Montana STATE UNIVERSITY

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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Dean, Graduate Division

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ABSTRACT

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INTRODUCTION

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

$$Zn \rightarrow Zn^{+2} + 2e \text{ at zinc electrode}$$

$$2H^+ + 2e \rightarrow H_2 \text{ at carbon electrode}$$
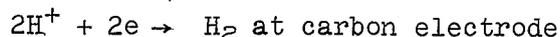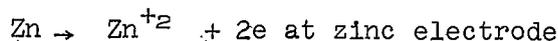
Originally, the evolved hydrogen formed bubbles on the positive electrode which resulted in generating a back e.m.f., called polarization (9). Then Leclanche' discovered that by surrounding the positive electrode with manganese dioxide, the formation of hydrogen gas is prevented to a considerable extent. The cell reactions (15) then being:

$$2MnO_2 + 2H^+ + 2e \rightarrow 2MnOOH$$

$$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e$$

or $$Zn + 2MnO_2 \rightarrow ZnO \cdot Mn_2O_3$$
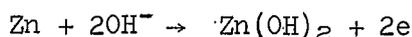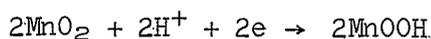
This reaction occurs on light discharge drains with zinc present, while on heavy drains with a deficiency of zinc ions, the reaction is assumed to be

$$2MnO_2 + 2NH_4^+ + 2e \rightarrow 2MnOOH + 2NH_3$$
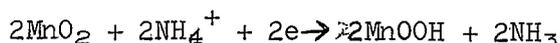
It was also found that only certain crystalline phases of manganese dioxide could act as a depolarizer in dry cells, these phases being principally gamma and rho types.

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:

$$3MnSO_4(aq) + 2KMnO_4(aq) + 2H_2O(1) \rightarrow 5MnO_2 + K_2SO_4(aq) + 2H_2SO_4(aq)$$
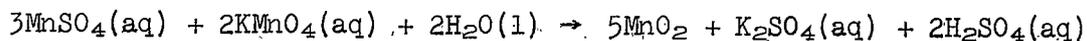
Some work has been done on the kinetics and mechanism of the reaction. Tompkins (18) found that the precipitation of manganese dioxide is hinder-

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 re-

duced to Mn^{+++}, which is further reduced to Mn^{++} by the mechanism:

$$2Mn^{+++} \rightarrow Mn^{++++} + Mn^{++}$$
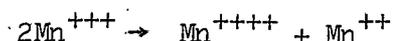
The Mn^{++++} ion is then hydrolyzed to form the dioxide. In absence of

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, Tomp-

kins suggests the following mechanism:

(1) $Mn^{++} + MnO_4^- + H_2O \rightarrow Mn^{+++} + HMnO_4^- + OH^-$

(2) $HMnO_4^- + Mn^{++} + OH^- \rightarrow 2MnO_2 + Mn^{++}$

(3) $2Mn^{+++} \rightarrow Mn^{++++} + Mn^{++}$

(4) $Mn^{++++} + H_2O \rightarrow Mn^{+++} + OH + H^+$

(5) $Mn^{++} + OH \rightarrow Mn^{+++} + OH^-$

(6) $Mn^{++++} + 4OH^- \rightarrow Mn(OH)_4 \rightleftarrows MnO_2 + 2H_2O$
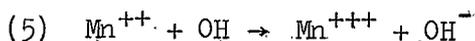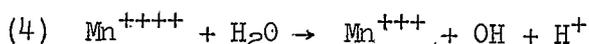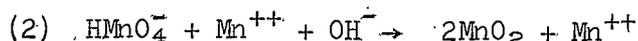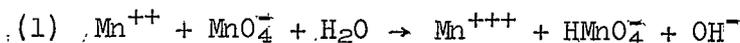
It is postulated that reaction 6 is accountable for the major part

of the production of MnO_2 because reaction 2 is believed to be slow. In

oxidations by permanganate, where hydrated manganese dioxide is precipi-

tated, 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 hetero-

geneous 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
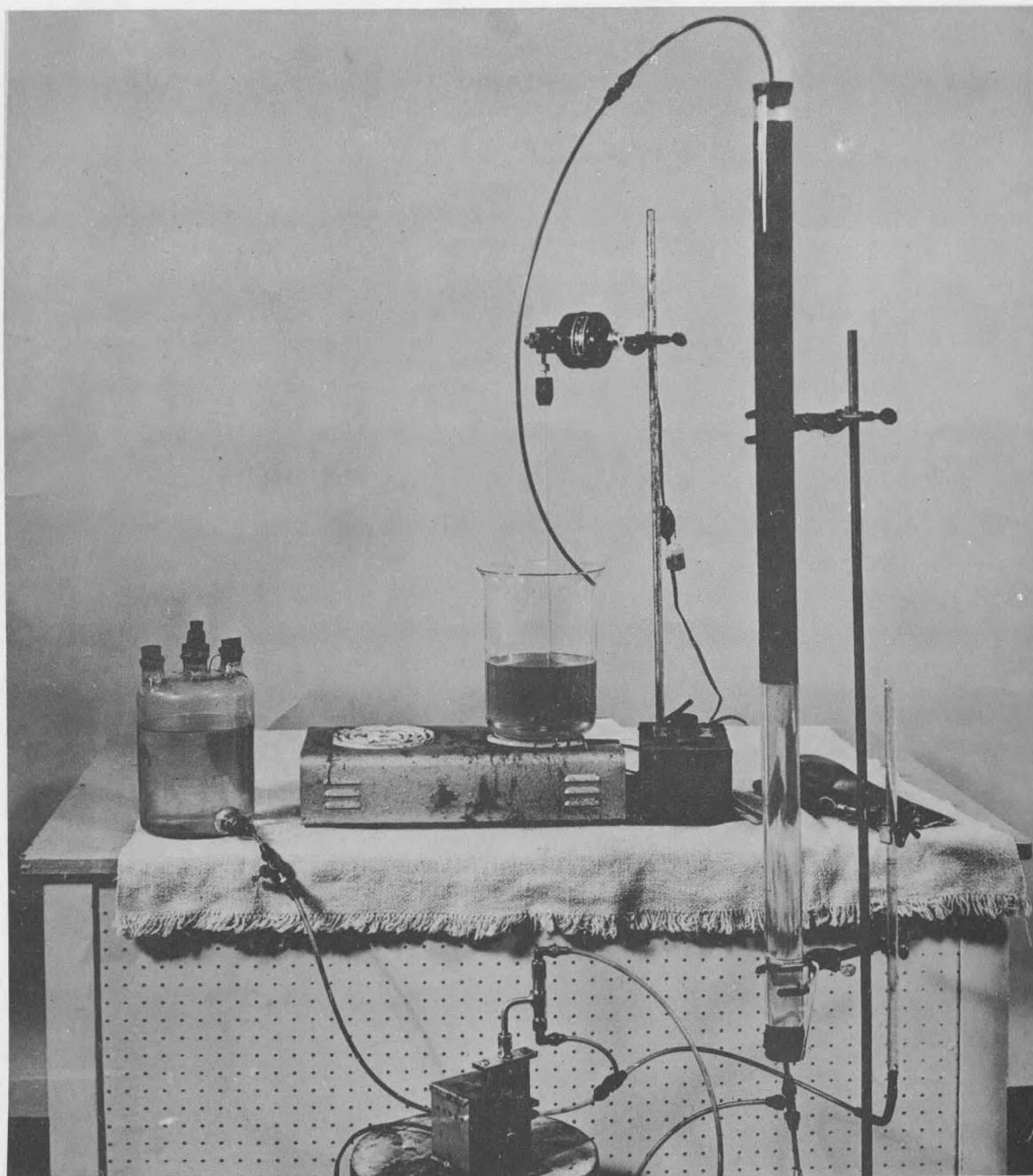
Figure 1. Reactor for Producing MnO_2 by Guyard Reaction.

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:

	Low Drain	High Drain
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.

Sample	Temp.	$MnSO_4$ Conc.	$KMnO_4$ Conc.	Contact Time	High Drain	Low Drain	Delayed Capacity
640	78°C	0.15 mole/l.	0.33 mole/l.	5 hrs.	6.3 hrs.	115 hrs.	100 hrs.
641	85	------	------		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 1.	0.25	0.75
x_3	Concentration of $KMnO_4$ — gm. mole per 1.	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". Treat-

ments 651, 652, and 655 gave 7.2, 6.4, and 6.6 hours high drain, respec-

tively, 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

$$x_1 = \frac{temp. - 80}{10}, \quad x_2 = \frac{conc. \ MnSO_4 - 0.50}{0.25}, \quad x_3 = \frac{conc. \ KMnO_4 - 0.25}{0.10},$$

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

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	$F_{5, \ 38} = \frac{4.2}{.53} = 7.92$
Lack of Fit	38	20	.53	
Total	43	41		

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	$F_{(5,38)} = 14.3$
Lack of Fit	38	5708	150	
Total	43	16399		

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 con-

ditions 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.

	Factor	Factor Level -1	Factor Level +1
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

$$x_1 = \frac{Temp. - 75}{10}, \quad x_2 = \frac{Conc. \ of \ MnSO_4 - 0.15}{0.05}, \quad x_3 = \frac{Conc. \ KMnO_4 - 0.10}{0.03},$$

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

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	30	6.23	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	30	1001	33.4	$F_{(5,30)} = 1.23$
Total	35	1206		

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_i'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 $KMnO_4$ con-

centration, 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
A +	129	127

TABLE XI. INTERACTION AC

	C	
	−	+
A −	129	125
A +	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 inter-

action 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 man-

ganous 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

Treatment	Average Low Drain	Average 3 Months Delayed Capacity	% of Initial Low Drain
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