



Electrolytic synthesis of battery-active manganese dioxide
by Arthur M Magnuson

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering at Montana State College
Montana State University
© Copyright by Arthur M Magnuson (1950)

Abstract:

The primary purpose of this investigation was to develop a process for the production of a battery-grade manganese dioxide from Montana ores.

An investigation was carried but in order to determine the influence on current efficiency and on quality of the product of the following process variables: acid concentration; manganous sulfate concentration; cell temperature; current density; and anode to cathode spacing.

The laboratory scale process which was developed resulted in the electrolytic deposition of a battery-active manganese dioxide on the anodes of a cell consisting of chemical-lead, cathodes, AGR graphite anodes and manganous sulfate in dilute sulfuric acid as the electrolyte.

The best conditions found were as follows: temperature, 93 °C.; current density, from 6 to 7 amps./sq.ft.; sulfuric acid concentration, 95 grams/liter; and manganous sulfate concentration, 150 grams/liter. Under the above conditions current efficiencies of around 70 per cent were obtained.

ELECTROLYTIC SYNTHESIS OF BATTERY-
ACTIVE MANGANESE DIOXIDE

by

ARTHUR M. MAGNUSON

A THESIS

Submitted to the Graduate Faculty

in

partial fulfillment of the requirements

for the degree of

Master of Science in Chemical Engineering

at

Montana State College

Approved:

Lloyd Bengtson
Head, Major Department

Lloyd Bengtson
Chairman, Examining Committee

J. D. Nelson
Dean, Graduate Division

Bozeman, Montana
September, 1950

MONTANA STATE COLLEGE
LIBRARY
BOZEMAN

N378
M275e
Cap. 2

2.

Table of Contents

	Page
Abstract.....	3
I. Introduction.....	4
II. Equipment, Materials and Methods.....	7
A. Equipment.....	7
B. Materials.....	9
C. Methods.....	10
III. Sample Calculations.....	17
IV. Results.....	22
V. Summary.....	31
VI. Acknowledgment.....	33
VII. Literature Cited.....	34
VIII. Appendix	35

Gift Graduate Committee

JAN 25 '51

96018

ABSTRACT

The primary purpose of this investigation was to develop a process for the production of a battery-grade manganese dioxide from Montana ores.

An investigation was carried out in order to determine the influence on current efficiency and on quality of the product of the following process variables: acid concentration; manganous sulfate concentration; cell temperature; current density; and anode to cathode spacing.

The laboratory scale process which was developed resulted in the electrolytic deposition of a battery-active manganese dioxide on the anodes of a cell consisting of chemical-lead cathodes, AGR graphite anodes and manganous sulfate in dilute sulfuric acid as the electrolyte. The best conditions found were as follows: temperature, 93 °C.; current density, from 6 to 7 amps./sq.ft.; sulfuric acid concentration, 95 grams/liter; and manganous sulfate concentration, 150 grams/liter. Under the above conditions current efficiencies of around 70 per cent were obtained.

I INTRODUCTION

It was known as early as the year 1918 that a battery-grade of manganese dioxide could be anodically deposited by the electrolysis of a manganous sulphate solution. Electrolytic manganese dioxide in recent years has been found to be far superior to the best natural ores especially under heavy drain conditions.

Of the many world deposits of naturally occurring manganese dioxide, the deposit located on the African Gold Coast is the only source which gives satisfactory activity under heavy battery-drain conditions. In the event that this source were cut off, the United States would therefore be entirely dependent on the synthetic product for dry cells.

Preliminary results on the electrolytic deposition of manganese dioxide were published in May of 1918 by Van Arsdale and Maier (5). Nichols (3), in a paper dated September 1932, describes research work carried out by The Burgess Battery Company in which rhodochrosite was used as the source of manganese. The most important recent work was that carried out by The Georgia Institute of Technology for the United States Army Signal Corps (2). In this investigation the electrolyte was first produced from a C.P. grade of manganous sulphate monohydrate and

later from a commercial-grade of manganous oxide.

In order that an electrolytic method be economically feasible, a cheap source of manganese soluble in dilute sulphuric acid must be available. The deposits of high-grade rhodochrosite near Butte, Montana meet these demands. The ore can be easily ground to a powder and practically its entire manganese content is soluble in dilute sulfuric acid. Silica, which is the main impurity, may readily be removed in the leaching process. Furthermore, because of its low calcium carbonate and magnesium carbonate content, the sulphuric acid losses would be at a minimum.

The deposits of pyrolusite at Phillipsburg, Montana offer another good source of manganese. After this ore is roasted in a reducing furnace the manganese content in the form of the lower oxides should also be soluble in the same acid.

The effectiveness of the manganese dioxide as a depolarizer for dry batteries can only be determined by the actual testing of the batteries. A combination of preliminary tests, however, which serves to give an indication of how the product will perform are the following: Chemical analysis; X-ray diffraction; electron diffraction; and electron microscope. These tests of

the dioxide and also tests on batteries made up from this depolarizer are performed by The Squier Signal Laboratory of the U. S. Army Signal Corps. Tests run by this laboratory in recent years have shown that gamma phase manganese dioxide is the structure best suited for use in dry batteries.

An electrical engineer was assigned to this project to work out problems of an electrical nature. Details on this aspect of the investigation are given in a thesis by Edward F. Sylvain (4).

II EQUIPMENT, MATERIALS AND METHODS

A. Equipment

Power Supply

The power supply in the electrolysis consisted of a motor-generator set that was capable of producing current densities up to 40 amps. per square foot. The direct current generator had a rating of 15 amperes at 50 volts. Good control of its voltage output was obtained by placing a Variac in the rectifier circuit. An additional resistor was included in the circuit when smaller currents were required. A schematic diagram is shown in Figure 1 of the appendix.

Electrolysis Cells and Heat Supply

For runs 1 through 6 and for runs 8 and 12, the cell vessels consisted of two-liter Pyrex beakers in which the electrolyte volume was maintained at 1850 cc. The remainder of the runs were made using 6 inch O.D. x 12 inches tall Pyrex cylinders containing an electrolyte volume of 3900 cc. Each cell was equipped with a siphon arrangement for use in the withdrawal of solution. This consisted of a small-bore glass tube formed into a U with a short length of rubber tubing and a screw clamp attached to one end.

Electric hot plates with two-heat control

were used as the source of heat. By placing a variac in the line leading to each hot plate excellent control was obtained.

The small cells were placed directly on the hot plates without danger of their tipping. The tall cells, however, were supported by means of a wooden rack, which was so constructed as to accommodate a series of six units. The rack was securely attached to the top of a laboratory table and it also served to hold the terminals from which contact could be made to any one cell or to any group of cells.

Electrodes and Electrode Supports

The cathodes used throughout this investigation consisted of two sheets of 1/16-inch chemical-lead sheet per cell. In the small cells sheets $3\frac{1}{2}$ inches x 7 inches were used while for the larger cells the size of the sheets was 4 inches x $10\frac{3}{4}$ inches.

As anodes for runs 1 through 6, two $\frac{7}{8}$ inch Arc-light carbon rods eight inches in length were replaced by one flat slab of AGR graphite four inches wide by $\frac{1}{2}$ -inch thick. Except where a definite anode surface area was required, the length of these anodes was standardized at $10\frac{3}{4}$ inches.

To serve as a support for the electrodes and to act as an insulator between the anodes and the cathodes, a sheet of $\frac{1}{4}$ -inch polystyrene was used. Portions of the electrodes were extended through openings in the polystyrene and the electrodes were attached to the sheet by means of small clamps and bolts. With the exception of the cell used in run eight, where the spacings were varied, the electrodes were so arranged as to give a cathode to anode spacing of one inch.

Laboratory Equipment

The filtering apparatus consisted of a table type Buchner filter, nine inches in diameter. Vacuum was maintained by means of a water aspirator.

For drying the anodes and for drying the samples of manganese dioxide a 110° C. electric oven with variable temperature control was used.

The additional items of laboratory equipment used were a Beckman Laboratory Model pH Meter and a Lumetron Photoelectric Colorimeter.

B. Materials

Ores

For runs 12 and 22, the source of the manganese was roasted pyrolusite from the reducing furnaces of The Domestic Manganese Company of Butte. This material

varied in color from a greyish-black to a light-green and it contained manganese in the form of its lower oxides.

Butte rhodochrosite obtained from the Anaconda Copper Mining Company was the manganese source for all other runs. This ore is a light pink in color and because of the presence of large amounts of silica its surface is glazed.

Typical Assays on both types of ore are given in Table IV of the Appendix.

Sulfuric acid

The sulfuric acid used in this investigation was technical grade.

C. Methods

Ore Grinding and Leaching

The ore was first put through a jaw crusher where it was broken up into pieces of about 1/2-inch diameter. It was then reduced to a powder by grinding in a steel ball mill for one hour. The few particles which had not been ground at the end of an hour were separated from the powder by the use of a 20-mesh screen and were added to the next batch.

The first step in the leaching process was to weigh 1200 grams of the ground ore and to add it slowly, with agitation, to the 10-normal sulfuric acid. The quantity of acid used was ten per cent in excess of that

quantity required to react theoretically with the manganese bearing compounds in the ore. If carbonates other than manganese were present, an additional amount of acid was added.

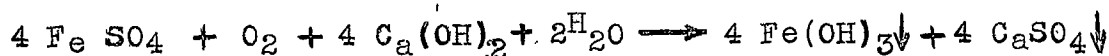
When rhodochrosite was used as the starting material, a large volume of carbon dioxide was given off. It was therefore not feasible to apply heat during the first part of the leaching process as the increased gas evolution would force the material over the sides of the container. After half an hour had elapsed however, the reaction had subsided sufficiently so that heat could be applied by means of a Bunsen burner. The reaction mixture was heated to a temperature of around 80° C. and it was kept at this temperature for an additional 1 1/2 hours.

When roasted pyrolusite was used as the source of the manganese a similar procedure was followed except that no outside heat was supplied. The large quantity of heat given off by the reaction served to hold the mixture at the desired temperature.

Purification and Filtration

With the solution from the leaching process still at a temperature of around 50° C., a lime slurry was added with continuous stirring until the p^H of the solution had reached a value of six as determined by the

Beckman pH Meter. The nearly neutral solution was then oxidized by allowing compressed air to bubble through it for approximately twenty hours. This treatment resulted in the ferrous iron being thrown out of the manganous sulfate solution in the form of ferric hydroxide precipitate together with the calcium hydroxide. The reaction may be expressed by the following equation:



Clemens (1) has shown that ferrous iron is thrown out of solution at a pH range of from 7 to 8, which is very close to the pH at which manganese is thrown out. However, by converting the ferrous compound to ferric hydroxide, as outlined above, a complete separation is effected at a pH of from 5.5 to 6.5 with no appreciable loss of manganese.

After the mixture was aerated it was filtered through the Buchner filter fitted with a coarse-grade of filter paper. Although suction was provided by means of a water aspirator, the time required to filter the contents of each container was about two hours.

In order to wash the precipitate it was returned to the glass cylinder and was mixed with distilled water. This was then followed by a second filtration. The last traces of precipitate were removed from the

solution by filtration through a fine-grade of filter paper. By the addition of distilled water the solution was made up to the desired concentration.

Testing the Solutions

A colorimetric method was used in testing the neutral solution and the electrolyte in the cells for manganous sulfate content. As the sample must not contain over 30 mg. of manganese per 100 cc when this method is used (6), the solution was first diluted with water to one part in 1000. Two 10 cc. portions were then pipetted into separate beakers. After the addition of 5 cc. of phosphoric acid, 0.3 gram of potassium periodate and 50 cc. of water to each beaker, the samples were boiled from 2 to 3 minutes on a hot plate. A blank, containing only phosphoric acid, water and potassium periodate was included with each set of samples run.

In order that a reference reading might be obtained, a standard sample from a C.P. grade manganous sulfate monohydrate had previously been made up and run. By a direct ratio this reading was then used in calculating the concentrations of the samples tested.

The acidity of the neutral solutions was

determined directly by the use of a Beckman pH meter. In obtaining the grams per liter of acid in the electrolyte, however, a curve of gms H_2SO_4 / liter versus pH was first drawn up.

Electroplating

The electrolyte was made up in each cell to contain the desired concentrations by the addition of neutral solution and of technical-grade sulfuric acid. Tests were run on these solutions and corrections were made as required.

The solutions were heated slowly at first, then more rapidly until they had attained a temperature of 93°C . The electrodes were put in place and were connected to the power circuit. The motor was started and the voltage adjusted to the proper value by means of the Variac. Because of fluctuations in voltage and temperature it was necessary to make frequent adjustments during the runs.

While the cell was in operation the manganese concentration of the solution decreased and the sulfuric acid content increased. The total cell reaction may be expressed by the following equation:



In order to adjust the solutions for changes in concentration brought about by this reaction, a calculated amount of acid solution was withdrawn and a calculated volume of neutral manganous sulfate solution was added at regular hourly intervals. The electrolyte in each cell was tested after every five hours of operation.

The effect that certain of the process variables might have on the current efficiency and on the quality of manganese dioxide produced was determined by making runs in which one condition was varied at a time. The variables which were studied were the following: acid concentration; manganous sulfate concentration; cell temperature; current density; and anode to cathode spacing.

Anode Stripping and Preparation of Samples

The samples of manganese dioxide that were used for analysis were stripped from the anodes by means of a wood chisel. Thin deposits were removed by scraping with the chisel while deposits $1/32$ -inch or more in thickness were removed by inserting the chisel between the layer of manganese dioxide and the anode and prying the deposit loose.

In another stripping method that was investigated, the anode was put back in the cell with no current flowing, but with the cell container filled with spent electrolyte. The solution was boiled vigorously for three hours and was then filtered to remove the manganese dioxide that had fallen from the anode. Any deposit that remained on the anode was then easily removed with a chisel.

The stripping procedure was followed by the grinding of the manganese dioxide to a fine particle size in a mortar and pestle. It was then dried in an electric oven at 80° C. for 12 hours. The samples from runs 7 and 22 were given a wash with water prior to the oven drying to remove the occluded and adsorbed acid.

III SAMPLE CALCULATIONS

A. Volume of Acid Required to Leach The Ore:

Rhodochrosite - This ore contains 16.4 per cent manganese, which corresponds to $16.4 \times \frac{114.9}{54.9} = 34.3$ per cent MnCO_3 . The chemical reaction involved may be expressed by the following equation:



Ore sample = 1200 grams.

Grams of H_2SO_4 theoretically required.

$$(1200) (0.343) \left(\frac{98.1}{114.9} \right) = 352$$

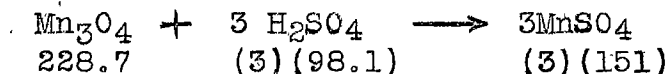
Volume of 10N H_2SO_4 theoretically required

$$1000 \left(\frac{3.52}{(10)(49.04)} \right) = 718 \text{ cc.}$$

Volume of 10N H_2SO_4 actually used 718

10% excess = 790 cc.

Roasted Pyrolusite - This ore contains about 48 per cent manganese in the form of the lower oxides. In the calculations to follow it was considered that all of the manganese existed as the oxide Mn_3O_4 . The percentage of this compound in the ore would then be indicated by the following equation:



Ore sample = 1200 grams.

18.

Grams of H_2SO_4 theoretically required to react with
the Mn_3O_4 $(1200)(.666)\left(\frac{98.1 \times 3}{228.7}\right) = 1028$

Grams of H_2SO_4 theoretically required to react with
the 10% CaO present $(120)\left(\frac{98.1}{56.1}\right) = 210$

Total Grams H_2SO_4 theoretically required $1028 +$
 $210 = 1238$

Volume of 10N H_2SO_4 theoretically required
 $1000 \left(\frac{1238}{(10)(49.04)} \right) = 2520 \text{ cc.}$

Volume of 10N H_2SO_4 actually used

$2520 + 10\% \text{ excess} = 2770 \text{ cc.}$

B. Volume of Acid Required Per Liter of Manganous
Sulfate (150 grams/liter) Produced:

Rhodochrosite	Ore sample	1200 grams
---------------	------------	------------

Grams of $MnCO_3$	1200×0.343	=	412
-------------------	---------------------	---	-----

Grams of $MnSO_4$ theor. obtained	$412 \times \frac{151}{114.9}$	=	542
-----------------------------------	--------------------------------	---	-----

Liters of $MnSO_4$ theor. obtained	$542/150$	=	3.61
------------------------------------	-----------	---	------

Volume of 10N H_2SO_4 used per liter of $MnSO_4$ obtained	$790/3.61$	=	219 cc.
--	------------	---	---------

Roasted Pyrolusite	Ore sample	1200 grams
--------------------	------------	------------

Grams of Mn	1200×0.48	=	575
---------------	--------------------	---	-----

Grams of $MnSO_4$ theor. obtained	$575 \times \frac{151}{54.9}$	=	1580
-----------------------------------	-------------------------------	---	------

19.

Liters of MnSO_4 theor. obtained
 $1580/150 = 10.54$

Volume of 10N H_2SO_4 used per liter of MnSO_4 obtained
 $2770/10.54 = 263 \text{ cc.}$

C. Volume of Electrolyte to Draw Off and Volume of Neutral Solution To Add Per Hour:

At 100 per cent anode current efficiency, the quantity of manganese dioxide that would be deposited per hour for each ampere of electricity flowing is

$$\frac{(3600) (86.9)}{(96,494) (2)} = 162 \text{ grams.}$$

Data:

Anode surface area 0.576 sq. ft. Gms. MnSO_4 /liter 150

Current density 6.7 amps./sq.ft. Gms. Mn per cell 212.5

Electrolyte volume 3.9 liters/cell Gms. H_2SO_4 /liter 95

Assumed current eff. 70 per cent Gms. H_2SO_4 /cell 370.5

Grams Mn per liter in the neutral solution 54.9

Gms. MnO_2 actually deposited
 $(1.62)(0.576)(6.7)(0.70) = 4.38$

Gms of Mn actually deposited
 $4.38 \times \frac{54.9}{86.9} = 2.77$

Grams of H_2SO_4 increase
 $2.77 \times \frac{98.1}{54.9} = 4.95$

20.

$$\begin{array}{r} \text{Volume of solution to be withdrawn} \\ \frac{4.95}{(371 - 4.95)} (3900) = 51 \text{ cc.} \end{array}$$

$$\begin{array}{r} \text{Mn in the solution withdrawn} \\ \frac{(212.5 - 2.77)(51)}{3900} = 2.74 \text{ Gms.} \end{array}$$

$$\begin{array}{r} \text{Grams of manganese to be added} \\ 2.74 + 2.77 = 5.51 \end{array}$$

$$\begin{array}{r} \text{Volume of neutral solution to be added} \\ 5.51 / 0.0549 = 100 \text{ cc.} \end{array}$$

If the results of the tests which were run at five-hour intervals showed that the concentrations were not as calculated, the calculations were repeated using a different assumed efficiency.

D. Calculation of Anode Current Efficiency:

Data:

Length of run	10 hours
Current density	10 amps. per sq. ft.
Grams of MnO ₂ produced	64.1
Anode surface area	0.576 sq. ft.

$$\begin{array}{r} \text{Grams MnO}_2 \text{ at 100 per cent efficiency} \\ (1.62)(10)(0.576)(10) = 93.3 \end{array}$$

$$\begin{array}{r} \text{Per cent current efficiency} \\ \frac{100 (64.1)}{(93.3)} = 68.7 \end{array}$$

E. Kilowatt Hours of Electricity Per Pound of
MnO₂ Produced:

21.

Data:

Cell voltage 1.91 volts

Cell current 5.8 amperes

Grams MnO_2 deposited
per hour 6.5

Kw-hr per pound of MnO_2
$$\frac{(1.91)(5.8)(0.454)}{6.5} = 0.77$$

IV RESULTS

A. Leaching The Ore:

About 95 per cent of the manganese present in the rhodochrosite ore was leached out with the acid under the conditions used in this investigation while 83 per cent of that present in the roasted pyrolusite was dissolved. However, because of the difference in manganese content between the two types of ore, approximately $1/3$ as many grams of the roasted ore were required as the rhodochrosite to obtain one liter of solution.

B. Kw-hrs Required Per Pound of MnO_2 Produced:

a. Effect of Change In Sulfuric Acid Content - Over the sulfuric acid range used in this investigation (33.5 to 150 grams/liter) the Kw-hrs per pound MnO_2 varied from 0.75 at the lowest concentration to 1.80 at a concentration of 150 grams/liter. Over the range of acid content from 33.5 to 125 grams/liter however, this quantity stayed in the range of $0.85 \pm .1$ as shown in Figure 3. In these runs the manganous sulfate content was held at 137.5 grams/liter and the current density at 10 amps./sq.ft.

b. Effect of Change in Manganous Sulfate Content -

Over the range of 100 to 150 grams/liter the Kw-hrs per pound MnO_2 decreased from 1.22 to 0.72 while the current efficiency increased from 43.2 to 73.4 per cent. In the range of from 150 to 175 grams/liter the Kw-hrs stayed within the limits of $0.85 \pm .1$ while the current efficiencies dropped off as much as 20 per cent as shown in Figure 4. The current density was 10 amp./sq.ft. and the acid concentration 67 grams/liter for these runs.

c. Effect of Change in Current Density - At

current densities much below 5 amps./sq.ft., the cell voltage approaches the minimum value for the electrolysis to proceed, which is frequently referred to as the cut off point. This fact would explain the sudden increase in Kw-hrs required at low current densities as shown in Figure 2. Between 5 and 6.7 amps./sq.ft. the Kw-hrs/lb. MnO_2 decreased rapidly from 0.98 to a low of 0.67. A gradual increase was then obtained over the range of from 6.7 to 18.6 amps./sq. ft. and a more rapid increase over the range of from 18.6 to 39. For these runs the manganous sulfate content was held at 137.5 grams/liter and the acid concentration

was maintained at 67 grams/liter.

d. Effect of Change of Anode to Cathode Spacing -

The Kw-hrs per pound MnO_2 remained constant over the anode to cathode spacings of 0.44 inches to 1.75 inches as shown in Figure 5.

C. Cell Voltage:

a. Effect of Change in Sulfuric Acid Content -

At acid concentrations below 33.5 grams/liter the cell voltage increased rapidly as the acidity was lowered. Thus at an acid content of 10 grams/liter the cell voltage was 2.42 while at 33.5 grams/liter it was 2.01. From 33.5 to 150 grams/liter however, the cell voltage stayed within the limits of $1.95 \pm .05$ as shown in Figure 3.

b. Effect of Change in Manganous Sulfate Content -

The cell voltage remained constant at a value of 1.9 volts over the range of manganous sulfate concentrations of from 100 to 175 grams/liter as shown in the data of Table I.

c. Effect of Change in Current Density - Over the current density range of 3.37 to 39 amps./sq. ft. the cell voltage increased steadily from 1.6 to 2.57 volts as shown in Figure 2. This is the effect that would

follow from Ohm's Law for an increase in current when the resistance is held constant.

d. Effect of Change in Anode to Cathode Spacing -

The cell voltage increased gradually from a value of 1.7 to 1.9 volts over the range of anode to cathode spacings of 0.44 to 1.75 inches as shown in Figure 5.

It is possible that the increase in voltage at the wider spacings was due to the increased resistance of the electrolyte.

D. Anode Stripping:

Deposits of manganese dioxide under 1/32-inch in thickness were found to be more difficult to strip than heavier coatings. Nearly all of the deposits however, could be removed by the chisel alone. The rest were loosened sufficiently by a three-hour boil to where they could be easily scraped off.

Another difficulty which was encountered in stripping the anodes was that a considerable amount of graphite was removed along with the manganese dioxide. This remained in the samples as a contaminant.

E. Effect of Process Variables:

a. Type of Anodes - Runs 1 through 6 were the only runs made with the hard-carbon or arc-light anodes. Under the same conditions, the current ef-

ficiencies obtained by the use of this type anode were around 10 per cent lower than those obtained with the AGR graphite anodes. The hard-carbon anodes were also found to deteriorate rapidly while the graphite anodes did not.

b. Cell Temperature - Run 6 in Table I was the only run made in which a series of temperatures was used. Over the range of temperatures from 41°C. to 92°C. the current efficiency was found to increase from 11.5 per cent. to 21.8 per cent. The anode deterioration however, was much greater at the lower temperatures. For example, after seven hours of operation the anodes from the cells at 77°C. and 92°C. showed only slight deterioration while the anodes from the cells at 41°C. and 60°C. were badly damaged.

The results obtained at the various cell temperatures of this investigation are in good agreement with those obtained by Nichols (3) and by The Georgia Institute of Technology (2).

c. Acid Concentration - Figure 3, which is a plot of the data taken from runs 13 and 15 over the range of 10 to 150 grams/liter, shows that the highest current efficiency, 72 per cent, was obtained

with an acid content of 95 grams/liter. The most rapid change in efficiency was an increase from 4.5 per cent to 59 per cent when the sulfuric acid concentration was increased from 10 to 33.5 grams/liter. At acid concentrations above the optimum, the current efficiency dropped off steadily to a value of 29.3 per cent at an acid content of 150 grams/liter.

The low efficiencies obtained at concentrations below 30 grams/liter may be attributed to the low conductivity of neutral manganous sulfate solutions.

The quantity of the lower oxides of manganese present in the MnO_2 increases as the acid concentration decreases as shown in Table I.

d. Manganous Sulfate Concentration - As is shown in Figure 4, the highest current efficiency, 73.4 per cent, was obtained at a concentration of 150 grams manganous sulfate per liter. The curve then drops off on both sides of this point, but it drops off much more rapidly for values below than above the optimum. The lowest efficiency, 43.2 per cent, was obtained at a manganous sulfate content of 100 grams/liter. The data used in plotting Figure 4 were taken from runs 14, 18 and 20 of Table I.

e. Current Density - The runs made to determine the effect of current density were runs 1 through 5 and also runs 9, 10, 16, 17 and 19. Data for these runs are given in Table I. The results from runs 4, 5, and 17 are unreliable as explained in the Table notes. Values obtained from the remaining runs were used in the plot of Figure 2. Over the range of current density from 3.37 to 39 amps./sq.ft., the highest efficiency obtained was a value of 63.5 per cent at a current density of 6.7. At values below 5 amps./sq. ft. the current efficiencies dropped off rapidly to a low of 15.9 per cent at 3.37 amps./sq. ft. This may be attributed to the effect of the cut off point as discussed under Kw-hrs per pound of MnO_2 .

f. Anode to Cathode Spacings - Run 8 was the only run made in which the spacings between the anode and cathode were changed from one inch. Over the range of 1/2-inch to 1 3/4-inches the current efficiency increased from 52 per cent to 58.8 per cent as shown in Figure 5.

F. Analysis of the Product by The Squier Signal

Laboratory (Tables II & III)

a. Iron Content - Of the samples that were analyzed, the samples from runs 12 through 22 had been

produced from a purified solution. The sample from run 15, cell 2 contained an iron content of 0.5 per cent, which was the lowest value reported. Other samples low in iron were the sample from run 15, cell 1 with 1.1 per cent and the sample from run 12 with 1.2 per cent. The results from runs 13 and 15 show that the iron content in the sample varies inversely with the acid concentration of the electrolyte.

b. Graphite Content - Graphite was the main contaminant of all of the samples which were analyzed.

c. Crystalline Structure --Except for the sample from run 13, cell 1 all of the samples of manganese dioxide that were tested showed predominantly a gamma structure. The samples from run 15, cell 2 and run 12 contained the largest amount of the gamma dioxide.

d. Available Oxygen as Per Cent MnO_2 - Sample 15, cell 2 contained an available oxygen content of 87.1 per cent while the sample from run 12 contained a value of 82 per cent. The remainder of the samples tested contained values ranging from 41.7 to 75.6 per cent.

e. Total Manganese as Per Cent Mn. - The sample from run 15, cell 2 also contained the largest Mn content with a value of 57.7 per cent. Samples 12 and 7 were next with values of 54.7 per cent and 54.6 per cent. The remainder of the samples showed values ranging from 34.8 per cent to 50 per cent manganese.

f. Battery Test - Table III gives the results of the initial battery tests on batteries made from a sample of manganese dioxide from run 7. The result obtained for the $16 \frac{2}{3}$ ohm test was 5.5 hours which was also the value given in the specifications. For the $166 \frac{2}{3}$ ohm test the result obtained, 109.4 hours, was 16 per cent lower than the value of 130 hours called for in the specifications.

V SUMMARY

The following generalizations may be drawn from the results found in this investigation:

1. Approximately 16 per cent more acid is required to leach roasted pyrolusite than to leach rhodochrosite. Of the manganese present in both types of ore about 95 per cent is soluble from rhodochrosite and 83 per cent from the roasted ore under the conditions of this investigation.
2. Batteries, which are made up with electrolytic manganese dioxide from Montana ores give satisfactory initial tests.
3. Electrolytic manganese dioxide produced from either type of ore exists predominantly in the gamma phase.
4. Temperatures of around 93°C. are necessary for the attainment of the highest current efficiencies accompanied by the least damage to the graphite anodes.
5. Acid concentrations of 95 grams per liter and manganous sulfate concentrations of 150 grams per liter give the highest current efficiencies.
6. Current densities of between 6 and 7 amps. per

32.

square foot give the highest current efficiencies.

7. Under the proper conditions current efficiencies of around 70 per cent may be obtained.

VI ACKNOWLEDGMENT

The author acknowledges with thanks the courtesy of The United States Army Signal Corps, who ran the analyses on the manganese dioxide samples and who sponsored the fellowship under which this work was carried out.

VII LITERATURE CITED

- (1) Clemens, R. F., U.S. Pat. 2,424,958 (1947).
- (2) Kissin, G. H., Electrolytic Synthesis of Battery Active Manganese Dioxide Georgia Institute of Technology, Atlanta, Georgia. 1949.
- (3) Nichols, G. W., Trans. Electrochem. Soc. 62, 393 (1932)
- (4) Sylvain, E. F., M.S. Thesis, Montana State College, (1950).
- (5) Van Arsdale, G. D. and Maier, C. G., Trans. Amer. Electrochem. Soc., 109 (1918).
- (6) Willard, H. H., and Diehl, H., Advanced Quantitative Analysis D. Van Nostrand Co., Inc. 176-7, 1943.

VIII APPENDIX

page

Table I - Electrolytic MnO_2 Data	36
Notes on Table I	41
Table II - Analysis of Electrolytic MnO_2	42
Table III- Battery Test Data.	44
Table IV - Typical Assays on Rhodochrosite and Roasted Pyrolusite Ores.	45
Figure 1.- Schematic Diagram of the Electrical Apparatus Used in the Electrolysis	46
Figure 2 - The Relation of Current Efficiency, Energy Requirements and Cell Volt- age to Various Current Densities	47
Figure 3 - The Relation of Current Efficiency, Energy Requirements and Cell Volt- age to Various Electrolyte Acid Concentrations	48
Figure 4 - The Relation of Current Efficiency and Energy Requirements to Various Electrolyte Manganese Sulphate Con- centrations.	49
Figure 5 - The Relation of Current Efficiency, Energy Requirements and Cell Volt- age to Electrode Spacing	50

Table I. Electrolytic MnO₂ Data

RUN AND CELL	SPACING ANODE-CATHODE (inches)	ANODE CATHODE	RUN TIME (hours)	MnO ₂ YIELD (grams) (uncorrected)	CURRENT EFFICIENCY (per cent) (uncorrected)	CURRENT DENSITY (amps./ft. ²)	CURRENT ACTUAL (amperes)	AVERAGE VOLTAGE PER CELL	KW-HR PER POUND MnO ₂	TEMPERATURE (Centigrade)	ELECTROLYTE MnSO ₄ Conc. H ₂ SO ₄ Conc. (gm./l.)
Carbon 1 Av. of 2 Cells	1	Hard Carbon Chemical Lead	26.5	35	23	15.5	3.53	2	2.43	91	<u>137.5</u> 67
Carbon 2 Discont. after 5 hrs.											
Carbon 3 1 Cell	1	Hard Carbon Chemical Lead	5	13.6	23.3	33.2	7.2	2.4	2.89	92	<u>137.5</u> 67
Carbon 4 1 Cell	1	Hard Carbon Chemical Lead	3	7.5	14.2	45	10.8	2.8	5.5	92	<u>137.5</u> 67
Carbon 5 1 Cell	1	Hard Carbon Chemical Lead	3	10.4	14.3	60	15	3.2	6.28	92	<u>137.5</u> 67
Carbon 6 Cell 1	1	Hard Carbon Chemical Lead	7	17.6	21.8	32	7.1	3	3.85	92	<u>137.5</u> 67
Carbon 6 Cell 2	1	Hard Carbon Chemical Lead	7	14	17.3	32	7.1	2.6	4.18	77	<u>137.5</u> 67

Table I. Electrolytic MnO₂ Data (continued)

RUN AND CELL	SPACING ANODE-CATHODE (inches)	ANODE CATHODE	RUN TIME (hours)	MnO ₂ YIELD (grams) (uncorrected)	CURRENT EFFICIENCY (per cent) (uncorrected)	CURRENT DENSITY (amps./ft. ²)	CURRENT ACTUAL (amperes)	AVERAGE VOLTAGE PER CELL	KW-HR. PER POUND MnO ₂	TEMPERATURE (°Centigrade)	ELECTROLYTE MnSO ₄ Conc. H ₂ SO ₄ Conc. (gm./l.)
Carbon 6 Cell 3	1	Hard Carbon Chemical Lead	7	8.3	10.3	32	7.1	3.05	8.26	60	<u>137.5</u> 67
Carbon 6 Cell 4	1	Hard Carbon Chemical Lead	7	9.3	11.5	32	7.1	2.95	7.15	41	<u>137.5</u> 67
Carbon 7 Av. of 5 Cells	1	Soft Carbon (2) Chemical Lead	17.5	86.2	50	10	6.06	1.92	1.07	93	<u>137.5</u> 67
Carbon 8 Cell 6	.438	Soft Carbon Chemical Lead	18	61.9	52	10.1	4.1	1.71	.905	93	<u>137.5</u> 67
Carbon 8 Cell 7	1.75	Soft Carbon Chemical Lead	18	70.3	58.8	10.1	4.1	1.92	.898	93	<u>137.5</u> 67
Carbon 9 Cell 1 (3)	1	Soft Carbon Chemical Lead	5	28.7	30.8	39	11.5	2.56	2.33	93	<u>137.5</u> 67
Carbon 9 Cell 2	1	Soft Carbon Chemical Lead	5	17.1	18.4	30.4	11.5	2.6	3.98	93	<u>137.5</u> 67
Carbon 9 Cell 6	1	Soft Carbon Chemical Lead	5	50.1	54	18.6	11.5	2.1	1.094	93	<u>137.5</u> 67

Table I. Electrolytic MnO₂ Data (continued)

RUN AND CELL	SPACING ANODE-CATHODE (inches)	ANODE CATHODE	RUN TIME (hours)	MnO ₂ YIELD (grams) (uncorrected)	CURRENT EFFICIENCY (per cent) (uncorrected)	CURRENT DENSITY (amps./ft. ²)	CURRENT ACTUAL (amperes)	AVERAGE VOLTAGE PER CELL	KW-HR PER POUND MnO ₂	TEMPERATURE (°Centigrade)	ELECTROLYTE H ₂ SO ₄ Conc. (gm./l.)
Carbon 10 Cell 1	1	Soft Carbon Chemical Lead	12	27.4	63.7	6.72	1.94	1.77	.684	93	$\frac{137.5}{67}$
Carbon 10 Cell 2	1	Soft Carbon Chemical Lead	12	34.4	91.2	5	1.94	1.71	.526	93	$\frac{137.5}{67}$
Carbon 10 Cell 6 (4)	1	Soft Carbon Chemical Lead	12	6	15.9	3.37	1.94	1.58	2.79	93	$\frac{137.5}{67}$
Carbon 11 (5)											
Carbon 12 1 Cell	1	Soft Carbon Chemical Lead	17.25	60.5	58	9.98	3.72	1.8	.865	93	$\frac{137.5}{67}$
Carbon 13 Cell 1	1	Soft Carbon Chemical Lead	8	3.4	4.5	9.9	5.8	2.42	15	93	$\frac{137.5}{10}$
Carbon 13 Cell 2	1	Soft Carbon Chemical Lead	8	44.3	59	9.9	5.8	2.01	.965	93	$\frac{137.5}{33.5}$
Carbon 13 Cell 3	1	Soft Carbon Chemical Lead	8	51.7	68.8	9.9	5.8	1.91	.776	93	$\frac{137.5}{100}$
Carbon 14 Cell 1	1	Soft Carbon Chemical Lead	14.5	58.8	43.2	10.6	5.8	1.901	1.23	93	$\frac{100}{67}$

Table I. Electrolytic MnO₂ Data (continued)

RUN AND CELL	SPACING ANODE-CATHODE (inches)	ANODE-CATHODE	RUN TIME (hours)	MnO ₂ YIELD (grams) (uncorrected)	CURRENT EFFICIENCY (per cent) (uncorrected)	CURRENT DENSITY (amps./ft. ²)	CURRENT ACTUAL (amperes)	AVERAGE VOLTAGE PER CELL	KW-HR PER POUND MnO ₂	TEMPERATURE (°Centigrade)	ELECTROLYTE MnSO ₄ Conc. H ₂ SO ₄ Conc. (gm./l.)
Carbon 14 Cell 2	1	Soft Carbon Chemical Lead	14.5	99.8	73.4	10.6	5.8	1.901	.735	93	<u>150</u> 67
Carbon 14 Cell 3		Soft Carbon Chemical Lead	14.5	82.5	60.6	10.6	5.8	1.90	.88	93	<u>165</u> 67
Carbon 15 Cell 1		Soft Carbon Chemical Lead	15	101.7	72	9.97	5.8	1.904	.741	93	<u>137.5</u> 95
Carbon 15 Cell 2		Soft Carbon Chemical Lead	15	78	55.3	9.97	5.8	1.904	.965	93	<u>137.5</u> 125
Carbon 15 Cell 3		Soft Carbon Chemical Lead	15	41.3	29.3	9.97	5.8	1.903	1.82	93	<u>137.5</u> 150
Carbon 16 1 Cell (6)		Soft Carbon Chemical Lead	5.5	36.9	37	28.2	11.2	2.42	1.83	93	<u>137.5</u> 67
Carbon 17 1 Cell		Soft Carbon Chemical Lead	10	21.1	45.25	5	2.88	1.834	1.14	93	<u>137.5</u> 67
Carbon 18 Cell 1		Soft Carbon Chemical Lead	10	50.2	53	10.1	5.86	1.865	.988	93	<u>125</u> 67
Carbon 18 Cell 2		Soft Carbon Chemical Lead	10	54.7	57.7	10.2	5.86	1.86	.906	93	<u>137.5</u> 67

Table I. Electrolytic MnO₂ Data (continued)

RUN AND CELL	SPACING ANODE-CATHODE (inches)	ANODE CATHODE	RUN TIME (hours)	MnO ₂ YIELD (grams) (uncorrected)	CURRENT EFFICIENCY (per cent) (uncorrected)	CURRENT DENSITY (amps./ft. ²)	CURRENT ACTUAL (amperes)	AVERAGE VOLTAGE PER CELL	KW-HR PER POUND MnO ₂	TEMPERATURE (°Centigrade)	ELECTROLYTE MnSO ₄ Conc. H ₂ SO ₄ Conc. (gm./l.)
Carbon 18 (7) Cell 3	1	Soft Carbon Chemical Lead	10	36.6	38.6	10	5.86	1.88	1.37	93	<u>140</u> 67
Carbon 18 Cell 4	1	Soft Carbon Chemical Lead	10	53.7	56.6	10.4	5.86	1.864	.925	93	<u>160</u> 67
Carbon 19 1 Cell	1	Soft Carbon Chemical Lead	15	35.8	50.7	5	2.9	1.75	.966	93	<u>137.5</u> 67
Carbon 20 Cell 1	1	Soft Carbon Chemical Lead	10	64.1	68.3	10	5.8	1.83	.752	93	<u>152.</u> 67
Carbon 20 Cell 2	1	Soft Carbon Chemical Lead	10	56.9	60.5	10	5.8	1.85	.855	93	<u>176.</u> 67
Carbon 21 1 Cell	1	Soft Carbon Chemical Lead	11	49	70.4	6.77	3.9	1.81	.719	93	<u>150</u> 95
Carbon 22 (5) Cell 1	1	Soft Carbon Chemical Lead	50	264.3	83.5	6.74	3.88	1.84	.615	93	<u>150</u> 95
Carbon 22 (5) Cell 2	1	Soft Carbon Chemical Lead	50	272.5	86.0	6.74	3.88	1.84	.596	93	<u>150</u> 95

Table I (continued)

NOTES

* Run Carbon 4 and run Carbon 5 are inaccurate due to the fact that deterioration of the anodes caused considerable carbon to be suspended in the electrolyte and this could not be easily separated from the manganese dioxide.

(1) Carbon rods 7/8 inches in diameter with inscription "510 Plania EFFEKT."

(2) National Carbon Company anodes, A. G. R. type graphite, are 1/2 inch thick and 4 inches wide.

(3) Made a re-run on this point (Carbon 16).

(4) Due to the fact that MnSO_4 concentrations were not consistent, the data of this run are not reliable.

(5) Solution prepared from roasted pyrolusite.

(6) Anode plated on one side only.

(7) Possible error in weights.

Table II Analysis of Electrolytic MnO₂

CARBON AND STRUCTURE CELL		AVAILABLE O ₂ AS % OF MnO ₂	% Mn.	% Fe.	% Pb.	RATING
Carbon 1 Cell 1	Gamma	70.6	48.3	1.4	0.15	----
Carbon 7 All Cells	Gamma	75.6	54.6	2.5	0.13	2
Carbon 9 Cell 1	Gamma	48.5	37.8	---	0.11	6
Carbon 9 Cell 2	Gamma	65.0	50.0	1.9	0.13	3
Carbon 9 Cell 6	Gamma	53.0	39.8	1.4	0.11	5
Carbon 10 Cell 1	Gamma	41.7	34.8	1.8	0.08	7
Carbon 10 Cell 2	Gamma	64.4	47.2	---	0.17	4
Carbon 12 1 cell	Gamma	82.0	54.7	1.2	----	1
Carbon 13 Cell 1	not MnO ₂	22.1	20.9	---	----	7
Carbon 13 Cell 2	Gamma	72.2	51.5	4.6	----	6
Carbon 14 Cell 1	Gamma	75.4	51.0	1.9	----	4
Carbon 14 Cell 2	Gamma	76.8	51.6	1.8	----	5
Carbon 14 Cell 3	Gamma	81.3	54.2	1.8	----	2

Table II Analysis of Electrolytic MnO_2 (Continued)

CARBON AND STRUCTURE CELL	AVAILABLE O ₂ AS % OF MnO ₂	% Mn.	% Fe.	% Pb.	RATING
Carbon 15 Cell 1	Gamma	81.6	54.2	1.1	---- 3
Carbon 15 Cell 2	Gamma	87.1	57.7	0.5	---- 1

Table III. Battery Test Data

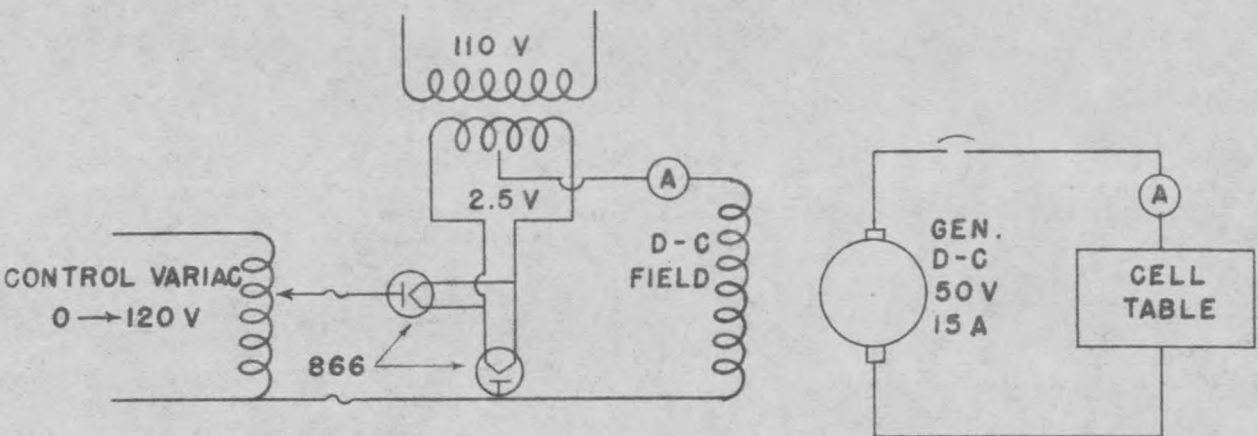
SAMPLE	DISCHARGE RESISTANCE (ohms)	TYPE OF DISCHARGE	TEST END VOLTAGE	AVERAGE INITIAL SERVICE (hours)	INITIAL CAPACITY REQUIRE- MENTS (specs.)
Carbon 7	16 2/3	Continuous	1.0	5.5	5.5
Carbon 7	166 2/3	Continuous	1.13	109.4	130

Table IV.

Typical Assays on Rhodochrosite and
Roasted Pyrolusite Ores

Rhodochrosite			
Component	Per Cent	Component	Per Cent
Manganese	16.4	Gold	0.37
Zinc	2.5	Phosphorus	0.04
Lead	1	Iron	3.0
Copper	0.16	Sulfur	3.2
Silver	1.24	Silicon Dioxide	40.0

Roasted Pyrolusite			
Component	Per Cent	Component	Per Cent
Manganese	48.6	Calcium oxide	7.8
Copper	0.07	Aluminum oxide	1.71
Iron	3.8	Silicon dioxide	14.56
Zinc	0.10	Phosphorus	0.114
Lead	0		



Apparatus Used in the Electrolysis.

Figure 2 - The Relation of Current Efficiency, Energy Requirements and Cell Voltage to Various Current Densities.

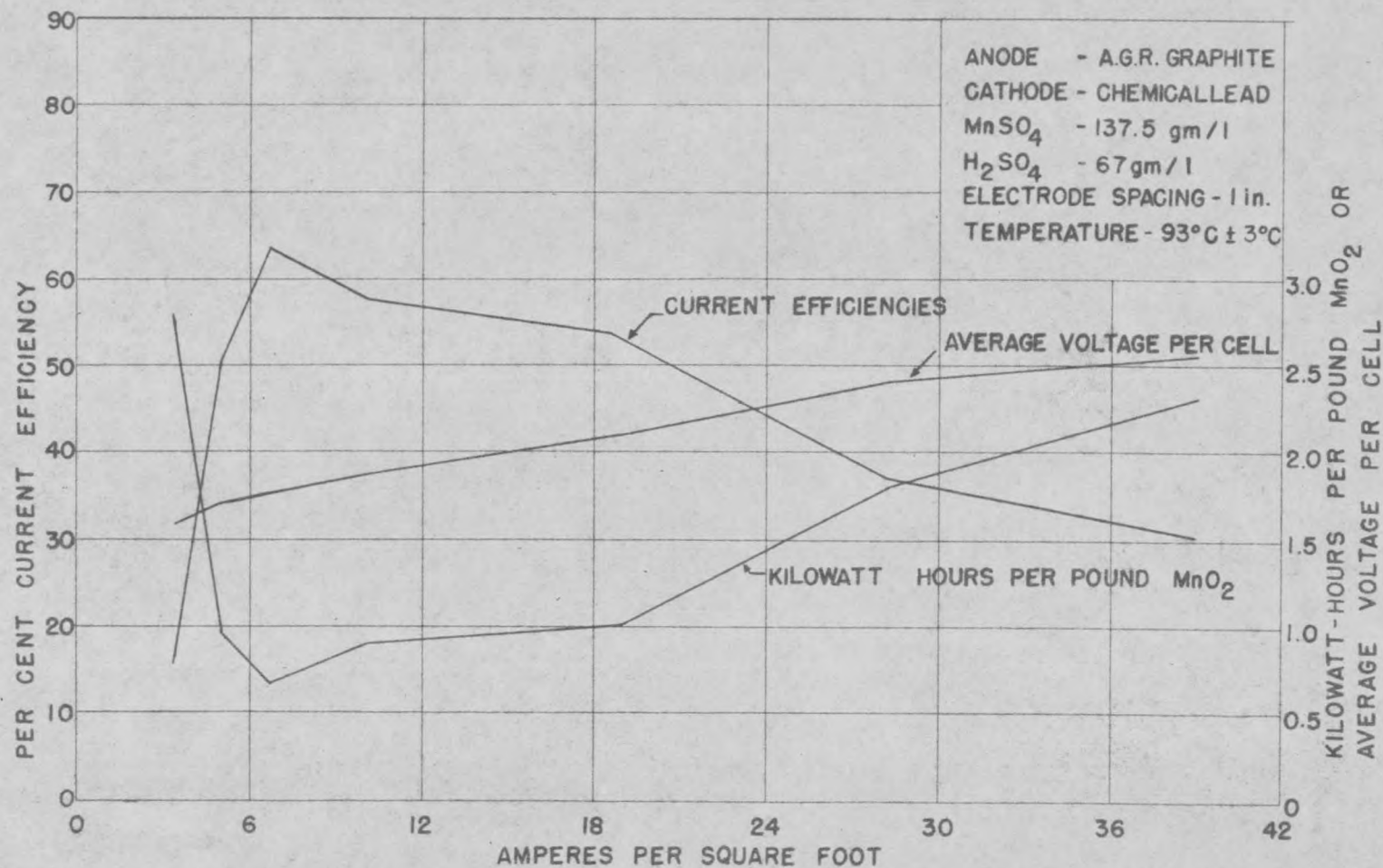
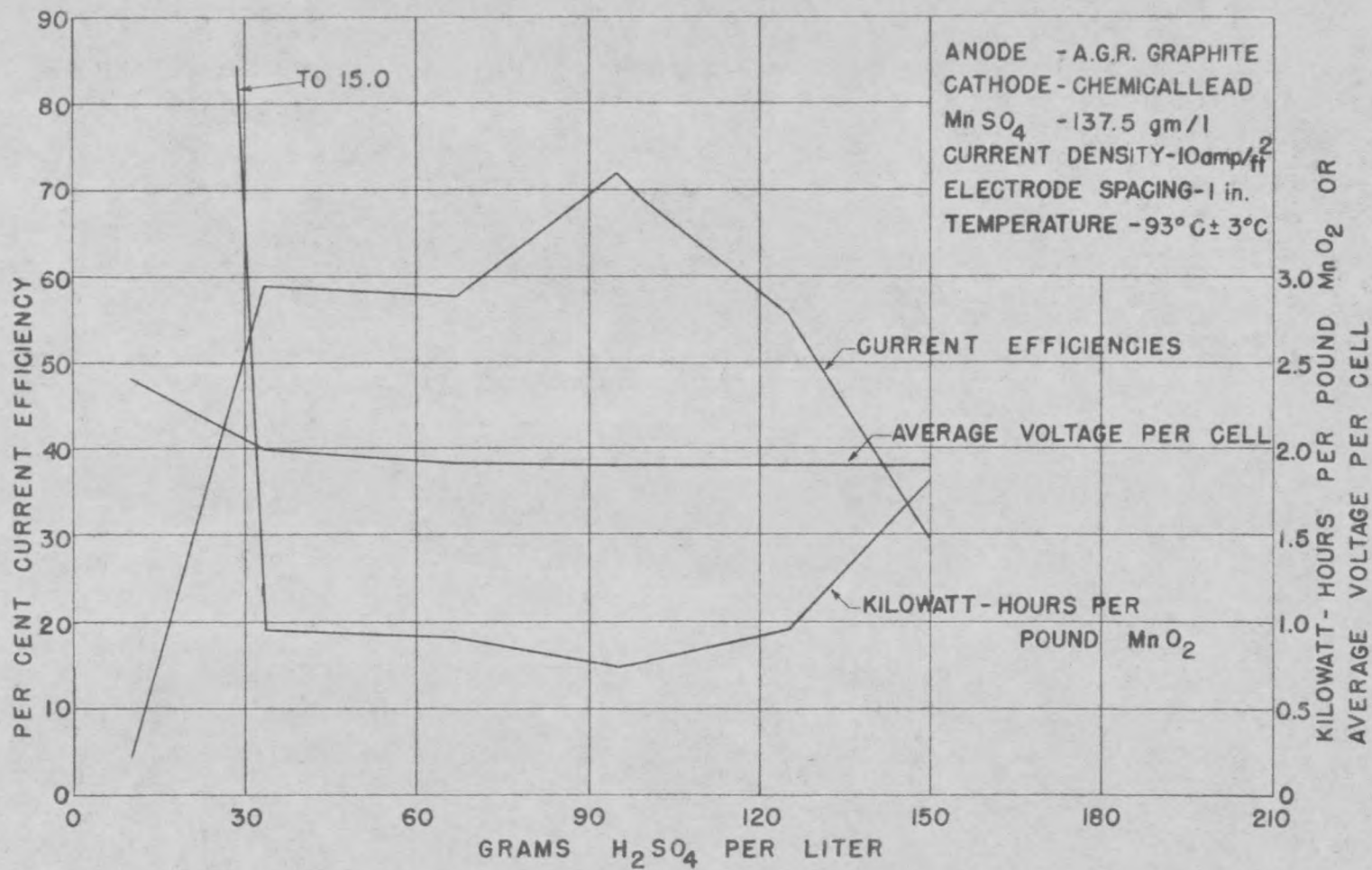


Figure 3 - The Relation of Current Efficiency, Energy Requirements and Cell Voltage to Various Electrolyte Acid Concentrations.



ANODE - A.G.R. GRAPHITE
 CATHODE - CHEMICAL LEAD
 H_2SO_4 - 67 gm/l
 CURRENT DENSITY - 10 amp/ft²
 ELECTRODE SPACING - 1 in.
 TEMPERATURE - 93°C ± 3°C

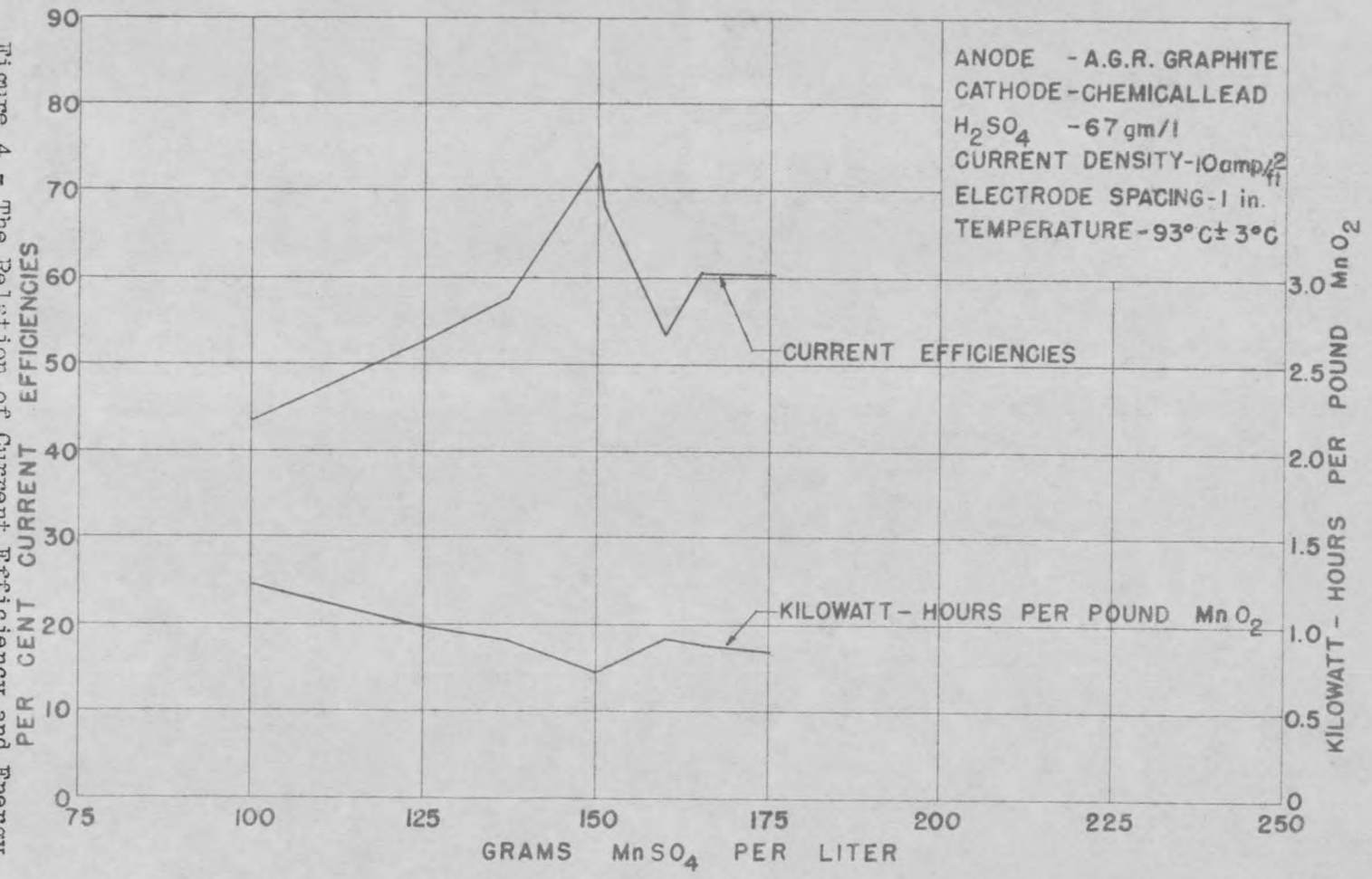


Figure 4 - The Relation of Current Efficiency and Energy Requirements to Various Electrolyte Manganese Sulphate Concentrations.

ANODE - A.G.R. GRAPHITE
 CATHODE - CHEMICAL LEAD
 H_2SO_4 - 67 gm/l
 $MnSO_4$ - 137.5 gm/l
 CURRENT DENSITY - 10 amp/ft²
 TEMPERATURE - 93°C ± 3°C

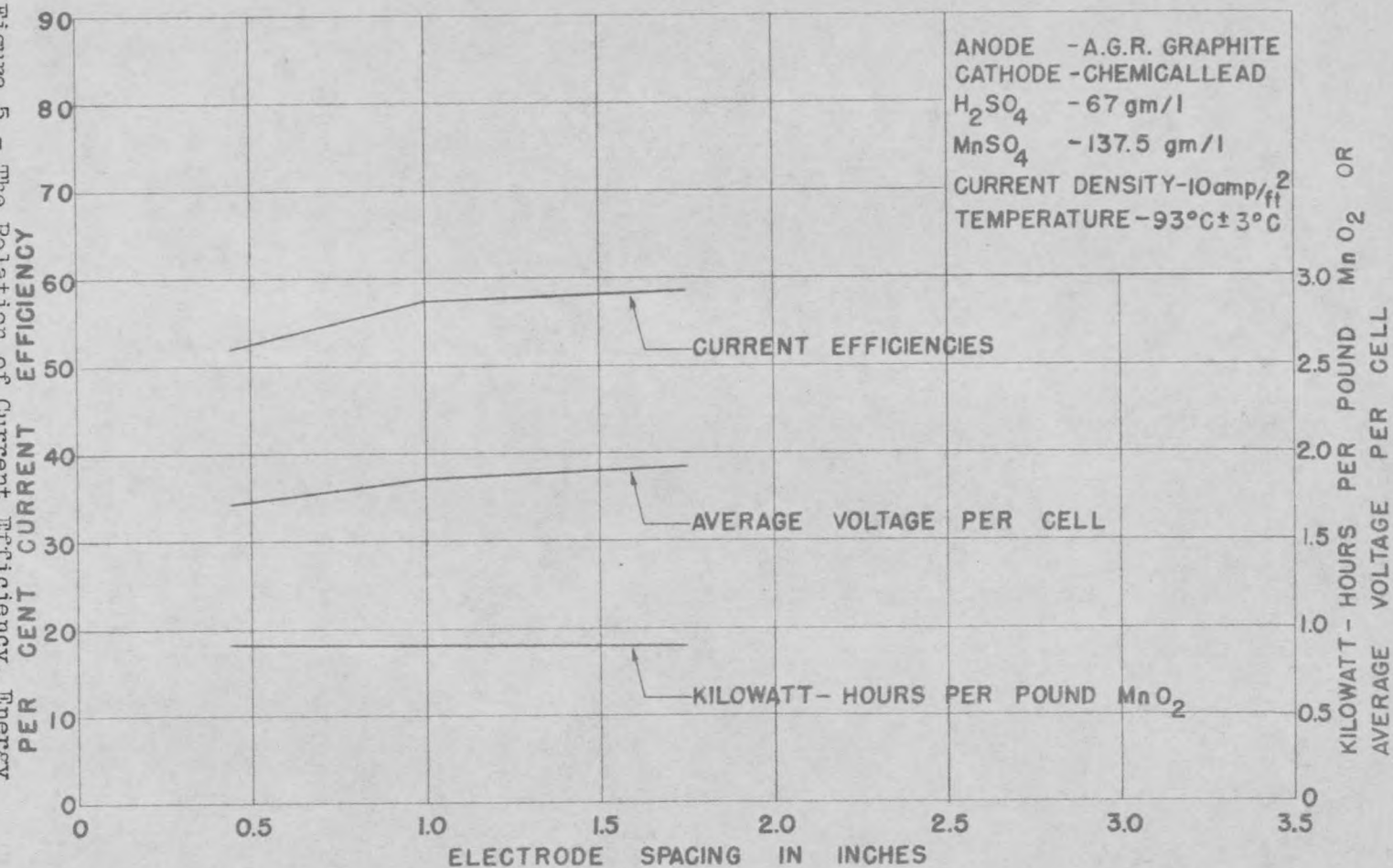


Figure 5 - The Relation of Current Efficiency, Energy Requirements and Cell Voltage to Electrode Spacing.

96018

SUBJECTS

3 1762 10014821 0

N378 96018
M275e [REDACTED]
cop.2 Magnuson, A. M.
Electrolytic synthesis of
battery-active manganese
dioxide.
DATE ISSUED TO
NOV 6 '62 Lang M. J. [REDACTED]
JUL 27 '74 728 5 Trade
INTERLIBRARY
N378
M275
cop.2
[REDACTED]

96018