Chemical synthesis of battery-active manganese dioxide
by William G Moore

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
of Master of Science in Chemical Engineering
Montana State University
© Copyright by William G Moore (1953)

Abstract:
Part of the results of the second year of investigation of chemical syntheses of battery active
-manganese -dioxide is presented here. The ultimate goal of the work is the development of a
commercially feasible chemical process for the manufacture of a battery active manganese dioxide
which will meet tentative United States Arngr Signal Corps specifications for synthetic manganese
dioxide.

A discussion of seven reactions which will produce battery active manganese dioxide is presented.
Chemical analyses, which includes total manganese, available oxygen, moisture -content, and pH, are
tabulated for each manganese dioxide sample as are the apparent density, bobbin weight, initial drain
test performance, and drain test performance after three months storage.

Two reactions which produce manganese-dioxide- of sufficient activity to meet specifications for initial
drain tests are: the nitric acid leach of bixbyite or hausmannite, and the chlorine oxidation of
manganese hydroxide. The thermal decomposition of manganese carbonate produces manganese
dioxide which is superior to Gold Coast ore and shows good capacity maintenance after three months
storage.

CHEMICAL SYNTHESIS OF BATTERY-ACTIVE
MANGANESE DIOXIDE

by

WILLIAM G. MOORE

A THESIS

Submitted to the Graduate Faculty

in

partial fulfillment of the requirements

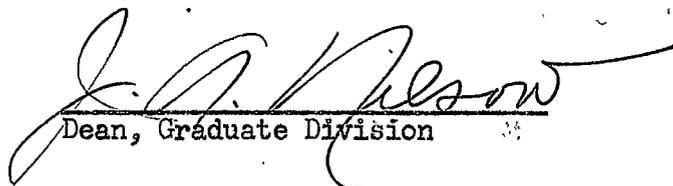for the degree of

Master of Science in Chemical Engineering

at

Montana State College

Approved:

Lloyd Berg

Head, Major Department

Lloyd Berg

Chairman, Examining Committee

J. A. Nelson

Dean, Graduate Division

Bozeman, Montana
July, 1953

TABLE OF CONTENTS

ABSTRACT

Part of the results of the second year of investigation of chemical syntheses of battery active manganese dioxide is presented here. The ultimate goal of the work is the development of a commercially feasible chemical process for the manufacture of a battery active manganese dioxide which will meet tentative United States Army Signal Corps specifications for synthetic manganese dioxide.

A discussion of seven reactions which will produce battery active manganese dioxide is presented. Chemical analyses, which includes total manganese, available oxygen, moisture content, and pH, are tabulated for each manganese dioxide sample as are the apparent density, bobbin weight, initial drain test performance, and drain test performance after three months storage.

Two reactions which produce manganese dioxide of sufficient activity to meet specifications for initial drain tests are: the nitric acid leach of bixbyite or hausmannite, and the chlorine oxidation of manganese hydroxide. The thermal decomposition of manganese carbonate produces manganese dioxide which is superior to Gold Coast ore and shows good capacity maintenance after three months storage.

INTRODUCTION

Manganese dioxide is used as a depolarizer in Leclanche type dry batteries. The quality of the manganese dioxide is one of the most important variables which determine the initial and delayed capacity of the dry cell. The activity of a given dioxide is determined by making batteries in which the only variable of composition is the dioxide, and subjecting these batteries to standard drain tests. The number of hours of battery life as evaluated by the drain tests determine the quality or activity of the manganese dioxide. Generally, the drain tests are compared to the performance of similar cells made with a natural manganese dioxide from the Gold Coast of Africa (Gold Coast ore). An A size dry cell made with Gold Coast ore will have a battery life of about 4 hours, high drain, and 80 hours, low drain, when discharged according to the specifications on page 7.

Prior to World War II, synthetic manganese dioxide was not competitive with Gold Coast ore to any great extent. The reasons were principally related to the type of service demands of the greatest volume of dry cells: civilian consumption, where acceptance of bulky high capacity cells was general. The need for improved dry cells became apparent during the war when battery powered portable electronic equipment was often inoperative due to battery failure. The poor capacity maintenance of cells after prolonged tropical storage, unsatisfactory low temperature discharge characteristics, and the desirability of small high capacity cells led to the investigation of sources of manganese dioxide which would give more satisfactory dry cell performance.

The Signal Corps has sponsored several research programs with a goal of developing a commercially feasible process for the manufacture of a manganese dioxide which has depolarizing action superior to Gold Coast ore. The first successful endeavor was the production by electrolysis of manganous sulfate solutions of a dioxide which met or exceeded the Signal Corps tentative specifications. While specification grade dioxide may be produced electrolytically, the cost of the product is rather high. Also present electrolytic dioxide production would not supply the domestic demand should the Gold Coast ore supply be interrupted in time of war.

The Signal Corps has sponsored a research program at Montana State College for the investigation of chemical syntheses yielding battery active manganese dioxide. Theses by Nickelson (1) and Davidson (2) include the first year's work. Theses by Fahlgren (3) and Sadagopachari (4) and this thesis report the second year's work.

The second year of investigation has been directed toward the development of the more favorable reactions reported by Nickelson (1) and Davidson (2) and testing other reactions not previously attempted at Montana State College. Fifteen reactions were investigated; seven are reported here and eight are reported by Fahlgren (3).

SPECIFICATIONS

The specifications following have been tentatively established by the Army Signal Corps as of November 17, 1949, for acceptable synthetic manganese dioxide depolarizers. These specifications were taken from Bulletin SCL-3117-A (8).

Chemical Composition

Available oxygen as % MnO_2	85.0% min
Total manganese as % Mn	58.0% min
Absorbed moisture as % H_2O	3.0% max
Iron as % Fe (soluble in HCl)	0.2% max
Silicon as % SiO_2	0.5% max
Other metallic impurities	0.1% max
pH range	4 to 8

Crystalline Phase

From crystallographic and microstructural analyses predominance of the crystallized phase known as gamma manganese dioxide should be evident.

Particle Morphology

The particle shall present irregular shapes with no evidence of cleavage (that is, with non-rectilinear profiles having nebulous rather than sharp, well-defined edges) when examined at direct magnification from 5,000 to 20,000 diameters.

X-Ray Diffraction Pattern

Specimen diffraction pattern should be characterized by the diffuse-line pattern of gamma manganese dioxide. Significant lines, d, of gamma manganese dioxide and their respective relative intensities, I, for iron

radiation comprising this specification are as follows:

d	I
4.00	5
2.45	7
2.14	7
1.65	10
1.40	5

Figure 3, in the Appendix, shows the various diffraction patterns of the seven types of manganese dioxide.

Particle Size

Particles should be of such a size that 95 percent of the specimen shall pass through a U. S. Standard Sieve No. 325.

Apparent Density

The bulk density of the specimen as measured by a Scott volumeter should be not less than twenty grams per cubic inch.

Battery Life

The specifications for discharge of standard A size dry cells are as follows:

	Low drain	High drain
Type discharge	continuous	continuous
Discharge resistance	166.7 ohms	16.67 ohms
End voltage	1.13 volts	1.00 volts
Temperature	70°F	70°F
Relative humidity	50%	50%
Battery life	130 hours	5.5 hours

MATERIALS AND METHODS

Reagents

Although the goal of this project is to develop chemical syntheses
for producing battery-active manganese dioxide from commercially available
ores, only C. P. grade chemicals have been used in this study. The
immediate problem was to produce specification grade product, leaving
purity difficulties inherent in work with ores to be overcome during a
later phase of the project. Data obtained in this study with pure reagents
will be used as a guide in selecting processes suitable for study in adap-
tations of commercial ores.

Syntheses

Methods of preparations of samples discussed in this report are shown
in the Appendix in Table II. Important variables encountered were reaction
temperature, concentration, and reaction time. Some tendencies were in-
dicated with respect to correlation of specimen properties with reaction
variables; these tendencies are noted in the discussion section. The wide
scope of this investigation and time limitations have prevented the mak-
ing of complete studies of reaction variables. Studies that have been
made were on batchwise reactions, leaving continuous processing as a
future development.

Battery Fabrication and Testing

Standard A size dry cells were constructed in accordance with usual
cell assembly techniques; Signal Corps specifications were followed in
proportioning the various mixtures and solutions that were used. A
mixture containing 80% by weight of the MnO_2 sample, 18% Shawinigan

carbon black, and 12% NH_4Cl were mixed in a pebble mill for 20 minutes to assure uniform consistency. This mixture was dampened with a wetting solution consisting of 5.8% NH_4Cl by weight, 8.6% $ZnCl_2$, and 85.6% H_2O until material acceptable for tamping was obtained.

From the mixture described above, bobbins were tamped in an apparatus as shown in the Appendix, Figure 1. Due to the corrosiveness of the mix-ture used in bobbin making, stellite and methacrylate plastic were utilized for the parts of the apparatus which would contact the mixture. Use of the stellite die also was advantageous since it produced smooth-sided bobbins.

Still in accord with Signal Corps specifications, the bobbins were wrapped in cotton gauze and set in zinc cans with a cold paste electrolyte containing a ratio of 50 ml of a solution consisting of 23.7% NH_4Cl by weight, 22.3% $ZnCl_2$, 0.1% $HgCl_2$, and 53.9% H_2O to 10.7 gm of a mixture containing 74.7% cornstarch and 25.3% flour. A paper washer was placed around the carbon rod, a brass cap was pressed on the rod, and then the bobbin was sealed in the can with wax.

After a period of four days the batteries were discharged through test resistances as partially diagrammed in the Appendix, Figure 2. The test rack consisted of eight 16.67 ohm resistances and twenty-four 166.7 ohm resistances. End voltages for the two drain tests were 1.13 volts for the 166.7 ohm drain, low drain, and 1.00 volts for the 16.67 ohm drain, called high drain.

<u>Oxygen Analysis</u>

Available oxygen determinations were made in accordance with Signal Corps methods as stated in <u>Bulletin SCL-3117-A</u> (8). The determination

was made as follows: To 0.2175 gm of dried MnO_2 was added 50 ml of 0.20 N $Fe(NH_4)_2(SO_4)_2$ solution containing 175 ml con H_2SO_4 per liter. Another 50 ml of the $Fe(NH_4)_2(SO_4)_2$ solution was pipetted into a second beaker to run as a control sample. Both samples were diluted to 200 ml with distilled water and digested on a steam plate. After digestion they were readjusted to the original 200 ml volume and titrated with 0.2 N $K_2Cr_2O_7$ solution. Since a suitable indicator was not available, a potentiometric titration was run using a type K potentiometer, calomel cell, and platinum electrode. The available oxygen was computed as four times the difference in volume of dichromate solution used in the sample and blank and reported as percent manganese dioxide.

Total Manganese Analysis

Portions of the specimen weighing 0.10 gm were dissolved in 10 ml water and 5 ml con HCl and the solution was evaporated almost to dryness. To this mixture was added 25 ml con H_2SO_4 and 10 ml con HNO_3 and the contents were heated till all traces of brown fumes were expelled. After cooling the solution, 275 ml water and 3 gm $NaBiO_3$ were added. Excess oxidant was removed with a sintered-glass funnel and the material was also washed free of permanganate with hot water. This filtrate was poured into 50 ml of an oxalate solution and the excess was titrated with 0.1 N $KMnO_4$.

pH Determination

A part of the manganese dioxide specimen weighing 0.75 to 1.00 gm was digested with 100 times its weight of distilled water for ten minutes at the boiling point. Volume was readjusted to the original and the solution was cooled. The pH of the supernatant liquid was then determined with a

Beckman pH meter.

Density

Densities were determined by running the specimen through a Scott volumeter into a cubic inch container. The apparent densities were then reported as grams per cubic inch.
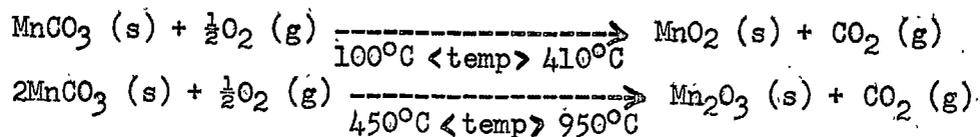
Moisture Content

A sample weighing one to three grams was dried for sixteen hours at a temperature of 110°C. The loss in weight was taken as the moisture content.

DISCUSSION OF RESULTS

Methods of preparation and analytical and test data for the manganese dioxide specimens produced in this study are shown in the Appendix, in Table I and Table II. A code was used to designate different samples, the first letter indicating the source of the manganese used in the synthesis (O for manganese oxides, OH for manganese hydroxide, S for manganese sulfate, C for manganese carbonate, or N for manganese nitrate), the second letter indicating the treatment (Cl for chlorine oxidation, H for heating, M for permanganic acid oxidation), and the number differentiates the reactions of a given type (C-H-1, C-H-2, etc.). The addition of the letters B or WB indicate the sample was ground in a ball mill, dry (B) or wet (WB).

Thermal Decomposition of Manganese Carbonate

Manganese carbonate decomposes to manganese oxides when heated to temperatures of $100^{\circ}C$ or above. Decomposition of the carbonate in air at temperatures below $410^{\circ}C$ yields predominately manganese dioxide. Lower oxides of manganese are produced at temperatures higher than $410^{\circ}C$ at atmospheric air pressure.

$$MnCO_3 \text{ (s)} + \tfrac{1}{2}O_2 \text{ (g)} \xrightarrow[100^{\circ}C \,<\text{temp}>\, 410^{\circ}C]{} MnO_2 \text{ (s)} + CO_2 \text{ (g)}$$

$$2MnCO_3 \text{ (s)} + \tfrac{1}{2}O_2 \text{ (g)} \xrightarrow[450^{\circ}C \,<\text{temp}>\, 950^{\circ}C]{} Mn_2O_3 \text{ (s)} + CO_2 \text{ (g)}$$

The rate at which the reaction proceeds to the right is determined by the temperature; at $110^{\circ}C$ only enough dioxide is produced in 24 hours to give the white carbonate a slight brown coloration, whereas about 80% of the carbonate is converted to manganese dioxide when heated at $400^{\circ}C$ for

24 hours. Decomposition of the carbonate in the presence of pure oxygen or under air pressure greater than atmospheric would probably increase the conversion for a given temperature. In all thermal decomposition of manganese carbonate reactions reported in Table II, the removal of unreacted carbonate was effected with dilute acid solutions. The possibility exists that the maximum reaction temperature could be increased above 400°C without decomposition of the dioxide to bixbyite (Mn_2O_3) by an increase in the oxygen partial pressure. The decomposition of manganese dioxide to bixbyite occurs over the temperature range 200°C to 550°C depending on the type of dioxide and the partial pressure of oxygen. Manganese carbonate decomposition to yield manganese dioxide at temperatures higher than 400°C would be desirable because the reaction rate would be increased at higher temperatures.

Comparison of the battery life of C-H-10 (6.3 and 111 hours, initial, and 103 hours after three months), which was prepared at 400°C, with C-H-16 (6.2 and 100 hours, initial, and 102 hours after three months), which was prepared at 290-340°C, shows no difference in the product which can be attributed to the reaction temperature. The highest temperature which will not produce bixbyite (Mn_2O_3) is recommended for this reaction. Sample C-H-13, which was prepared at 410°C, contained a considerable amount of bixbyite (as shown by the low oxygen to manganese ratio, Table I), and C-H-14, which was prepared at 490°C was almost pure bixbyite.

The source of the manganese carbonate is of doubtful significance since manganese dioxide of approximately equal activity was produced by the thermal decomposition of manganese carbonate made by three different syntheses. Decomposition of manganese carbonate made from ammonium carbonate and manganous sulfate was tried in four reactions: C-H-4 (3.9 and 70 hours), C-H-7 (.1 and 33 hours), C-H-8 (1.7 and 83 hours), and C-H-9 (1.7 and 103 hours). Samples C-H-11 (1.8 and 91 hours) and C-H-12 (1.9 and 100 hours) were prepared from manganese carbonate synthesized from sodium carbonate and manganous sulfate. The comparison of the drain tests of C-H-8, C-H-9, C-H-11, and C-H-12 shows these samples to be very similar and indicates the probability of 5 to 6 hour and 110 hour performance of C-H-8 and C-H-9 after these samples have been ball milled. Sample C-H-11, which was ground in a mortar before battery fabrication, gave a battery life of 1.8 and 91 hours for a bobbin weight of 8.3 grams. A portion of C-H-11 was ball milled dry for two hours and designated C-H-11B. Battery tests of C-H-11B were 6.2 and 110 hours and the bobbin weights were 9.0 grams. Similarly, C-H-11WB was ball milled wet and made into batteries which gave 6.3 and 108 hour performance. C-H-12, which was ground in a mortar, gave 1.9 and 100 hour battery life, whereas the ball milled portion of C-H-12, designated C-H-12B, had 5.2 and 121 hour battery life.

The great increase in battery life of the ball milled portions of C-H-11 and C-H-12 led to ball milling of the carbonate before decomposition. Two samples, C-H-15 and C-H-18, were prepared from ball milled

carbonate and the initial drain tests of 5.6 and 104 hours and 5.4 and 106 hours for the respective samples indicate the grinding was beneficial. Further ball milling of the products of these two reactions may better the drain tests.

The exact function of the ball milling is not known, but the physical appearance, apparent density, amount of electrolyte wetting solution necessary for good bobbin tamping qualities, and the bobbin weights all change when a given dioxide is ball milled. A general observation concerning apparent density is that if the density of the mortar ground sample is less than about 10 to 14 grams per cubic inch, the density after ball milling will approach this value, and conversely, if the density of the mortar ground sample is higher than 10 to 14, the density after ball milling will usually decrease to this value. The bobbin weights of ball milled samples were heavier than those of the corresponding mortar ground sample in every case but one.

The use of a fluid energy mill for the decomposition of the carbonate may increase the conversion due to simultaneous particle size reduction at the decomposition temperature. With air classification and recycle of oversize material, this type of mill is capable of producing a -325 mesh product in accordance with Signal Corps specifications. Should sufficiently high conversions be obtained, the acid leach for unreacted carbonate removal may be eliminated.

Although none of the manganese dioxide samples made by the thermal decomposition of manganese carbonate gave specification drain tests, the battery life of the best samples was close enough to specifications

to warrant further study. The stability of the dioxide produced by this type of reaction is very good; the delayed capacity tests of C-H-4, -5, -10, -11, -12, and C-H-16 showed very little deterioration of the dioxide after three months storage.

The bobbin weights of all the C-H- samples reported in Table I were one to two grams below the specified 9.5 to 10.5 gram limits and this low bobbin weight may well account for the lack of specification drain tests. Research to remedy this fault is desirable, if for no other reason than to eliminate the effect of bobbin weight on drain tests as a little known factor in dry cell performance. Bobbin weight and drain test data of samples C-H-11, -11B, -11WB, -12 and C-H-12B show the high drain tests of the ball milled portions increased 200 to 300 percent and the low drain tests increased 20 percent for a bobbin weight increase of less than 10 percent. While no prediction of similar increases in battery life for a like increase in bobbin weights can be made, the data shows the best battery tests were obtained from the heavier bobbins. The degree of particle size reduction and particle size distribution are probable variables which in part determine the bobbin weight of a given dioxide sample.

The thermal decomposition of manganese carbonate to yield battery active manganese dioxide has been the subject of several patents (5) but the reaction has not been demonstrated to produce a dioxide of sufficient activity to meet Signal Corps specifications. Commercial application of the reaction has been attempted by at least one large

battery manufacturer who reports the process not economically attractive when limited to small scale production. Improvement in the quality of the dioxide produced by this process to the point where it is competitive with electrolytic ore would in all probability change the economic feasibility of the reaction.

Permanganic Acid Oxidation Manganese Compounds

The permanganic acid oxidation of manganese carbonate was tried principally to determine the phase type of the resulting dioxide. The reaction products of C-M-1 and C-M-3 were evaluated by the Signal Corps micro-optical section as essentially gamma manganese dioxide. The low density of this material was probably a contributing factor to the extremely low bobbin weights obtained. The lack of any drain test performance of these samples probably indicates faulty cell construction or introduction of impurities, since almost any type of manganese dioxide, or for that matter, any manganese oxide will give at least a few hours of battery life. The chemical analysis of the samples C-M-1 and C-M-2 show a good manganese content but poor oxygen content; this information plus the gamma dioxide micro-optical report apparently means the presence of a considerable amount of unreacted manganese (divalent) carbonate. Insufficient quantities of the two samples were prepared for ball milling, acid leaching for carbonate removal or retesting. No commercial application of this reaction type is probable due to the high cost of synthesizing permanganic acid.

The permanganic acid oxidation of manganous sulfate solutions yielded a product which had a battery life about like Gold Coast ore.
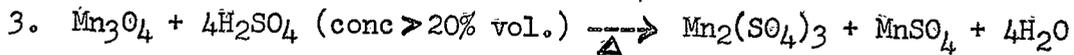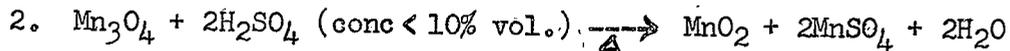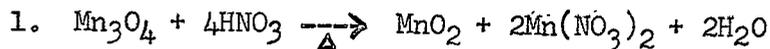
The effect of ball milling a portion of M-S-4 was noteworthy: from Table I, the data on M-S-4, which was ground in a mortar, read, density, 13.6; bobbin weight, 8.2; high drain, 1.4 hours; and low drain, 122 hours, while the data of the ball milled portion, M-S-4B, read, density, 10.5; bobbin weight, 9.0; high drain, 5.3 hours; and low drain, 82 hours. The manner in which the data varies makes an analysis somewhat difficult. The density decreased, yet the bobbin weight increased, the high drain life increased by a factor of almost four and the low drain life decreased by more than 30 percent. The capabilities of the dioxide produced by this synthesis are somewhat better than Gold Coast ore, but not sufficiently better to justify the cost of the permanganic acid.

Thermal Decomposition of Manganous Nitrate Solutions

The samples N-H-8 and N-H-9 are typical of the thermal decomposition of manganous nitrate. The dioxide so produced has always been classified as beta phase material and the relatively poor battery tests verify the phase determination. This reaction is more attractive as a source of pure reagent grade manganese dioxide than as a source of battery active manganese dioxide.

Nitric Acid Leach of Hausmannite (Mn_3O_4)

The reaction of hausmannite with nitric acid was reported by Nickelson (1) as the "nitric acid oxidation of hausmannite." The yields and reaction products of the reactions reported in Table II (O-H- series) lead to the verification of the following reaction:

1. $Mn_3O_4 + 4HNO_3 \xrightarrow{\Delta} MnO_2 + 2Mn(NO_3)_2 + 2H_2O$

2. $Mn_3O_4 + 2H_2SO_4$ (conc $< 10\%$ vol.) $\xrightarrow{\Delta} MnO_2 + 2MnSO_4 + 2H_2O$

3. $Mn_3O_4 + 4H_2SO_4$ (conc $> 20\%$ vol.) $\xrightarrow{\Delta} Mn_2(SO_4)_3 + MnSO_4 + 4H_2O$

The acid used, whether nitric or sulfuric, acts not as an oxidizing agent, but as a source of hydrogen ions. The x-ray diffraction analysis of many samples of hausmannite by Signal Corps personnel has established Mn_3O_4 as a chemical compound and not a physical mixture of MnO and MnO_2. However, the reactions one and two indicate the divalent nature of two of the manganese atoms of the hausmannite molecule. Reaction three is a side reaction which occurred to the extent of 5 to 10% in those reactions where the initial sulfuric acid concentration was 20% by volume. The reaction may be compared to the well known oxidation of ferrous to ferric ion by manganese dioxide in the presence of excess acid:

$$2Fe^{++} + MnO_2 + 4H^+ \longrightarrow Mn^{++} + 2Fe^{+++} + 2H_2O$$

$$2Mn^{++} + MnO_2 + 4H^+ \longrightarrow Mn^{++} + 2Mn^{+++} + 2H_2O$$

The formation of manganic (Mn^{+++}) ion was not observed to take place under any conditions of temperature or concentration when nitric acid was the acid used.

The results of Nickelson's work indicate that concentrated nitric acid produces a good product as far as chemical analysis is concerned, but at reaction temperatures higher than $115^\circ C$ an undesirable phase type (beta) is produced. This beta MnO_2 formation can come from only two sources, the hausmannite during the leaching or from the decomposi-

tion of the manganous nitrate formed. To eliminate the possibility of
the inclusion of beta material from the decomposition of manganous
nitrate, dilution of the nitric acid is recommended. The decomposition
temperature of aqueous solutions of manganous nitrate is a function of
the concentration of the nitrate. The stability of 50 percent man-
ganous nitrate solutions to temperatures as high as 157°C has been
demonstrated so no difficulty should occur if the manganous nitrate
effluent is controlled to a concentration of 50 percent or less.

The optimum concentration of nitric acid for the leaching of
hausmannite has not been determined. Commercialization of this process
would indicate use of the highest acid concentration which will not give
beta MnO_2 from decomposition of the manganous nitrate produced in the
leach.

The nitric acid used in all syntheses involving this reagent was
chemically pure, 69.2% acid. This acid was diluted to a concentration
of 200 ml. per liter for the reactions designated as O-H-18, -19, -20,
-23. The battery tests of this group approximate Gold Coast ore per-
formance. The hausmannite used in these syntheses was of doubtful purity.
The hausmannite made by carbon reduction of beta MnO_2 was incomplete and
introduced beta MnO_2 into the product. The carbon arc reduction of
MnO_2 to produce hausmannite was not very successful since the leached
product was essentially beta, with only minor phases of gamma-rho
dioxide present. An essentially pure hausmannite was produced by thermal
reduction of beta MnO_2 (95% pure) at 1100°C. The battery tests and
analytical data for O-H-36 indicate the importance of using a pure

Mn_3O_4 in the reaction. The drain tests on O-H-36 of 5.9 and 128 hours closely approach a specification grade dioxide. The capacity maintenance of this material is fairly good; the three months test of 118 hours indicates a rather stable dioxide.

Generally good conversion was effected on all nitric acid leaches of hausmannite with the samples containing 85 to 95% O_2 as MnO_2. The exception was a sample run at room temperature where less than five percent of the hausmannite reacted to form MnO_2. This latter trial verified Nickelson's conclusions that heat is essential in initiating the reaction, and as a result, all reactions were run near the boiling point of the solution. Most of the hausmannite reacted in the first five to ten minutes of contact with the acid as indicated by a rapid increase in temperature for this period of time. The reaction could probably be made to take place almost instantaneously by raising the reaction temperature to $120^{\circ}C$ or higher. The higher temperatures could be obtained by running the reaction under pressure, thereby elevating the boiling point of the solution. As previously discussed, the maximum temperature should not exceed the decomposition temperature of the manganous nitrate present in the leach solution.

Another example of this effect of purity of the hausmannite can be seen by comparing the battery tests and chemical analysis of O-H-36 with O-H-45. The latter sample was prepared from hausmannite made by thermal reduction at $1250^{\circ}C$ of beta MnO_2 of 99.6% purity. The drain tests of O-H-45 of 6.4 and 139 hours exceed both high and low drain specifications and are the best drain tests for any nitric acid leach of hausmannite.

There is no question as to the ability of this reaction to produce a battery active MnO_2 which will meet Signal Corps specifications for initial drain tests and the delayed capacity tests of O-H-36 indicate the probability that this material will meet the Signal Corps specifications of 85% of the initial drain tests on 1 year's storage at 70°F and 50% relative humidity. To produce such an active material the following reaction conditions should be observed:

1. Hausmannite of high purity should be used.

2. Reaction temperature, for nitric acid concentrations up to 70%, should be above 60°C and preferably near the boiling point of the solution, but below the decomposition temperature of the manganous nitrate formed in the reaction.

3. Reaction time is a function of concentration of reagents, but should be long enough to produce a dioxide having an oxygen content of 85% or higher.

4. The nitric acid concentration may be almost any value up to 70%. The law of mass action favors the use of more concentrated solutions. An acid concentration high enough to cause decomposition of the manganese nitrate formed in the leach is undesirable. The use of nitric acid containing appreciable quantities of dissolved NO_2 is also undesirable, since an aqueous solution of this gas reduces MnO_2 to manganous ion.

Sulfuric Acid Leach of Hausmannite

The battery tests of O-H-21, -22, and O-H-30 seem to indicate that sulfuric acid is an undesirable acid for the reaction with hausmannite

to produce a high grade battery active dioxide. These results are by no means conclusive, and as will be shown later in the section on Sulfuric Acid Leach of Mn_2O_3, the use of sulfuric acid in leaching hausmannite to produce good battery active ore is not only feasible, but is a practical way of combining chemical and electrolytic MnO_2 production. The sulfuric acid concentration used in the above syntheses was 200 ml. of 95 percent H_2SO_4 per liter of water. The reaction followed those mechanisms outlined on page 19 for sulfuric acid. Manganese dioxide was produced, but in less than the theoretical quantities. The formation of the dark red manganic ion precludes the reaction three, page 19. Micro-optical examination showed a predominance of the alpha phase dioxide for all sulfuric acid leaches in the O-H- series where the sulfuric acid concentration was 20% by volume. Battery tests of alpha MnO_2 are generally unsatisfactory, usually considerable lower than the battery life of Gold Coast ore. The use of acid concentrations of less than ten percent would probably produce manganese dioxide comparable to that produced by nitric acid leaches. This prediction is not made from analyzing data on sulfuric acid leaches of hausmannite, but from the sulfuric acid leaches of bixbyite (Mn_2O_3), a compound that reacts almost identically with hausmannite.

Nitric Acid Leach of Bixbyite (Mn_2O_3)

Bixbyite is prepared in the same manner as hausmannite but at lower temperatures (600 to 900°C). Pure bixbyite was produced by thermal reduction of beta manganese dioxide (99.6% pure) at 710°C for 72 hours. The lower temperature necessary for the formation of

bixbyite as compared with the hausmannite synthesis makes bixbyite a somewhat more desirable oxide for the type of reaction outlined below:

$$Mn_2O_3 + 2HNO_3 \longrightarrow MnO_2 + Mn(NO_3)_2 + H_2O$$
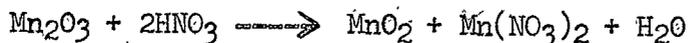
The added advantage of producing only one mol of manganese nitrate per mol of manganese dioxide from the leach of bixbyite also favors the use of this oxide over hausmannite.

The first syntheses of battery active dioxide from bixbyite were designated O-H-24, -25, and O-H-28. The technical grade Mn_2O_3 used in these syntheses contained five to ten percent impurities, of which Si, Al, Fe, K, and Mg are present to the extent of 1, 1, 2, .3-1, and 0.8 percent respectively. Since Si is present as SiO_2 of $SiO_3^=$, Al as Al_2O_3, and Fe probably as the oxide, the total impurities are considerable. The presence of silica or silicates makes the probability great that this technical grade bixbyite was prepared by the thermal reduction of Gold Coast ore. The battery test of the first dioxide prepared from this technical grade bixbyite were not outstanding but were very encouraging when the chemical analysis of the samples were considered. The oxygen content of these samples was about 80 to 85 percent, and the manganese analysis only 54 to 56 percent. The battery tests of O-H-28 of 5.3 and 124 hours were good enough to warrant a full scale investigation of leaching bixbyite with nitric acid. Samples O-H-31, -32, and O-H-34 verified the results of the first bixbyite leaches. The specification high drain tests of O-H-32 and O-H-34 are attributed to ball milling these samples before battery fabrication. The battery tests of O-H-28 (5.3 and 124 hrs.) which was

ground in a mortar, and the tests of the same material, O-H-28WB
(6.0 and 131 hours) which was ball milled, illustrate the benefits of
ball milling.

A relatively pure bixbyite, prepared by thermal reduction of
99.6 percent beta manganese dioxide at 910°C for 18 hours was used in
the reaction designated O-H-42. The reaction conditions of O-H-42
are almost identical to those of O-H-32 with the exception of the bix-
byite purity. The comparison of initial drain tests of O-H-32 (6.5
and 109 hours) and O-H-42 (6.2 and 142 hours) shows a 30 percent
increase in low drain performance due to the use of the chemically
purer bixbyite.

The similarity of the reaction of hausmannite and bixbyite with
nitric acid to form battery active dioxide is shown by comparison of
the drain tests of O-H-42 (6.2 and 142 hours) which was synthesized
from bixbyite, and O-H-45 (6.4 and 139 hours) which was synthesized
from hausmannite. This similarity is of extreme value since it
greatly decreases the degree of temperature control necessary in either
the synthesis of bixbyite or hausmannite. If, during the synthesis of
bixbyite, the temperature should get so high as to decompose some or
all of the bixbyite to hausmannite, the quality of dioxide produced
from this mixture will be as good as from pure bixbyite.

Sulfuric Acid Leach of Bixbyite

The leach of technical grade bixbyite with sulfuric acid at a
concentration of 200 ml per liter of water was unsuccessful in pro-
ducing a good battery active dioxide. Micro-optical examination of

the two samples (O-H-26 and O-H-27) made at the latter concentration
of sulfuric acid showed essentially alpha manganese dioxide and the
battery tests were correspondingly poor. The formation of manganic
ion was noted during the leach of both O-H-26 and O-H-27. To avoid
the formation of manganic ion, the sulfuric acid concentration was
reduced to 100 ml per 2.4 liters of water in O-H-33 and O-H-41. These
reactions produced a dioxide having good initial activity with drain
tests of about 6.0 and 115 hours. Poor conversion of the bixbyite to
dioxide was effected in O-H-41 since the oxygen content was but 81 per-
cent. The drain tests of O-H-41 were good enough (6.2 and 120 hours)
to warrant the prediction that specification grade dioxide can be
produced by the sulfuric acid leach of bixbyite (and hausmannite since
it reacts similarly to bixbyite). The determination of the highest
acid concentration which is tolerable is of the utmost importance to
the success of this reaction. The acid concentration of 200 ml per
liter produces good conversion of bixbyite to dioxide, but the product
is of an undesirable phase type. Concentration of 100 ml per 2.4 liters
produce a dioxide having good battery activity, but the conversion in
a reasonable reaction period is rather low.

Commercial Possibilities of the Nitric Acid Leach of Bixbyite

As previously stated, the ultimate goal of this Signal Corps
sponsored project is the development of a commercially feasible chemical
process for the manufacture of a battery grade manganese dioxide which
will meet or exceed Signal Corps specifications for synthetic dioxide.
A process which will allow recycle of chemical reagents ordinarily is

the most desirable type, the exception being when the reagents involved are extremely cheap. The nitric acid leach of bixbyite or hausmannite is a process which lends itself to a cyclic type of operation. The following reactions will illustrate the sequence of reactions necessary for producing a specification grade manganese dioxide from a low grade pyrolusite such as is found in abundance around the Butte, Montana area:

1. MnO_2 (aqueous suspension) + $2NO_2$ $\xrightarrow{\Delta}$ $Mn(NO_3)_2$

2. $Mn(NO_3)_2$ $\xrightarrow{\Delta}$ MnO_2 + $2NO_2$ (recycle)

3. $2MnO_2$ $\xrightarrow{\Delta}$ Mn_2O_3 + $\frac{1}{2}O_2$

4. Mn_2O_3 + $2HNO_3$ $\xrightarrow{\Delta}$ MnO_2 + $Mn(NO_3)_2$ (recycle

These reactions are simplified since purification steps to effect the removal of impurities (principally iron in most ores) are not included.

Reaction 1 is the leach of the ore by aqueous solutions of gaseous NO_2 which is oxidized by MnO_2 to nitrate ion and the manganese is reduced to manganous ion. The side reaction of NO_2 occurs also:

$3NO_2$ + H_2O $\longrightarrow$ $2HNO_3$ + NO

This side reaction is beneficial in extracting that portion of the manganese present as MnO ($MnCO_3$, Mn_2O_3, Mn_3O_4, etc.). However, the nitric acid present will extract most of the iron present in the ore. The final leach solution will contain manganese and other nitric acid soluble metallic ions as nitrates plus some free nitric acid. Only pilot plant studies on a specific ore will establish the best purification treatment. Iron is generally removed by adjusting the pH of its aqueous solutions to about 3.5 to 6.5, blowing the solution with air

to oxidize the ferrous ion to ferric ion which will then precipitate
as $Fe(OH)_3$. The iron-free manganous nitrate solution is concentrated
and decomposed according to reaction 2. The decomposition temperature
of manganous nitrate varies with the concentration and pressure, but
a temperature of 200°C would effect complete decomposition of manga-
nous nitrate. Any Ca, Na, K, or Mg present as nitrates will remain as
such since they are quite stable at this temperature. The undecomposed
nitrates may be removed from the MnO_2 of reaction 2 by water washing.

The MnO_2 from reaction 2 is decomposed to bixbyite by calcining
at 600 to 900°C. The bixbyite is leached with nitric acid to form a
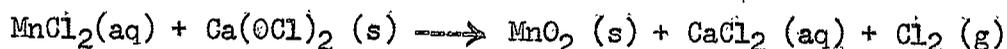dioxide of high quality as outlined in the previous section.

The recycle of the nitrogen dioxide from reaction 2 is an impor-
tant feature of this process. Part of the NO_2 is recycled to the ore
leach step (reaction 1) and part is absorbed in water in the presence
of air to form the nitric acid used in the leach of reaction 4. The
manganous nitrate produced in reaction 4 is recycled to reaction 2.
The nitrogen loss in the system occurs when the Ca, Na, Mg, or K
nitrates are washed out of the dioxide produced in reaction 2. These
nitrates could be concentrated and sold as fertilizer material if they
represent an appreciable nitrogen loss. Make up NO_2 is probably most
economically produced by the catalytic air oxidation of anhydrous
ammonia.

Cost calculations on this process based on a Butte pyrolusite,
current reagent costs as listed in Chemical and Engineering News, and
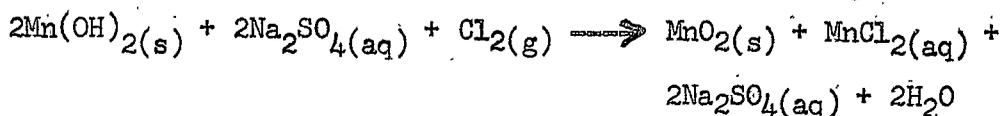a production rate of ten tons per day of battery active dioxide indi-

cate a profitable selling price of 15 to 20 cents per pound of dioxide. The current market price of synthetic manganese dioxide which will meet Signal Corps specifications is around 30 cents per pound.

Chlorine Oxidation of Manganese Hydroxide

Fahlgren (3) has reported the reaction of sodium and calcium hypochlorite with manganous salts to produce a battery active manganese dioxide. The hypochlorite oxidation of the manganous salts may be represented by the following reactions:

$$MnCl_2(aq) + Ca(OCl)_2 (s) \longrightarrow MnO_2 (s) + CaCl_2 (aq) + Cl_2 (g)$$

$$Mn(NO_3)_2 (aq) + Ca(OCl)_2 (s) \longrightarrow MnO_2(s) + Ca(NO_3)_2(aq) + Cl_2(g)$$

$$Mn(NO_3)_2(aq) + 2NaOCl(aq) \longrightarrow MnO_2(s) + 2NaNO_3(aq) + Cl_2(g)$$

A somewhat similar reaction was proposed to eliminate the intermediate formation of the hypochlorite. The reaction of manganese salts with sodium hydroxide to form manganese hydroxide followed by the chlorination would eliminate the synthesis of the sodium hypochlorite. The reactions S-Cl-1 and -2 are the reaction of manganous sulfate with caustic to form manganese hydroxide followed by chlorine oxidation:

$$2MnSO_4(aq) + 4NaOH(aq) \longrightarrow 2Mn(OH)_2(s) + 2Na_2SO_4(aq)$$

$$2Mn(OH)_2(s) + 2Na_2SO_4(aq) + Cl_2(g) \longrightarrow MnO_2(s) + MnCl_2(aq) +$$
$$2Na_2SO_4(aq) + 2H_2O$$

The reactions were run two stage as shown with cooling between the manganese hydroxide formation and the oxidation step. The pH of the oxidation reaction was observed at three hour intervals and the pH, initially at 11.9, fell rapidly to the acidic region and slowly approached a final pH of 1.8. The pH change to the acidic region is

accounted for by noting the reaction products of the following reaction:

$$Cl_2 + H^+ + OH^- \rightleftharpoons HCl + HOCl$$
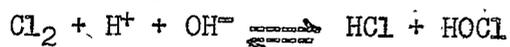
The reaction proceeds to the right if sufficient base is present to neutralize the HCl formed. In the case of chlorine oxidation of manganese hydroxide, the manganese hydroxide functions both as a base to neutralize the HCl and as a reducing agent for reaction with the hypochlorous acid.

As noted above, the pH of the reaction approached 1.8 after passing chlorine through the solution for a 24 hour period. A duplication of S-Cl-1 on a longer scale was attempted, but the chlorine supply was exhausted after six hours of oxidation. The pH measurements on this reaction after six hours was 2.7 and after an additional 18 hour agitation with no further chlorination, the pH was 1.8. The presence of any significant amounts of manganese hydroxide at such a low pH was not thought to be possible, however, examination of the solid residue showed a considerable amount of the white hydroxide. This information leads to some doubt that pH readings could be used as a satisfactory means of determining the endpoint of the reaction.

The reactions S-Cl-1 and S-Cl-2 differed only in the concentration of the reagents, S-Cl-2 being twice as concentrated as S-Cl-1. The battery tests and chemical analyses of these samples were similar in all respects. The initial high drain tests of S-Cl-1 (7.2 hours) and S-Cl-2 (7.6 hours) were far better than those of other chemically pre-pared manganese dioxide samples reported in Table I.

The stability of the manganese dioxide produced by chlorine oxida-

tion of manganese hydroxide has not been determined since three months

tests are not available at this time. The questionable stability stems

from Signal Corps observations that some manganese dioxide which shows

high initial activity sometimes reverts to a more stable, but less

active phase type of dioxide after prolonged contact with the electro-

lyte of the battery. A large decrease in battery performance after

three months storage may indicate such an unstable dioxide.

The formation of manganese dioxide in the presence of alkali metal

ions is sometimes conducive to an undesirable phase type of dioxide.

In the S-Cl- reactions, a considerable amount of sodium ion is present.

The specification initial drain tests of both S-Cl-1 and S-Cl-2 do not

indicate an unfavorable dioxide structure, however, the chlorine oxi-

dation of manganese hydroxide in the absence of sodium ion was run to

establish the function of the sodium ion in the reaction. The reaction

OH-Cl-1 was performed in a manner similar to the S-Cl- reactions with

the exception that the Na_2SO_4 was removed from the precipitated man-

ganese hydroxide before the chlorine oxidation. This reaction proceeds

as follows:

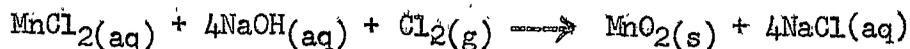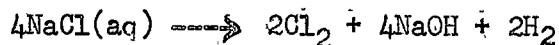$$2Mn(OH)_{2(s)} + Cl_{2(g)} \longrightarrow MnO_{2(s)} + MnCl_{2(aq)} + 2H_2O$$

The analytical and drain test data of OH-Cl-1 are similar to that of

the S-Cl- products except the high drain test of OH-Cl-1 was only 5.0

hours. The comparison of three months tests of OH-Cl- and S-Cl- may

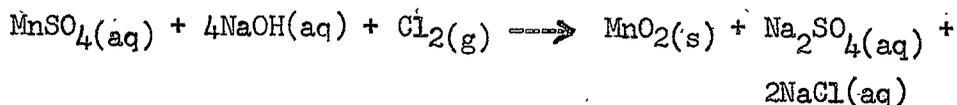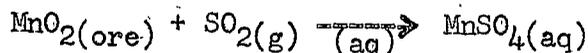determine whether sodium is harmful in this type of reaction.

Until the capacity maintenance of the batteries made from this

type of dioxide is evaluated, very little can be said for the commercial

possibilities of the chlorine oxidation of manganese hydroxide. The most probable commercial syntheses to produce manganese dioxide from this type of reaction may be outlined as follows:

Source of caustic and chlorine is the electrolysis of sodium chloride.

$$4NaCl(aq) \longrightarrow 2Cl_2 + 4NaOH + 2H_2$$

$$2H_{2(g)} + 2Cl_{2(g)} \longrightarrow 4HCl(aq)$$

$$MnO_{2(ore)} + 4HCl_{(aq)} \longrightarrow MnCl_{2(aq)} + 2H_2O + Cl_{2(g)}$$

$$MnCl_{2(aq)} + 4NaOH_{(aq)} + Cl_{2(g)} \longrightarrow MnO_{2(s)} + 4NaCl(aq)$$

The use of manganese sulfate as in the S-Cl- reactions offers no particular advantage unless a cheap source of SO_2 is available. The reaction of SO_2 with pyrolusite to form manganese sulfate followed by the hydroxide addition and oxidation may be as follows:

$$MnO_{2(ore)} + SO_{2(g)} \xrightarrow[(aq)]{} MnSO_4(aq)$$

$$MnSO_{4(aq)} + 4NaOH(aq) + Cl_{2(g)} \longrightarrow MnO_2(s) + Na_2SO_{4(aq)} +$$
$$2NaCl(aq)$$

The use of SO_2 instead of HCl for extraction of the manganese from the ore allows net production of chlorine which may allow better integration with an existing chlorine consuming industry.

SUMMARY

1. Ball milling manganese dioxide made by thermal decomposition of manganese carbonate or by the nitric acid leach of bixbyite usually improves the battery performance of the dioxide.

2. Manganese dioxide made by the thermal decomposition of manganese carbonate gives better battery performance than Gold Coast ore.

3. Manganese dioxide which will meet initial drain test specifications can be synthesized by the nitric acid leach of bixbyite or hausmannite, and by the chlorine oxidation of manganese hydroxide.

4. In the sulfuric acid leach of bixbyite, the sulfuric acid concentration is critical. Acid concentrations of 20 percent by volume or greater produce an inactive dioxide; acid concentrations of less than 10 percent by volume produce a dioxide which gives a battery performance superior to Gold Coast ore.

-34-

ACKNOWLEDGEMENT

LITERATURE CITED

(1) Nickelson, R. L., M. S. Thesis, Montana State College, 1952.

(2) Davidson, J. A., M. S. Thesis, Montana State College, 1952.

(3) Fahlgren, C. E., M. S. Thesis, Montana State College, 1953.

(4) Sadagopachari, R., M. S. Thesis, Montana State College, 1953.

(5) Bolen, M. and B. H. Weil, Literature Search on Dry Cell Technology, Atlanta, Engineering Experiment Station Georgia Institute of Technology, 1948.

APPENDIX

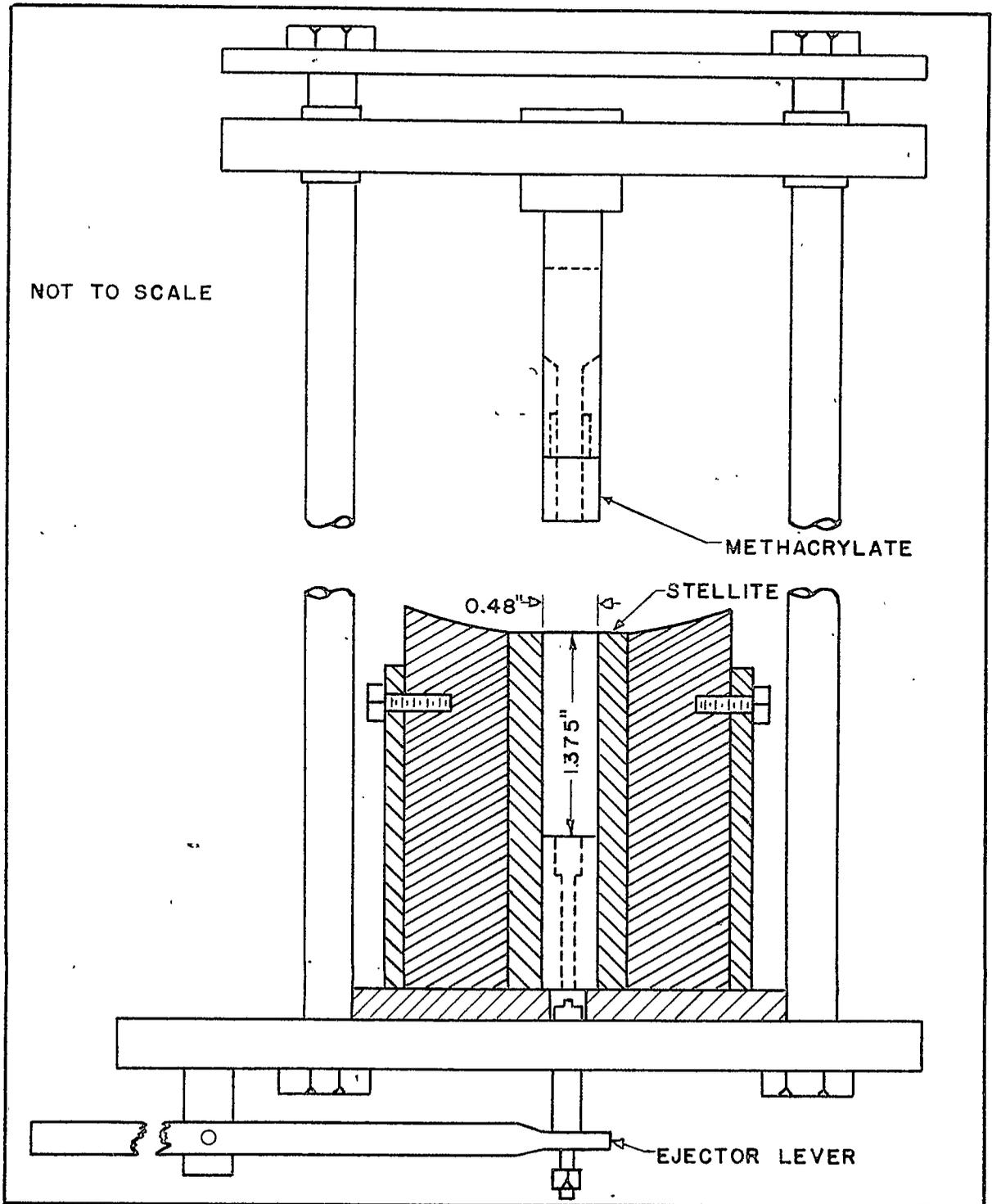NOT TO SCALE

METHACRYLATE

STELLITE

0.48"

1.375"

EJECTOR LEVER

Figure 1. Bobbin Tamping Apparatus
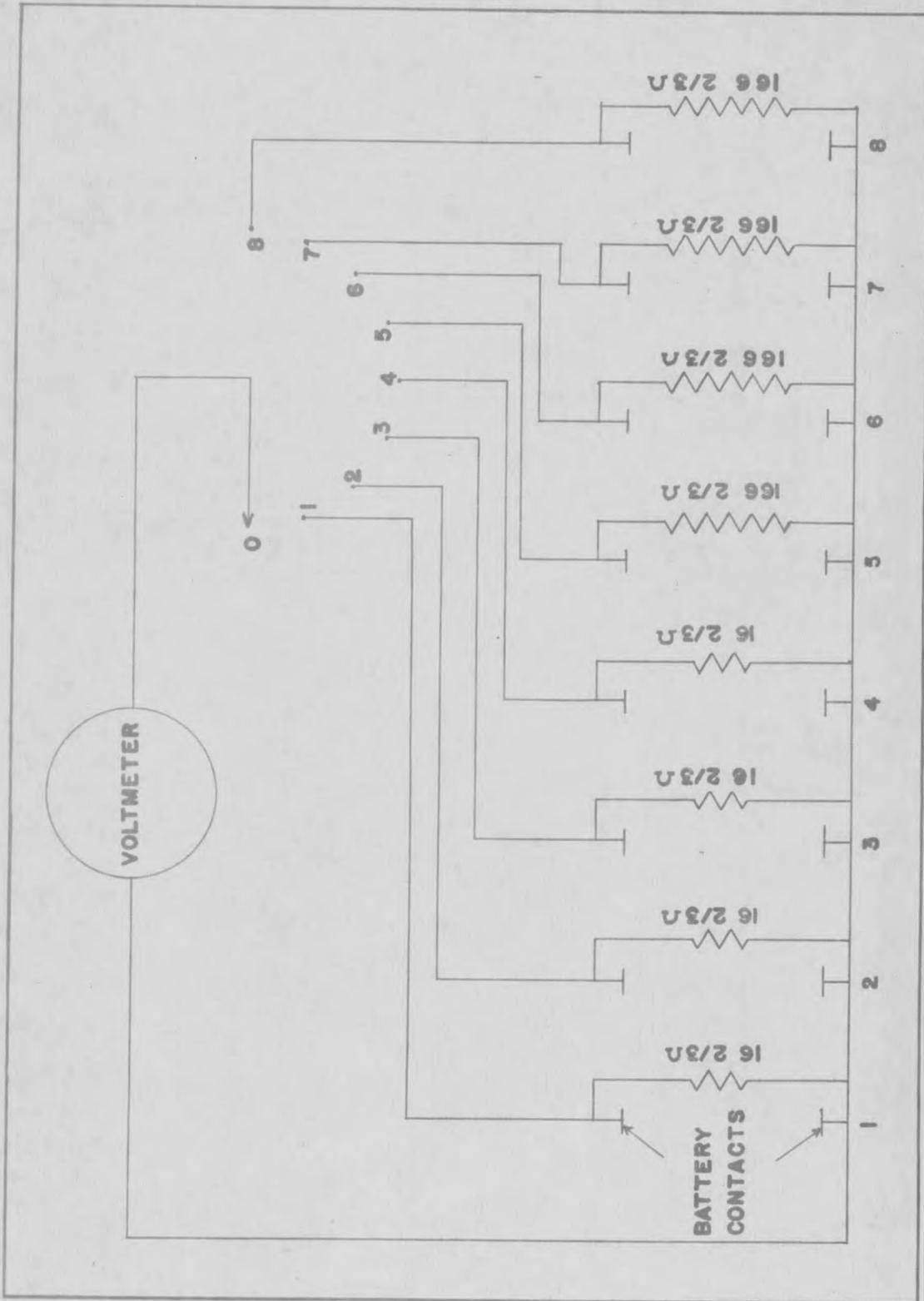
Figure 2. Schematic Diagram of Battery Test Rack

TABLE I
ANALYTICAL AND TEST DATA

Sample	O_2 as % MnO_2	% Mn	% H_2O	pH	gm/in^3	Bobbin wt. (gms)	Initial 16 2/3	Drain Tests 166 2/3	Three months test 166 2/3
C-H-3	88.0	57.2	.4	4.1	7.5	8.1	3.2	92	60
-4	60.3	54.5	1.4	6.4	7.8	8.0	3.9	70	62
-5	88.6	57.5	.7	6.2	8.8	8.2	5.1	122	110
-6	87.5	58.4	1.5	6.7	6.2	7.9	.3	37	15
-7	92.2	56.9	2.2	4.5	6.7	8.1	.1	33	13
-8	93.3	54.5	1.2	5.2	7.6	8.2	1.7	83	6
-9	87.5	56.8	1.1	4.2	9.9	8.3	1.7	103	45
-10	89.1	52.5	1.0	3.9	7.8	8.5	6.3	111	103
-11	93.0	58.8	.8	4.5	7.6	8.3	1.8	91	92
-11B	92.0	58.8	.8	4.5	11.8	9.0	6.2	110	102
-11WB	92.0	58.8	.8	4.5	10.1	9.0	6.3	108	85
-12	88.7	58.7	2.2	7.9	7.3	8.3	1.9	100	96
-12B	88.7	58.7	2.2	7.9	12.4	8.9	5.2	121	99
-13	72.2	58.0	.8	6.4	6.9	8.0	4.7	80	65
-13B	72.2	58.0	.8	6.4	10.6	8.7	4.6	102	84
-14	56.1	64.0	.3	6.0	5.8	8.2	.9	17	12
-15	91.2	59.8	.7	3.7	11.8	8.8	5.6	104	84
-15AM	91.2	60.2	.3	4.9	11.7	8.7	-	17	50
-16	88.7	59.8	1.7	7.0	10.4	8.7	6.2	110	102
-18	89.0	59.8	.0	7.1	11.5	8.7	5.4	106	90
C-M-1	77.5	58.4	6.8	4.2	7.0	7.7	0	0	0
-3	84.0	54.5	4.7	5.4	2.6	6.7	0	0	0
M-S-3	93.6	57.9	.6	4.2	18.3	8.8	.8	49	14
-4	92.6	58.3	3.0	6.6	13.6	8.2	1.4	122	31
-4B	87.0	58.8	3.0	6.6	10.5	9.0	5.3	82	85
-6	92.6	60.2	1.0	6.5	13.4	9.4	4.8	110	83
N-H-8	92.5	60.1	.5	7.1	29.0	10.2	2.3	50	-
-9	96.5	57.0	.3	4.9	19.0	10.0	2.9	70	-
O-H-18	97.5	57.3	.5	6.6	10.0	8.4	4.7	112	-
-18B	97.5	57.3	.5	6.6	16.8	9.7	4.5	108	86