble matter in K_2MnO_4

.522 grams per 5 grams = 10.4%

.525 grams per 5 grams = 10.5%.

Run #6

Anode potentials

Area of anode exposed = 18.6 sq.cm.

Standard cell = 1.0159^v

KClO₃ solution 20° C

Potentiometer readings

St. cell	V total	V anode	Current
.4092	-.1V	-.127	0
.0965	+12.6V	1.0047	1.5
.0955	21.0V	1.1385	3.1
.0965	25.4V	1.537	4.45

Chrome alum solution 45° C.

St. cell	V total	V anode	Current
.4097	0.20	.0400	0
.1414	3.42	.8371	1.55
.1428	3.80	.8654	2
.1436	4.08	.9067	3
.1437	4.30	.9262	4
.1453	4.57	.9513	5

K₂MnO₄ solution 1 N. NaOH 20° C.

St. cell	V total	V anode	Current
.4120	.29	.0327	0
.1520	3.90	.4656	1.6
.1563	4.20	.4733	2.0
.1689	4.90	.5081	3.0
.1853	5.5	.5280	4.0
.1799	6.1	.5389	5.0