



Battery active manganese dioxide by chemical synthesis
by Fred P Baughman

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering
Montana State University
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Abstract:

It has been established that the battery activity of manganese dioxide used in the fabrication of dry cells is a function of the crystalline phase type of the manganese dioxide. This paper presents a comprehensive study of the chemical synthesis of manganese dioxide by all methods of synthesis which might be expected to yield manganese dioxide of suitable phase type to be battery active. The manganese dioxide has been evaluated according to the methods set forth in U.S. Army Signal Corps Specification SCL-3117D, IS March 1952, entitled Manganese Dioxide Synthetic.

Methods of preparation of manganese dioxide are classified into the following groupings: (A) oxidation of manganous salts by chlorine and chlorine containing compounds, (B) oxidation of manganous salts by permanganates, (C) thermal decomposition of heat labile manganese compounds, (D) acid treatment of mixed oxides of manganese, and (E) miscellaneous methods of synthesis. The manganese dioxide resulting from each method of synthesis is evaluated by comparison of pertinent physical and chemical data as well as battery drain test data. These data are compared with accepted specifications for synthetic manganese dioxide. Figures include a reference chart showing the X-ray diffraction patterns for all seven phase types of manganese dioxide. Additional figures are graphs which give power curves for a typical chemical manganese dioxide compared with Gold Coast and electrolytic manganese dioxides.

Manganese dioxide of suitable activity to meet or exceed synthetic specifications results from methods falling into classifications (A), (B), and (D) but methods classified under (C) and (E) do not yield manganese dioxide of proper phase type and therefore, these products do not meet specifications.

A correlation of the chemical and physical factors which result in acceptable battery activity of chemically produced manganese dioxide has led to the establishment of limits for the various chemical and physical properties of chemical manganese dioxides. They are: O₂ as % MnO₂ 83.6% (min)
% Mn 58.7% (min)
% H₂O 1.7% (max)
pH 4.3 to 6.9
gm/in³ 11.6 (min)
"A" size bobbin weight-gms 8.9 to 10.3
Phase type Gamma, rho, or gamma-rho

BATTERY ACTIVE MANGANESE DIOXIDE

BY

CHEMICAL SYNTHESIS

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Fred P. Baughman

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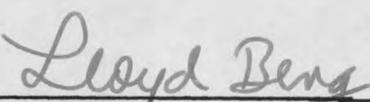
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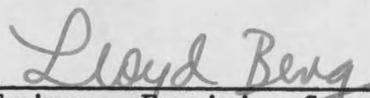
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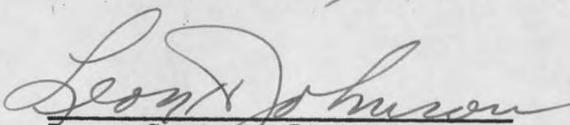
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ABSTRACT

It has been established that the battery activity of manganese dioxide used in the fabrication of dry cells is a function of the crystal-line phase type of the manganese dioxide. This paper presents a comprehensive study of the chemical synthesis of manganese dioxide by all methods of synthesis which might be expected to yield manganese dioxide of suitable phase type to be battery active. The manganese dioxide has been evaluated according to the methods set forth in U. S. Army Signal Corps Specification SCL-3117D, 18 March 1952, entitled Manganese Dioxide Synthetic.

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Manganese dioxide of suitable activity to meet or exceed synthetic specifications results from methods falling into classifications (A), (B), and (D) but methods classified under (C) and (E) do not yield manganese dioxide of proper phase type and, therefore, these products do not meet specifications.

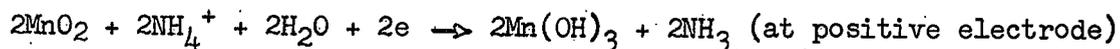
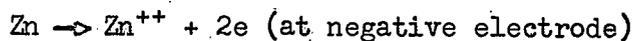
A correlation of the chemical and physical factors which result in acceptable battery activity of chemically produced manganese dioxide has led to the establishment of limits for the various chemical and physical properties of chemical manganese dioxides. They are:

O ₂ as % MnO ₂	83.6% (min)
% Mn	58.7% (min)
% H ₂ O	1.7% (max)
pH	4.3 to 6.9
gm/in ³	11.6 (min)
"A" size bobbin weight-gms	8.9 to 10.3
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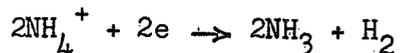
INTRODUCTION

The common dry cell has long been used as a portable power source for both military and civilian needs. The military uses have been principally in the area of communications in the past, but development of many modern weapons in the guided missile and rocket fields has resulted in increased requirements for compact, portable power sources. Current widespread civilian use of dry cells in portable lights, hearing aids, portable radios, and many other devices as well as new uses arising from the development of transistors point to an expanding development and use of dry cells.

Although there has been improvement in the manufacture of dry cells arising from new techniques and methods (1) and dry cell technology has been the source of many patents by manufacturers, the greatest possibility for improvement of dry cells appears to be through improvement of the manganese dioxide component of the cell. Although the manganese dioxide does not enter into the cell reaction directly, it does serve as a depolarizer. The cell reaction mechanism is postulated as follows (5):



The actual depolarization reaction is not definitely established, but a possible explanation is to be found in the following two-step reaction:



Thus it may be seen that, unless the hydrogen is depolarized as formed, the conductivity of the cell is decreased to the point where no current is produced. How effective the manganese dioxide in the cell will be as a depolarizer is a function of its phase type and the manganese dioxide phase type may well be the limiting factor in the life of a given dry cell. The meaning of the term 'phase type' has been defined by William Nye as follows (18):

"These manganese dioxide samples are being made under non-equilibrium conditions and are, therefore, mesocrystalline materials, that is they are very poorly crystallized. There are but two polymorphs of MnO_2 - the tetragonal form (if well crystallized, it is called pyrolusite or beta MnO_2) and the orthorhombic form (the mineral Ramsdellite). The seven basic phase types we use here are modifications of these two basic polymorphs - we call them phase types - not phase in the strict sense of the word. 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 type 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."

Although manganese dioxide of each phase type gives some degree of battery activity, it has been established by the Army Signal Corps that material which corresponds to gamma, rho, or gamm-rho intermediate phase types appear to give the highest degree of battery activity when compounded into dry cells. The most active, naturally occurring, manganese dioxide ores are those in which the phase type is principally gamma. Figure 1 is a reference chart showing the various X-ray diffraction pat-

terms for all seven phase types of manganese dioxide.

Extensive research (7, 8, 10, 11, 17, 20) has been carried out on the electrolytic production of manganese dioxide. When conditions were regulated to produce gamma or rho phase type manganese dioxide, the drain characteristics were superior to natural ores (impure gamma). The success of this method of synthesizing manganese dioxide which is suitable for use in dry cells is attested to by the fact that one plant is currently in operation devoted to the production of electrolytic manganese dioxide for use in dry cells (16).

In addition to its phase type, there are other factors which will affect the activity of the manganese dioxide as a depolarizer. The presence of such impurities as cobalt and nickel is detrimental to the battery activity immediately upon fabrication of the cell and the presence of iron may cause deterioration of the activity after cell storage. Variation of other component parts of the cell will affect the power output of the cell considerably. The physical and chemical characteristics of the manganese dioxide can affect the battery activity. The amount of manganese dioxide which can be tamped into a cell bobbin is a function of the apparent density of the material, and, since a cell's power output depends upon the total amount of manganese dioxide present in that cell, low density may contribute to poor cell performance. The actual assay value of the sample (i.e., % MnO_2) may be a factor, particularly if the assay (% MnO_2) is low. Other factors affecting drain performance are the pH and water hydration or crystallization of the manganese dioxide. The

problem is one of making manganese dioxide of proper phase type which also has the correct physical and chemical properties for high battery activity.

The best natural ore is found in abundance in Gold Coast, Africa and this ore is principally gamma phase type, but impurities and inactive phase type dioxide limit the activity of this material; the only domestic source of natural ores is limited quantities of less active ores which are found in the Philipsburg, Montana area. Current production of electrolytic manganese dioxide is of gamma phase type of high purity and correspondingly good drain characteristics. A third possible path to the production of battery active manganese dioxide is by means of some suitable chemical synthesis. A number of different ideas for chemical syntheses have been proposed (1) and patents have been issued on some chemical processes for battery active manganese dioxide, but no large-scale commercial production has yet developed. The possible unavailability of Gold Coast ore in case of war and the attractive possibility that a chemical process might be developed for the continuous production of this strategic chemical have led to this study of chemical methods of synthesis.

The United States Army Signal Corps has been interested in the possibilities of the chemical path to MnO_2 to the extent that research has been sponsored by that organization at Montana State College in Bozeman, Montana and at Western Electrochemical Company in Culver City, California. Also, private research has continued in this field and one process has been reported in the pilot plant stage of development (14).

In addition to the research sponsored by the Signal Corps from June 15, 1951 to June 15, 1954, a continuing program of research is being carried out at Montana State College under the auspices of the Engineering Experiment Station.

METHODS AND PROCEDURES

In order to evaluate correctly the worth of any particular method of chemical synthesis of manganese dioxide, it is necessary to synthesize at least 80 grams of product so that a sufficient quantity will be available for the fabrication of "A" type dry cells to be tested for drain capacity. Since official specifications have not been established upon which to base requirements of the chemical manganese dioxide, methods and procedures of analysis and testing as established by the United States Army Signal Corps manganese dioxide specifications SCL-3175 (19) were followed: The capacity tests used for evaluation of the battery activity are defined (19) as follows:

"4.6.1 Fifteen (15) each dry cells, size "A", prepared as described in 4.5 shall be used for each of the following initial capacity tests.

	<u>Low Drain</u>	<u>High Drain</u>	<u>BA-270/U Test</u>
a. Type of Discharge	Continuous	Continuous	Continuous- Intermittent
b. Discharge Resistance	166 2/3 ohms	16 2/3 ohms	26.25 ohm/2 min, 52.5 ohm/18 min
c. Test end voltage	1.13 volts	1.0 volts	1.1 volts
d. Discharge Temp	70°F(50% RH)	70°F(50% RH)	70°F(50% RH)"

In order to do this study, it was necessary to make some modifications in the dry cell testing procedures. The number of cells fabricated for test purposes was kept to the minimum number with which the evaluation of the battery activity could be completed. A batch of mix which was sufficiently large to yield 7 to 10 "A" cells was made in the exact proportions specified in SCL-3175 and these cells were used to evaluate only five-day high and low drain performance and three-month low drain performance of the samples. By this procedure the following results were achieved: (1) the size of samples required for evaluation of battery activity was held at a minimum and, (2) cell storage space and test equipment outlay was not excessively great, thus permitting evaluation of a maximum number of chemical methods under the plan of this research. Extensive testing will be required if pilot plant studies are to be made on any of these methods of synthesis, but the very scope of this work has not permitted prolonged cell life studies (except for the three-month low drain test) or BA-270/U Test evaluations of the samples.

For the purpose of determining the possible merit of a particular synthesis, several reactions were run, each under different reaction conditions, and the manganese dioxide product from each run was evaluated as to chemical and physical properties as well as drain characteristics. Any synthesis which yielded a product with acceptable chemical and physical properties and which gave battery tests equal to or better than Gold Coast ore was further examined to determine the feasibility of meeting the synthetic battery-grade manganese dioxide specifications. These

specifications are listed as the first item of Table III for comparison.

An examination of the possible chemical methods of making manganese dioxide revealed that the syntheses could be classified logically into five groupings:

- A. oxidation of manganous salts by chlorine and chlorine compounds,
- B. oxidation of manganous salts by permanganates,
- C. thermal decomposition of heat labile manganese compounds,
- D. acid treatment of lower oxides of manganese, and
- E. miscellaneous methods of synthesis.

Each method of synthesis has thus been given a letter designation depending upon which group it falls into; following the letter is a number which designates a particular sub-group depending upon the manganese salt used in the synthesis; following this number is a second number which differentiates between syntheses within the sub-group. The chemical reactions which have been investigated are listed in Table II. Listed in Table III are analytical and test data indicative of the better results obtained from each method of synthesis. Listed in Table IV are methods of preparation of samples reported in Table III. Although Table III is a report of only 45 typical samples, it should be noted that the investigations at Montana State College have resulted in the synthesis of approximately 600 samples of manganese dioxide. Many of these samples were synthesized as a part of the effort to evaluate the effects of reaction variables in a particular synthesis and, in those cases in which the reaction conditions were unfavorable, the manganese dioxide product had

different physical, chemical, and drain characteristics than the sample reported in Table III. The results reported in Table III have been verified by running additional experiments.

EXPERIMENTAL RESULTS

A. Oxidation by chlorine and chlorine compounds has proved to be a versatile approach to high quality manganese dioxide. One possible method is to use chlorine gas in the presence of alkali to oxidize a manganous salt. The base used may be the basic salt, manganese carbonate, (13) as in reaction A.1.1 or sodium hydroxide as in reactions A.2.1, A.2.2, A.3.1, A.4.1, and A.4.2. In the case of oxidation of manganese carbonate, the manganese dioxide is essentially rho phase type, but the failure to meet drain specification is probably due to residual traces of manganese carbonate in the product. Chlorine oxidation of manganous salts in the presence of sodium hydroxide gives material of phase types rho and gamma-rho, and the reaction seems to proceed equally well whether the salt used is manganese chloride (A.2.1, A.2.2), and manganese nitrate (A.3.1), or manganese sulfate (A.4.1, A.4.2). In general, this synthesis yields a gamma-rho phase type manganese dioxide giving drain tests which meet or exceed specifications in most cases. It should be noted that a sample of manganese dioxide, made by oxidation of manganese chloride in the presence of sodium hydroxide with chlorine (A.2.2), gave the longest low drain performance (183 hours initial and 160 hours three-month test) of any sample tested in this program. This initial test exceeds

the specification by more than 40% and is 100% greater than Gold Coast ore. Capacity maintenance, that is the three-month test, is a little low for the samples made from manganese sulfate, but this is believed to be due to occluded salts rather than a serious defect in the synthesis method. The use of calcium hydroxide as a base in this type of reaction was investigated (A.2.5) with manganese chloride as the source of manganese and the product is again gamma-rho phase type which meets or exceeds all drain specifications.

Another method of synthesis, which was considered, is the oxidation of manganese salts with sodium hypochlorite (A.2.6, A.3.3, A.4.5) and, although this produces material of desirable phase type, the samples fail to meet both drain specifications. When manganese salts are oxidized with sodium hypochlorite solutions, chlorine is evolved, so sodium hydroxide is added to the oxidizing solution in 2:1 molar ratio of sodium hydroxide to sodium hypochlorite and this solution is used as the oxidant (A.2.3, A.4.4). Again the product is of the proper phase type, but drain specifications are not met. A similar synthesis makes use of calcium hypochlorite as the oxidant for manganese salts (A.2.4, A.3.2, A.4.3). The use of manganese chloride as the source of manganese yields rho phase type dioxide which easily exceeds drain specifications. The use of manganese nitrate as the source of manganese yields gamma-rho phase type which also exceeds drain specifications, but when manganese sulfate is used with this oxidant, in spite of rho phase type product, drain specifications are not met. It is believed that the calcium sulfate which is

formed in the latter case is retained as an impurity in the product and the extreme insolubility of this salt makes complete removal difficult.

It has been reported (6) that an excellent quality manganese dioxide can be produced by oxidation of manganese sulfate in acidic solutions using sodium chlorate as the oxidant (A.4.7). This material is essentially rho phase type and drain tests meet or exceed specifications readily. Other similar reactions using different chlorates as the oxidant have been tried and results are less promising (13). Oxidation of manganese sulfate with potassium chlorate (A.4.6) gives alpha phase type, with correspondingly short cell life. An attempt to use chloric acid, in place of the sodium salt has been reported (6); this yields manganese dioxide of rho phase type with excellent low drain test, but the high drain test falls short of specifications.

Experiments using chlorine dioxide gas to oxidize manganese hydroxide have been reported (6), but the product of this reaction (A.5.1) shows very little activity.

B. Oxidation of manganous salts by permanganates is a particularly attractive method of making battery active manganese dioxide, since the reaction is of the reduction-oxidation type and results in essentially 100% of all the manganese from the reducing agent (manganous salt) and the oxidant (permanganate compound) being converted to battery active product.

Potassium permanganate was used as the oxidant for three manganous salts: manganese chloride (B.2.1), manganese nitrate (B.3.3), and manganese sulfate (B.4.2). Each of these syntheses produces specification

material both from the standpoint of battery-drain tests and phase type. It should be noted that the products of these syntheses show little or no loss of life after storage.

Permanganic acid has been used to oxidize manganese carbonate (B.1.1) and the product gives very short cell life although the phase type is gamma. Permanganic acid oxidation of manganese nitrate (B.3.1), manganese sulfate (B.4.1), and manganese hydroxide (B.5.1) fails to give material which meets drain specifications (2).

Oxidation of manganese nitrate with barium permanganate (B.3.2) yielded such poor quality manganese dioxide that, after several unsuccessful attempts to adapt this synthesis to production of battery-grade manganese dioxide, further investigation was deemed unprofitable.

C. Thermal decomposition of heat labile manganese compounds has been investigated and there seems to be small possibility of making synthetic manganese dioxide this way. The heat treatment of manganese carbonate (C.1.1) in an oxidizing atmosphere at temperatures between 100°C and 410°C causes decomposition of the manganese carbonate with subsequent formation of manganese dioxide (12). Although the decomposition product is predominately manganese dioxide, it is necessary to remove unreacted manganese carbonate by dilute acid treatment. The product is basically gamma and has excellent high drain characteristics, but fails to meet the low drain specification.

Thermal decomposition of permanganic acid (C.2.1) by hot spraying of an aqueous solution of this compound on a granite slab gives material

which is characterized as gamma, but the high drain test is not met by this product and although the initial low drain tests meet specification, the delayed capacity tests are below specification (2).

Thermal decomposition of manganese nitrate (C.3.1) always gives beta manganese dioxide and the drain tests are correspondingly low (12). It is reported that gamma manganese dioxide has been made by this method of synthesis in pilot plant operation (13), but the reported procedures and methods of cell evaluation do not permit battery test comparisons, since the reported cell size and type of test used do not conform to standards of the battery industry.

Attempts to make manganese dioxide by thermal decomposition of manganese oxalate (C.4.1) fail to produce manganese dioxide and yield instead lower oxides of manganese (4). When these oxides are treated with dilute acids, the resulting dioxide is alpha and is a poor depolarizer.

Thermal decomposition of manganese sulfate (C.5.1) results in a product of gamma-rho phase type, but the drain tests on this material fail to meet specifications.

Thermal decomposition of manganese chlorate (C.6.1) has been evaluated (6) and the product is principally rho phase type which meets high drain specifications, but fails on both low drain tests and three-month low drain tests.

It is doubtful if thermal decomposition of heat labile compounds is a practical method of producing battery active manganese dioxide because of the probability of either making a product which contains lower oxides of

manganese or leaving undecomposed material in the product.

D. Acid treatment of lower oxides of manganese with a dilute acid yields manganese dioxide and the manganous salt of the acid (12, 13). If the acid used is nitric or sulfuric, then the resulting salt may be concentrated and subjected to thermal decomposition to yield lower oxides, which can be acid treated to make more manganese dioxide and manganese salt. If the acid oxide can be recovered and recycled this process may be feasible. Patents have been issued for Nossen's nitric acid cycle (13), which used nitric acid as the leach acid. Another possible source of lower oxides is the heat treatment of pyrolusite ore (MnO_2). Depending upon the temperature of heating, the product is either bixbyite (Mn_2O_3) or hausmannite (Mn_3O_4). Acid treatment of both of these oxides has been evaluated and the results are promising.

When hausmannite is treated with dilute nitric acid (D.1.1), the product is gamma-rho manganese dioxide of excellent physical and chemical properties and both high and low drain performance exceed specifications. However, a similar treatment of hausmannite with dilute solutions of sulfuric acid (D.1.2) gives dioxide of uncertain phase type and the product fails to meet drain specifications.

Again, when bixbyite is treated with dilute nitric acid (D.2.1), the product is gamma-rho manganese dioxide of excellent physical and chemical properties and all drain tests exceed specifications. A similar treatment of bixbyite with dilute sulfuric acid (D.2.2) gives dioxide which is characterized as gamma-rho and which meets initial specifications but

fails to meet three-month specifications.

Since the temperature required to convert pyrolusite to bixbyite is lower than that required to convert to hausmannite and since acid treatment of bixbyite results in a mol of dioxide for each mol of bixbyite with only one mol of manganese salt for recycle, whereas the hausmannite would result in two mols of manganese salt for recycle, it seems evident that this acid treatment method of synthesis is more practical for use with bixbyite as the source of manganese.

Attempts to produce battery active manganese dioxide by air oxidation of manganese hydroxide resulted in failure. The resulting product, which is believed to be manganite ($MnOOH$), after acid treatment with dilute nitric acid (D.3.1) has fairly good physical and chemical properties, but the battery activity is comparable to Gold Coast ore (2).

E. Miscellaneous methods of synthesis include all methods which have been evaluated that do not fit any of the other four groups. It is significant that none of these methods give material of the correct phase type and the battery tests are correspondingly poor (2, 14, 12, 13).

PHYSICAL AND CHEMICAL CHARACTERISTICS
OF CHEMICAL MANGANESE DIOXIDE
RELATED TO BATTERY ACTIVITY

As explained under METHODS AND PROCEDURES, official specifications have not been established for chemical manganese dioxide. The specifications which are currently established for synthetic battery-grade manganese dioxide generally seem to apply to the manganese dioxide made by

the various chemical methods of synthesis. An attempt to make correlations of chemical and physical properties with drain characteristics for the various chemically synthesized manganese dioxides has been reported (15) and the resulting correlations are general in nature. A survey of the 600 samples which have been synthesized in the course of this work brings out a basic fact concerning the crystalline phase type of chemical manganese dioxide. Of all the samples for which X-ray diffraction patterns are available, the only samples which met or exceeded both high and low drain specifications (initial) were of the gamma, rho, or gamma-rho phase types. Of the 45 samples reported in Table III, for which drain test data are available, 19 samples meet or exceed high drain specifications, 20 exceed low drain specifications, and 14 exceed both specifications. The following table shows how the chemical and physical properties for these 14 samples compare with the existing specifications for battery-grade manganese dioxide synthetic:

TABLE I

	<u>O₂ as % MnO₂</u>	<u>% Mn</u>	<u>% H₂O</u>	<u>pH</u>	<u>Density gm/M₃</u>	<u>"A" size bobbin weight-grams</u>
Chemical MnO ₂	83.6 min	58.7 min	1.7 max	4.3 to 6.9	11.6 min	8.9 to 10.3
Specifi- cation	85 min	58 min	3.0 max	4.0 to 7.0	18.0 min	9.5 to 10.5

The principal discrepancy occurs in the density and bobbin weights of the samples made by chemical methods of synthesis. The minimum density of

these 14 samples was 11.6 instead of the 18.0 required in the specifications. In fact, some samples of chemical manganese dioxide out of the 600 total samples have met or exceeded both specifications in spite of densities as low as 10.1 gm/in³. The chemical manganese dioxide samples generally have densities in the range of 10.0 to 17.0 gm/in³. In addition, although most of the samples yield "A" size cell bobbins in the 9.5 to 10.5 gram weight range, numerous samples which yielded bobbin weights less than 9.5 to as low as 8.9 grams have met or exceeded both high and low drain specifications. In the light of this evidence of excellent drain life from manganese dioxide samples of densities considerably below the 18.0 gm/in³ specified and with cell bobbins lighter than the 9.5 gram minimum, it seems that these two specifications should be revised for chemical manganese dioxide.

Figures 2 and 3 are characteristic drain test curves for a natural ore, a sample of chemical manganese dioxide, and a sample of electrolytic manganese dioxide. The natural ore is a sample of Gold Coast ore, the chemical manganese dioxide was made by permanganate oxidation of manganese nitrate, and the electrolytic manganese dioxide is a commercial sample which meets specifications. In Figure 2 the cell voltage is plotted as a function of time for the high drain test and in Figure 3 the cell voltage is plotted as a function of time for the low drain test of these same three samples. Although the number of hours of cell life for the sample of chemical manganese dioxide compare well with the sample of electrolytic manganese dioxide, it is to be noted that due to the lower voltage of the

battery made from chemical manganese dioxide the actual power output (area under the curve) is lower for the chemical product than it is for the electrolytic product. This is generally true of chemical manganese dioxide.

SUMMARY

1. Manganese dioxide of excellent physical and chemical properties which meets or exceeds both the initial high and low drain specifications is produced through use of chlorine or chlorine compounds in the following cases:

- a. when chlorine gas is used to oxidize aqueous solutions of manganese chloride, manganese nitrate, or manganese sulfate in the presence of sodium hydroxide,
- b. when chlorine gas is used to oxidize aqueous manganese chloride in the presence of calcium hydroxide,
- c. when calcium hypochlorite is used to oxidize aqueous solutions of manganese chloride or manganese nitrate, and
- d. when sodium chlorate is used to oxidize aqueous, acidic solutions of manganese sulfate.

2. The use of potassium permanganate to oxidize aqueous solutions of manganese chloride, manganese nitrate, or manganese sulfate produces manganese dioxide which meets or exceeds both the initial high and low drain specifications and the product has excellent physical and chemical properties.

3. Nitric acid leaching techniques have been successfully applied to convert both bixbyite (Mn_2O_3) and hausmannite (Mn_3O_4) to battery active manganese dioxide of excellent physical and chemical properties. The product of these leaches easily meets or exceeds initial high and low drain specifications. Sulfuric acid leaching has been applied with equal success to the conversion of bixbyite to manganese dioxide.

4. Three-month low drain tests on the samples made and tested under this program indicate that, in general, chemical manganese dioxide has excellent shelf life and may be expected to give good capacity maintenance after storage.

5. Thermal decomposition of heat labile manganese compounds does not give specification manganese dioxide directly, but this approach may be used to produce lower oxides for acid leaching methods.

6. The feasibility of chemically making battery active manganese dioxide which meets or exceeds existing drain test specifications is established, since 14 of the 46 methods of synthesis gave material which meets or exceeds these specifications for initial drain tests.

7. The chemical manganese dioxide is usually of lower density than the 18.0 gm/in^3 specified and "A" size cell bobbin weights from these materials vary from 8.9 to 10.3 grams. This is not a serious deflection, however, since the drain specifications are met or exceeded by the chemical manganese dioxide samples.

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TABLE II

CHEMICAL METHODS OF SYNTHESIS OF MnO_2

A. Oxidation of manganous salts by chlorine and its compounds:

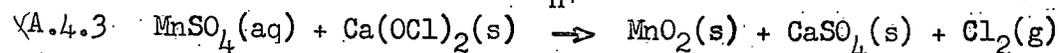
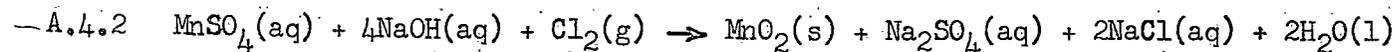
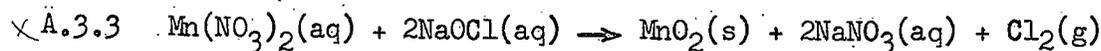
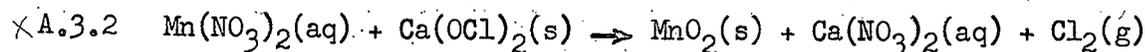
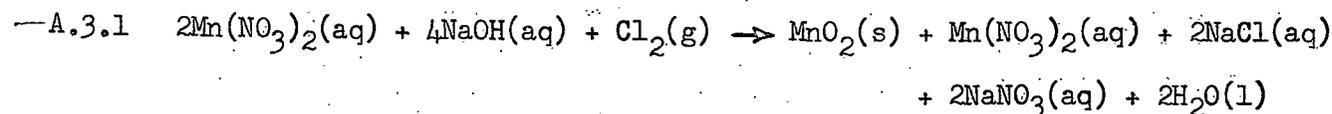
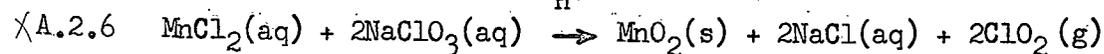
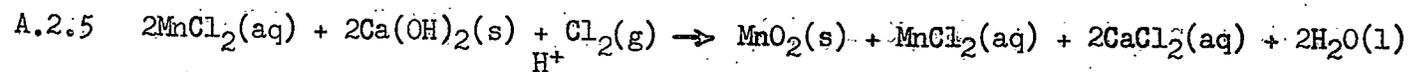
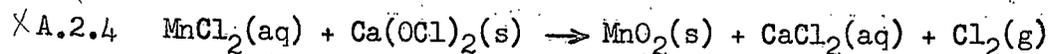
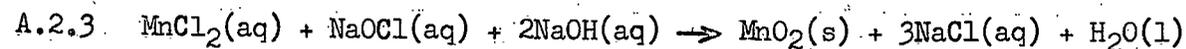
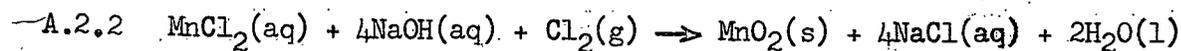
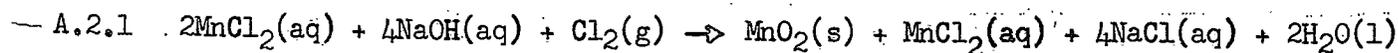
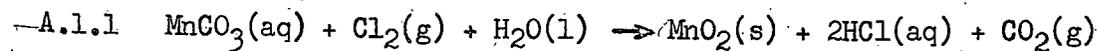
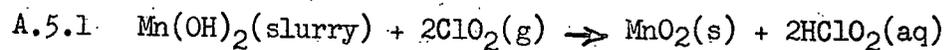
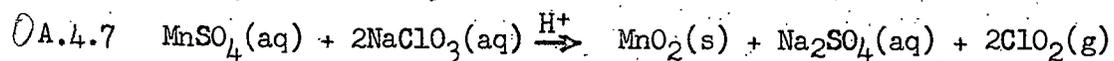
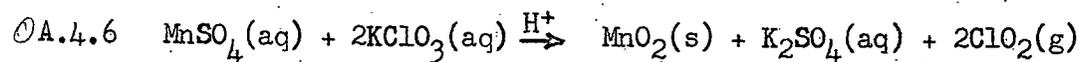
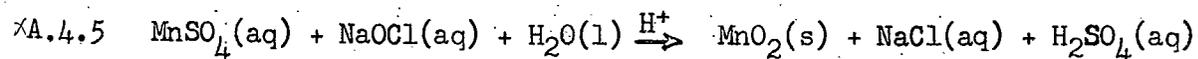
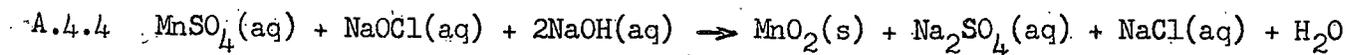


TABLE II (Cont'd)

CHEMICAL METHODS OF SYNTHESIS OF MnO₂

B. Oxidation of manganous salts by permanganates:

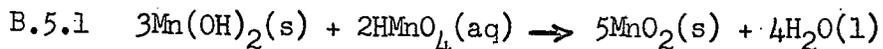
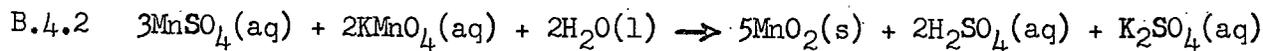
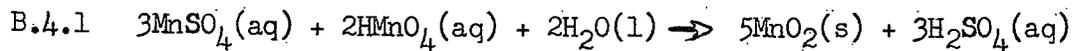
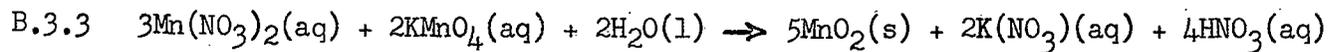
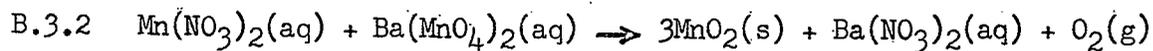
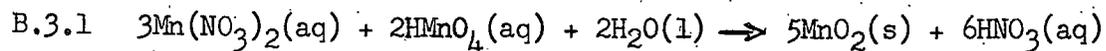
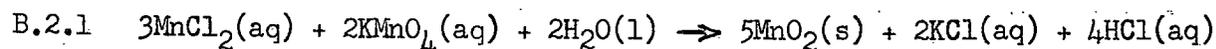
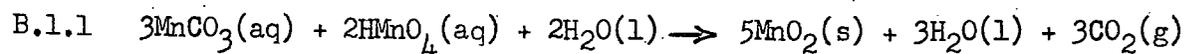
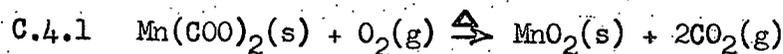
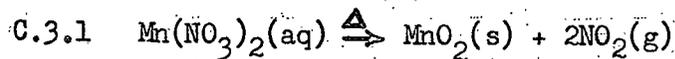
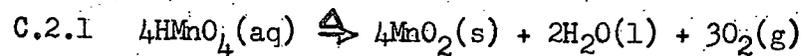
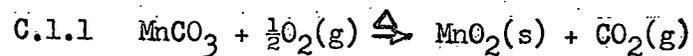


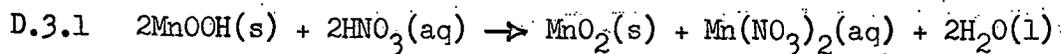
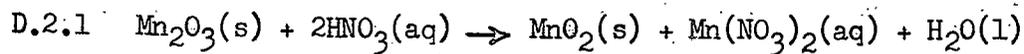
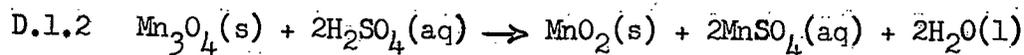
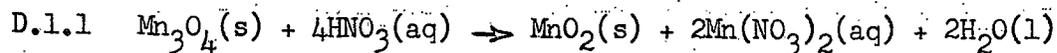
TABLE II (Cont'd)

CHEMICAL METHODS OF SYNTHESIS OF MnO₂

C. Thermal decomposition of heat labile manganese compounds:



D. Acid treatment of lower oxides of manganese:



E. Miscellaneous methods of synthesis:

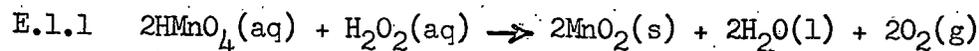


TABLE II (Cont'd)

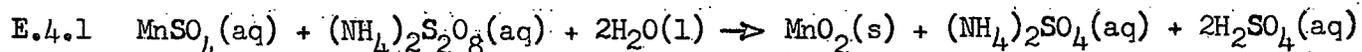
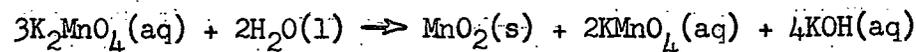
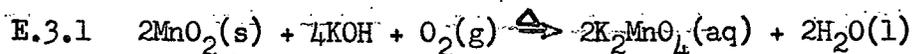
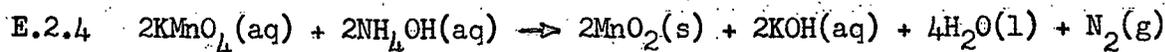
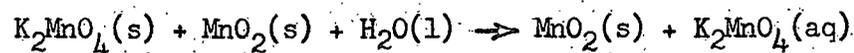
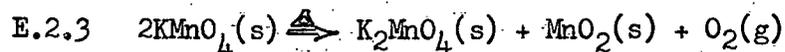
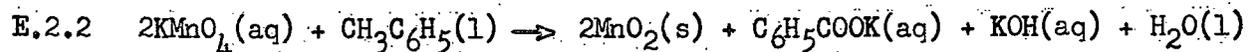
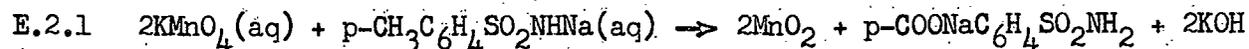
CHEMICAL METHODS OF SYNTHESIS OF MnO₂

TABLE III

ANALYTICAL, PHYSICAL, AND TEST DATA

Code	% O ₂ as % MnO ₂	% Mn	% H ₂ O	pH	Density gm/in ³	Crystalline Phase	Bobbin Wt grams	High Drain (5 day test) hrs	Low Drain (5 day test) hrs	Low Drain (3-month test) (hrs.)
Specifi- cations	85 min.	58 min.	3.0 max.	4.0 to 7.0	18.0 min.	Gamma, Rho, or Gamma-Rho	9.5 to 10.5	5.5	130	No spec.-Est. 85% original.
A.1.1	94.1	63.0	1.0	5.0	17.3	Rho	9.3	3.2	126	67
A.2.1(a)	94.3	62.0	1.6	5.8	14.0	Gamma-Rho	9.5	7.3	128	84
A.2.1(b)	88.3	61.3	1.5	6.4	14.7	Gamma-Rho	9.8	4.8	156	150
A.2.2(a)	94.6	62.6	1.3	5.7	13.5	Rho	9.7	5.5	135	117
A.2.2(b)	92.3	61.0	0.8	5.8	13.2	Gamma-Rho	9.9	2.9	183	160
A.2.3	83.5	58.7	2.7	10.5	13.8	---	---	---	---	---
*A.2.4	89.2	58.7	0.1	5.6	13.6	Rho	8.9	5.7	149	133
A.2.5	81.7	61.4	0.6	6.2	11.6	Gamma-Rho	9.1	5.7	130	112
*A.2.6	91.0	58.9	0.9	3.2	30.1	---	---	---	---	---
A.3.1	90.9	61.9	1.5	6.2	13.1	Gamma-Rho	9.4	5.6	144	128
*A.3.2	90.5	62.5	0.5	6.6	15.9	Essentially Gamma-Rho	9.7	5.7	146	127
*A.3.3	92.2	61.0	0.5	6.2	14.4	Principally Gamma-Rho	9.8	5.4	140	106
A.4.1	89.6	61.1	1.3	4.4	14.2	Principally Gamma-Rho	9.3	7.6	140	104
A.4.2	88.0	62.5	1.3	4.9	12.0	Gamma; trace Epsilon	9.5	5.6	152	101
*A.4.3	91.2	62.2	2.5	6.5	10.6	Rho	9.4	4.8	122	108
A.4.4	94.9	57.8	0.7	6.7	12.8	Principally Gamma; some R	9.8	3.9	152	50
*A.4.5	91.9	59.8	1.5	6.7	14.2	Rho	---	5.9	128	---
*A.4.6	83.1	57.1	2.4	3.2	---	Alpha	---	2.2	49	---
o A.4.7	91.8	59.0	0.5	6.9	32.2	Rho; trace Alpha	---	7.4	143	137
A.4.8	94.2	58.6	0.3	6.2	30.7	Rho	---	5.0	145	141
A.5.1	93.5	59.1	1.8	6.9	7.5	---	---	0.0	18	---
B.1.1	77.5	58.4	6.8	4.2	7.0	Gamma; Alpha	7.7	0.0	0	0
B.2.1	92.2	59.9	0.8	6.3	15.4	Gamma	10.1	5.5	130	134
B.3.1	94.0	61.8	0.7	7.0	13.2	Gamma	9.8	3.6	104	65
B.3.2	78.0	55.3	5.5	2.8	9.0	---	---	---	---	---
B.3.3	90.7	61.4	1.7	6.6	14.6	Gamma	10.1	5.8	136	135

TABLE III (Cont'd)

ANALYTICAL, PHYSICAL, AND TEST DATA

Code	% O ₂ as % MnO ₂	% Mn	% H ₂ O	pH	Density gm/in ³	Crystalline Phase	Bobbin Wt grams	High Drain (5 day test) hrs	Low Drain (5 day test) hrs	Low Drain (3-month test) hrs
Specifi- cations	85 min.	58 min.	3.0 max.	4.0 to 7.0	18.0 min.	Gamma, Rho, or Gamma-Rho	9.5 to 10.5	5.5	130	No spec.-Est. 85% original
B.4.1	92.6	60.2	1.0	6.5	13.4	Rho	9.4	4.8	110	83
B.4.2	90.7	61.4	1.7	6.6	14.6	Gamma-Rho; trace Alpha, Beta	10.1	6.2	131	120
B.5.1	93.1	61.1	0.8	4.1	8.2	Poorly crystallized Alpha	8.6	5.5	90	36
C.1.1	92.0	58.8	0.8	4.5	11.8	Gamma; traces Beta, Rho, MnCO ₃	9.0	6.2	110	102
C.2.1	83.3	61.9	2.5	6.6	27.1	Gamma	8.9	4.5	132	109
C.3.1	87.9	57.9	0.7	6.1	16.1	Beta	10.0	2.6	70	66
C.4.1	57.0	68.0	0.3	5.9	10.5	Alpha	9.3	1.1	22	10
C.5.1	91.3	58.3	2.9	6.1	9.8	Gamma-Rho	8.2	3.7	109	107
C.6.1	90.2	58.9	1.1	6.1	26.5	80% Rho - 20% Alpha	---	6.6	118	114
D.1.1	92.3	62.0	1.3	5.3	12.8	Gamma-Rho	8.7	6.4	139	122
D.1.2	86.4	59.9	1.6	4.5	11.9	Distorted Beta	8.7	5.1	109	50
D.2.1	95.5	61.4	0.8	4.5	13.6	Gamma-Rho	10.0	6.0	143	137
D.2.2	83.6	61.1	0.4	6.0	16.9	Gamma-Rho	10.0	5.85	130	98
D.3.1	87.5	61.0	2.2	3.8	16.0	Rho; trace Alpha	8.8	3.2	76	---
E.1.1	87.3	60.3	7.4	4.2	3.8	Delta	6.9	0.0	0	0
E.1.2	85.9	---	---	5.2	13.6	Alpha	9.5	0.4	39	6
E.2.1	81.8	57.8	2.1	7.5	5.7	Delta; Epsilon	7.3	0.0	1	0
E.2.2	79.4	58.1	3.9	6.9	13.7	Delta; Epsilon	8.0	2.9	100	---
E.2.3	80.8	56.8	2.6	7.2	7.2	Epsilon	7.6	0.0	67	---
E.2.4	82.0	56.5	3.3	7.2	12.1	Delta	8.2	0.0	8	---
E.3.1	89.2	60.6	3.4	7.1	18.2	Beta; Epsilon	9.0	3.3	68	98
E.4.1	85.7	58.3	3.7	3.3	10.6	Alpha	---	0.9	28	11

TABLE IV

METHOD OF PREPARATION OF SAMPLES REPORTED IN TABLE III

<u>Code</u>	<u>Preparation</u>
A.1.1	A slurry of 200 grams MnCO_3 in 3 liters of water was chlorinated at 0-10°C for 3 hours.
A.2.1(a)	A slurry of Mn(OH)_2 was made by reacting 1584 grams $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 12 liters of water with 640 grams NaOH in 2 liters of water. This slurry was chlorinated at 5°C for 69 hours. A 115 gram portion of the dried product of this reaction was treated with 50 cc of concentrated H_2SO_4 in one liter of water at 87°C for 2 hours.
A.2.1(b)	A solution of 480 grams NaOH in 7.5 liters of H_2O was chlorinated and a solution of 1188 grams $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 1.5 liters of H_2O was added dropwise. The slurry was chlorinated at 6°C for 24 hours. An 80-gram portion of the dried product of this reaction was treated with 10 cc of concentrated HCl in one liter of water at 87°C for 2 hours.
A.2.2(a)	A solution of 320 grams NaOH in 3 liters of water was chlorinated and a solution of 396 grams of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 0.5 liter of water was added dropwise. The slurry was chlorinated at 21°C for 21 hours. A 100-gram portion of the dried product was treated with 100 cc of concentrated HCl in one liter of water at 87°C for 2 hours.
A.2.2(b)	A solution of 480 grams of NaOH in 7.5 liters of water was chlorinated and a solution of 1188 grams of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 1.5 liters of water was added dropwise. A solution of 480 grams of NaOH was added dropwise during the last half of the reaction time. The slurry was chlorinated at 25°C for 24 hours. A 100-gram portion of the product was treated with 22 cc of concentrated HCl in one liter of water for 2 hours at 87°C.
A.2.3	A solution of 240 grams $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 4.5 liters of water was reacted with 5 pounds of NaOCl solution (5-6%) and 96 grams of NaOH in 0.6 liter of H_2O . The NaOCl was added over a 3-hour period. The temperature varied from 92°C at the start of the reaction to 60°C at the end of the reaction.

TABLE IV (Cont'd)

METHOD OF PREPARATION OF SAMPLES REPORTED IN TABLE III

<u>Code</u>	<u>Preparation</u>
A.2.4	A solution of 400 grams $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 10 liters of water was reacted with 200 grams $\text{Ca}(\text{OCl})_2$ powder wetted with 200 cc of water. The $\text{Ca}(\text{OCl})_2$ was added in small batchwise additions over a 3.5 hour period and the temperature was 30°C .
A.2.5	A slurry of 148 grams of $\text{Ca}(\text{OH})_2$ in 3 liters of water was chlorinated and a solution of 396 grams of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 0.5 liter of water was added dropwise. The slurry was chlorinated at 25°C for 23 hours.
A.2.6	A solution of 197.9 grams of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 50 grams of H_2SO_4 in 430 cc of total solution was added dropwise to 500 cc of solution containing 213 grams of NaClO_3 . Addition time was 1.5 hours and the reaction temperature was 90°C .
A.3.1	A slurry of $\text{Mn}(\text{OH})_2$ was made by reacting 716 grams of $\text{Mn}(\text{NO}_3)_2$ solution (50%) in 2.7 liters of water with 160 grams NaOH in 0.5 liter of water. This slurry was chlorinated at 29°C for 21.5 hours.
A.3.2	A solution of one pound (50% solution) of $\text{Mn}(\text{NO}_3)_2$ diluted to 2 liters with water was reacted with 290 grams of $\text{Ca}(\text{OCl})_2$ wetted with 0.2 liter of water. The $\text{Ca}(\text{OCl})_2$ was added in small batchwise additions over a 2 hour period and the average temperature was 40°C .
A.3.3	A solution of one pound (50% solution) of $\text{Mn}(\text{NO}_3)_2$ diluted to 10 liters with water was reacted with 2.8 liters of NaOCl solution (4-5%). The total reaction time was 5 hours and the average temperature was 50°C .
A.4.1	A slurry of $\text{Mn}(\text{OH})_2$ was made by reacting 338 grams of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 2.5 liters of water with 160 grams of NaOH in 0.5 liter of water. This slurry was chlorinated for 24 hours at 2°C .
A.4.2	A solution of 240 grams of NaOH in 2.8 liters of water was chlorinated and 338 grams of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 0.7 liter of water was added dropwise over a 3 hour period. This slurry was chlorinated for 24 hours at an average temperature of 30°C .

TABLE IV (Cont'd)

METHOD OF PREPARATION OF SAMPLES REPORTED IN TABLE III

<u>Code</u>	<u>Preparation</u>
A.4.3	A solution of 338 grams of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 2 liters of water was reacted with a solution of 300 grams of $\text{Ca}(\text{OCl})_2$ in 1.5 liters of water. Addition time was 3 hours and the average temperature was 26°C . The dried product of this reaction was treated with 76 cc of concentrated HCl in 2 liters of water at 93°C for 2 hours.
A.4.4	A solution of 300 grams of NaOH in 2 liters of water was chlorinated until half of the NaOH had been reacted with Cl_2 and the molar ratio of NaOH to NaOCl was 2:1. This solution was added, dropwise, to a solution of 338 grams of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 1.5 liters of water. Addition time was 3 hours, total reaction time was $12\frac{1}{2}$ hours at an average temperature of 30°C . A 100-gram portion of the dried product was treated with 100 cc of dilute H_2SO_4 (100 gm H_2SO_4 /liter) for 1 hour at 94°C .
A.4.5	A solution containing 74.5 grams of NaOCl (16% solution) was added, dropwise, to a solution of 151 grams MnSO_4 and 100 grams H_2SO_4 at the boiling point of the solution ($95^\circ\text{-}100^\circ\text{C}$). The total volume of the combined solutions was one liter and the total reaction time was 2 hours.
A.4.6	A solution containing 169 grams of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and 100 grams HNO_3 in one liter of water was reacted with 245 grams of KClO_3 in 0.5 liter of water. The KClO_3 solution was added, dropwise, over a 2 hour period and the ClO_2 gas was removed as fast as formed; reaction temperature was 90°C .
A.4.7	A solution containing 487 grams/liter of MnSO_4 was reacted continuously with a solution containing 667 grams/liter of NaClO_3 . The acidity of the reaction was maintained at the proper level by holding the reaction slurry at a concentration of 150 grams/liter of H_2SO_4 . Reaction temperature was $90^\circ\text{-}100^\circ\text{C}$; total reactor volume was 3 liters and slurry withdrawal was at the rate of one liter/7 hours.
A.4.8	A solution containing 259 grams/liter of MnSO_4 was reacted continuously with a solution containing 215 grams/liter of HClO_3 . Reaction temperature was $90^\circ\text{-}95^\circ\text{C}$; total reaction time was 15 hours. The filtered and washed product was digested for 3 hours at the boiling point in one liter of 150 grams/liter of H_2SO_4 .

