



Battery-active manganese dioxide
by Clifford Frank Poor

A THESIS Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree
of Doctor of Philosophy in Chemical Engineering at Montana State College
Montana State University
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Abstract:

Of approximately 30,000 short tons of battery-active manganese dioxide consumed per year in the United States, only 1400 tons are produced domestically. Because Montana possesses great quantities of manganese ore, an investigation on the utilization of the ore commercially was conducted.

A reaction which looked promising for producing manganese dioxide was the oxidation of manganous sulfate by potassium permanganate. The manganese dioxide produced by this reaction was evaluated, according to U.S. Army Signal Corps Specifications SCL-3117-D). The results obtained, as well as chemical and physical data, are reported and interpreted in this thesis.

It was found that battery-active manganese dioxide meeting U. S.

Signal Corps specifications could be produced by this reaction when commercial-grade reagents were used.

In addition, the manganese dioxide which met specifications was blended with Philipsburg, Montana low-grade battery ore. A mixture containing 20% specification manganese dioxide and 80% Philipsburg ore was sufficient to surpass the quality of imported. Gold Coast manganese dioxide.

When manganese dioxide is made from the chlorination of manganous hydroxide or from the oxidation of manganous carbonate with air, it is necessary to acid leach the manganese dioxide to enhance the battery activity. This thesis also contains a study of acid leaching of manganese dioxide produced from the chlorination of manganous hydroxide.

B A T T E R Y - A C T I V E M A N G A N E S E D I O X I D E

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Head, Major Department

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Dean, Graduate Division

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ABSTRACT

Of approximately 30,000 short tons of battery-active manganese dioxide consumed per year in the United States, only 1400 tons are produced domestically. Because Montana possesses great quantities of manganese ore, an investigation on the utilization of the ore commercially was conducted.

A reaction which looked promising for producing manganese dioxide was the oxidation of manganous sulfate by potassium permanganate. The manganese dioxide produced by this reaction was evaluated according to U. S. Army Signal Corps Specifications SCL-3117-D. The results obtained, as well as chemical and physical data, are reported and interpreted in this thesis.

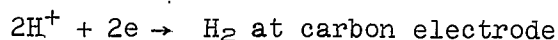
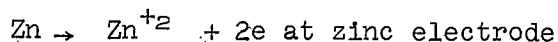
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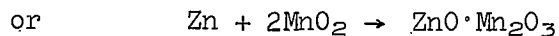
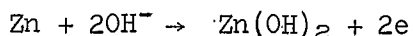
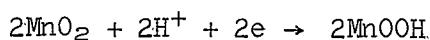
When manganese dioxide is made from the chlorination of manganous hydroxide or from the oxidation of manganous carbonate with air, it is necessary to acid leach the manganese dioxide to enhance the battery activity. This thesis also contains a study of acid leaching of manganese dioxide produced from the chlorination of manganous hydroxide.

INTRODUCTION

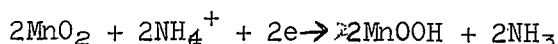
The basic reactions in a dry cell battery may be represented as follows:



Originally, the evolved hydrogen formed bubbles on the positive electrode which resulted in generating a back e.m.f., called polarization (9). Then Leclanche' discovered that by surrounding the positive electrode with manganese dioxide, the formation of hydrogen gas is prevented to a considerable extent. The cell reactions (15) then being:



This reaction occurs on light discharge drains with zinc present, while on heavy drains with a deficiency of zinc ions, the reaction is assumed to be



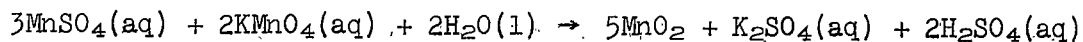
It was also found that only certain crystalline phases of manganese dioxide could act as a depolarizer in dry cells, these phases being principally gamma and rho types.

In the years past, the so-called battery-active manganese dioxide has been imported principally from Gold Coast, Africa. Of a total of 30,102 short tons of battery grade ore consumed in 1957, 28,102 tons were imported, while only 1400 tons were produced domestically. (13).

Because Montana has a vast supply of manganese in Butte and low grade battery-active manganese dioxide in Philipsburg, the Chemical Engineering Department at Montana State College has undertaken to develop economically feasible processes which could utilize Montana manganese ore in the production of manganese dioxide.

Since June 1951 laboratory research has been conducted by the Chemical Engineering Department on the chemical synthesis of battery-grade manganese dioxide. This research was sponsored from June 1951 to June 1954 by the Army Signal Corps, who were interested in developing dry cell batteries for military use. The research was then sponsored from June 1954 to June 1955 by Manganese, Incorporated of Henderson, Nevada, and from June 1955 to the present by the Montana State College Engineering Experiment Station. From the knowledge and techniques gained in this research, it appeared that three reactions showed promise of being utilized to develop Montana manganese ore deposits. The reactions were: the oxidation of manganous sulfate with potassium permanganate, the oxidation of manganous hydroxide with chlorine (14), and the oxidation of manganous carbonate with air (17).

The over-all reaction for the oxidation of manganous sulfate with potassium permanganate, which is known as the Guyard reaction, is as follows:



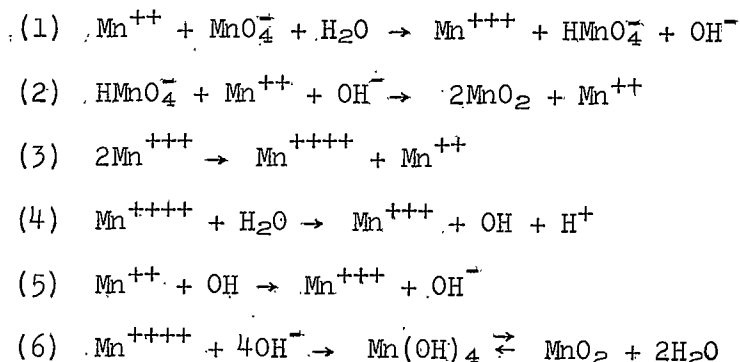
Some work has been done on the kinetics and mechanism of the reaction.

Tompkins (18) found that the precipitation of manganese dioxide is hindered

ed by anions which complex with the Mn^{+++} ion and the more stable the complex, the greater the retardation. For example, the sulfate ion, $SO_4^{=}$, forms the stable complex $[Mn(SO_4)_2 \cdot 2H_2O]^-$ in 6N H_2SO_4 , but hydrolyzes to manganese dioxide on dilution. This indicates that MnO_4^- is first reduced to Mn^{+++} , which is further reduced to Mn^{++} by the mechanism:



The Mn^{++++} ion is then hydrolyzed to form the dioxide. In absence of complex-forming anions, Tompkins found that the rate is proportional to the concentration of the permanganate and manganous ions, and inversely proportional to the hydrogen ion concentration. Using these facts, Tompkins suggests the following mechanism:



It is postulated that reaction 6 is accountable for the major part of the production of MnO_2 because reaction 2 is believed to be slow. In oxidations by permanganate, where hydrated manganese dioxide is precipitated, complications arise from heterogeneous reactions at the surface of the precipitate and the kinetics of the overall reaction can become highly complicated (1). Definite processes are not postulated for the heterogeneous reaction.

Polissar (16) found that the Guyard reaction is catalyzed by MnO_2 and when MnO_2 is added to the solution, the induction period, which is the time required to attain the maximum rate, is diminished. The complexing anions which form complexes with manganic ions increase the induction time.

But Tompkins found that the catalytic effect of the manganese dioxide is greatly reduced when the slurry is vigorously stirred, which indicates that the catalytic effect is probably a surface effect.

Kleinfelder (10) was the first at Montana State College to experiment with the oxidation of manganous sulfate with potassium permanganate to produce battery-active manganese dioxide. Although a complete study was not made on all reaction variables, poor battery-grade manganese dioxide was obtained from the experiments performed. This led to the belief that specification-grade dioxide could not be produced by the Guyard reaction.

A year later, Domning (6) continued experimentation with the permanganate oxidation of manganous sulfate using mostly C.P. reagents. While very few of his manganese dioxide samples met specifications, his overall results were better than those obtained by Kleinfelder. The possibilities of the reaction producing specification manganese dioxide were drawing nearer.

Because of the simplicity in preparing manganese dioxide by the Guyard reaction, it was decided to conduct a more extensive investigation of the Guyard reaction using only commercial reagents. A few exploratory experiments indicated that specification manganese dioxide could be made using manganous carbonate ore from Butte, Montana as a raw material. The

major part of this thesis will be concerned with producing battery-grade manganese dioxide by the oxidation of manganous sulfate with potassium permanganate.

As previously stated, other reactions that look favorable both economically and technically are the oxidation of manganous hydroxide with chlorine and the oxidation of manganous carbonate with air. The end product manganese dioxide in both of these reactions must be acid leached to enhance the battery-activity. As a result, a few experiments were executed to study the acid leaching variables. This, also, will be presented in this thesis.

EXPERIMENTAL CONSIDERATIONS

Because the data obtained from the experiments were to be used in evaluating and designing a commercial plant, technical grade reagents were used in a majority of the experiments. By doing this, time was saved in attaining the objective, a more practical evaluation of the product was made possible, and more knowledge on the limitations of the reaction was acquired.

The manganous sulfate was obtained by leaching two 50-lb. batches of concentrated manganous carbonate from the Anaconda, Montana smelter with the stoichiometric amount of technical sulfuric acid. The acid solution was 20% by weight of sulfuric acid. The two batches of manganous sulfate were then combined and with the exception of filtering the insolubles, the manganous sulfate solution was not purified. Technical potassium permanganate was purchased from the Carus Chemical Company of LaSalle, Illinois. All dilution and washing was done with tap water. Spectrographic analysis

of the potassium permanganate crystals and the solid obtained by evaporating the manganous sulfate solution to dryness are illustrated in Tables XXIV and XXV in the Appendix.

Because the project had limited funds, very few analyses, such as X-ray diffraction, electron diffraction, and spectrographic analysis, were performed on the manganese dioxide produced. Therefore, most of the decisions and planning were based on the performance of manganese dioxide in the dry cell battery.

EXPERIMENTAL EQUIPMENT

Standard bench-scale glassware was used. Four-liter beakers and 30-liter battery jars were used as reaction and washing vessels. Fultork labmotors with glass stirrers provided the necessary agitation. For pumping the permanganate solution, two Research Appliance Company bellows pumps were utilized, while the permanganate feed columns were pyrex glass, 48-in. in length and 48mm. in diameter. Heating of the solutions was provided by electric hot plates, controlled by Varitron variacs. Filtering was achieved with a 10-in. diameter suction filter with water aspirators providing the suction. The hydrogen ion concentration was measured with a Beckman pocket pH meter. The samples were dried in a Freas electric oven and ball-milled in 3.5-gal. ball mills, which contained approximately five pounds of cylindrical-shaped balls. A U. S. standard sieve No. 100 and a Ro-tap sieve shaker separated the -100 mesh manganese dioxide, which was used in the batteries.

Batteries were made and evaluated on specialized dry cell battery fabrication and testing equipment.

EXPERIMENTAL PROCEDURE

Figure 1 indicates the set-up for the production of manganese dioxide by the oxidation of manganous sulfate with potassium permanganate. The manganous sulfate solution was first diluted with tap water to the desired concentration in 4-liter beakers or 30-liter battery jars. Upon dilution, the pH of the solution would increase from 1.8 to approximately 3.0; this pH depended upon the amount of dilution. The pH of the solution was re-adjusted with concentrated sulfuric acid to 1.8 ± 0.1 . The manganous sulfate solution was then heated on a hot plate to the desired temperature, which was kept constant by a variac. After dissolving the potassium permanganate in tap water, the solution was put into the feed column(s). When the sulfate solution reached the desired temperature, the pump(s) was turned on. By pumping carbon tetrachloride into the feed column, the permanganate solution was displaced into the manganous sulfate through Saran tubing at the desired rate. The carbon tetrachloride displacement technique was used because the potassium permanganate would have corroded the pumps. Over the total reaction time, the slurry was continually stirred with a glass stirrer connected to a Fultork laboratory motor.

Following the complete addition of the permanganate, the slurry was digested for one hour with constant agitation. Then the manganese dioxide was filtered, placed in a 30-liter battery jar and washed with tap water to a pH of 6 to 7. After washing, the manganese dioxide was again

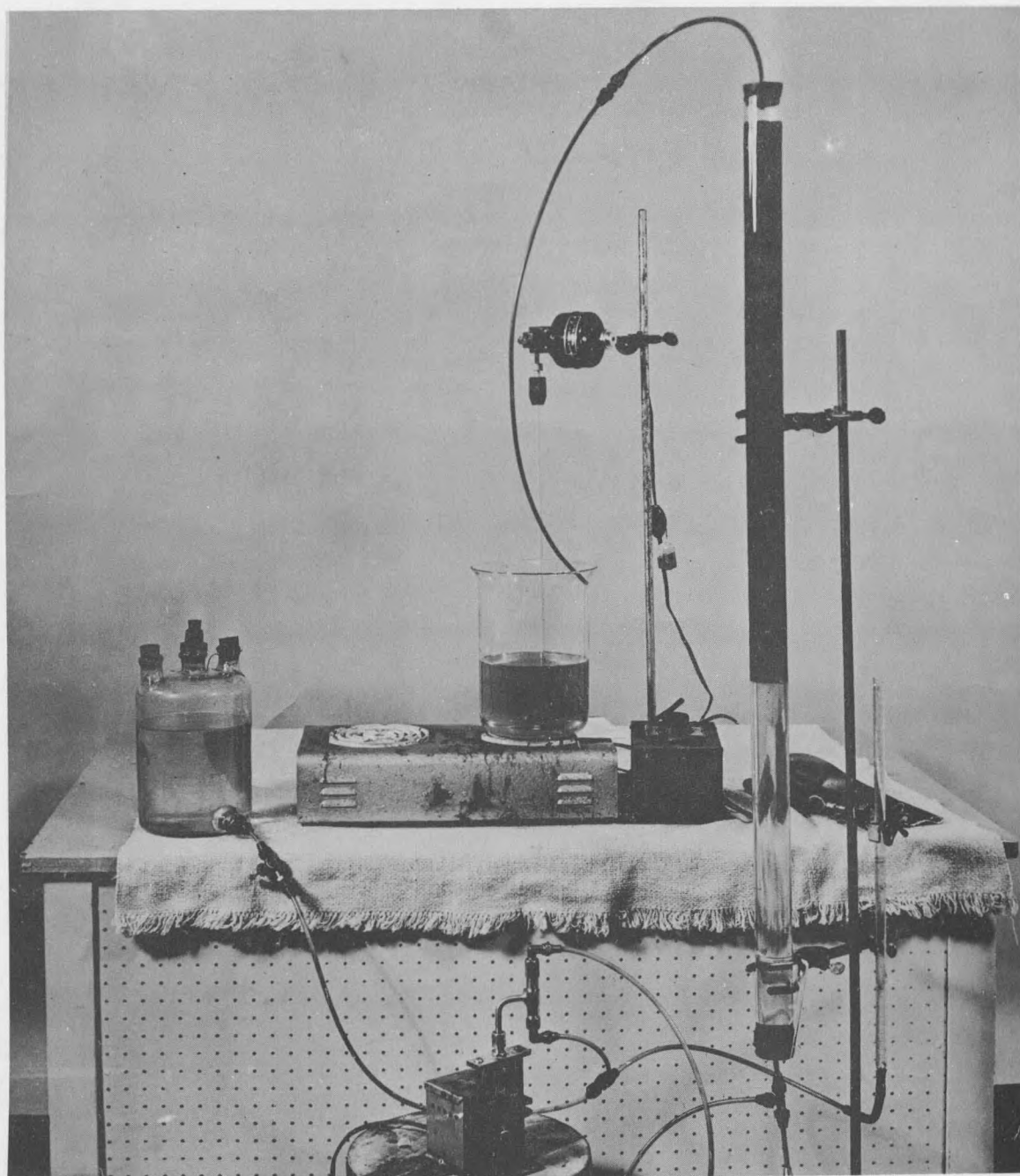


Figure 1. Reactor for Producing MnO_2 by Guyard Reaction.

filtered, dried at 110°C for 24 hours and ball-milled for two hours. The -100 mesh dioxide was separated and made into dry cell batteries, which were fabricated and evaluated according to Signal Corps specifications SCL-3117-D (Table XXXIV in Appendix).

Usually six batteries, size "A", were made for the test rack, which had the following capacity tests:

	<u>Low Drain</u>	<u>High Drain</u>
Type of Discharge	Continuous	Continuous
Discharge Resistance	166-2/3 ohms	16-2/3 ohms
Test End Voltage	1.13 volts	1.0 volts
Discharge Temperature	70°F	70°F

After five days of aging, two batteries were tested on high drain and two on low drain. The remaining two were used for the three months delayed capacity test.

When acid leaching a manganese dioxide sample, the sulfuric acid solution was adjusted to the desired concentration and heated to temperature. The manganese dioxide sample, filtered from the reaction liquor, was put into the sulfuric acid solution and stirred with a glass stirrer connected to a Fultork labmotor. Subsequently, the sample was filtered, washed, dried, ball-milled, and fabricated into dry cell batteries.

EXPERIMENTAL APPROACH

Potassium Permanganate Oxidation

Because the object was to optimize high and low drain characteristics, the method of steepest ascent as outlined in Design and Analysis of Industrial Experiments (5) and Experimental Designs (4) was used.

Generally, when all the experiments as outlined by a particular design were completed, an equation which represents the relation between the variables was calculated by statistical methods. An F-test was performed to determine how "good" the equation was. From the equation it was possible to estimate which path to take to reach optimum conditions.

When four variables are studied, a full factorial design gives estimates of interactions which usually have little or no effect. It is possible to reduce the number of experiments required by including the interactions with other major effects (7). By using this technique, a full 2^5 factorial which has 32 treatments can be reduced to 16 treatments. The actual design, from Experimental Designs, had 16 treatments and 6 center points to estimate the experimental error.

The five factors or variables investigated were temperature, concentration of manganous sulfate, concentration of potassium permanganate, rate of addition of potassium permanganate, and digestion time after every 30-minute addition of permanganate.

Sample calculations for the statistical analysis used are in the Appendix.

Acid Leaching

In performing the experiments on acid leaching, one factor was varied while the others were kept constant. The variables studied were temperature, contact time, ratio of concentrated acid to manganese dioxide, and acid concentration. The major part of the study was performed on one sample of manganese dioxide, and the acid leaching was done with C.P.

sulfuric acid. One experiment was performed to compare C.P. with technical sulfuric acid.

A statistical design could have been applied to this study which would have estimated interactions as well as major effects, but the author was unfamiliar with such techniques when the experiments were performed.

EXPERIMENTAL RESULTS

POTASSIUM PERMANGANATE OXIDATION OF MANGANOUS SULFATE

Exploratory Runs:

Before an experimental design was used, exploratory runs 640 and 644, which aided in designing the statistical approach as well as determine feasibility of reaction to produce battery-active manganese dioxide from commercial ore, were first attempted. For the exploratory treatments, fifty pounds of Anaconda Company rhodocrosite float, designated as AR-1, was leached with thirty-two pounds of technical grade sulfuric acid in 130 pounds of water. From the spectrographic analysis of the solids obtained for the manganous sulfate solution, the percentage of the elements in the solution was calculated. This analysis is in Table XXIII in the Appendix. Chemical grade potassium permanganate was also used.

Table I gives the results of the exploratory runs. These treatments indicated that battery-active manganese dioxide could be produced from unpurified manganous sulfate obtained from rhodocrosite ore. Actually, the results obtained were very good.

The manganous sulfate solutions of runs 640 and 644 had initial pH's of approximately 2.0, while runs 642 and 643 initial pH's were 3.5. Upon

TABLE I. EXPLORATORY RUNS FOR OXIDATION OF MANGANOUS SULFATE WITH POTASSIUM PERMANGANATE.

<u>Sample</u>	<u>Temp.</u>	<u>MnSO₄ Conc.</u>	<u>KMnO₄ Conc.</u>	<u>Contact Time</u>	<u>High Drain</u>	<u>Low Drain</u>	<u>Delayed Capacity</u>
640	78°C	0.15 mole/l.	0.33 mole/l.	5 hrs.	6.3 hrs.	115 hrs.	100 hrs.
641	85	0.15	0.33		6.2	109	108
642	86	0.15	0.33	4.5	6.3	127	116
643	88	0.15	0.33	3.0	7.1	128	114
644	85	0.25	0.33	4.5	6.3	132	118
645	86	0.15	0.33	0.25	0.1	62	---
646	87	0.25	0.33	1.0	0.33	74	---

heating the sulfate solutions of runs 642 and 643, some ferrous and manganous hydroxide precipitated. In these particular runs the precipitated hydroxides did not interfere with or have an effect upon the drain capacities.

Treatments 642 and 643 were identical with the exception that the manganese dioxide from treatment 642 was acid leached with 3 liters of 100 gm. per liter sulfuric acid at 87°C. Although the low drains were practically the same, the high drain was reduced from 7.1 hours to 6.3 hours. Also, run 641 was an acid leached portion of run 640. The drain results of run 641, as indicated in Table I, are slightly less than the drains of run 640.

In addition to having an initial pH of 2, iron was removed from the sulfate solution of run 644. The manganese dioxide produced from run 644 met both high and low drain specifications, even though the manganous sulfate concentration was higher than that of runs 640 and 643.

Spectrographic analysis of runs 640, 643, and 644 are in Table XXVI of the Appendix. Surprisingly, the analysis shows that the manganese dioxide from these runs contains the same percentage of iron -- 0.5%. But samples 640 and 644, which had low initial pH's for the manganous sulfate solution, had 0.01% and 0.05% sodium, respectively, while sample 643 had 0.5% sodium. Likewise, the percentage copper for samples 640 and 644 were, respectively, 0.01% and 0.005%, and the percentage copper for sample 643 was 0.01%. Both samples, 640 and 644, contain no barium, but sample 643 contained 0.01% barium which could react with sulfate ion to

form barium sulfate that could be detrimental to the drain capacities. Outside of the three elements mentioned, the samples all contained the same amount of impurities.

If the purification step of the manganous sulfate could be by-passed, the capital cost of a commercial plant would be reduced and the process simplified. Even though treatments 642 and 643 gave good results, there is a greater probability for co-precipitation and increased adsorption of the precipitated ferrous and manganous hydroxide. Hence, it was felt that it would be safer to have a lower initial pH to prevent the precipitation of the ferrous and manganous hydroxide. Therefore, the initial pH of the manganous sulfate solution for all treatments of the experimental design used was approximately 2.0.

The manganese dioxide from runs 645 and 646 gave poor drain results. In run 645 all the permanganate was added at once and the dioxide formed was digested for ten minutes, while for run 646 the permanganate was added as in run 645 but was digested for one hour. The longer digestion had a slight positive effect on the high and low drain. Consequently, a one-hour digestion period was adopted for subsequent runs.

These exploratory runs served as a guide for determining the levels of the first set of treatments in the experimental design.

First Experiment:

The levels for the first experiment are given in Table II.

TABLE II. FACTOR LEVELS OF THE FIRST EXPERIMENT.

		Factor Level	
		-1	+1
x_1	Temperature - degrees C.	70	90
x_2	Concentration of $MnSO_4$ - gm. mole per l.	0.25	0.75
x_3	Concentration of $KMnO_4$ - gm. mole per l.	0.15	0.35
x_4	Addition time of $KMnO_4$ - hrs.	2.0	4.0
x_5	Digestion time - min. digestion per 30-min. addition	0.0	20.

The design used and the results obtained are arranged in Table III.

Nineteen of the 22 treatments gave poor high and low drain capacities.

Actually, of the 19 treatments, none had low drains which were equal to Gold Coast low-grade manganese dioxide, that has low drain capacities of approximately 80 hours. Only five treatment of these nineteen -- 651, 652, 656, 659, and 663, surpassed five hours high drain.

Of the 22 treatments, only three can be classified as "good". Treatments 651, 652, and 655 gave 7.2, 6.4, and 6.6 hours high drain, respectively, and the low drains were 103, 122, and 102, respectively. All are characterized by a relatively low addition time of two hours, and a $MnSO_4$ concentration of 0.25 gm. mole per liter. Treatments 651 and 655 had reaction temperatures of 70°C. The reaction conditions of these three treatments were, generally, similar to those of the exploratory runs.

Although treatments 651, 652, and 655 gave an inkling as to the path of optimizing the drain characteristics, the techniques of experimental designs were used to determine the next levels of the factors. From the results obtained, the linear equation for high drain calculated to be:

$$\hat{y} = 4.61 + 0.18x_1 + 0.74x_2 + 0.05x_3 + 0.25x_4 + 0.0x_5$$

TABLE III. EXPERIMENTAL DESIGN AND RESULTS - FIRST EXPERIMENT

Sample	Temp. x_1	MnSO ₄ Conc. x_2	KMnO ₄ Conc. x_3	Addition x_4	Digestion x_5	High Drain hrs.		Low Drain hrs.	
651	-1	-1	-1	-1	1	7.1	7.2	97	108
2	1	-1	-1	-1	-1	6.3	6.5	120	123
3	-1	1	-1	-1	-1	2.7	3.2	72	74
4	1	1	-1	-1	1	4.3	4.3	60	63
5	-1	-1	1	-1	-1	6.5	6.6	97	102
6	1	-1	1	-1	1	4.7	5.0	58	61
7	-1	1	1	-1	1	4.0	4.4	61	62
8	1	1	1	-1	-1	4.1	4.2	51	64
9	-1	-1	-1	1	-1	5.1	5.3	97	100
660	1	-1	-1	1	1	4.5	4.7	57	60
1	-1	1	-1	1	1	4.3	4.3	52	54
2	1	1	-1	1	-1	3.7	4.4	53	57
3	-1	-1	1	1	1	5.0	5.1	72	72
4	1	-1	1	1	-1	4.6	4.7	57	59
5	-1	1	1	1	-1	4.6	4.6	62	62
6	1	1	1	1	1	4.0	4.2	51	53
7	0	0	0	0	0	4.1	4.4	59	59
8	0	0	0	0	0	3.6	3.8	51	71
9	0	0	0	0	0	3.6	4.0	46	54
670	0	0	0	0	0	4.6	4.6	59	62
1	0	0	0	0	0	3.9	4.0	54	57
2	0	0	0	0	0	4.0	4.0	54	57

and for the low drain:

$$\hat{y} = 67.60 - 6.16x_1 - 0.74x_2 - 0.05x_3 - 0.25x_4 + 0.0x_5$$

where $\hat{y}$ is the drain in hours, and

$$x_1 = \frac{\text{temp.} - 80}{10}, \quad x_2 = \frac{\text{conc. MnSO}_4 - 0.50}{0.25}, \quad x_3 = \frac{\text{conc. KMnO}_4 - 0.25}{0.10},$$

$$x_4 = (\text{addition time} - 3), \text{ and } x_5 = \frac{\text{digestion time} - 10}{10}$$

The constants 4.61 and 67.6 were the average high and low drain, respectively, of all the batteries in the first experiment and the minus sign before the coefficients of the variable gave the indication that the levels of the variables had to be reduced.

An F-test was performed to determine the reliability of the linear equations. Tables IV and V illustrate the analysis of variance of the high and low drains.

TABLE IV. ANALYSIS OF VARIANCE OF HIGH DRAIN - FIRST EXPERIMENT

	d.f.	s.s.	m.s.
Linear Model	5	21	4.2
Lack of Fit	<u>38</u>	<u>20</u>	.53
Total	43	41	

$F_{5, 38} = \frac{4.2}{.53} = 7.92$

The value of F at 0.05 level with $v_1 = 5$ and $v_2 = 38$ is 4.46. Since $F = 7.42$ and $F_{.05} (5, 38) = 4.46$, the response surface for high drain was assumed to be linear.

TABLE V. ANALYSIS OF VARIANCE OF LOW DRAIN - FIRST EXPERIMENT.

	d.f.	s.s.	m.s.
Linear Model	5	10691	2138
Lack of Fit	<u>38</u>	<u>5708</u>	150
Total	43	16399	

$F(5,38) = 14.3$

With the test being highly significant, the low drain response surface was linear for the results obtained. For example, the low drain capacity for treatment 661 was 53 hours and when substituting the reaction conditions into the low drain equation, the calculated low drain became 53.6 hours. Because the high and low drain equations were linear within the range of the reaction conditions as outlined in Table II, the slopes, or coefficients, of the variables were used to outline the next set of levels for the factors. The calculations are illustrated in Tables XXVII and XXVIII in the Appendix.

Second Experiment:

From the calculations of the path of steepest ascent, the new levels of the factors for the second set of treatments are given in Table VI.

TABLE VI. FACTOR LEVELS OF THE SECOND EXPERIMENT.

<u>Factor</u>	<u>Factor Level</u>	
	<u>-1</u>	<u>+1</u>
x ₁ Temperature - degrees C.	65	85
x ₂ Concentration of MnSO ₄ - gm. mole per liter	0.10	0.20
x ₃ Concentration of KmnO ₄ - gm. mole per liter	0.07	0.13
x ₄ Addition time of KMnO ₄ - hrs.	1.0	2.0
x ₅ Digestion Time - Min. digestion per 30 min. addition	0.0	10.0

TABLE VII. . . EXPERIMENTAL DESIGN AND RESULTS - SECOND EXPERIMENT.

Sample	Temp. x_1	MnSO ₄ Conc. x_2	KMnO ₄ Conc. x_3	Addition x_4	Digestion x_5	High Drain hrs.		Low Drain hrs.	
681	-1	-1	-1	-1	1	6.7	6.8	126	142
2	1	-1	-1	-1	-1	7.8	7.9	127	129
3	-1	1	-1	-1	-1	7.1	7.3	132	134
4	1	1	-1	-1	1	7.0	7.3	133	133
5	-1	-1	1	-1	-1	6.2	6.7	121	126
6	1	-1	1	-1	1	7.2	7.5	121	129
7	-1	1	1	-1	1	6.2	6.5	126	128
8	1	1	1	-1	-1	7.4	8.1	124	125
9	-1	-1	-1	1	-1	7.0	7.1	123	125
690	1	-1	-1	1	1	6.9	6.9	127	128
1	-1	1	-1	1	1	7.3	7.4	122	126
2	1	1	-1	1	-1	7.0	7.8	130	133
3	-1	-1	1	1	1	6.3	6.7	125	128
4	1	-1	1	1	-1	7.2	7.2	135	136
5	-1	1	1	1	-1	5.6	6.3	120	127
6	1	1	1	1	1	5.8	6.3	111	124
7	0	0	0	0	0	7.0	7.1	114	130
8	0	0	0	0	0	7.4	7.7	127	129

Generally, the results (Table VII) obtained using the second set of levels had from good to excellent drain capacities. All of the sets with the exception of treatment 696 which had an average low drain of 118 hours, averaged over 120 hours low drain. One battery of treatment 696 gave the lowest low drain of 111 hours, and the highest low drain was from treatment 681 with 142 hours. Similarly, high drain capacities of all the treatments surpassed specification, which is 5.5 hours. The best high drain was from treatment 688 which gave 8.1 hours on one battery; the worst being 5.6 hours from treatment 695.

The linear equations representing the second experiment for high and low drain were, respectively,

$$\hat{y} = 7.0 + 0.25x_1 - 0.05x_2 - 0.25x_3 - 0.15x_4 - 0.15x_5$$

$$\hat{y} = 127.0 + 0.44x_1 - 0.63x_2 - 2.06x_3 - 1.13x_4 - 0.56x_5$$

where

$$x_1 = \frac{\text{Temp.} - 75}{10}, \quad x_2 = \frac{\text{Conc. of MnSO}_4 - 0.15}{0.05}, \quad x_3 = \frac{\text{Conc. KMnO}_4 - 0.10}{0.03}$$

$$x_4 = \frac{\text{Addition Time} - 1.5}{0.5}, \quad x_5 = \frac{\text{Digestion Time} - 5}{5}$$

The constant 7.0 represented the average high drain capacities of all the batteries of the second experiment and the constant 127 was the average low drain capacity for all the batteries. For the first experiment, the average high drain was 4.6 hours and the average low drain was 67.6 hours. Thus, the average high drain of the second set was 52% greater than the first set, and likewise, the average low drain of the second experiment was 87.5% better than the first experiment.

The F-test on the high drain results as shown in Table VIII gave a significant test at the 5% level and thus it was concluded that the response surface of the high drain tests was linear.

TABLE VIII. ANALYSIS OF VARIANCE OF HIGH DRAIN - SECOND EXPERIMENT.

	d.f.	s.s.	m.s.
Linear Model	5	5.69	1.14
Lack of Fit	<u>30</u>	<u>6.23</u>	0.21
Total	35	11.92	

$$F_{(5,30)} = 5.5$$

$$F_{(.05)(5,30)} = 4.5$$

The Analysis of Variance for low drain gave a highly insignificant F-test, indicating that the low drain linear response surface had changed, possibly to a curved response surface.

TABLE IX. ANALYSIS OF VARIANCE OF LOW DRAIN - SECOND EXPERIMENT.

	d.f.	s.s.	m.s.
Linear Model	5	205	41
Lack of Fit	<u>30</u>	<u>1001</u>	33.4
Total	35	1206	

$$F_{(5,30)} = 1.23$$

Because of the change from being linear to a curved surface for the low drain, two factor interactions were examined. Strictly from chemical considerations, it is doubtful if the digestion time had any effect upon the low drain capacities, especially on the results obtained from the second experiment. Consequently, the one-half replicate of a 2^5 fac-

torial is transformed to a full 2^4 factorial. As a result, the major effects and two factor interactions have no aliases; i.e., in fractional factorial designs a required effect also estimates one or more effects, but in full factorial designs, all major factors and interactions are measured independently. Using capital letters instead of x_1 's, the major effects are represented as follows:

- A = Temperature
- B = Concentration of MnSO_4
- C = Concentration of KMnO_4
- D = Addition Time

The levels of the factors were as shown in Table VI. There was no appreciable interaction between temperature and MnSO_4 concentration (Table X), but there was interaction between temperature and KMnO_4 concentration, with the best combination being a KMnO_4 concentration of 0.07 gm. mole per liter, and the temperature varying between 65 and 85°C. Interaction AD (temperature and addition time) in Table XII appears to indicate that an addition time of one hour of 0.07 gm. mole per liter KMnO_4 should be used with the temperature between 65 and 85°C to give good low drain capacities. These conditions are depicted by treatments 681, 682, 683, and 684, which gave average low drains of 134, 128, 133, and 133 hours, respectively.

The interaction between MnSO_4 concentration and KMnO_4 concentration is shown in Table XIV, which indicates that at a KMnO_4 concentration of 0.07 gm. mole per liter, the MnSO_4 concentration can vary from 0.10 to 0.20 gm. mole per liter to yield near-specification low drain tests, but at KMnO_4 concentration of 0.13 gm. mole per liter, the MnSO_4 concentration

TABLE X . INTERACTION AB

		B	
		-	+
A	-	127	127
	+	129	127

TABLE XI. INTERACTION AC

		C	
		-	+
A	-	129	125
	+	130	126

TABLE XII. INTERACTION AD

	D	
	-	+
A		
-	129	125
+	128	128

TABLE XIII INTERACTION BC

	C	
	-	+
B		
-	128	128
+	130	123

TABLE XIV. INTERACTION BD

	D	
	-	+
B	128	128
	129	124

TABLE XV. INTERACTION CD

	D	
	-	+
C	132	127
	125	126

should be at the lower concentration of 0.10 gm. mole per liter. When both the KMnO_4 and MnSO_4 were at their higher concentrations, relatively poorer drains were obtained as exemplified by runs 687, 695, and 696.

With an addition time of one hour, the concentration of MnSO_4 can be from 0.10 to 0.20 gm. mole per liter, but at an addition time of two hours of KMnO_4 solution, the concentration of MnSO_4 should be 0.10 gm. mole per liter to produce good battery-active manganese dioxide.

Table XV for the concentration of KMnO_4 and addition time interaction discloses that the best results could be obtained with a one-hour addition time with the KMnO_4 concentration varying from 0.07 to 0.13 gm. mole per liter.

Of the remaining four variables, temperature, concentration of manganous sulfate, and concentration of potassium permanganate appeared to be the most important with the addition time being somewhat dependent upon the concentration of reagents. Runs 700 and 701 were made in which the reaction conditions were identical to runs 684 and 644 with the exceptions that the permanganate solutions were heated to 82°C and then they were added instantaneously to the manganous sulfate.

As demonstrated in Table XVI, the treatments 700 and 701 did not measure up to treatments 684 and 694. Sample 700 is about the same quality as Gold Coast manganese ore.

TABLE XVI. EFFECT OF INSTANTANEOUS ADDITION OF KMnO_4 .

Treatment	Temp.	Conc. MnSO_4	Conc. KMnO_4	Addition Time	High Drain	Low Drain
684	85	0.20	0.07	1 hr.	7.2	133
700	85	0.20	0.07	0	4.3	84
694	85	0.10	0.13	2	7.2	136
701	85	0.10	0.13	0	4.5	103

Samples 643 and 644, which had very similar drain tests to those in the second experiment, were blended with Philipsburg, Montana battery-ore to upgrade the drain capacities to that of Gold Coast ore. The blends of samples 643 and 644 were designated as B-643 and B-644. As illustrated in Table XVII, 20% of either sample 643 or 644 was sufficient to upgrade Philipsburg manganese dioxide to the quality of Gold Coast ore.

TABLE XVII. BLENDS OF PHILIPSBURG MnO_2 AND MANGANESE DIOXIDE PREPARED BY GUYARD REACTION.

Sample	% Philipsburg	High Drain	Low Drain
Gold Coast	0	4.2	82
Philipsburg	100	3.7	80
B-643	80	4.1	90
B-644	80	4.0	85

Delayed Capacity:

Although the low drain capacities of the first experiment batteries were predominantly poor, the shelf life of the batteries generally was good. As illustrated in Table XVIII, ten of the 22 sets had excellent delayed drain capacities (above 85% initial), while nine gave from poor

TABLE XVIII. THREE MONTHS DELAYED CAPACITY RESULTS. -- FIRST EXPERIMENT

<u>Treatment</u>	<u>Average Low Drain</u>	<u>Average 3 Months Delayed Capacity</u>	<u>% of Initial Low Drain</u>
651	102 hrs.	110 hrs.	106
-4	62	63	102
-6	60	61	102
-7	62	66	107
-9	99	96	98
661	53	49	93
-2	55	57	104
-7	59	52	88
-9	50	47	94
672	56	49	88
652	122	100	82
-3	73	55	75
-8	58	43	74
660	58	43	75
-3	72	57	79
-4	58	45	78
-5	62	45	73
-6	52	42	81
671	56	46	83
668	61	41	67
670	61	34	56
655	99	---	---

to good results. Only two samples, 668 and 670, gave poor results.

The reasons for the failure or deterioration of dry cells during storage are the loss of moisture in the cell and slow chemical reactions which take place in the battery (9). The batteries tested were stored in polyethylene bags which no doubt hindered the evaporation of water from the batteries. As a result, samples 651, 654, 656, 657, and 662 had delayed capacities greater than their respective initial low drain capacities.

Of approximately 150 batteries fabricated in the first experiment, 13 were discarded because of corrosion. Three of the eight batteries made from sample 670 were badly corroded, and the one tested for shelf life was slightly corroded. Apparently, this set of batteries contained some impurities which accelerated the corrosion of the cells.

Unlike the initial drain capacities, the delayed capacities showed no correlation with the reaction conditions. Storage conditions are usually the most influencing factor on shelf life. All in all, the delayed capacities of the batteries tested were of good quality.

Interpretation of Results:

To explain the effect of variable levels between the first experiment which had an average high drain of 4.6 and an average low drain of 68 hours, and the second experiment, which had an average high and low drain of 7.0 and 127 hours, respectively, X-ray diffraction patterns and spectrographic analysis of two representative samples from each set of treatments were taken. Also, X-ray patterns were taken for three of the

exploratory runs.

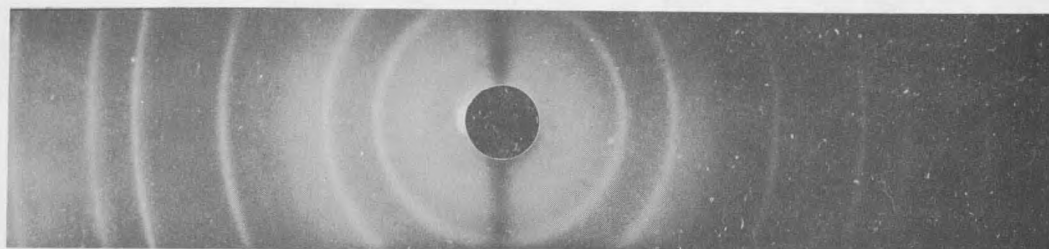
Figure 2 illustrates the diffraction patterns of samples 660 and 694 from the first and second set of treatments, respectively. Sample 660 gave a very good pattern of alpha manganese dioxide, while sample 694 gave a gamma-form of manganese dioxide. In performing the X-ray diffraction patterns for the exploratory runs, the Signal Corps interpreted the crystal phase of samples 640, 643, and 644 to be 50% alpha and 50% rho. Whether sample 694 contained some alpha was only of secondary importance. The X-ray patterns as shown illustrate a definite phase change from Experiment One to Experiment Two.

The pattern of #694 was not as good as #660 because the crystal development was not as perfect. The effect of the reaction conditions on crystal development can best be explained by the influence of orientation and aggregation velocity.

The effect of digesting a precipitate is to enhance its particle size. In the formation of the precipitate, the aggregations first formed are more amorphous. Upon digestion, the crystals grow and the molecules tend to approach equilibrium by loss of energy with the crystal lattice being more ordered. The speed of this process is called the orientation velocity (11).

The crystal structure is also dependent on the aggregation velocity, which is a function of the supersaturation (11). With greater supersaturation, the separate aggregates will be less regular. The aggregation velocity will have more effect on the precipitated particles than the

-36-



Sample #660

Alpha Manganese dioxide



Sample #694

Gamma Manganese dioxide

Figure 2. X-Ray Diffraction Patterns.

orientation velocity when the supersaturation is very large and because of large supersaturation the particles will become amorphous and will not give X-ray patterns. Gradually the unstable precipitate transforms into a more stable crystalline state.

Assuming that #652, which had drain characteristics similar to the treatments of the second experiment, possessed the same crystal structure as #694, the effect of reaction time is exemplified within the first experiment. Sample 652 had a high and low drain of 6.4 and 122 hours, respectively, while 660 gave a high drain of 4.6 hours and a low drain of 58 hours. The reaction conditions of these treatments were identical with the exception that #652 had a total reaction time of three hours, while #660 had a total reaction time of 7.3 hours. Sample 694, which gave 7.2 hours high drain and 136 hours low drain, had the same reaction time as #652, but the reagent concentrations of #694 were more dilute. The discrepancy between the drain characteristics of #694 and #652 was less than between #694 and #660. Thus, the increased drain characteristics of the second experiment batteries resulted primarily from an increased addition rate and a decreased reaction time, both of which accounted for less crystalline development of the manganese dioxide.

Table XIX shows the spectrographic analysis of samples 660 and 694. Both are identical as to the amount of impurities with the exception that #660 had 0.05% sodium and intermediate amounts of potassium, while #694 contained no sodium and 0.1% potassium. Schilling (17) found qualitatively that sodium gave a detrimental effect on drain characteristics and, like-

TABLE XIX. SPECTROGRAPHIC ANALYSIS OF SAMPLES 660 AND 694.

Sample	660	694
<u>Element</u>		
Manganese	Major Constituent	Major Constituent
Potassium	Intermediate Constituent	-----
	<u>Minor Constituents</u>	
Aluminum	1 %	1 %
Calcium	1	1
Iron	1	1
Silicon	0.5	0.5
Potassium	-----	0.1
Magnesium	0.05	0.05
Sodium	0.05	-----
Barium	0.01	0.01
Copper	0.01	0.01
Strontium	0.01	0.01
Titanium	0.005	0.005
Vanadium	0.001	0.001
Chromium	Trace	Trace
Lead	None found	None found
Nickel	None found	None found
Tungsten	None found	None found
Zinc	None found	None found
Rare Earths	None found	None found

wise, the potassium no doubt has a similar negative effect on the drain results. The spectrographic analyses for these particular samples were used only to determine the relative differences between #660 and #694, because a material balance using the spectrographic analysis of the reagents and manganese dioxide indicated that more iron was precipitated with the dioxide than was originally present in the reaction solutions. The addition of iron during the course of processing was doubtful because glassware, plastic tubing, and ceramics were used throughout. Likewise, the material balance showed that more aluminum and calcium exited than entered. Since the ceramic balls used in the ball mill contain corundum, the addition of aluminum was plausible. The increased amount of calcium could have come from the tap water used to wash the precipitated manganese dioxide.

A material balance on sample 644 indicated that of 2.24 gms. of iron that entered the reaction mixture, only 0.78 gms. was precipitated with the manganese dioxide. Similarly, all of the aluminum, zinc, copper, lead, titanium, and boron present in the reaction solution did not precipitate with the dioxide. From a chemical standpoint, this is possible for the initial pH of the reaction solution was approximately 2.0 and the final pH was 0.9.

In comparing the percentage of manganese dioxide in the samples from the two blocks of treatments, no significant difference was found. In addition, the percentage yields were all about the same, which was 100% or better because of manganese dioxide forming a hydrate ($\text{MnO}_2 \cdot \text{XH}_2\text{O}$).

A trend developed for the apparent densities (gms. per cu. in.) of the samples. Generally, for the representative samples in the first experiment, the densities ranged from 11.6 to 13.1, while for the second experiment the apparent densities were usually in the range of 13.0 to 14.8.

CONCLUSIONS

1. When reacting manganous sulfate, prepared by dissolution of concentrated Anaconda Company rhodocrosite in technical-grade sulfuric acid, with commercial-grade potassium permanganate, battery-grade manganese dioxide meeting Signal Corps specifications can be produced using the following conditions:

- A. by having the reaction temperature between 65°C and 85°C.
- B. by having the manganous sulfate solution at an initial pH of 2.0.
- C. by adding the potassium permanganate to the manganous sulfate solution, agitated sufficiently to keep the slurry dispersed, at a rate of 0.66 moles of potassium permanganate per mole of manganous sulfate per hour if the permanganate concentration is 0.07 gm. moles per liter with the manganous sulfate varying from 0.10 to 0.20 gm. moles per liter,

or by adding the potassium permanganate at a rate of 0.33 moles of potassium permanganate per mole of manganous sulfate per hour if the potassium permanganate concentration is 0.13 gm. moles per liter and the manganous sulfate concentration of 0.10 gm. moles per liter.

- D. by digesting the reaction slurry one hour after the complete addition of potassium permanganate.
- E. by filtering the manganese dioxide from the reaction solution and then washing the manganese dioxide to a pH of approximately 7.0 using tap water.
- F. by drying the product to approximately 3% moisture at a temperature of 110°C.

G. by ball-milling the manganese dioxide to a mesh which will give the maximum drain characteristics.

2. The reaction conditions of the oxidation of manganous sulfate by potassium permanganate influence the crystal structure of the manganese dioxide produced. The longer reaction time produces the more stable alpha phase manganese dioxide while a relatively shorter reaction time gives an alpha-rho or gamma-form manganese dioxide.

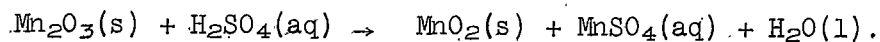
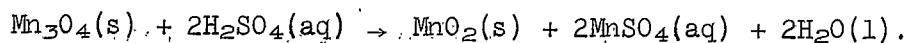
3. A mixture of 20% manganese dioxide, meeting Signal Corps specifications, prepared from the potassium permanganate oxidation of manganous sulfate and 80% battery-grade Philipsburg, Montana manganese dioxide possesses better drain characteristics than imported Gold Coast manganese dioxide.

ACID LEACHING

Previously, some of the chemically-prepared manganese dioxide had been acid leached with hydrochloric or sulfuric acid to improve the battery activity (2). For example, a 100-gm. sample MCl-18, prepared from manganese sulfate, chlorine, and caustic, gave zero hours high drain and six hours low drain. After being leached with 12.45 gms. of sulfuric acid diluted in 120 ml. of tap water, the sample's high and low drains were 4.4 hours and 135 hours, respectively. Another sample, MCl-1, with a similar preparation to MCl-18, leached with 29 cc. of hydrochloric acid dissolved in one liter of tap water, gave a high drain of 4.5 hours and a low drain of 153 hours, while the unleached portion gave 1.8 hours high drain and 88 hours low drain. Sample A 0-4 prepared from the air oxidation of manganese carbonate gave 7.1 hours high drain and 124 hours low drain after

being acid leached with sulfuric acid, but the unleached portion gave 5.3 hours high drain and 106 hours low drain (17).

The improvement of battery-activity was brought about by dissolving unreacted reagents such as manganous hydroxide in the chlorination reaction, or as in the case of air oxidation, the dissolving of manganous carbonate. Also, the lower oxides of manganese such as bixbyite (Mn_2O_3) and hausmanite (Mn_3O_4) were dissolved. The reactions of these oxides with sulfuric acid are:



The leaching of these oxides and unreacted reagents was exemplified by the increase in percentage of manganese dioxide. Sample MC1-1 percentage manganese dioxide changed from 78.0 to 95.5, while for sample MC1-18, the percentage increased from 83.0 to 90.4% manganese dioxide.

It was also postulated that most of the iron impurities were likewise leached from the dioxide, but a spectrographic analysis of a leached and unleached sample disprove this postulate. Table XX shows the spectrographic analysis of unleached sample 450 and leached sample 451 which were made from unpurified $MnSO_4$ solution prepared from Anaconda rhodocrosite. Both samples contain 1% iron. Possibly, the dissolution of the iron was made difficult by internal adsorption of the iron particles or occlusion of the mother liquor.

Temperature Effect:

Of the variables studied in acid leaching, temperature had the great-

TABLE XX. SPECTROGRAPHIC ANALYSIS OF LEACHED AND UNLEACHED SAMPLES.

Element	Sample No.	
	450	451
	<u>Approximate Quantity</u>	
Iron	1 %	1 %
Aluminum	0.5	0.5
Calcium	0.1	0.1
Silicon	0.1	0.1
Magnesium	0.05	0.05
Copper	0.005	0.005
Lead	0.001	0.005
Boron	0.001	0.001
Titanium	0.001	0.001
Barium	None found	None found
Chromium	None found	None found
Nickel	None found	None found
Tungsten	None found	None found
Rare Earths	None found	None found
Manganese	Major Constituent	

est effect upon the high drain characteristics. As shown in Figure 3, high drain increased with temperature with other variables being constant. For example, sample 403, leached at 32°C gave 5.6 hours high drain, while sample 401 yielded 6.7 hours high drain when leached at 92°C. Sample 408, with 7.0 hours high drain after leaching at 90°C, produced 5.8 hours when slurried with sulfuric acid at 35°C. These examples as well as other observations indicated rather conclusively that for given acid leaching conditions, a high temperature acid leach improved high drain characteristics of the manganese dioxide.

The effect of temperature on low drain was not as clear-cut as for high drain. Sample 403, which had a high drain 16.4% better than sample 401, had a low drain of 106 hours, while sample 401 had a low drain of 111 hours.

As indicated in Table XXI, no definite trend as for high drain can be established for low drain even though the acid concentrations and ratios are greatly different. As far as low drain improvement is concerned, the drain time was poor with no leaching. Although leaching improved the drain characteristics, the temperature of the acid solution did not improve the low drain as it usually did the high drain. Table XXI also indicates that a temperature of approximately 55°C was sufficient to have good low drain characteristics. For samples 441 through 444 the low drains are fairly equal, regardless of temperature or acid conditions, but there is a discrepancy between the two duplicate sets. This, again, exemplifies that low drain is not as sensitive to acid leaching conditions as high drain.

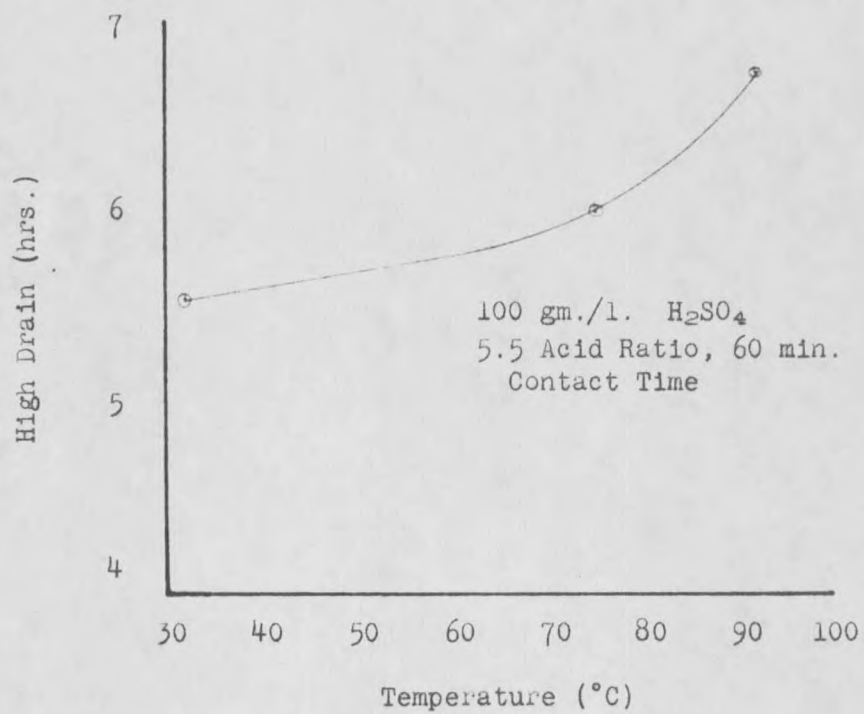


Figure 3. High Drain vs. Temperature

TABLE XXI. ACID LEACHING CONDITIONS AND RESULTS.

<u>Sample</u>	<u>Acid Conc.</u>	<u>Acid Ratio</u>	<u>Temp.</u>	<u>Contact Time</u>	<u>High Drain</u>	<u>Low Drain</u>
401	100 gm/l	5.7	92°C	60 min.	6.7	111
403	100	5.7	32	60	5.6	106
407	5	0.14	83	5	5.8	116
415	5	0.14	58	5	5.7	124
441	50	0.4	90	60	7.7	132
442	50	0.4	90	60	7.4	132
443	8.4	0.3	55	10	5.6	125
444	8.4	0.3	55	10	6.0	146

Acid Ratio Effect:

As previously explained, acid ratio refers to the grams of concentrated sulfuric acid per gram of manganese dioxide. While the data reveals trends of acid ratio and concentration of acid on delayed capacity, the amount of acid and the concentration desired can vary from sample to sample. Naturally, if a sample is known to have a great amount of unreacted reagents, such as manganous carbonate or manganous hydroxide, a greater amount of acid and higher concentration will be used than for a sample that has a relatively smaller amount of impurities.

The effect of acid ratio and concentration upon three months delayed capacity showed a definite trend. Specifications require that the battery-active manganese dioxide must retain 85% of its initial low drain discharge after one year. For practical purposes, three months delayed capacity tests were made instead of one year.

Table XXII shows the effect of acid ratio and concentration on shelf life. Although the data is somewhat erratic, it indicates that the 50 gm. per liter leaches at an approximate acid ratio of 1.5 gave excellent

TABLE XXII. ACID LEACHING CONDITIONS AND SHELF LIFE.

Sample	Acid Conc. gm/liter	Acid Ratio	Temp. °C.	Contact Time Min.	Low Drain Hrs.	3 Months Drain Hrs.	% of Initial Low Drain
401	100	5.7	92	60	111	75	68
403	100	5.4	32	60	106	69	65
404	100	5.7	75	60	90	75	84
412	100	3.7	87	20	112	70	63
414	100	2.5	80	5	125	106	85
408	50	1.6	85	60	116	109	94
409	50	1.6	87	20	118	117	99
410	50	1.5	87	5	120	118	98
413	50	1.3	77	1.5	110	105	96
402	5	0.14	80	1.5	108	93	86
405	5	0.14	90	60	113	69	61
406	5	0.14	89	20	117	63	54
407	5	0.14	83	5	116	108	93
415	5	0.13	58	5	124	89	72
416	5	0.10	63	60	111	73	66
411	---	---	---	---	112	95	85
441	50	0.4	90	60	132	88	67
442	50	0.4	90	60	132	90	67
443	5	0.3	55	10	125	84	67
444	5	0.3	55	11	146	84	58

shelf life, but the 100 and 5 gm. per liter acid leaches gave mostly poor delayed capacity results. The average percentage of initial low drain for the 100 and 5 gm. per liter leaches were 73 and 72, respectively, while sample 411, which was not acid leached, yielded a delayed capacity of 85% of its initial low drain. The average for the 50 gm. per liter is 96.7%.

The effect of low acid ratio was again exemplified by samples 441 to 444. The initial low drain results were excellent, but the shelf life of the samples was poor. Duplicate samples 441 and 442 seem to indicate that shelf life was more dependent on acid ratio than acid concentration.

It can only be postulated why the delayed capacities were markedly different because so many things influence shelf life. For the low acid ratio, one is inclined to say that all the impurities were not dissolved by the acid. For the high acid ratio, the only plausible explanation was that all the sulfate ions were not removed when the samples were washed and, consequently, calcium ions reacted with the sulfate ions to form calcium sulfate, which would form on the surface of the manganese dioxide. Secondly, the more severe acid leaching conditions could have produced a crystal structure change, but X-ray results received from the Signal Corps showed that there was no phase change (Table XXXIII in Appendix).

Actually, shelf life is greatly influenced by storage conditions. Specifications state that the batteries should be stored at 70°F with a relative humidity of 50%. While the storage temperature ranged from 64 to 77°F, the relative humidity during the winter months would approach zero. Consequently, the amount of wetting solution per sample and seal-

ing of the battery with wax influences shelf life.

Generally, the data indicated that for a given sample of manganese dioxide produced in a certain way, there are certain acid leaching conditions which have an influence on shelf life, assuming that all other variables are held constant.

Contact Time Effect:

Figures 4 and 5 point out the effect of contact time on drain characteristics. There was a definite increase in high drain for the 50 gm. per liter leach with the maximum being attained near the 20 min. contact time, but the 5 gm. per liter leach showed no trend. With the high drain being more sensitive to leach conditions, the 5 gms. per liter and 0.14 acid ratio were probably not severe enough to effectively remove the impurities. The low drain for both the 5 and 50 gm. per liter leaches reach a maximum at approximately 45 min. contact time with the drain capacities leveling off from there. Because a longer contact time did not hinder low drain, a 30 min. contact time was required to markedly increase both the high and low drains.

Economics:

Economically, technical grade sulfuric acid is the only acid that could be used. While most of the samples leached were with a C.P. acid, samples 431 and 432 demonstrate that technical sulfuric acid can be used in place of C.P. sulfuric acid. Sample 431's high and low drains were 7.8 and 134 hours, respectively, while sample 432, which was leached with

Legend: $\odot$ 50 gm. per l. H_2SO_4

1.6 acid ratio, $87^\circ C$ Temp.

Δ 5 gm. per l. H_2SO_4

0.14 acid ratio, $85^\circ C$ Temp.

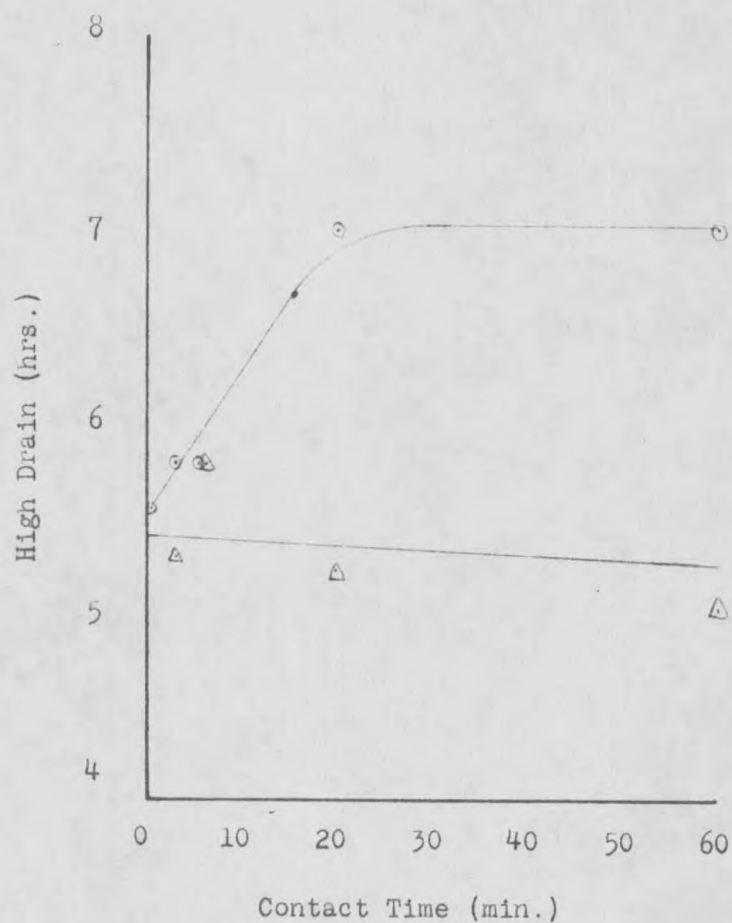


Figure 4. High Drain vs. Contact Time

Legend: $\odot$ 50 gm. per l. H_2SO_4
1.6 acid ratio, 87°C Temp.
 $\triangle$ 5 gm. per l. H_2SO_4
0.14 acid ratio, 85°C Temp.

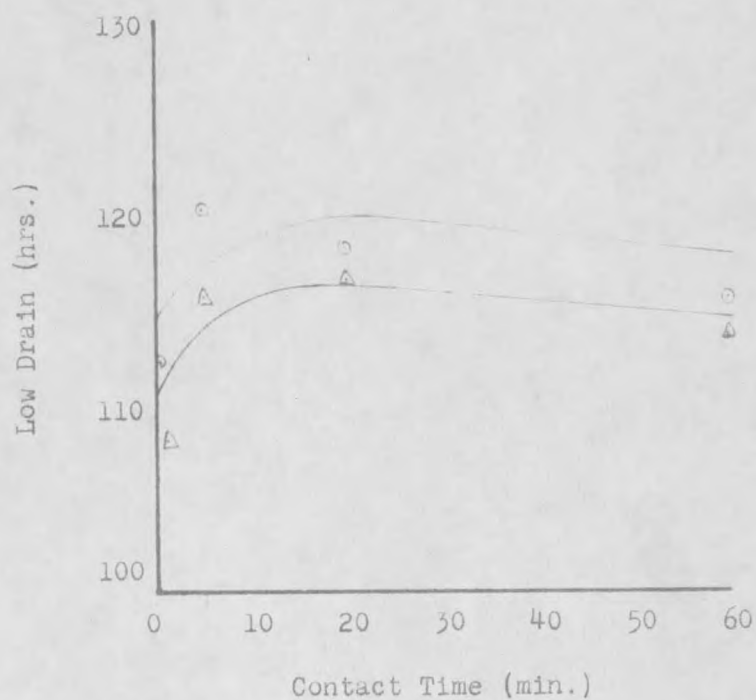


Figure 5. Low Drain vs. Contact Time

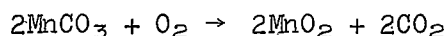
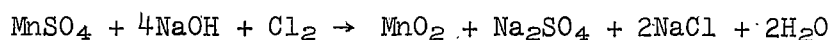
technical grade acid, had high and low drains of 7.5 and 129 hours, respectively. Both the drain characteristics of these samples were equal for all practical purposes.

Although hydrochloric acid is just as efficient as sulfuric acid, it is much more expensive and manganese dioxide is very soluble in concentrated hydrochloric acid. On a commercial scale more control of leaching conditions would be necessary when using hydrochloric acid.

If experimental design techniques were used on the acid leaching study, the effect of interactions as well as experimental error could have been estimated. In addition, an equation representing the given system under study would correlate the relationship among the variables and interactions.

SUMMARY

1. Acid leaching improved battery activity of samples made by the following reactions:



2. High drain was more sensitive to acid leaching conditions. To obtain maximum high drain, the temperature of the leach solution should be approximately 90°C.
3. A temperature of 55°C was sufficient to improve low drain, but the temperature required for high drain did not hinder the low drain.
4. A contact time of at least 30 minutes was needed to enhance both the high and low drain characteristics.

5. For a sample of manganese dioxide prepared in a given manner, there are certain acid leaching conditions which help or hinder the delayed capacity of the dioxide, assuming all other variables are constant.
6. Technical grade sulfuric acid was as efficient as chemical grade sulfuric acid for leaching battery-active manganese dioxide.

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APPENDIX

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TABLE XXIII. ANALYSIS OF MANGANOUS SULFATE USED FOR EXPLORATORY RUNS.

<u>Element</u>	<u>% in Solids*</u>	<u>% in Solution</u>	<u>Parts/Million</u>
Fe	1	0.274	2740
Al	0.5	0.138	1380
Si	0.1	0.0274	274
Zn	0.1	0.0274	274
Ca	0.05	0.0138	138
Cu	0.01	0.00274	27.4
Pb	0.01	0.00274	27.4
Ti	0.01	0.00274	27.4
Boron	0.005	0.00138	13.8
Cr	0.001	0.0000274	0.274

* 173.6 gms. of solids in 631.8 gms. of $MnSO_4$ solution.

TABLE XXIV

ANALYSIS OF MANGANOUS SULFATE SOLUTION USED FOR STATISTICAL DESIGN.

<u>Element</u>	<u>% in Solids*</u>	<u>% in Solution</u>	<u>Parts/Million</u>
Mg	1	0.27	2700
Al	0.5	0.135	1350
Fe	0.5	0.135	1350
Si	0.5	-----	-----
Ca	0.05	0.0135	135
Zn	0.05	0.035	135
Na	0.01	0.0027	27
Cu	0.005	0.00135	13.5

* 172.3 solids in 637 gms. MnSO_4 solution.

TABLE XXV. SPECTROGRAPHIC ANALYSIS OF POTASSIUM PERMANGANATE.

<u>Element</u>	
Manganese, Potassium	Major Constituents
	<u>Minor Constituents</u>
Silicon	0.5 %
Aluminum	0.1
Magnesium	0.01
Copper	0.001
Iron	0.001
Titanium	Trace
Barium	None found
Lead	None found
Nickel	None found
Calcium	None found
Chromium	None found
Sodium	None found
Strontium	None found
Zinc	None found
Rare Earths	None found

TABLE XXVI. SPECTROGRAPHIC ANALYSIS OF MANGANESE DIOXIDE
SAMPLES 640, 643, and 644.

Sample	640	643	644
<u>Element</u>			
Manganese			Major Constituent
Potassium	1 %	1 %	1 %
Aluminum	0.5	0.5	0.5
Calcium	0.5	0.5	0.5
Iron	0.5	0.5	0.5
Magnesium	0.1	0.1	0.1
Silicon	0.1	0.1	0.1
Copper	0.01	0.01	0.005
Sodium	0.01	0.5	0.05
Strontium	0.01	0.01	0.01
Lead	0.005	0.005	0.005
Boron	0.001	0.001	0.001
Titanium	0.001	0.001	0.001
Barium	None found	0.01	None found
Chromium	None found	None found	None found
Nickel	None found	None found	None found
Tungsten	None found	None found	None found
Rare Earths	None found	None found	None found

SAMPLE CALCULATIONS

These sample calculations will be concerned with the high drain results from the first experiment.

The coefficients of the variables (x_1) in the linear equation are calculated from the expression

$$b = \frac{\sum yx}{2 \sum x^2}$$

The divisor 2 is necessary because there were two batteries tested per sample. The y represents the drain capacity of the battery and the x signifies a plus or minus one, which depends on a particular sample. The calculations for b_1 in the high drain equation are as follows:

$$\begin{aligned} \sum yx &= (6.5 + 6.3 + 4.3 + 4.3 + \dots + 4.7 + 4.6 + 4.0 + 4.0) \\ &\quad - (7.1 + 7.2 + 3.2 + 2.7 + \dots + 5.0 + 5.1 + 4.6 + 4.6) = -5.8. \\ \sum x^2 &= 32 \end{aligned}$$

hence $b = -5.8/32 = -0.18$

After all the coefficients are calculated, an analysis of variance of the drain capacities is performed. The linear model sum of squares is calculated from the equation

$$\text{Linear model ss} = \sum_{i=1}^k (\sum xy)^2 / 2 \sum x^2$$

Thus, $(5.8)^2 + (23.8)^2 + (1.6)^2 + (8)^2 + (0)^2 / 32 = 20.83$.

The total sum of squares can be obtained by use of the equation

$$\text{Total ss} = \sum y^2 - \frac{(\sum y)^2}{N}$$

Consequently, total ss = $(7.1)^2 + (7.2)^2 + \dots + (4.0)^2 + (4.2)^2 -$

$$\frac{(7.1 + 7.2 + \dots + 4.0 + 4.2)^2}{32}$$

The sum of squares for lack of fit is obtained by difference.

The total degrees of freedom is equal to the total number of observations minus one, while the degrees of freedom for linear model is equal to the number of independent variables. The lack of fit degrees of freedom is also obtained by difference.

Following the determination of the degrees of freedom and the calculation of sum of squares, an Analysis of Variance Table is constructed, as in case, Table IV on page 22. Then the F-test is performed.

The next step is the calculation of the direction which would optimize the drain capacities as shown in Table XXVII or for low drain in Table XXVIII.

In Table XXVII, line (1) gives the base level of the factors, line (2) indicates the unit, i.e., the change in level corresponding to the change from 0 to 1 in the design, and line (3) gives the slopes of the linear equation. For example, for every 0.18 units in which x_1 is decreased, x_2 will decrease by 0.74 units. Likewise, for every decrease of 1.8°C , the MnSO_4 concentration should be decreased by -0.185 gm. mole per liter. Thus, line (4) describes the path of steepest ascent, while line (5) illustrates the changes when taking a convenient increment of x_1 . The quantities of line (5) are added to the base level to give the path of steepest ascent, from which the levels for the next set of runs can be estimated.

TABLE XXVII. PATH OF STEEPEST ASCENT FOR HIGH DRAIN - FIRST EXPERIMENT.

Variable	x_1	x_2	x_3	x_4	x_5
(1) Base Level	80	0.50	0.25	3	10
(2) Unit	10	0.25	0.10	1	10
(3) Estimate Slope b	-0.18	-0.74	-0.05	-0.25	0.0
(4) Unit x b	-1.80	-0.185	-0.005	-0.25	no effect
(5) Change in level per -5°C in x_1	-5.0	-0.514	-0.0139	-0.695	
(6) Path of steepest ascent	80	0.50	0.25	3	
	75	0	0.24	2.3	
	70	0	0.22	1.6	

TABLE XXVIII. PATH OF STEEPEST ASCENT FOR LOW DRAIN - FIRST EXPERIMENT.

Variable	x_1	x_2	x_3	x_4	x_5
(1) Base Level	80	0.50	0.25	3	10
(2) Unit	10	0.25	0.10	1	10
(3) Estimate Slope b	-6.16	-12.16	-6.50	-7.97	-6.53
(4) Unit x b	-61.6	-3.04	-0.650	-7.97	-65.3
(5) Change in level per $\pm 5^\circ\text{C}$ in x_1	-5	-0.246	-0.059	-0.65	-5.30
(6) Path of Steepest ascent	80	0.50	0.25	3	10
	75	0.25	0.19	2.35	4.7
	70	0	0.13	1.7	0

TABLE XXIX. ANALYTICAL DATA OF SAMPLES FROM OXIDATION OF MANGANOUS SULFATE BY POTASSIUM PERMANGANATE.

Sample	O ₂ as % MnO ₂	% H ₂ O	Apparent Density gm/in ³	Bobbin Wt. gms.	Milliliters of Wetting Solution per 50 gms. MnO ₂
640	82.5	3.76	13.6	9.1	16.2
1	86.0	3.12	13.4	9.2	14.9
2	82.6	2.15	11.7	9.2	16.0
3	82.6	3.14	13.2	9.3	16.5
4	83.5	2.34	15.5	9.4	15.5
5	83.5	4.80	10.0	8.4	14.4
6	82.4	5.77	12.2	9.0	15.7
651	80.6	4.13	14.1	9.1	16.0
2	79.8	3.29	13.4	9.2	15.0
3	78.4	3.15	12.1	9.2	12.8
4	78.4	3.06	12.6	8.9	15.7
5	79.0	3.22	12.4	9.2	15.5
6	80.0	2.70	12.9	9.2	16.2
7	78.8	3.54	12.0	8.4	18.4
8	79.0	3.02	12.1	8.9	17.3
9	80.6	4.36	13.0	8.9	17.3
660	78.8	2.89	13.1	9.1	15.0
1	80.0	3.02	11.8	8.6	17.0
2	80.6	3.21	11.6	8.8	15.0
3	80.4	2.38	12.6	9.3	16.7
4	79.8	2.04	12.9	9.4	15.9
665	79.5	2.71	11.7	8.9	17.4
6	80.0	3.56	12.4	9.0	18.6
7	81.5	3.45	12.1	9.0	16.5
8	81.3	3.32	12.0	8.9	15.0
9	80.0	2.80	11.5	9.1	17.2
670	81.5	3.37	11.9	9.2	17.2
1	80.0	3.09	11.9	8.9	15.0
2	81.0	2.49	11.6	8.9	17.6
681	82.6	3.92	12.1	9.3	16.5
2	83.6	2.98	15.5	9.1	16.5
3	81.5	4.94	13.7	9.2	15.5
4	81.5	3.58	14.8	9.2	15.5
5	80.6	5.18	14.2	9.3	15.1
6	83.0	3.65	13.9	9.1	15.6
687	79.8	5.26	11.9	9.0	16.0
8	83.6	3.30	13.3	9.1	15.5
9	82.6	3.92	13.7	9.1	16.0

TABLE XXIX - continued.

Sample	O ₂ as % MnO ₂	% H ₂ O	Apparent Density gm/in ³	Bobbin Wt. gms.	Milliliters of Wetting Solution per 50 gms. MnO ₂
690	81.5	2.86	13.8	9.0	19.8
1	79.1	3.95	13.5	9.1	15.0
2	81.3	3.27	13.9	9.2	17.3
3	80.0	4.03	13.5	9.2	15.8
4	80.4	3.18	13.8	9.2	15.1
5	78.0	4.10	13.6	9.1	15.8
6	79.9	3.31	13.0	9.4	16.0
7	81.0	3.82	13.8	9.2	15.0
698	80.4	3.58	14.5	9.2	16.0
700	80.5	4.13	12.5	9.4	16.0
1	79.5	4.73	13.2	9.4	12.2

TABLE XXX. ACID LEACHING DATA AND RESULTS

Sample	Acid Conc. gm/liter	Acid Ratio	Temp. °C.	Contact Min.	High Drain Hrs.	Low Drain Hrs.	3 Months Hrs.
400	---	---	---	---	5.6	112	95
401	100	5.7	92	60	6.7	111	75
402	5	0.29	80	1.5	5.3	108	93
403	100	5.4	32	60	5.6	106	69
404	100	5.7	75	60	6.0	90	75
405	5	0.14	90	60	5.0	113	69
406	5	0.14	89	20	5.2	117	63
407	5	0.14	83	5	5.8	116	108
408	50	1.6	85	60	7.0	116	109
409	50	1.6	87	20	7.1	118	117
410	50	1.5	87	5	5.8	120	118
411	---	---	---	---	5.6	112	95
412	100	3.7	87	20	6.4	112	70
413	50	1.3	77	1.5	5.8	110	105
414	100	2.5	80	5	5.1	125	106
415	5	0.13	58	5	5.7	124	89
416	5	0.10	63	60	6.3	111	73
430	---	---	---	---	3.0	52	---
431	100	2.9	88	60	7.8	134	116
432	100	3.0	91	60	7.5	129	78
440	---	---	---	---	5.0	112	---
441	50	0.4	90	60	7.7	132	88
442	50	0.4	90	60	7.4	132	90
443	8.4	0.3	55	10	5.6	125	84
444	8.4	0.3	55	11	6.0	146	84
450	---	---	---	---	6.5	105	75
451	100	1.7	85	60	6.2	114	68

TABLE XXXI. ANALYTICAL DATA OF ACID LEACHED SAMPLES.

Sample	O ₂ as % MnO ₂	% H ₂ O	Apparent Density gm/in ³	Bobbin Wt. gms.	Milliliters of Wetting Solution per 50 gms. MnO ₂
400	76.7	4.26	14.1	9.5	14.0
401	89.3	4.50	13.2	9.7	16.6
402	77.8	5.93	13.8	9.5	14.3
403	76.5	3.67	13.9	9.8	14.3
404	68.6	2.84	14.4	9.8	13.8
405	77.0	2.97	15.3	10.1	14.0
406	75.9	2.97	16.1	10.0	14.2
407	76.7	5.26	14.0	9.7	14.5
408	74.7	2.72	14.7	9.9	14.4
409	78.7	1.84	14.9	9.7	14.2
410	77.0	2.27	14.7	10.0	14.0
411	76.7	4.76	14.1	9.5	14.0
412	72.3	3.20	14.5	9.7	14.1
413	80.4	1.14	14.6	9.8	15.1
414	81.9	2.20	14.9	9.8	14.2
415	77.3	4.16	13.5	9.7	14.5
416	75.3	1.6	14.0	9.6	14.0
430	---	1.43	---	---	14.6
431	87.6	2.10	---	9.6	15.2
432	78.2	2.63	---	9.6	16.2
440	---	---	---	9.7	12.6
441	89.0	2.26	14.0	9.8	14.0
442	90.8	1.13	14.5	9.5	14.5
443	84.0	3.97	15.0	9.7	13.8
444	83.7	3.77	14.9	9.8	13.5
450	77.0	7.76	11.1	9.1	16.2
451	84.5	5.30	12.0	9.2	14.9

TABLE XXXII. METHODS OF PREPARATION

Sample

400

Two hundred pounds of MnSO_4 was diluted to 10% MnSO_4 and reacted with 28 pounds of NaOH to form 45 gallons of $\text{Mn}(\text{OH})_2$ slurry, which was chlorinated to a pH of 3 at a temperature of 33°C . A portion of this sample was used for the acid leaching study with the remaining being shipped to battery manufacturers.

430

Six hundred pounds of 10% MnSO_4 was reacted with 56 pounds of NaOH . The 90 gallons of $\text{Mn}(\text{OH})_2$ slurry was chlorinated for 14 hours to a pH of 4. Most of the sample was acid leached with 50 gm. per liter H_2SO_4 for 2 hours at 90°C and then sent to battery manufacturers. A small portion of the unleached MnO_2 was used in the acid leached study.

440

Four moles of C.P. MnSO_4 was reacted with 14 moles of NaOH forming 8 liters of $\text{Mn}(\text{OH})_2$ slurry, which was chlorinated continuously in a 4-foot, 2-inch glass reactor. The contact time was approximately 20 minutes and the temperature 35°C .

450

Eight moles of MnSO_4 solution (AR-1) was diluted to 9 liters, which was reacted with 640 gms. of NaOH dissolved in 1 liter of tap H_2O . The slurry was chlorinated as in sample 440 with a contact time of 65 min. at 36°C .

TABLE XXXIII. X-RAY DIFFRACTION CHARACTERIZATION DATA.

Acid Leached Samples

<u>Sample No.</u>	<u>Phase</u>
405	Corundum (α Al_2O_3); gamma-rho MnO_2 .
410	Same as above
411	Same as above
415	Same as above

Guyard Reaction Samples

640	50% α , 50% rho
643	Same as above
644	Same as above
660	Alpha
694	Gamma

TABLE XXXIV. EXCERPTS FROM SCL-3117-D SPECIFICATION

3. REQUIREMENTS

3.3 Chemical Composition. The synthetic manganese dioxide shall show, on analyses as described in 4.3, the following chemical composition:

Available oxygen as % MnO_2	85% min.
Total manganese as % Mn	58% min.
Absorbed moisture as % H_2O	3% max.
Iron as % Fe (soluble HCl)	0.2% max.
Silicon as % SiO_2	0.5% max.
Metallic Impurities (e.g., Cu, Cd, Ni, Pb, Sb, etc.)	0.1% max.
pH	4.0-8.0

3.4 Particle Size. The synthetic manganese dioxide shall be of such size that at least 95 percent of the material shall pass through a U.S. Standard Sieve #325 (see 4.2).

3.5 Crystalline Phase. When the crystallographic and micro-structural analyses of the synthetic manganese dioxide are made as described in 4.4, there shall be evidence of a predominance of the imperfectly crystallized phase known as gamma MnO_2 .

3.5.1 Particle Morphology. When examined in the micron and sub-micron size range, at direct magnification from 5,000 to 20,000 diameters, the particle shall present irregular shapes with no evidence of cleavage, i.e., with non-rectilinear profiles having powdery or nebulous rather than sharp, well-defined edges.

3.5.2 X-Ray Diffraction Pattern. The X-Ray diffraction pattern shall be characterized by the diffuse-line pattern of gamma MnO_2 . For the purpose of this specification, the significant lines (d) of gamma MnO_2 and their respective relative intensities (I) for iron radiation are as follows:

<u>d</u>	<u>I</u>
4.00	5
2.45	7
2.14	7
1.65	10
1.40	5

3.6 Capacity. When discharged as described in 4.6, the minimum allowable capacity for each "A"-size cell, fabricated as described in 4.5.1, shall be as follows:

TABLE XXXIV - continued.

(a) High Drain Test 5.50 hours

(b) Low Drain Test 130.0 hours

4.3 Chemical Analyses.

4.3.1 Preparation of Sample. The sample shall be dried for 16 hours at a temperature of 100 C. All analyses (except determination of moisture) shall be done on the dry basis.

4.3.2 Determination of Moisture. About 20 grams of the original sample are dried for 16 hours at a temperature of 110 C. The loss in weight is taken as the water content of the sample.

$$\text{Moisture as } \% \text{ H}_2\text{O} = \frac{\text{Loss in wt. of sample} \times 100}{\text{Original wt. of sample}}$$

4.4 Crystallographic and Micro-Structural Analyses.

4.4.3 X-Ray Diffraction. X-Ray diffraction patterns are obtained by the usual techniques, using either a Debye powder camera or a Geiger counter X-Ray spectrometer. The use of filtered FeK alpha radiation in a Debye powder camera having a dispersion of 1 degree of 20mm of film is recommended, with an exposure of 6 to 12 hours in order to bring out the gamma MnO₂ pattern.

4.5 Dry Cell Fabrication Program.

4.5.1 Construction. "A" size dry cells shall be constructed as follows in accordance with existing standard cell assembly techniques.

(a) The following dry mix formulation shall be used:

80% MnO₂

8% Carbon Black

12% NH₄ Cl

4.6 Capacity Tests

4.6.1 Twenty (20) each dry cells, size "A", prepared as described in 4.5.1, shall be used for each of the initial capacity tests* as follows:

TABLE XXXIV - continued.

	<u>Low Drain</u>	<u>High Drain</u>
(1) Type of Discharge	continuous	continuous
(2) Discharge Resistance	166-2/3 ohms	16-2/3 ohms
(3) Test End Voltage	1.13 volts	1.0 volt.
(4) Discharge Temperature	70 F (50% R.H.)	70 F (50% R.H.)

* - Inasmuch as an evaluation of each sample is required in not more than 1 month's time, the evaluation must of necessity be based upon initial capacity tests only. However, in order to prove each evaluation, sufficient dry cells are made from each sample, as previously described in 4.5.1 and 4.6.1, and set aside for delayed capacity tests after storage periods of 3, 6, 12, 18, and 24 months at a temperature of 70 F.

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