Chemical synthesis of battery-active manganese dioxide
by Jack A Davidson

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
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manganese dioxide which would meet specifications tentatively established by the United States Army
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syntheses discussed in this paper was the hot spraying of permanganic acid on a granite slab at
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exceed low drain specifications with 131.5 hours. Tests indicate that further study could produce a
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MANGANESE DIOXIDE

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A THESIS

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Approved:

Lloyd Berg

Head, Major Department

Lloyd Berg

Chairman, Examining Committee

J. A. Nelson

Dean, Graduate Division

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ABSTRACT

The purpose of this investigation was to determine a suitable chemical synthesis for a battery-grade manganese dioxide which would meet specifications tentatively established by the United States Army Signal Corps and which could be adapted to commercial ores. From a literature review of the known chemical syntheses for manganese dioxide, eighteen were selected for study. Samples were synthesized by these using laboratory chemicals and given standard Signal Corps tests. Due to time and scope of the study, optimum variable conditions were not determined, but the possibilities of these syntheses as indicated by micro-optical analysis and battery tests were established.

Since a joint investigation was conducted, the results for nine of the syntheses are presented in this thesis and the remainder are presented in a thesis by R. L. Nickelson. The most promising of the syntheses discussed in this paper was the hot spraying of permanganic acid on a granite slab at 150-200^{0}C. Although material produced by this method did not meet all specifications, battery life did exceed low drain specifications with 131.5 hours. Tests indicate that further study could produce a manganese dioxide which would meet Signal Corps Specifications.

I INTRODUCTION

Research within the battery industry has shown that seven basic types of phases of manganese dioxide (alpha, beta, delta, epsilon, gamma, rho, and ramsdellite) can be detected by x-ray diffraction and the electron microscope. There are but two polymorphs of manganese dioxide - the tetragonal form (if well crystallized, it is called pyrolusite or beta manganese dioxide) and the orthorhombic form (the mineral ramsdellite). The seven types designated by the Signal Corps are modifications of these two basic polymorphs - called phases - although they are not phases in the strict sense of the word. Battery tests have shown that the imperfectly crystallyzed form designated as gamma has superior properties as a depolarizer for dry cells and will give longer life than any of the six remaining structures. Although somewhat inferior to gamma, imperfectly crystallized rho possesses sufficiently suitable depolarizing properties so that a predominant mixture of the two will meet specifications for natural ore. The remaining five types ordinarily show poor depolarizing qualities and fail to meet specifications.

The only good natural source of this gamma material is located on the African Gold Coast. Due to the present world situation, the United States Signal Corps has stimulated research within the battery industry to develop a method for converting the commercial ores within the United States to the gamma structure. Several good sources of manganese ore have been located within the United States. Among these are pyrolusite deposits at Phillipsburg, Montana; and a high-grade of rhodochrosite near Butte, Montana.

Up to the present time, the majority of the work sponsored by the Signal Corps has been done with the electrolysis of manganous sulfate solu-

tions. Research in this field has been carried out by A. M. Magnuson (2) and The Tennessee Corporation (5), and has been reported to be successful in producing a high quality gamma manganese dioxide. At the present time plants capable of commercial production using this process are being constructed. However, the Signal Corps has felt that further research could possibly develop a cheaper chemical process and has contracted Montana State College to make such an investigation.

The problem was approached by making a literature review to determine the known chemical methods for producing manganese dioxide and select those which seemed feasible. Literature which was reviewed included A Literature Search on Dry Cell Technology (1), The Chemical Elements and Their Compounds (4), and several inorganic chemistry textbooks. This material indicated that chemical synthesis for manganese dioxide dry cell depolarizers was patented at least as far back as 1913. However, none of these are being used commercially to produce gamma manganese dioxide as indicated by present literature.

From this search eighteen type reactions were selected for trial. Samples were then synthesized and given the standard Signal Corps tests which included determination of pH, density, available oxygen, manganese content, moisture, battery tests in "A" cells at high and low drain, x-ray diffraction, and electron microscope analysis. Data from the latter two tests were received from the Squier Signal Laboratory of the United States Army Signal Corps and The Eagle-Picher Company of Joplin, Missouri.

This problem has been investigated jointly and the data received have been divided into two portions. The findings for nine of the eighteen type reactions which were studied are given in this thesis while the remaining ones are discussed in a thesis by R. L. Nickelson (3).

II. MATERIALS AND METHODS

A. Materials

Reagents

Although the ultimate goal of this research is to develop a chemical synthesis for producing battery grade manganese dioxide from commercial ores, only laboratory grade chemical reagents were used in this study. Laboratory reagents were used so that the properties of the manganese dioxide from each reaction could be determined accurately. These data will be used in selecting a suitable process to be adapted to commercial ores.

In general, high grade reagents of a C. P. or reagent quality were used to minimize the presence of metallic ions which have been found to be extremely detrimental to battery life. One exception was the use of a technical grade manganous sulfate since large quantities of this reagent were consumed. A manganese analysis showed this material to contain 65.6 percent manganous sulfate which indicates the presence of large amounts of impurities. However, no excessive metallic contents were encountered as indicated by product analysis.

B. Methods

Synthesis

The methods of preparation for the various samples are shown in Table I. The most important variables which were encountered in this study were temperature, concentration, reaction time, and particle size. In some reactions tendencies were indicated as far as variables were concerned, but in no reaction has this study been extensive enough to determine optimum variable conditions. The scope of the investigation and time have prevented such deter-

minations.

In some cases absolute control of these variables was practically impossible. For example, in hot spraying reactions the temperature would fluctuate as the mist was passed over the granite slab due to the consumption of heat for reduction. In such cases the variables have been reported within limits.

Very little difficulty was experienced in obtaining the proper pH. In all syntheses except two this was accomplished by water washes. The two exceptions are pointed out in the discussion of results.

Battery Fabrication and Testing

Standard "A" size dry cells were constructed in accordance with standard cell assembly techniques. A mixture containing 80% MnO_2, 8% Shawinigan carbon black, and 12% NH_4Cl, were mixed in a ball mill for 20 minutes to assure a uniform consistency. This material was dampened with a solution containing 5.8% NH_4Cl, 8.6% $ZnCl_2$, and 85.6% H_2O until the proper tamping conditions were obtained.

From this mixture standard "A" bobbins were tamped in the apparatus shown in Figure 1. Due to the corrosiveness of the material, bakelite and polystyrene plastic were used in all parts which contacted the bobbin while the remainder was of steel construction. Before plastic dies were obtained, attempts were made to use nickel, but this was dissolved and contaminated the bobbins to such an extent that the results were not reproducible. The bobbins were wrapped in cotton gauze and set in zinc cans with a cold paste containing a ratio of 50 cc of a solution consisting of 23.7% NH_4Cl, 22.3% $ZnCl_2$, 0.1% $HgCl_2$, and 53.9% H_2O to 10.7 g of mixture containing 74.7%

cornstarch and 25.3% flour. A brass cap was pressed on the carbon anode, a paper disk was placed on top of the bobbin, and then it was sealed with wax.

After sitting 4 days these were discharged continuously through the test resistances shown in Figure 2. This test rack consisted of four 16 2/3 ohm resistances and twelve 166 2/3 ohm resistances which were connected to a voltmeter. The panel was constructed in two parts which were connected in parallel. To avoid repetition only 8 of the resistances are shown in Figure 1. A similar panel containing 8 low drain resistances was omitted from the drawing. The cut-off voltages or voltages at which the cells were removed from the rack were 1.13 for low drains and 1.0 for high drains.

Oxygen Analysis

Available oxygen determinations were made in accordance with Signal Corps methods and are reported as percent manganese dioxide. The determination was made as follows: To 0.2175 g of dried MnO_2 was added 50 cc of 0.20 N $Fe(NH_4)_2(SO_4)_2$ solution containing 175 cc of concentrated H_2SO_4 per liter. Another 50 cc of $Fe(NH_4)_2(SO_4)_2$ solution was pipetted into a second beaker to run as a control sample. Both samples were diluted to 200 cc with distilled H_2O and digested on a steam plate. After digestion they were readjusted to the original 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 as percent MnO_2 was then computed as 4 times the difference in volume of $K_2Cr_2O_7$ solution used in the sample and blank.

Total Manganese Analysis

Portions of MnO_2 weighing 0.10 g were dissolved in 10 ml of H_2O and 5

ml of concentrated HCl and the solution evaporated almost to dryness. To this was added 25 ml of concentrated H_2SO_4 and 10 ml of concentrated HNO_3 and the contents heated to expel all traces of brown fumes. After cooling the solution, 275 ml of H_2O and 3 g of $NaBiO_3$ were added. The excess oxidant was removed with a sintered-glass funnel and washed free of permanganate with hot H_2O. This filtrate was poured into 50 ml of oxalate solution and the excess was titrated with 0.1 N $KMnO_4$.

pH Determination

A sample of MnO_2 weighing 0.75 to 1.00 g was digested with 100 times its weight of distilled H_2O for 10 minutes under boiling conditions. The volume was readjusted and the solution cooled. The pH of the supernatant liquid was then determined with a Beckman pH meter.

Density

Densities were determined by running the sample through a Scott-Paint Volumeter until one cubic inch of sample had been obtained. The density was then reported as gm/in^3.

Moisture

A sample weighing 1-3 g was dried for 16 hours at a temperature of 110°C. The loss in weight was taken as the moisture content.

III. SPECIFICATIONS

The following specifications have been tentatively extablished by the Signal Corps as of November 17, 1949, for suitable synthetic battery grade manganese dioxide. This material was taken from bulletin SCL-3117-A.

Chemical Composition

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

If the available oxygen and total manganese percentages are recalculated so as to determine a possible oxygen deficient formula, the following formation shall be obtained: 88-95% $MnO_{1.92}$ to $MnO_{1.95}$.

Particle Size

The particles shall be of such size that 95 percent of the material shall pass a U. S. Standard Sieve #325.

Crystalline Phase

From crystallographic and micro-structural analyses there shall be evidence of a predominance of the imperfectly crystallized phase known as gamma MnO_2.

Particle Morphology

When examined at direct magnification from 5,000 to 20,000 diameters,

the particle shall present irregular shapes with no evidence of cleavage,

i.e. with non-rectilinear profiles having powdery or nebulous rather than

sharp, well-defined edges.

X-Ray Diffraction Pattern

The X-ray diffraction pattern shall be characterized by the diffuse-

line pattern of gamma MnO_2. For the purpose of this specification, the

significant lines (d) of gamma MnO_2 and their respective relative intensi-

ties (I) for iron radiation are as follows:

$\underline{d}$	$\underline{I}$
4.00	5
2.45	7
2.14	7
1.65	10
1.40	5

A reference chart showing the various diffraction patterns for all seven

types of manganese dioxide is given in Figure 3.

Capacity

The minimum allowable capacity for each "A"-size cell shall be as

follows:

	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 volt
Discharge Temperature	70°F (50% R.H.)	70°F (50% R.H.)
Battery Life	130 hours	5.5 hours

IV. RESULTS

The method of synthesis and test data for the manganese dioxide samples prepared for this study are shown in Tables I through III. In some cases the samples were of insufficient size to make density determinations and battery tests. Also, in the early part of the study before battery testing equipment had been set up at Montana State College, samples were sent to the Squier Laboratory for battery fabrication so the bobbin weights for these are unavailable.

This discussion of results has been grouped according to type reactions and includes the chemical formula plus the possibilities of this reaction for producing battery grade manganese dioxide, but does not include optimum variable conditions for previously stated reasons. In some cases the by-products are uncertain, but the reactions have been formulated in the most probable manner.

1. Calcium Hypochlorite Oxidation of Manganous Salts

$$MnCl_2 + Ca(OCl)_2 \longrightarrow MnO_2 + CaCl_2 + Cl_2$$
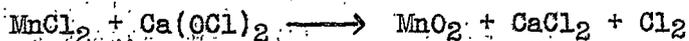
The variables in this reaction seemed to largely determine the type of structure which was obtained. These structures ranged from delta through epsilon and rho to a gamma-rho intermediate. The majority were of the gamma-rho type. Although these patterns were very close to gamma, the best battery drain tests were not as good as those which are reported for electrolytic samples, but were about the same as those received from Gold Coast ore. Incipient transformation between the epsilon and gamma-rho phases was indicated in the diffraction pattern for K-CH-2. Mr. William Nye of the Chemical-Physics Branch of Squier Signal Laboratory has given the following explanation

of incipient transformation between phases:

> "These manganese dioxide samples are being made under non-equilibrium conditions and are, therefore, mesocrystalline materials, that is they are very poorly crystallized. These phase types represent a continuous (or perhaps discontinuous) series of modifications of the basic phases. Based on their diffraction patterns, they are characterized as one or more of the seven phase types. Sometimes the diffraction patterns are intermediate between one phase and another. In these materials the electron microscope may also reveal a changing morphology. It is in these materials we use the term 'incipient crystallization or transformation'. In our use 'incipient' means beginning to change from one phase type to another."

The product density was far below the specified 20 g/in^3 which was typical of most precipitation reactions. Good oxidation was obtained and most samples were close to or above the specified available oxygen requirement, but the oxygen numbers were somewhat low. However, the specification for an oxygen number of 1.92-1.96 seems to be losing its significance since good battery materials have been obtained outside this limit.

Some of the materials synthesized by this reaction were found to give relatively good life on low drain as compared to high drain. In general, these samples were the ones with the light bobbin weights which would mean that density has more effect on the high drain test than on the low drain. This seems feasible since more rapid conductance is needed in the high drain test and therefore a more dense bobbin should be required.

Indications are that the best product can be obtained in a hot (around 70-80°C) concentrated solution with a relatively long reaction time, which is considered to be more than the few minutes obtained in the intermittent product removal as described in the synthesis of K-CH-4. This reaction was found to be exothermic.

The use of a 50 percent aqueous manganous nitrate solution for this

reaction instead of manganous chloride produced a rho diffraction pattern both at 80°C and 110-120°C. However, material produced at 30-50°C showed a gamma-rho structure. The material produced at 80°C was comparable in battery tests to the best material produced from manganous chloride while the others were not. The material produced at the highest temperature was found to be low in available oxygen. In all cases the density of the product was found to increase as the reaction temperature was decreased which was found to be generally true of all reactions.
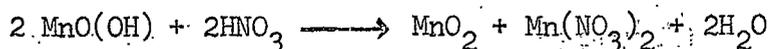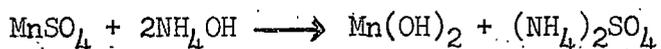
Since the rho and gamma diffraction patterns are similar as shown in Figure 3, heat treatments were tried as a means of making a conversion between the two. The gamma-rho material produced by the calcium hypochlorite oxidation of the manganous nitrate solution was used in this treatment. It was heat treated at 150, 170, and 220°C. From this meager data, plots of treating temperature versus battery life are shown in Figures 4 and 5. Although the phase of the product was not changed, the heat treatment at 170°C was found to improve the battery life of this material immensely. Battery life increased from 0.0 and 58 hours at room temperature to 3.9 and 102 hours at 170°C for high and low drains respectively. Although not so pronounced, similar results were obtained from the chlorination of carbonate as reported by Nickelson (3).

This investigation concludes that a battery material surpassing Gold Coast ore can be obtained by this type of reaction. However, the economics of such a process do not appear favorable unless calcium hypochlorite could be cheaply regenerated from the by-products.

Manganous sulfate could not be used in this reaction due to the high insolubility of the resulting calcium sulfate which would contaminate the

manganese dioxide. In a similar reaction sodium hypochlorite solution was used to oxidize manganous sulfate. The yield from this synthesis was so low that the amount was insufficient for battery fabrication. Micro-optical analysis indicated a rho and alpha structure.

2. Air Oxidation of Manganous Hydroxide Plus a Nitric Acid Oxidation

$$MnSO_4 + 2NH_4OH \longrightarrow Mn(OH)_2 + (NH_4)_2SO_4$$

$$2Mn(OH)_2 + 1/2 O_2 \longrightarrow 2MnO(OH) + H_2O$$

$$2 MnO(OH) + 2HNO_3 \longrightarrow MnO_2 + Mn(NO_3)_2 + 2H_2O$$

Air oxidation of manganous hydroxide by keeping it damp with water and allowing it to stand in air failed to produce manganese dioxide, but produced a brown lower oxide which was probably $MnO(OH)$ or $Mn_2O_3 \cdot H_2O$. Variations in reaction time and temperature failed to give favorable results. The majority of these were then oxidized with nitric acid to form a black manganese dioxide with good oxygen content. The yields obtained from this step were extremely low and not commercially feasible. Most of the products contained a rho or rho plus alpha structure, but did not give good battery performance although two samples (S-AD-4 and S-AD-5) did approach Gold Coast ore battery tests.

Attempts to obtain better oxidation by running the reaction in solution also failed to produce a good product after about 12 hours of oxidation. These oxidations were run by dispersing air in solutions containing manganous sulfate and ammonium hydroxide with and without nitric acid in the solution. The products and battery tests were comparable to those which were not oxidized in solution.

This type of reaction is not considered to be a feasible commercial

possibility.

3. Oxidation of Manganous Sulfate With Permanganic Acid

$$2HMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 + 3H_2SO_4$$
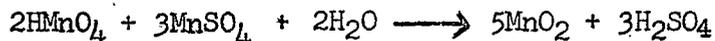
This reaction was run both at 25-30°C and 70-80°C with very little difference being found between the two. High available oxygen contents and relatively good densities were obtained considering the preparation was by precipitation, but the bobbin weights were not as heavy as would be expected from the bulk density. The bobbin weight, which is probably the more important of the two, does not seem to be a linear function of bulk density. This is partially true because the mesh of the samples on which the bulk densities were measured were not always the same, and partially due to a difference in tamping qualities between the various types of manganese dioxide.

Both products had a rho structure and gave battery life almost identical to that received from Gold Coast ore. No runs were made varying concentration or time because of difficulties in obtaining barium permanganate for the production of permanganic acid.

One of the biggest problems which would have to be solved in connection with any of the reactions involving permanganic acid would be a cheap synthesis for this material. Small scale tests were conducted in attempts to produce it by vacuum distillation of the anhydride (Mn_2O_7) from a mixture of concentrated sulfuric acid, potassium permanganate, and water. Although permanganic anhydride appeared to be formed in the reactor, only small traces of it were pulled over in the absorption train which was evacuated to 3-4 mm of Hg pressure. Attempts to oxidize manganese salts to permanganic acid with

BaO_2, PbO_2, and a mixture of concentrated H_2SO_4 failed to produce substantial quantities. From the standpoint of permanganic acid consumption, the reduction of manganous sulfate with it would be the most economical permanganic acid reaction since the majority of the manganese dioxide is produced from the sulfate.

Products from this reaction can be considered to be about comparable to Gold Coast ore.

4. <u>Thermal Reduction of Permanganic Acid</u>

$$4HMnO_4 \xrightarrow{\Delta} 4MnO_2 + 2H_2O + 3O_2$$
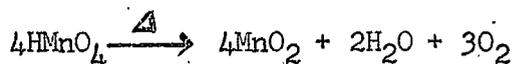
Thermal reduction of permanganic acid was conducted both by hot spraying an aqueous solution on a granite slab and by spontaneous decomposition at room temperature. That produced by the latter method showed a delta structure and did not give exceptionally good battery performance. The samples produced by hot spraying gave excellent low drain tests with one (M-H-3) exceeding synthetic specifications with 131.5 hours life. This was the only sample which surpassed this specification. The x-ray diffraction pattern for this material showed a poorly crystallyzed structure which is a property of the gamma phase. The sample was characterized as either gamma or beta, but the excellent low drain test tends to indicate a gamma structure. This sample was produced between 150 and 200°C.

A second sample produced by hot spraying permanganic acid at 150-275°C gave relatively good battery life considering it was characterized as alpha Mn_2O_3. The reaction temperature was obviously too high. The densities for both samples produced by hot spraying were good in comparison to that received from precipitation reactions. In general, those samples prepared by heat treatments were found to have good densities, but in these cases the

product density was also found to decrease as reaction temperature was in-
creased.

Although the low drain tests were one hour short of specifications, it
is thought that closer temperature control could possibly bring this up to
requirements. This reaction is considered to be the best of the nine dis-
cussed in this thesis, but as previously stated its success depends on the
possibility of finding a cheap supply of permanganic acid.

5. Reduction of Permanganic Acid With Hydrogen Peroxide

$$2HMnO_4 + H_2O_2 \longrightarrow 2MnO_2 + 2H_2O + 2O_2$$

Various concentrations of hydrogen peroxide and permanganic acid were
used in this synthesis, but a delta product was obtained in all cases.
Battery life was practically negligible for all the samples. The density of
the products were extremely low with $3-4$ g/in^3 which may partially account
for the poor battery tests. More dilute reagents seemed to slightly increase
the density, but it was so low that the effects of concentration were of
little value. In most reactions density increased with concentration, but
the vigorous reaction in this case is thought to be the reason for the diff-
erence. No possibilities are seen for this synthesis.

6. Ammonium Hydroxide Reduction of Potassium Permanganate

$$KMnO_4 + NH_4OH \longrightarrow NH_4MnO_4 + KOH$$

$$2 NH_4MnO_4 \longrightarrow 2MnO_2 + 4H_2O + N_2$$
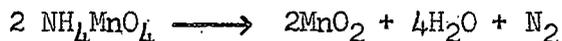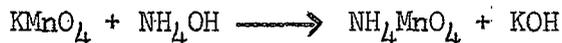
The products received from this reaction were brownish in color so one
of the samples was given a nitric acid wash to remove any lower oxides which
were present. The diffraction pattern of this sample was found to be alpha
while those samples prepared similarly without this wash showed a delta struc-

ture. Similar results were obtained with nitric acid washes as reported by Nickelson (3). This seems to indicate that nitric acid washes can cause a shift in phase structure.

The density of the products were very low with the most concentrated solution giving the denser product. The presence of a delta product in this synthesis disproves a previous belief that the presence of potassium ion always causes the production of an alpha structure. This result is further substantiated by other data in this thesis and in the one presented by Nickelson (3).

Due to the presence of potassium hydroxide as a by-product and excess ammonium hydroxide, the initial pH of this material was above the specifications. Very dilute sulfuric acid washes were used to bring it within limits.

Battery tests for these materials gave practically zero life in all cases. From these and micro-optical data this synthesis is considered impractical.

7. Fusion of Inactive Manganese Dioxide With Potassium Hydroxide Plus a Water Treatment

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$$

$$3\ K_2MnO_4 + 2H_2O \longrightarrow MnO_2 + 2KMnO_4 + 4KOH$$

All materials produced by this synthesis contained a beta-epsilon mixture which further substantiates that the presence of potassium ion does not always cause formation of alpha. The densities and oxygen contents were good, but the battery life did not equal that received from Gold Coast ore. Again, the only explanation for the good low drain test but poor high drain test for

O-KH-1 is its relatively low density as compared to the other two samples from this reaction. The use of potassium nitrate in the fusion as an additional oxidizing agent seemed to have practically no effect. No future is seen for this synthesis.

8. Toluene Reduction of Potassium Permanganate

$$2KMnO_4 + \text{(ring)}^{CH_3} \longrightarrow 2MnO_2 + \text{(ring)}^{COOK} + KOH + H_2O$$
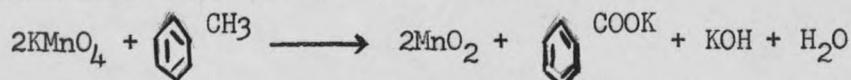
Battery life from this product (100 hours on low drain) was surprisingly long considering that the phase was characterized as delta-epsilon. Both the oxygen content and density were low, but a longer reaction time or change in concentration could possibly raise these. The presence of water seems to be required since small scale tests with only toluene and potassium permanganate failed to produce manganese dioxide. The pH of the product was also beyond limits and had to be lowered with a dilute sulfuric acid wash.

Further research with this reaction or a similar one using permanganic acid in place of potassium permanganate could possibly lead to the development of a good product. However, since the structure was not of a rho or gamma nature, this reaction is not considered exceptionally good.

9. Thermal Reduction of Manganous Carbonate

$$MnCO_3 \xrightarrow{\Delta} MnO + CO_2$$

$$2 MnO + O_2 \longrightarrow 2 MnO_2$$
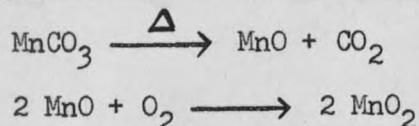
Manganous carbonate was thermally reduced at $210^\circ C$ and $300-420^\circ C$. At the latter temperature a mixture of beta and Mn_3O_4 was obtained which indicates too high a reaction temperature was used. Battery life for this material did not meet that received from Gold Coast ore. Micro-optical data for the sample prepared at $210^\circ C$ have not been received, but battery

tests did not show an exceptionally good product. Here again, the low density material was found to have relatively better life on the low drain test than the high drain. Both density and oxygen contents of the samples were poor.

An opinion seems to exist that the size of the manganese dioxide particle obtained is the same as that of the original carbonate. In this event density and probably battery performance are dependent on the properties of the manganous carbonate used. From the data obtained this reaction cannot be considered good, but perhaps a better product could be made by using different manganous carbonates.

Although none of the materials produced met all Signal Corps specifications, battery drain tests on the material produced by hot spraying permanganic acid were sufficiently long to warrant a full scale investigation of the possibilities of producing a cheap permanganic acid and determination of optimum operating conditions. It is believed that a manganese dioxide comparable to that produced by electrolysis of manganous sulfate solutions can be prepared by this method.

V. SUMMARY

The following generalizations have been drawn from the results found in this investigation.

1. The best reaction investigated from the standpoint of battery performance was the hot spraying of permanganic acid solutions. Manganese dioxide from this synthesis gave battery life in the range of that obtained from electrolytic samples.

2. Other type reactions which will produce manganese dioxide comparable or better than Gold Coast ore are the calcium hypochlorite oxidation of manganous salts and the oxidation of manganous sulfate with permanganic acid.

3. Thermal decomposition reactions generally produce a denser product than precipitation reactions.

4. A denser product is usually produced in cold, concentrated solutions.

5. Density seems to effect high drain tests more than low drain tests.

6. A heat treatment at 170°C will improve the battery life of a gamma-rho mixture, but will not change the phase.

7. Nitric acid washes may cause a shift in phase.

8. The presence of potassium ion does not always cause the formation of alpha manganese dioxide.

VI. ACKNOWLEDGEMENT

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VIII. APPENDIX

Table I Method of Preparation

Code	Preparation
K-CH-1	Twelve hundred g. of $MnCl_2.4H_2O$ was oxidized in hot aqueous solution with 870 g. $Ca(OCl)_2$.
K-CH-2	Four hundred g. of $MnCl_2.4H_2O$ dissolved in 2 l. of H_2O was heated to 75°C and oxidized with 290 g. of $Ca(OCl)_2$.
K-CH-3	Four hundred g. of $MnCl_2.4H_2O$ was dissolved in 350 cc of H_2O and oxidized with 290 g. $Ca(OCl)_2$.
K-CH-4	Four hundred g. of $MnCl_2.4H_2O$ was dissolved in 350 cc of H_2O and oxidized with 290 g. of $Ca(OCl)_2$. The hypochlorite was added in small amounts and the product filtered off after each addition. Temperature was 15-20°C.
K-CH-5	Four hundred g. of $MnCl_2.4H_2O$ was dissolved in 350 cc of H_2O and oxidized with 290 g. of $Ca(OCl)_2$. The hypochlorite was added in small amounts and the product filtered off after each addition. Temperature was 40°-50°C.
K-CH-6	Four hundred g. of $MnCl_2.4H_2O$ was dissolved in 2 l. of H_2O and oxidized with 290 g. $Ca(OCl)_2$ at 70°-75°C. This had a longer reaction time than K-CH-2.
K-CH-7	Four hundred g. of $MnCl_2.4H_2O$ was dissolved in 500 cc of H_2O was oxidized with 290 g. of $Ca(OCl)_2$ at 10-20°C. The total reaction time was six hours.
N-CH-1	Six hundred and eighteen g. of 50% aqueous $Mn(NO_3)_2$ was oxidized with 243 g. of $Ca(OCl)_2$. No heat was applied but the temperature rose to about 80°C.
N-CH-2	Six hundred and eighteen g. of 50% aqueous $Mn(NO_3)_2$ was heated to 110°C and oxidized with 160 g. of $Ca(OCl)_2$ at 110-120°C.
N-CH-3	Two thousand two hundred and twenty five g. of 50% aqueous $Mn(NO_3)_2$ solution was oxidized with 890 g. of $Ca(OCl)_2$ at 30-50°C with a total reaction time of $3\frac{1}{2}$ hours. A portion of this MnO_2 was heat treated at 150°C for 41 hours.
N-CH-4	A portion of the MnO_2 prepared in N-CH-3 was heat treated at 220°C for 48 hours.
N-CH-5	A portion of the MnO_2 prepared in N-CH-3 was heat treated at 170°C.

Table I (continued)

Code	Preparation

N-CH-6
A portion of the MnO_2 prepared in N-CH-3 was dried at room temperature.

S-AD-1
Twelve hundred g. of $MnSO_4$ were dissolved in 2400 cc of H_2O and mixed with 1000 cc NH_4OH to precipitate $Mn(OH)_2$. The $Mn(OH)_2$ was dried at 90°C. This product was heat treated at 300°C and then oxidized with 260 cc of HNO_3.

S-AD-2
Twelve hundred g of $MnSO_4$ were dissolved in $2\frac{1}{2}$ l. of H_2O and treated with 1 l. of NH_4OH. This $Mn(OH)_2$ was used in S-AD-2, S-AD-3 and S-AD-4. The portion of $Mn(OH)_2$ used in S-AD-2 was dried in air at 300°C with the temperature rising to 400°C at the end.

S-AD-3
This portion of the $Mn(OH)_2$ prepared in S-AD-2 was dried at 100°C.

S-AD-4
This portion of the $Mn(OH)_2$ prepared in S-AD-2 was dried at room temperature.

S-AD-5
Thirteen hundred g. of $MnSO_4$ was dissolved in 2700 cc H_2O and reacted with 1100 cc NH_4OH. The $Mn(OH)_2$ was kept damp at room temperature and allowed to oxidize for 8 days. The resulting material was oxidized at room temperature with 466 cc HNO_3 dissolved in 1 l. H_2O.

S-AD-6
Two hundred and seventy six g. of $Mn(OH)_2$ which had been dried at 100°C was oxidized overnight with 232 cc HNO_3 at room temperature.

S-AD-7
Two hundred and seventy six g. of $Mn(OH)_2$ which had been dried at 100°C was oxidized overnight with 232 cc HNO_3 dissolved in 500 cc H_2O.

S-AD-8
Thirteen hundred g. of $MnSO_4$ was dissolved in 2700 cc H_2O and the $Mn(OH)_2$ was precipitated with 1100 cc NH_4OH. This $Mn(OH)_2$ was used in S-AD-8 and S-AD-9. The portion in S-AD-8 was dried at 100°C in air and wet down several times to promote oxidation. The brown oxide was oxidized with 204 cc HNO_3 dissolved in 440 cc H_2O for $2\frac{1}{2}$ hours at 70-80°C.

S-AD-9
A portion of the $Mn(OH)_2$ prepared in S-AD-8 was oxidized for several days with additions of H_2O to keep it damp. The brown oxide was oxidized with 220 cc HNO_3 dissolved in 475 cc H_2O at room temperature.

Table I (continued)

Code	Preparation
S-A-1	Thirteen hundred and ninety g. of $MnSO_4$ was dissolved in 2200 cc H_2O and heated to 70°C. Air was dispersed through the solution simultaneously with the addition of 1140 cc of NH_4OH. Total reaction time was 10 hours. The brown oxide was then oxidized with 390 cc HNO_3 in 2 l. of H_2O.
S-A-2	Six hundred g. of $MnSO_4$ were dissolved in 1200 cc of H_2O and heated to boiling. To this 550 cc of NH_4OH and 200 cc of HNO_3 were added dropwise while air was blown through the solution. Ammonium hydroxide was added to keep the pH up to 8. The pH did get as low as 6. Temperature ranged from 75-95°C. Total reaction time was about 12 hours.
M-S-1	One hundred and seventeen g. of $MnSO_4$ was dissolved in 250 cc of H_2O and oxidized at 25-30°C with 450 cc of 10% $HMnO_4$.
M-S-2	One hundred and seventeen g. of $MnSO_4$ was dissolved in 250 cc of H_2O and oxidized at 70-80°C with 450 cc of 10% $HMnO_4$.
M-H-1	Two hundred and sixteen g. of $Ba(MnO_4)_2$ were dissolved in 600 cc of H_2O and reacted with 32 cc H_2SO_4. The $BaSO_4$ was filtered off and the $HMnO_4$ allowed to decompose spontaneously at room temperature.
M-H-2	Permanganic acid prepared as in M-H-1 was sprayed on a granite slab at 150-250°C. The temperature may have reached 300°C at times.
M-H-3	Permanganic acid prepared by dissolving one pound of $Ba(MnO_4)_2$ in 1270 cc H_2O and 67 cc H_2SO_4 and filtering off the $BaSO_4$. This was divided into two portions and used in M-H-3 and M-HP-3. The portion used in M-H-3 was sprayed on a granite slab at about 150-200°C.
M-H-4	Ten percent $HMnO_4$ was sprayed on a granite slab at 150-275°C.
M-HP-1	Two hundred and sixteen g. of $Ba(MnO_4)_2$ was dissolved in 600 cc of H_2O and reacted with 32 cc of H_2SO_4. The $BaSO_4$ was filtered off and the $HMnO_4$ was reduced with 30% H_2O_2.
M-HP-2	Permanganic acid was prepared as in M-HP-1 was diluted with 2 l. of H_2O before reducing it with 30% H_2O_2.
M-HP-3	One half of the $HMnO_4$ prepared in M-H-3 was reduced by slowly dripping in a 5% solution of H_2O_2. The temperature was kept below the room temperature with a H_2O bath.

Table I (continued)

Code	Preparation
P-AM-1	Seven hundred and twenty six g. of $KMnO_4$ were dissolved in 2900 cc of H_2O. To this was added 384 cc NH_4OH and the solution was reacted hot.
P-AM-2	Two hundred g. of $KMnO_4$ was mixed with 500 cc H_2O and 1100 cc NH_4OH. This was heated slightly until a reaction started and then was set overnight to react.
P-AM-3	Two hundred g. of $KMnO_4$ was mixed with 200 cc NH_4OH and heated intermittently to keep the reaction proceeding. Ammonium hydroxide was added intermittently to make up losses until a total of 500 cc had been added.
O-KH-1	Four hundred g. of inactive MnO_2 was fused with 516 g. KOH. The mixture was dissolved in H_2O and treated with CO_2.
O-KH-2	Two hundred g. of inactive MnO_2 which had been ground to pass 200 mesh was fused with 322 g. at about 260°C, cooled, and treated with 2 l. of H_2O.
O-KH-3	Two hundred g. of MnO_2 which had been ground to pass 200 mesh was fused with 322 g. of KOH and 116 g. of KNO_3 at about 260°C. This was cooled and treated with 2 l. of H_2O.
P-T-1	Two hundred g. of $KMnO_4$ was mixed with 1 l. of toluene and 500 cc of H_2O. The mixture was refluxed for about $2\frac{1}{2}$ hours.
S-NH-1	Three hundred and seven g. of $MnSO_4$ was dissolved in 650 cc H_2O and oxidized with 2,186 g. of NaOCl solution containing 5% available Cl. Reaction temperature was 80°C.
C-H-1	Five hundred g. of $MnCO_3$ was thermally decomposed for $2\frac{1}{2}$ hours in the presence of air at 300-420°C.
C-H-2	Two hundred g. of $MnCO_3$ was thermally decomposed at 210°C for $47\frac{1}{2}$ hours.

Table II Chemical Test Data

Code	O_2 as % MnO_2	% Mn	O_2 No.	% H_2O	pH
K-CH-1	79.6	56.8	1.88	3.43	5.2
K-CH-2	84.5	59.2	1.90	1.43	6.6
K-CH-3	75.2	58.1	1.81	0.84	6.4
K-CH-4	79.7	58.7	1.85	4.35	6.3
K-CH-5	87.4	61.1	1.90	1.13	7.2
K-CH-6	86.2	60.9	1.89	1.98	6.1
K-CH-7	81.6	59.9	1.86	2.93	5.8
N-CH-1	85.0	60.4	1.89	1.93	6.1
N-CH-2	58.2	58.3	1.63	1.15	6.2
N-CH-3	92.1	61.3	1.95	2.45	5.0
N-CH-4	93.4	61.2	1.96	1.73	5.5
N-CH-5	93.0	61.2	1.96	1.67	5.3
N-CH-6	87.5	60.8	1.91	3.49	4.5
S-AD-1	91.3	59.9	1.96	3.62	3.7
S-AD-2	16.0	51.5	—————	0.81	5.9
S-AD-3	9.4	50.0	—————	1.41	7.9
S-AD-4	61.6	65.2	1.60	1.47	6.4
*S-AD-5	9.1	34.2	—————	0.69	—————
S-AD-5	87.5	61.0	1.91	2.19	3.8
S-AD-6	85.3	60.6	1.89	3.50	3.6
S-AD-7	85.6	61.9	1.87	3.54	5.0
S-AD-8	87.4	61.1	1.90	3.16	2.7
*S-AD-8	8.6	39.2	—————	0.84	—————
S-AD-9	89.9	60.6	1.93	3.31	—————
S-A-1	86.5	58.7	1.93	5.83	3.8
S-A-2	34.0	66.2	—————	0.97	5.8
M-S-1	93.5	61.3	1.96	1.79	3.7
M-S-2	93.8	62.1	1.95	2.65	3.9
M-H-1	81.7	58.3	1.88	1.12	5.4
M-H-2	All material used in inconclusive battery test				
M-H-3	83.3	61.9	1.85	2.48	6.6
M-H-4	81.8	62.4	1.83	1.98	4.7
M-HP-1	77.7	58.8	1.84	3.84	5.3
M-HP-2	81.7	58.6	1.88	8.17	5.0
M-HP-3	87.3	60.3	1.91	7.40	4.2
P-AM-1	85.4	59.1	1.91	1.16	3.7
P-AM-2	83.8	56.7	1.93	2.68	7.1
P-AM-3	82.0	56.5	1.92	3.27	7.2
O-KH-1	85.6	59.1	1.92	4.27	5.2
O-KH-2	85.8	58.1	1.93	3.09	7.7
O-KH-3	89.2	60.6	1.93	3.34	7.1
P-T-1	79.4	58.1	1.86	3.91	6.9
S-NH-1	86.4	57.2	1.95	2.89	4.3
C-H-1	70.3	64.3	1.69	1.58	6.4
C-H-2	75.6	60.7	1.79	0.38	6.3

*Before HNO_3 oxidation.