Battery active manganese dioxide by chemical synthesis
by William G Moore

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

Abstract:
The reagents chlorine, sodium hydroxide, and manganese sulfate have been reacted by several techniques to yield manganese dioxide. The manganese dioxide was tested according to the U. S. Army Signal Corps specifications SCL-3H7-D for utility as a high grade depolarizer for Leclanche dry cells. The promising reactions were investigated extensively and treatment effects evaluated.

The synthesis methods investigated were: 1. Chlorine oxidation of manganese hydroxide 2. Chlorine oxidation of manganese sulfate 3. Basic hypochlorite oxidation of manganese sulfate 4. Miscellaneous methods which incorporate combinations of the first three methods Data on chemical and physical properties of the MhO2 together with X-ray diffraction analyses and battery tests are reported. Analysis of synthesis methods and operational difficulties are discussed.

The chlorine oxidation of manganese hydroxide was scaled up to 200 gallon semi-continuous operation with commercial reagents. The better runs yielded manganese dioxide which passed the chemical and drain test requirements of the Signal Corps Specification 31177-D for synthetic MnOg for military grade dry batteries. Analysis by X-ray diffraction shows the MhOg to be of the gamma-rho to rho crystalline structure.

Blends of Gold Coast ore and manganese dioxide prepared in the scaled up reactions were tested for indications of the commercial utility of the chemical depolarizer. A mutual upgrading effect is shown by the Gold Coast-chemical..ore blend in contrast to the linear variation of battery life with composition exhibited by electrolytic Mn02-Gold Coast ore blends. Specification battery tests are obtained with 55%-60% chemical ore, whereas 85-90% electrolytic ore is required! to upgrade Gold Coast ore to the same capacity.

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TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

TABLE OF CONTENTS (Cont'd)

ABSTRACT

The reagents chlorine, sodium hydroxide, and manganese sulfate have been reacted by several techniques to yield manganese dioxide. The manganese dioxide was tested according to the U. S. Army Signal Corps specifications SCL-3117-D for utility as a high grade depolarizer for Leclanche dry cells. The promising reactions were investigated extensively and treatment effects evaluated.

The synthesis methods investigated were:

1. Chlorine oxidation of manganese hydroxide
2. Chlorine oxidation of manganese sulfate
3. Basic hypochlorite oxidation of manganese sulfate
4. Miscellaneous methods which incorporate combinations of the first three methods

Data on chemical and physical properties of the MnO_2 together with X-ray diffraction analyses and battery tests are reported. Analysis of synthesis methods and operational difficulties are discussed.

The chlorine oxidation of manganese hydroxide was scaled up to 200 gallon semi-continuous operation with commercial reagents. The better runs yielded manganese dioxide which passed the chemical and drain test requirements of the Signal Corps Specification 3117-D for synthetic MnO_2 for military grade dry batteries. Analysis by X-ray diffraction shows the MnO_2 to be of the gamma-rho to rho crystalline structure.

Blends of Gold Coast ore and manganese dioxide prepared in the scaled up reactions were tested for indications of the commercial utility of the chemical depolarizer. A mutual upgrading effect is shown by the Gold Coast-chemical ore blend in contrast to the linear variation of battery life with composition exhibited by electrolytic MnO_2-Gold Coast ore blends. Specification battery tests are obtained with 55%-60% chemical ore, whereas 85-90% electrolytic ore is required to upgrade Gold Coast ore to the same capacity.

INTRODUCTION

The need for portable power sources has been satisfied by a variety of cell systems. Many of these cells utilize an oxidation-reduction reaction which features solution of a metal to yield metal ions at one electrode and evolution of hydrogen at the other electrode.

Researchers soon discovered that the evolution of hydrogen was undesirable, since it caused the cell potential to fall rapidly even when the current drain on the cell was light. This phenomenon, which caused a voltage decrease when the cell was under current drain, was termed polarization. Elimination of polarization, or depolarization, became the object of intensive study. Depolarization by reacting the hydrogen with an ozidizing agent to form inert reaction products was the approach which led to eventual success. The oxidizing agent which proved most efficient from the point of view of stability, availability, and effectiveness was the oxide of tetravalent manganese, manganese dioxide. Best known of manganese dioxide depolarized dry cells is the Leclanche dry cell, which utilizes the carbon-manganese dioxide: zinc metal couple.

Large naturally occuring deposits of high quality battery active manganese dioxide in Western Africa were instrumental in the success of the Leclanche cell. Note that the African natural manganese dioxide is described as battery active, implying that high quality MnO_2 exists which is not battery active, i.e., does not function well as a depolarizer despite its high assay of MnO_2.

Investigations by battery manufacturers and independent researchers led to improvements in dry cell manufacturing techniques, formulations, and storageability, but no significant improvement in the depolarizer was made as long as the Gold Coast ore was available to the world at a reasonable price. Other MnO_2 ores were evaluated as were a variety of synthetically prepared dioxides, but most were found to be inferior to Gold Coast ore in performance. Some investigators began to discover that the common denominator of battery activity of manganese dioxide was a rather nebulous sort of thing. When the analytical tools of X-ray diffraction and electron microscopy were brought to bear, the problem of differentiating battery active MnO_2 from the inactive dioxide began to be resolved. In general, the well defined, highly crystalline species which gave sharp diffraction patterns were poor depolarizers, while the active species tended toward an amorphous or meso crystalline structure and are characterized by diffuse diffraction patterns.

As an introduction to the use of electron micrographs and X-ray diffraction in evaluating battery active MnO_2, the reader is referred to Figures 1 through 8. Figure 1 was prepared by the micro-optical section of the Signal Engineering Laboratories as a guide in judging the merits of synthetic MnO_2. The gradations in crystal habit correlate rather well with battery activity for MnO_2 having similar chemical and physical properties such as $\%MnO_2$, free moisture, apparent density, and crystal phase.

The electron micrographs must be used in conjunction with the other analytical procedures to avoid unwarranted conclusions as the following instances will illustrate:

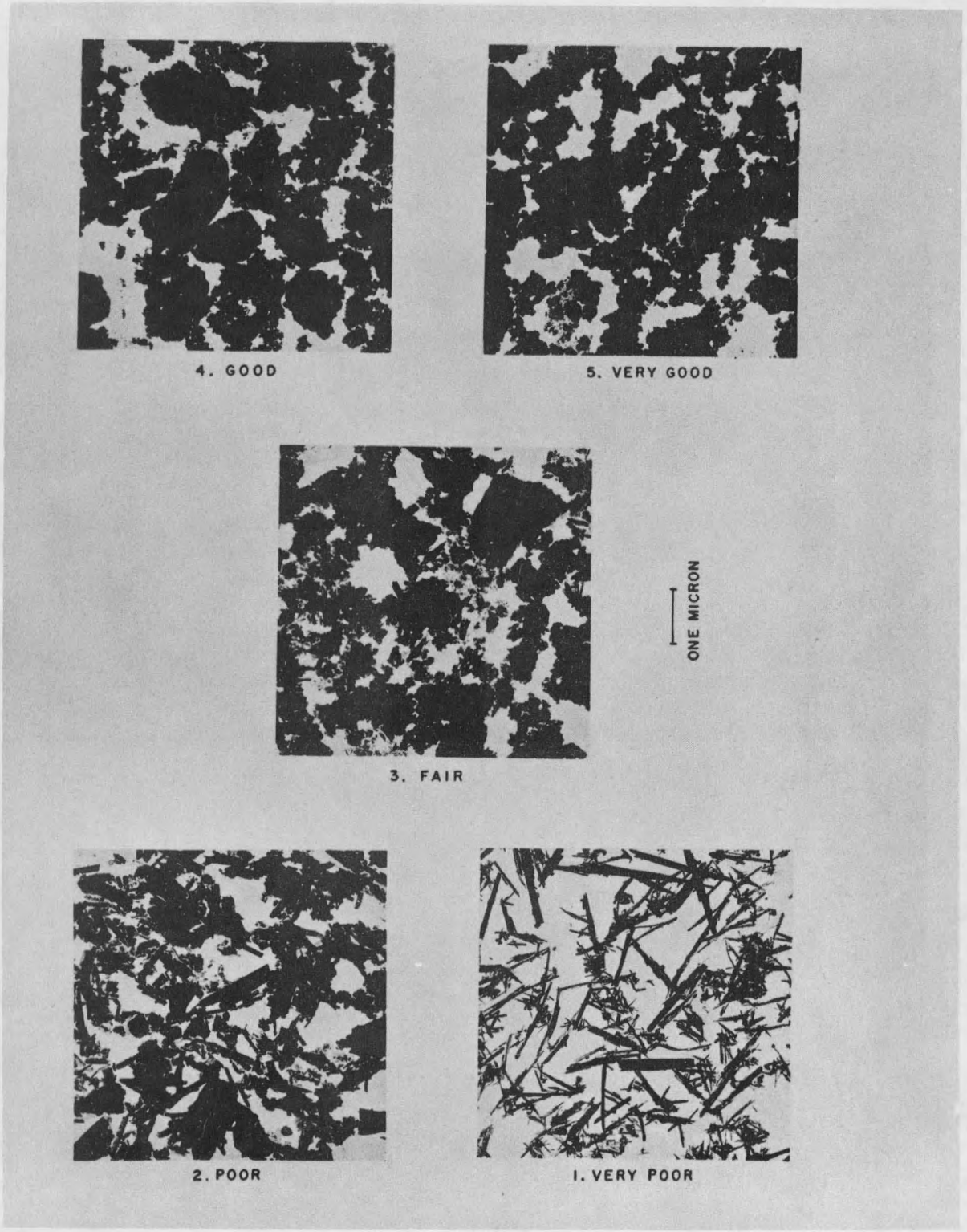

Figure 1 Reference Electron Micrographs

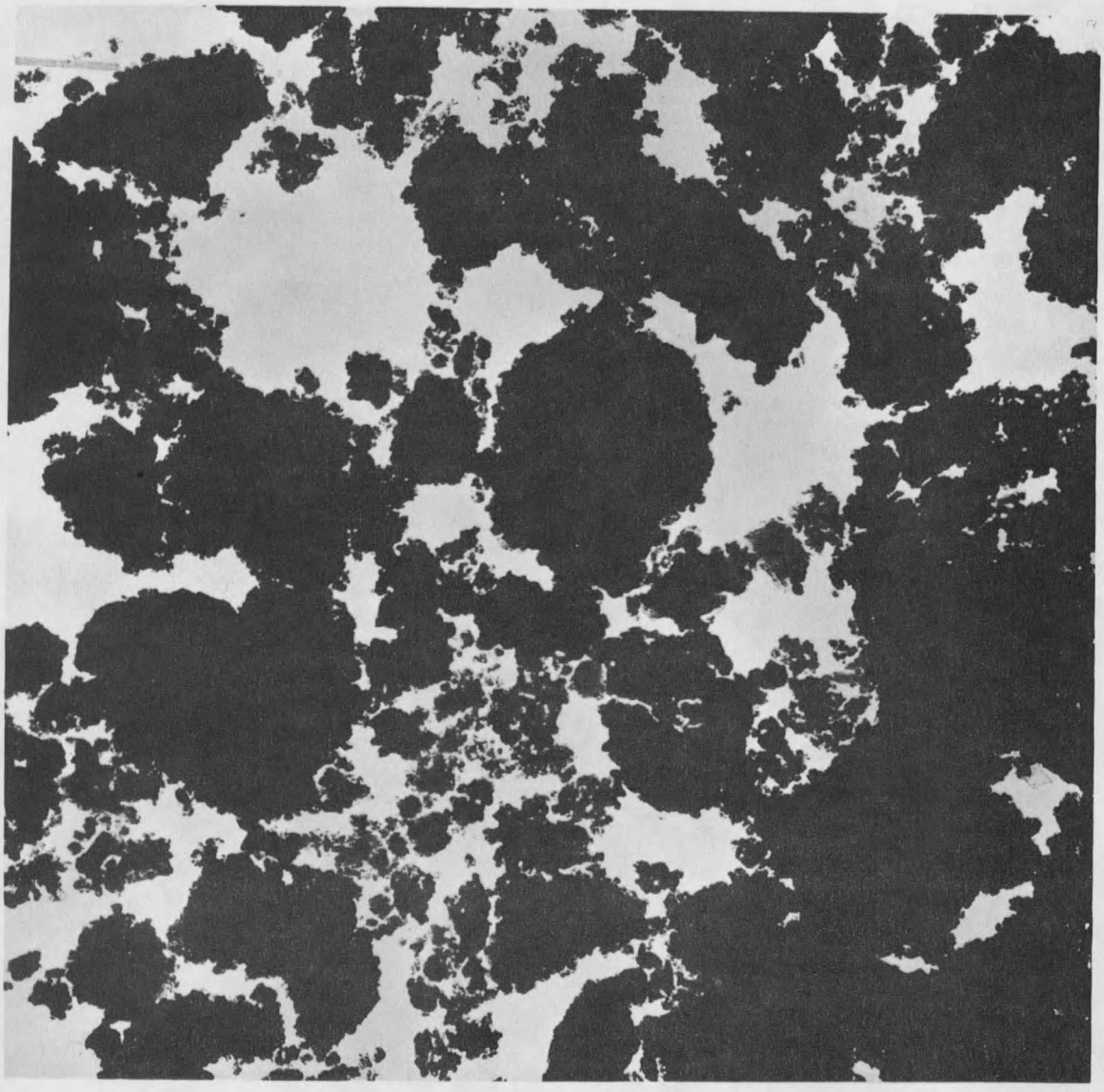

Figure 2 Electron Micrograph MnO_2 32,000X

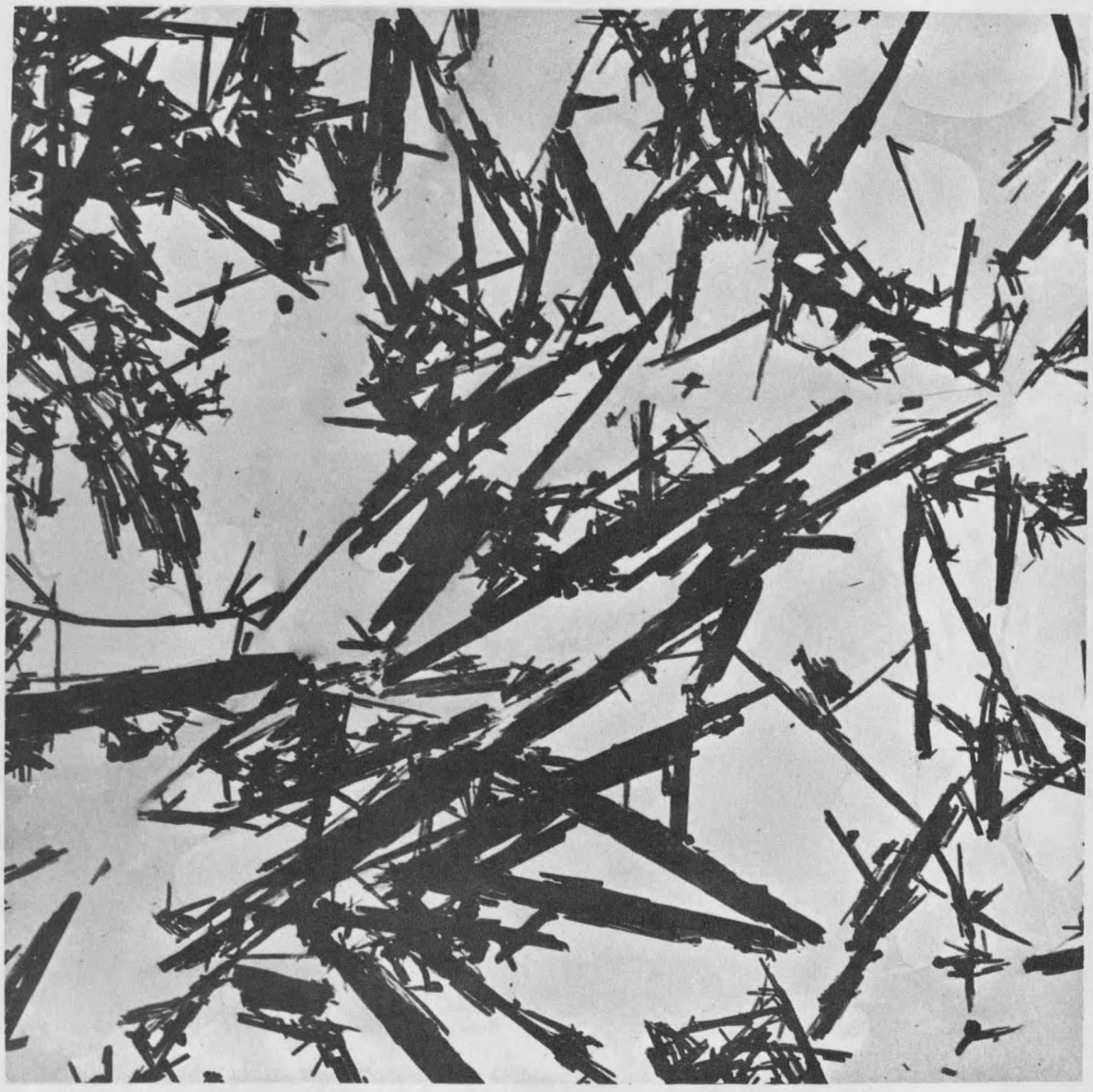

Figure 3 Electron Micrograph of MnO_2 - 32,000X

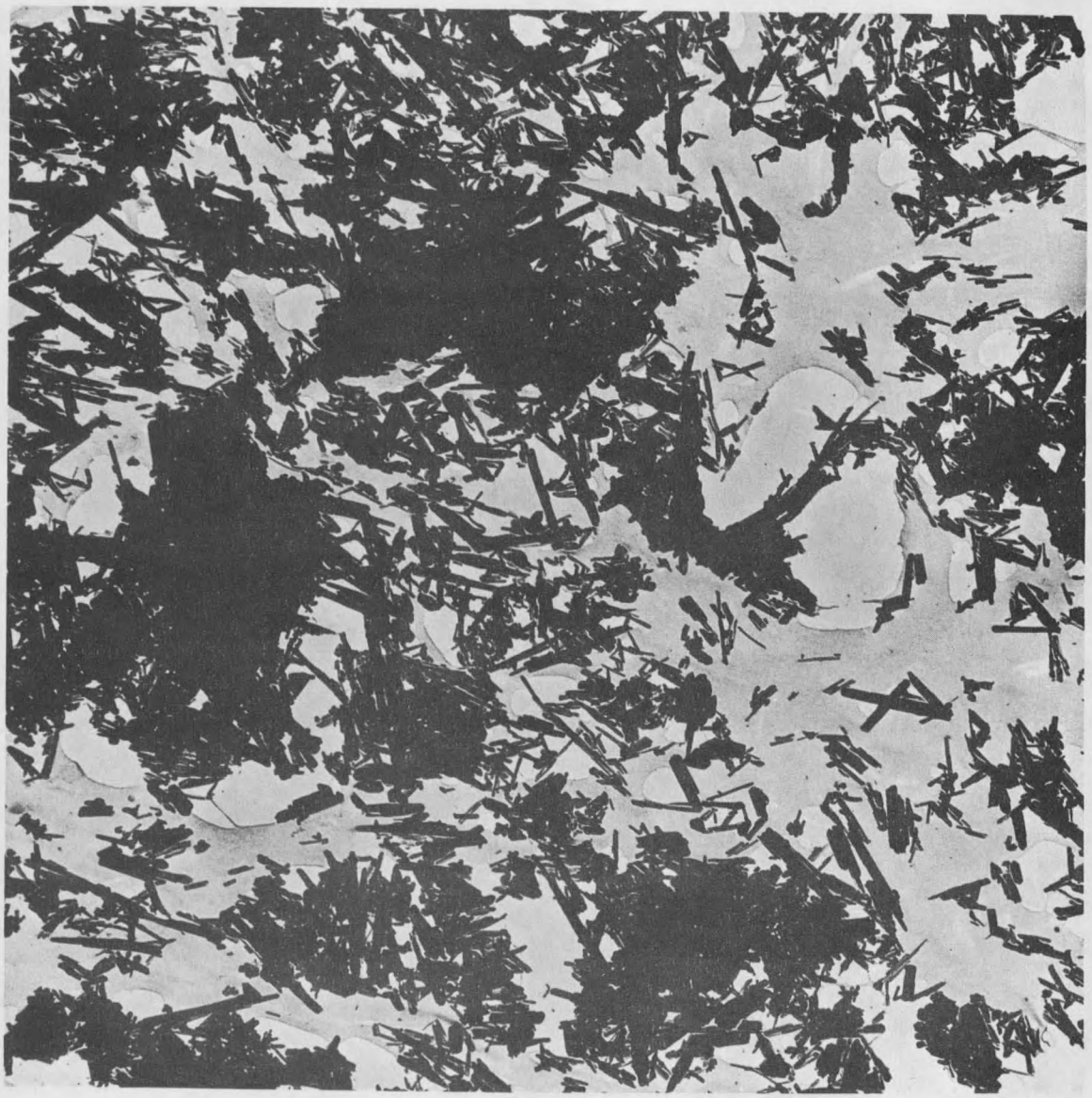

Figure 4 Electron Micrograph of MnO_2 - 32,000X

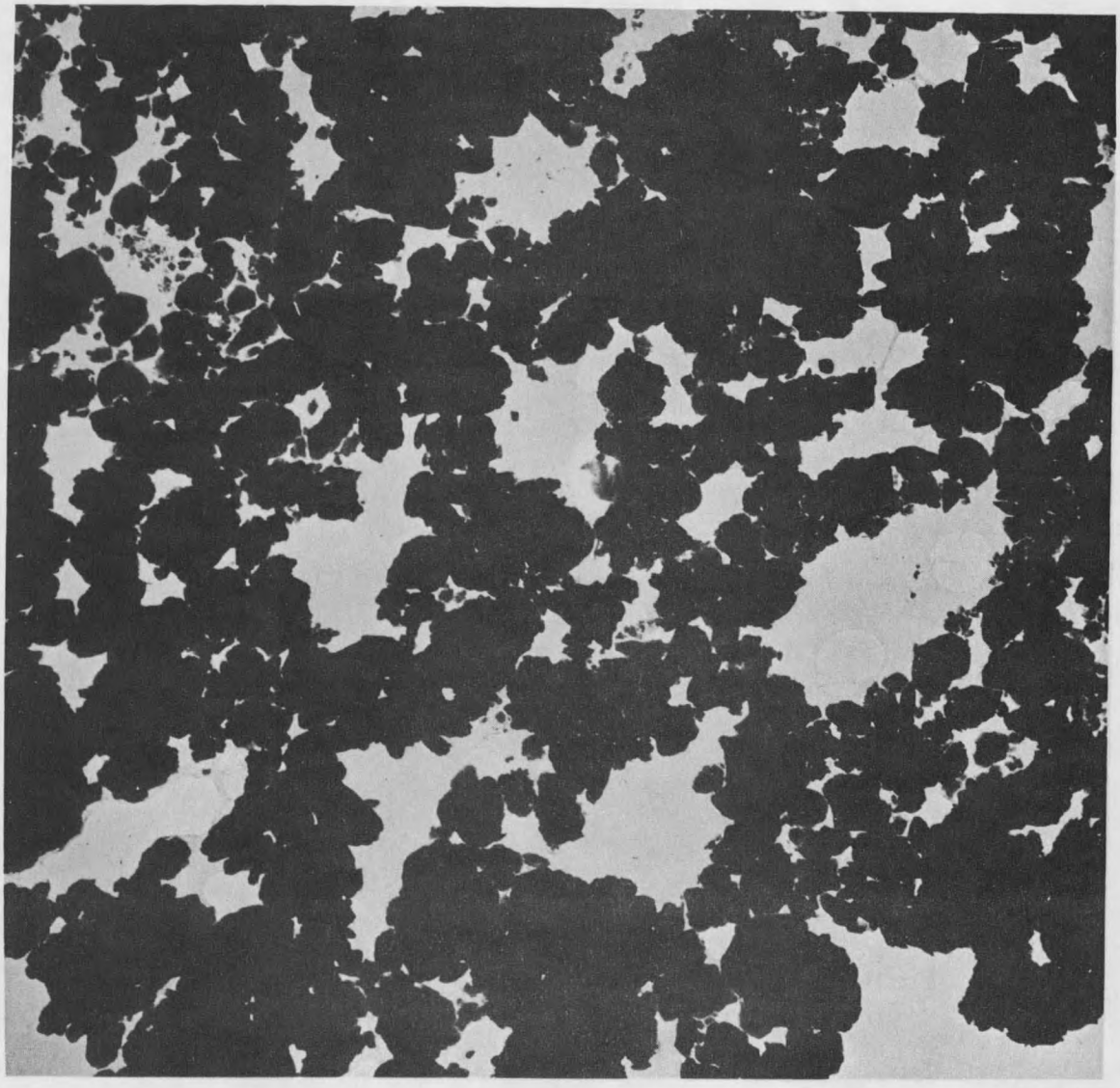

Figure 5 Electron Micrograph of MnO_2 - 32,000X

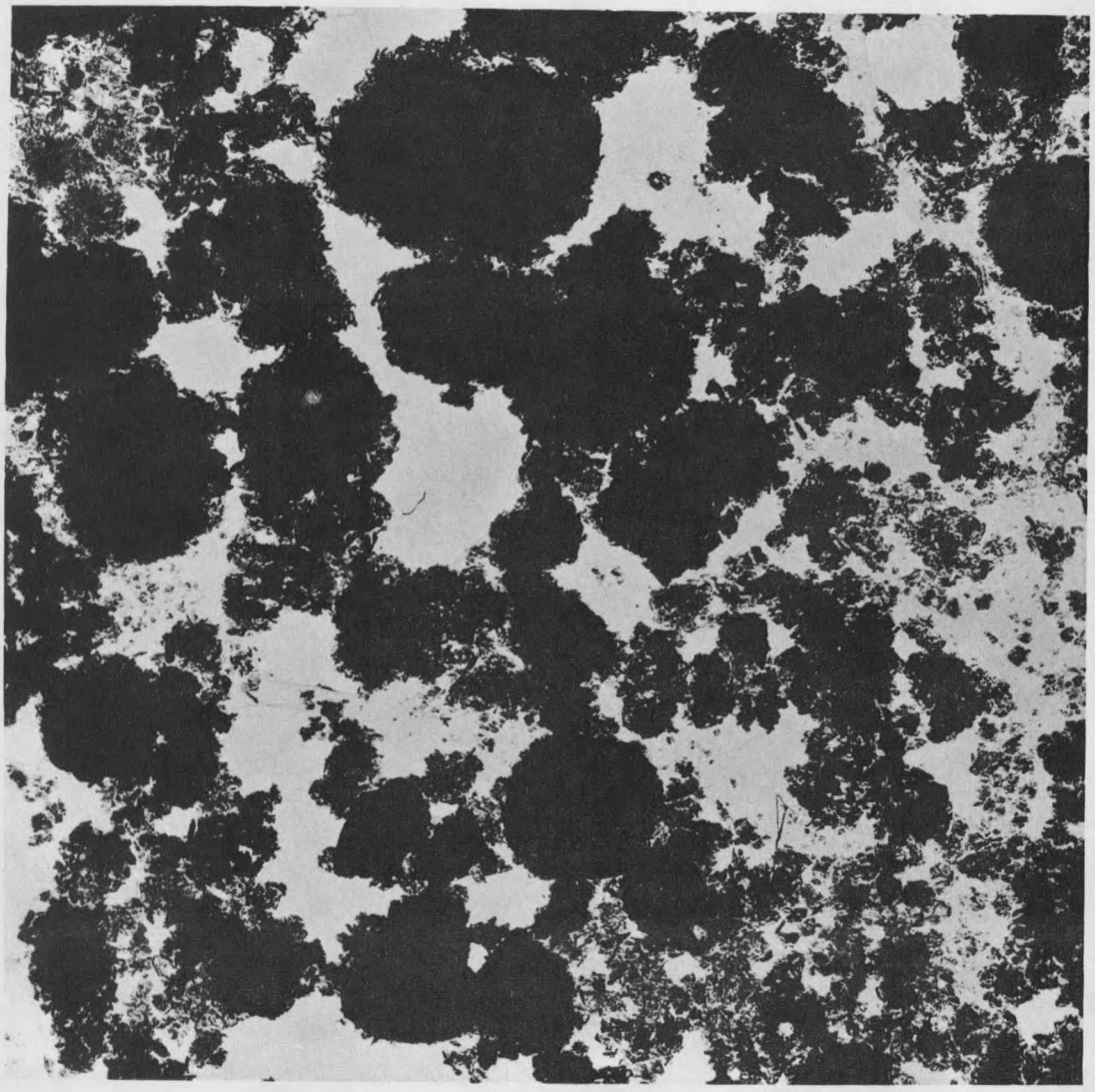

Figure 6 Electron Micrograph of MnO_2 - 32,000X

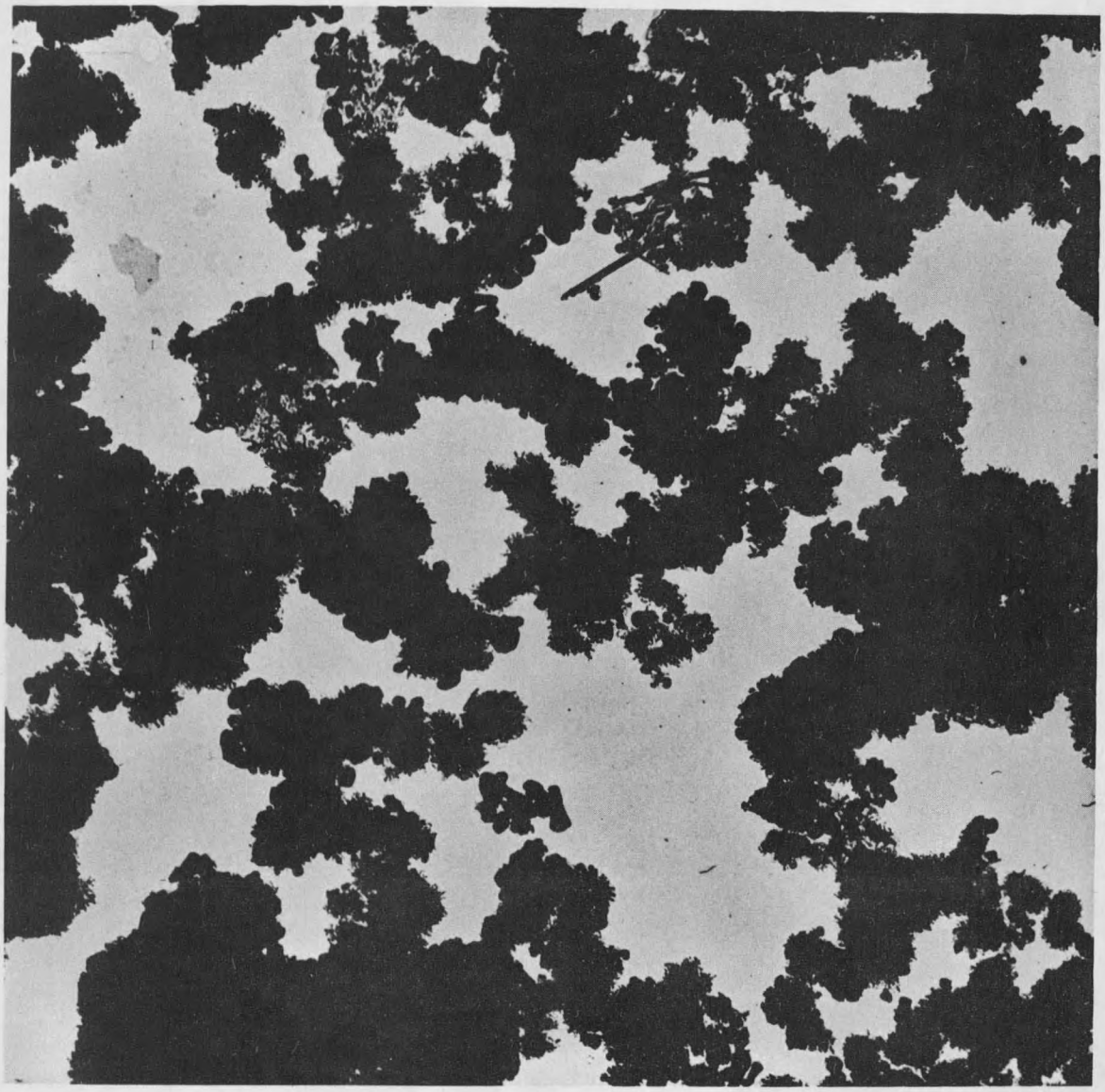

Figure 7 Electron Micrograph of MnO_2 - 32,000X

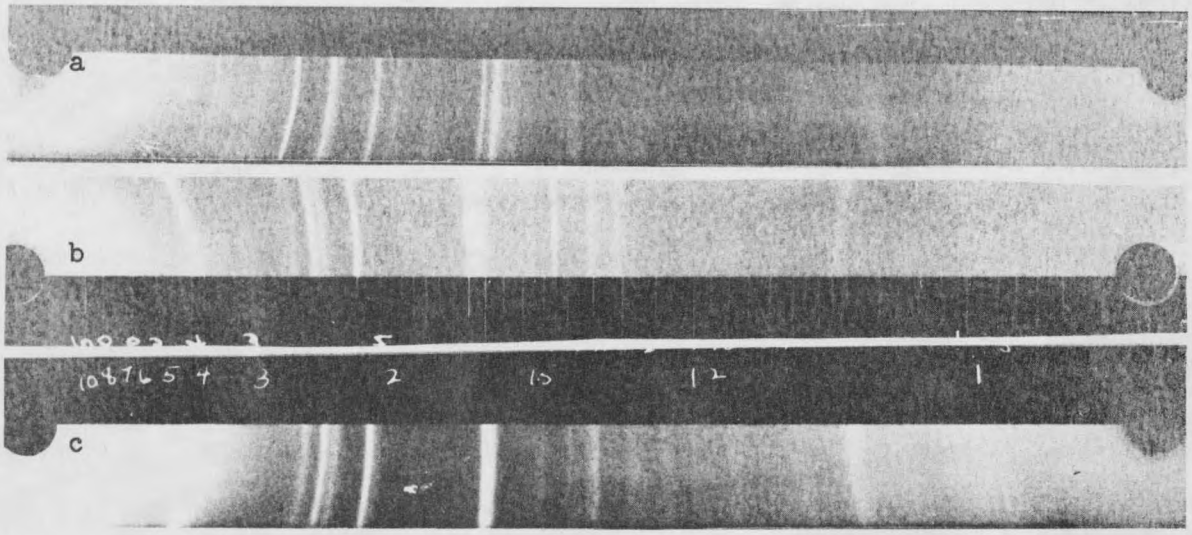

Figure 8. Shown above are X-ray diffraction patterns of (a) a typical beta manganese dioxide prepared by thermal decomposition of $Mn(NO_3)_2$, (b) rho phase MnO_2 prepared by chlorine oxidation of $MnCO_3$ and (c) rho phase MnO_2 prepared by $Ca(OCl)_2$ oxidation of $MnCl_2$ solution. The electron micrographs of the ultimate particles of these samples are shown in Figures 2, 4, and 5.

Comparison of Figures 1, 2, and 3 may lead to rating the MnO_2 of Figure 2 as good to very good morphology and the MnO_2 shown in Figure 3 as very poor. The battery activity of the two samples is actually as predicted, except that the best (Figure 2) is only mediocre as compared to the natural ore from the Gold Coast of Africa and decidedly inferior to the better synthetic MnO_2. The reason for these results is shown by the X-ray diffraction pattern of Figure 8a, the samples are both of the relatively inactive beta phase. The point demonstrated is that an undesirable phase can exhibit excellent particle morphology and mediocre battery activity, or may have poor morphology and show almost no battery activity.

The next two micrographs, Figures 4 and 5, show similar correlations for a desirable phase. Both samples have the rho crystal structure as shown by Figure 8b and c, but by the particle morphology ratings of Figure 1, the MnO_2 of Figure 5 must be rated much better than that of Figure 4. The battery tests verify the ratings and show the best sample to be almost twice as good as the Gold Coast ore.

Figure 6 illustrates the extremely fine, lacey particles associated with some chemical syntheses. The particular sample illustrated is a gamma-rho dioxide prepared by the low temperature chlorine oxidation of $MnCO_3$ slurries. The favorable phase and morphology do not account for the poor battery activity of the sample. The extremely low apparent density of this MnO_2 prevented proper cell fabrication and battery tests were very poor.

Figure 7 shows that several distinct types of crystal habit may occur in a given reagent system. This particular sample shows evidence of transformation of one phase type to another.

Since World War II the U. S. Army Signal Corps has put a great deal of effort into a program to improve the dry batteries used by the military. The goal was to establish domestic production of a high grade synthetic MnO_2 depolarizer as well as encouraging research leading to improvement of the other components of the Leclanche cell. To date, the program has been successful; new conducting gel systems, paper separators, and improved electrolyte formulations have been developed. Research sponsored by the Signal Corps led to the pilot plant and subsequent commercial production of a synthetic depolarizer which was sig-

nificantly better than the Gold Coast ore. The newly developed process produced the gamma phase of MnO_2 by the electrolysis of acidic $MnSO_4$ solutions. In addition to the development of the electrolytic process, the Signal Corps sponsored research on synthetic MnO_2 depolarizers prepared by chemical syntheses, a project undertaken at the Engineering Experiment Station at Montana State College.

As a scouting activity, the Signal Corps examined micro-optically numerous manganese dioxide samples made by a great variety of reaction types; those which produced meso-crystalline MnO_2 were chosen for further investigations at Montana State College. A review of the research done at M.S.C. in the period 1951 to 1955 was presented by Berg (2) and Baughman (1). This work was on the scale of a few hundred grams and the reactions run batchwise or semi-continuous. Of particular interest to Baughman was the reaction of $MnCl_2$ with caustic and chlorine followed by digestion of the product with dilute HCl at at elevated temperature. The following description represents the reaction sequence:

> A solution of 480 grams of NaOH in 7.5 liters of water was chlorinated and a solution of 1188 grams of $MnCl_2 \cdot 4H_2O$ 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.

This procedure has been successfully employed in synthesizing manganese dioxide which is about twice as effective as Gold Coast ore.

In an effort to extend the chemical synthesis of battery grade ore to the system NaOH, Cl_2, and $MnSO_4$, a series of experiments were designed

to evaluate the effect of treatment variables on the battery activity of the MnO_2.

Literature and patent disclosures (3) mention the oxidation of $MnSO_4$ solutions by a variety of oxidizing agents including several methods for the addition of caustic and chlorine. The reaction products are generally described as superior depolarizers, superior presumably to the natural ore from Africa. Since the reaction conditions of temperature, reactant ratios, contact time, and general technique were lacking in the above disclosures, a starting point in the experiment design was largely at the discretion of the experimentor.

The stoichiometry of the proposed reaction is:

I. $MnSO_4 + 4NaOH + Cl_2 \longrightarrow MnO_2 + Na_2SO_4 + 2NaCl + 2H_2O$

$Mn^{+2} \longrightarrow Mn^{+4} + 2e$

$2e + 2Cl_2 \longrightarrow 2Cl^{-1}$

$Mn^{++} + Cl_2 \longrightarrow Mn^{++++} + 2Cl^{-}$

The actual sequence of events depends on the manner of the reagent addition; for instance, Baughman has reported the dropwise addition of $MnSO_4$ to chlorinated caustic solutions.

II. $4NaOH + Cl_2 \longrightarrow NaOCl + NaCl + 2NaOH + H_2O$

III. $2NaOH + MnSO_4 + NaOCl \longrightarrow 2\ NaCl + Na_2SO_4 + H_2O + MnO_2$

The mol ratio of reagents was four mols NaOH per mol manganese, which fits the electronic requirements of equations II and III. The actual mechanism of oxidation is no doubt complex, since the pH of the reaction mixture, initially at 13+ hydrolyzes the $MnSO_4$ as fast as added to yield

the insoluble hydroxide, $Mn(OH)_2$, the chlorine added to a solution of this base strength and of extremely low effective concentration of manganous ion, reacts nearly quantitatively to form NaOCl and NaCl. The basic hypochlorite oxidation of $Mn(OH)_2$ has been demonstrated to yield a hydrated non-stoichiometric manganese oxide which has the oxidizing power corresponding to 85% of the manganese as MnO_2 and the rest as a divalent oxidation state. The actual compound(s) present have not been definitely identified, but are thought to be the tervalent oxide hydrate, manganite, $Mn_2O_3 \cdot H_2O$ or $MnO \cdot OH$, a compound which assumes both tetravalent and divalent character in acidic media. Continuing with the oxidation according to the method of Baughman, after completing the $MnCl_2$ addition, the chlorine is apparently evolved as fast as added, indicating a deficiency of base, therefore he specifies the dropwise addition of base to complete the oxidation. The oxidation could, and probably does proceed by alternate mechanisms at this stage, depending on the relative rates of caustic and chlorine addition. If the chlorine is in excess, the effective oxidant is probably HOCl, which occurs by reaction IV:

IV. $Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl$

This reaction will proceed to the right if base is added to neutralize the HCl formed; without base addition, equilibrium is apparently reached at a pH of about 1.8 - 2.0 at 25°C. If base is added more rapidly than Cl_2, the oxidant then becomes NaOCl. As the molar ratio of NaOH to Mn becomes closer to the 4:1 ratio theoretically needed to oxidize all the manganese to the tetravalent state, the reaction mechanism takes on a

different character. The relatively higher concentration of MnO_2, as compared to $Mn(OH)_2$, in the presence of NaOCl, leads to the formation of $NaMnO_4$ according to the reaction

V. $2NaOH + 2MnO_2 + 3NaOCl \longrightarrow 2NaMnO_4 + 3NaCl + H_2O$

$2(Mn^{+4} \xrightarrow{-3e} Mn^{+7})$
$2(Cl^{+1} \xrightarrow{+2e} Cl^{-1})$

The intensity of the permanganate color persists even though analysis of the manganese oxides shows that about 15% of the manganese is present as a quasi divalent state. Apparently the divalent manganese is coated by a covering of MnO_2 in such a way as to make the divalent material unavailable, thereby presenting a particle with the properties of MnO_2. The formation of permanganate under these conditions is always accompanied by a change in the appearance of the precipitate to the light brown "hydrate" characteristic of Volhard MnO_2. The hydrate is a non-stoichiometric oxide which is typically 75 - 85% MnO_2 (dry basis), and 55 - 60% Mn and is a poor depolarizer. Other characteristics of material made by this technique is an absorption phenomena at a particular point in the washing of the MnO_2. The MnO_2 precipitates were washed by successive dilution and decantation of the soluble salts. Where permanganate formed during the reaction it was noted to decrease in intensity as would be expected until the wash water was in the pH range of 4.0 to 5.0 where the MnO_4 suddenly disappeared and the manganese dioxide became colloidal, remaining dispersed for days. As the washing continued, the amount of MnO_2 in the dispersed phase increased. The pH and salt content of the wash water was the criteria for the end of the washing period; a pH of 6.5 to 7.0 and the

absence of a precipitate with the addition of .1 M $BaCl_2$ to a portion of the wash water was considered the end point. Even after this degree of washing, the resulting dried manganese dioxide would give an alkaline reaction when subjected to the pH determination outlined by the Signal Corps specification, SCL 3117-D, Table XV of the appendix.

The successful cure-all for the activation of the hydrated form of MnO_2 outlined above was the digestion with HCl at or near the boiling point. Baughman's opinion of the best leach condition was as follows: determine the amount of divalent manganese in the "hydrate" by utilizing the analysis of the sample as $\%MnO_2$ and % manganese in the following manner:

$$\% \text{ divalent manganese} = (\% \text{ total Mn}) - (\%MnO_2)\left(\frac{55 \text{ gm Mn}}{87 \text{ gm } MnO_2}\right).$$

The difference in the two values is the grams of divalent manganese present, and since it is associated with oxygen, the convention has been to convert the weight of divalent manganese to percent MnO by multiplying the above quantity by the molecular weight ratio of MnO:Mn or 71/55, which gives:

$$\%MnO = (1.29)x(\%Mn)-(.816)x(\%MnO_2)$$

A word of explanation of the reference to MnO and divalent manganese is in order. The actual existence of divalent manganese or MnO is not probable. However, several oxides of manganese such as Mn_2O_3, Mn_3O_4, and $Mn_2O_3 \cdot H_2O$ behave more like mixtures of MnO and MnO_2 in the presence of acids since solution to yield the manganous ion occurs and the insoluble portion contains a predominance of tetravalent manganese. Thus the

calculated quantity, % MnO, is hypothetical, but nevertheless useful in determining properties of a sample of MnO_2.

The amount of HCl necessary to activate the hydrate was that theoretically needed to remove all the divalent manganese. Acid concentration was typically 3 to 10% and the ratio of acid solution to hydrate manganese dioxide 10:1 by weight. The resulting dioxide was then washed, dried, and ground in a pebble mill to yield a very active depolarizer.

In reviewing this reaction sequence the following weaknesses are noted: the yield is about 80-85% per pass based on chlorine and caustic consumption, and there appears to be no method for putting the reaction on a continuous basis. Neither of these are serious objections, but are to be kept in mind when alternate syntheses are proposed.

The author, in 1952, demonstrated the chlorine oxidation of $Mn(OH)_2$ according to these equations:

VI. $MnSO_4 + 2NaOH \longrightarrow Mn(OH)_2 + Na_2SO_4$

VII. $2Mn(OH)_2 + Cl_2 \longrightarrow MnO_2 + MnCl_2 + 2H_2O$

The reaction was initially run two stage as shown with cooling between the $Mn(OH)_2$ formation and the addition of chlorine. The reaction was semi-continuous and was terminated after a 24-hour reaction period when the pH, initially at 9-10, had fallen to 1.8 - 2.0. The principal advantage of this scheme was the production of the $Mn(OH)_2$ by simple pH control, and no special attention was needed in the chlorination, since side reactions to form permanganate were not possible in the presence of appreciable concentrations of manganous ion. The reaction product could

be utilized after the customary washing, drying, and grinding, and without activation steps to yield a very good depolarizer. Although the yield of product based on the caustic and chlorine consumption is about 105%, the 50-55% conversion per pass necessitates a recycle manganese stream. Adaptation of the chlorination to a continuous counter flow system was feasible since no reagent addition other than chlorine was made during the oxidation.

The sodium hypochlorite oxidation of neutral $MnSO_4$ solutions has been reported (3). The reaction proceeds as follows:

VIII. $2NaOCl + MnSO_4 \longrightarrow Na_2SO_4 + MnO_2 + Cl_2$

$$\begin{matrix} 2Cl^{+1} & \xrightarrow{+2e} & 2Cl^{0} \\ Mn^{+2} & \longrightarrow & Mn^{+4} \end{matrix}$$

The reaction proceeds to the right with the evolution of Cl_2. The reaction product is recovered in quantitative yields and requires only the customary washing, drying, and grinding to be used as a good quality depolarizer. This reaction requires close control in the hypochlorite preparation since chlorination beyond the point of 3 gm/liter of free NaOH results in the spontaneous decomposition of the NaOCl:

IX. $NaOCl \longrightarrow NaCl + \frac{1}{2}O_2$

The overall chlorine and caustic consumption of reaction VIII is the same as in the two reactions I and VII; however, it should be noted that during the oxidation step the chlorine changes only one valence electron, a situation brought about by the low pH of the reaction mixture. Utilization of the maximum valence change of the "positive" chlorine requires a neutral or basic reaction medium.

It was concluded that this reaction would be worthy of further effort with some modifications in the chemistry to eliminate the chlorine evolution, i.e., maintain the reaction pH at the neutral point by caustic addition so the reaction would proceed as follows:

X. $4NaOH + Cl_2 \longrightarrow 2NaOH + NaOCl + NaCl$

XI. $2NaOH + NaOCl + NaCl + MnSO_4 \longrightarrow Na_2SO_4 + 2NaCl + MnO_2 + H_2O$

Reappraisal of the three reaction schemes in section I in the light of their commercial application leads to the choice of VII and XI as having more promise than I. However, the excellent battery activity of the manganese dioxide of I justified some effort toward utilizing $MnSO_4$ in the reaction step and H_2SO_4 in the activation step.

The first program adopted included investigation of reaction parameters of reactions I, VII, and XI on a batch or semi-continuous scale with reagent grade materials used throughout. Utilization of commercial grade reagents on a bench scale was to be the second stage so that impurity effects could be evaluated in closely controlled experiments. Assuming success in the second stage, demonstration of the reaction on a scale of 20 pound batches was to be attempted to determine scale-up factors not evident on the bench scale or 4 liter beaker stage. Data from the three phases were to be used in approximating capital requirements of a commercial venture.

METHODS AND PROCEDURES

Previous research at Montana State College has shown that the best method of evaluating depolarizer efficiency is to fabricate and test dry cells according to Signal Corps specifications, SCL-3117-D. The pertinent paragraphs of this specification which outline the materials and methods used in fabricating the "A" size test cells are included in the appendix. The type of drain tests that the cells are subjected to are the initial high drain and low drain and the delayed capacity low drain test. The conditions for these tests are listed below:

	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	1.00 volts
discharge temp (humidity not controlled)	65-75°F	65-75°F

The battery drain tests at Montana State College differ from the capacity tests of the Signal Corps specification in that only five days elapsed between the time of fabrication and the drain tests. The difference in drain between the five-day and ten-day aging period is negligible.

The Signal Corps specifies the aging conditions for delayed capacity tests to be 70°F and 50% relative humidity. Humidity and temperature were not controlled during the aging period at Montana State College and varied considerably. The temperature averaged 70-75°F, but the humidity was often in the zero to thirty per cent range. Moisture loss in the stored cells was serious and post mortems on stored cells showed the bobbins to be powdery and the conducting gel deteriorated or entirely crystallized. The resulting delayed capacity tests may not represent the

true capabilities of the test sample, but may be a more accurate indication of percent moisture loss.

The battery tests require eight cells, two for each initial drain test, four for delayed capacity at three, six and twelve months. When erratic performance on the initial tests was encountered, a check cell was run off. The amount of MnO_2 necessary for this scale of testing is easily prepared in 4-liter capacity beakers.

Chemical analysis and physical measurements were made in accordance with the SCL-3117-D specification for synthetic manganese dioxide.

Initially, chemically pure chemicals were used to prepare the manganese dioxide samples in batches of about 100-200 grams each. Treatment effects such as reactant ratios, temperature and reaction time were evaluated by changing only one variable at a time. Occasionally, larger batches were prepared so additional material was available for investigation of grinding, sizing, and acid digestion.

When suitable reaction conditions were found which produced manganese dioxide equaling or exceeding the SCL-3117-D specifications for synthetic MnO_2, the conditions were tried with commercial or technical grade reagents so that impurity effects on the product might be ascertained. When suitable purification techniques were discovered and the use of commercial reagents yielded a product meeting or closely approaching the synthetic MnO_2 specification, the design of continuous reaction systems was undertaken. Evaluation of operating variables peculiar to continuous operation were ascertained. The next phase involved the scale-up of the commercial reagent reactions from the 4-liter

beaker stage to the 100-250 gallon batch stage. The object of operation on this scale was to evaluate handling characteristics in semi-commercial equipment, determine suitable materials of construction, and to obtain samples of a size which would allow more extensive product quality determinations.

EXPERIMENTAL RESULTS

Combination of the reagents $MnSO_4$, NaOH, and Cl_2 to yield battery active MnO_2 is accomplished in a variety of procedures. In considering the systems which might be utilized, the simplest seems to be the simultaneous or sequential addition of the three reagents in the stoichiometric proportions to yield the product, MnO_2, and by-products, NaCl and Na_2SO_4. Several reactions illustrate the properties of manganese dioxide prepared by the addition of 4 mols of caustic to 1 mol of $MnSO_4$, followed by chlorination to an acidic endpoint. Reversal of the procedure, that is, chlorination of 4 mols of caustic followed by addition of 1 mol of aqueous $MnSO_4$ yields a product like that of MCl-1. Table I shows the physical and chemical analyses of these samples.

Table I

Sample	O_2 as $\%MnO_2$	%Mn	Density gm/in^3	Drain Tests high	low	3 mo.
MCl-7	83.4	58.0	11.8	1.4	118	12
MCl-1	78.0	56.0	12.5	2.5	84	84
MCl-1a	95.5	61.4	12.2	4.5	153	128

The products are the light brown hydrated MnO_2 typical of Volhard dioxide; that is, the precipitate commonly obtained by reduction of permanganate in neutral solutions. Calculation of possible chemical combi-

nations in the hydrate may be useful in deciding the merits of the synthesis type. The divalent manganese is commonly associated with tetravalent manganese in the form of Mn_2O_3, bixbyite, or the hydrated quasi-tervalent oxide, manganite, $Mn_2O_3 \cdot H_2O$ or $MnO \cdot OH$. Since manganite has been identified in the air oxidation products of $Mn(OH)_2$ and $Mn(OH)_2$ is present in both reactions under consideration, it follows that a logical choice is manganite. If the analyses of MCl-1 are considered, calculations of the quantity of tetravalent manganese as $MnO_2 \cdot H_2O$ associated with the divalent manganese as MnO leads to the following results:

	$\%O_2$ as MnO_2	%Mn	Actual % MnO_2	$Mn_2O_3 \cdot H_2O$ %Manganite	$\%H_2O$ hydration
MCl-1	78.0	56.0	67.4	21.2	11.4

The significance of the scaled down value for actual per cent MnO_2 is this: In an experiment to determine the effective depolarizer reaction in a Leclanche cell, several cells were discharged until they were completely polarized. Figure 9 shows the voltage vs. time plots of these discharge curves.

The ampere hour-chemical conversion relation is such that the equivalents of manganese dioxide actually present in the cell corresponds exactly to the equivalents of electricity summed over the high discharge voltage plateau, i.e., at cell potentials greater than .8 - .9 volt. The primary depolarization cell reaction is then:

XII. $H_2 + 2MnO_2 \longrightarrow Mn_2O_3 \cdot H_2O$

or

$\longrightarrow Mn_2O_3 + H_2O$

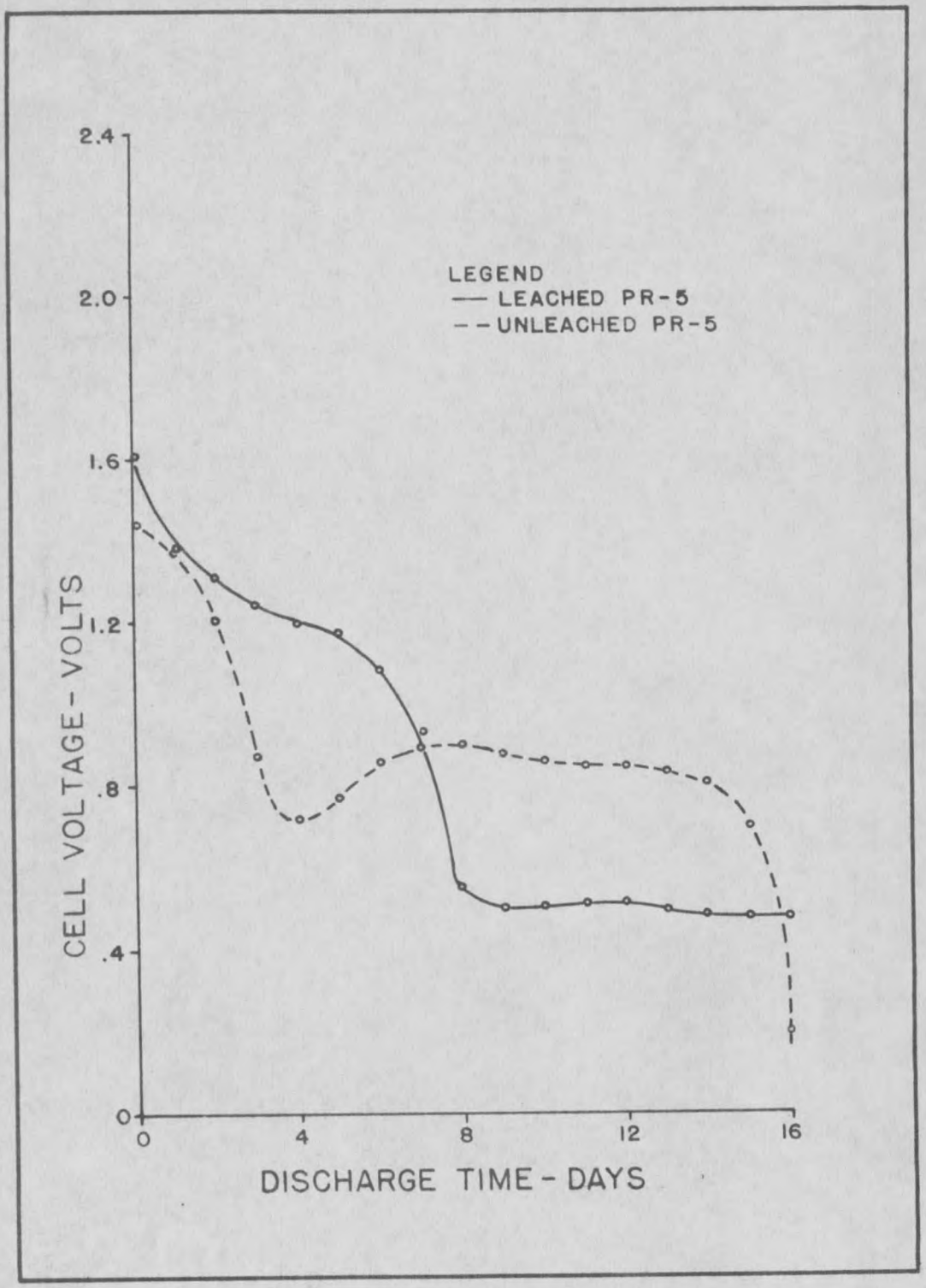

FIG 9 CELL VOLTAGE VS. TIME

and the shape of the curves indicates this reaction goes essentially to completion. A break in the voltage curve where all the MnO_2 is consumed is followed by another lower plateau which corresponds to the reaction

XIII. $3Mn_2O_3 + H_2 \longrightarrow 2Mn_3O_4 + H_2O$

Hausmanite has been identified by X-ray diffraction as the principle product of the completely discharged cells. The evidence is not conclusive since an extensive testing program would be necessary to pin down the actual cell depolarization reaction; however, the sequence of events as postulated seems sound enough to base the conclusion that the best depolarizer has a minimum divalent manganese content.

Stoichiometric manganese oxides of average Mn valence state less than four are unstable in acid media at elevated temperatures. For example, the compound Mn_2O_3 has been contacted with dilute H_2SO_4 (1) at the boiling point with the result that one half of the manganese dissolved to form $MnSO_4$ and the other half remained as manganese dioxide; a manganese dioxide which is of the meso crystalline gamma-rho variety and a very efficient depolarizer. Such an internal oxidation reduction reaction has been used to reduce the divalent manganese content of samples such as MCl-1 and produce a product with much enhanced depolarizer capacity.

Again considering the reaction MCl-1, it is apparent that an acid leach or activation step is necessary if a truly high quality depolarizer is needed. When MCl-1 was leached to remove the MnO with the result shown by the MCl-la data, a very effective depolarizer resulted. The efficiency of the overall process is not outstanding since some of the manganese is converted to permanganate in the oxidation and some must be redissolved

in the leach step and recycled through the process. The best bench scale yield data indicate about 85% per pass manganese conversions, 85% ultimate yield based on chlorine and caustic, and 95+% ultimate yield of the manganese.

The reaction is not as straightforward as has been indicated, however. Micro-optical analysis of reaction products made by this synthesis show some instances of formation of epsilon phase MnO_2. Epsilon MnO_2 seems to be an effective depolarizer initially, but is not stable in the presence of the battery electrolyte, as shown by a large drop in cell performance after three months' storage.

Some effort was expended in determining conditions which would yield MnO_2 with the activity of MCl-la without the necessity of a leach and if possible, better reagent yield figures.

A review of reaction conditions of MCl-l showed that the reaction was essentially the oxidation of Mn^{++} or $Mn(OH)_2$, depending on the relative amounts of NaOCl and NaOH. The tendency is to favor the oxidation of the hydroxide; the reasoning is as follows: The product contains appreciable divalent manganese even though MnO_4^- is evident at the end of the reaction, an anomolous situation since MnO_4^- rapidly is reduced by all divalent manganese compounds with the possible exception of rhodonite. The reaction apparently proceeded by oxidation of outer layers of the hydroxide gel structure in a manner which effectively sealed and prevented further attack on the remaining inner hydroxide. Near the endpoint of the reaction, the solution contained, for all practical purposes, "MnO_2" particles, NaOH and NaOCl, a combination effective in forming $NaMnO_4$ and NaCl.

The solution to the problem could appear from two quarters; elimination of the nonequilibrium conditions leading to the trapping of $Mn(OH)_2$ in the interstices of the MnO_2 particles, or reduction of the caustic-to-manganese ratio. The first course seemed more desirable since a 100% yield of MnO_2 would theoretically be the result; yet, practically, no efficient mixing or agitating mechanism was devised which altered the course of the reaction.

Investigation of the caustic-to-manganese ratio was studied rather extensively because of the immediate success of the first experiment of this nature. When one mol of manganese sulfate is reacted with two mols of caustic, a heavy white gelatinous precipitate of $Mn(OH)_2$ forms and the pH of the solution assumes a value of 9.5 - 10.5. When chlorine is admitted to the agitated solution at room temperature, dark particles of MnO_2 form around the Cl_2 bubbles. Since the chlorine has limited solubility, even at the freezing point of solution, the reaction proceeds rather slowly. A convenient experimental procedure was to chlorinate the solution in open agitated vessels at a rate which allowed a slight excess of chlorine. Results of chlorine oxidation of manganese hydroxide slurries at various temperatures and several concentrations show that product quality is not seriously affected by changes in reaction temperature over the range of $-5^{\circ}C$ to $40^{\circ}C$. Oxidation at higher temperatures proceeded by a different mechanism and yielded MnO_2 with the same physical and chemical properties as the low temperature product, but with very poor battery activity. The mechanism of the high temperature oxidation is thought to be via a manganite intermediate since the solutions become an intense orange-

brown color characteristic of manganite. The high assay of MnO_2 in the product plus the poor depolarizer capacity leads to the conclusion that a highly crystalline dioxide of the beta structure or a highly ordered, poor morphology of the rho phase is produced. Figures 3 and 4 show the results of high temperature chlorine oxidation of $MnCO_3$; both materials are poor depolarizers.

The chlorine oxidation of manganese hydroxide proceeds to the end-point pH of 2.0 without the formation of permanganate. The manganous hydroxide functions as both the base to neutralize the acid formed during the chlorine-water reaction to form HOCl and HCl and as a reducing agent for the HOCl. The 2:1 caustic ratio therefore results in only a 50+% conversion of the manganese to manganese dioxide per pass according to the sequence

XIV. $MnSO_4 + 2NaOH \longrightarrow Na_2SO_4 + Mn(OH)_2$

XV. $2Mn(OH)_2 + Cl_2 \longrightarrow MnCl_2 + MnO_2 + 2H_2O$

The product of reaction XV is typified by the following samples in Table II:

Table II

Sample	Ave. Temp.	O_2 as $\%MnO_2$	%Mn	Density gm/in^3	Drain Tests high	low	3 mo.
MCl-4	0°	92.2	59.2	13.8	7.2	133	119
MCl-5	2°	89.6	61.1	14.2	7.6	140	103
MCl-6	20°	92.1	60.2	12.8	5.5	129	112
MCl-3	27°	92.2	62.2	12.5	6.5	118	109
MCl-10	7°	90.2	60.6	11.0	5.2	119	105

The advantage of this reaction is the ease of control, no side reactions are encountered, the yield of product based on the caustic added is in the range

of 100-110%, and no activation step or acid digestion period is necessary to produce a depolarizer that is of the gamma rho crystalline structure and has sufficient activity to meet the Signal Corps specifications for synthetic MnO_2. The obvious disadvantage of such a process is the low conversion, inherent to the 2:1 caustic-to-manganese reagent ratio. The long 24 hour contact time used in the above syntheses was not deemed a disadvantage because it could be reduced to the order of .1 to .2 hour by a more efficient chlorination technique to be described in the next section.

In adjusting the reaction conditions of the 50% per pass manganese hydroxide chlorination to more realistic conditions, the contact time received most attention. As mentioned previously, the rate limiting variable appeared to be the low solubility of the oxidizing agent, Cl_2. Increasing the partial pressure of Cl_2 over the reaction mixture was the first and most significant effort in increasing the reaction rate. A few experiments were performed to determine the approximate reactor requirements. A small 1-liter suction flask agitated by a magnetic stirrer was charged with 500 ml of $Mn(OH)_2$ slurry of the same concentration as was used in the 24 hour atmospheric pressure runs. A pressure regulated, metered chlorine supply was connected through a stoppered opening at the top of the flask. As might be expected, the reaction rate was rapid at first and declined gradually to zero after one hour. The rate was very dependent on degree of agitation even in the early stages of the reaction. Temperature of the reaction mixture was not controlled and varied from 24°C to 33°C. A portion of the product was washed and dried according to standard practices, and was submitted for X-ray diffraction analysis. Figures 10g and h show

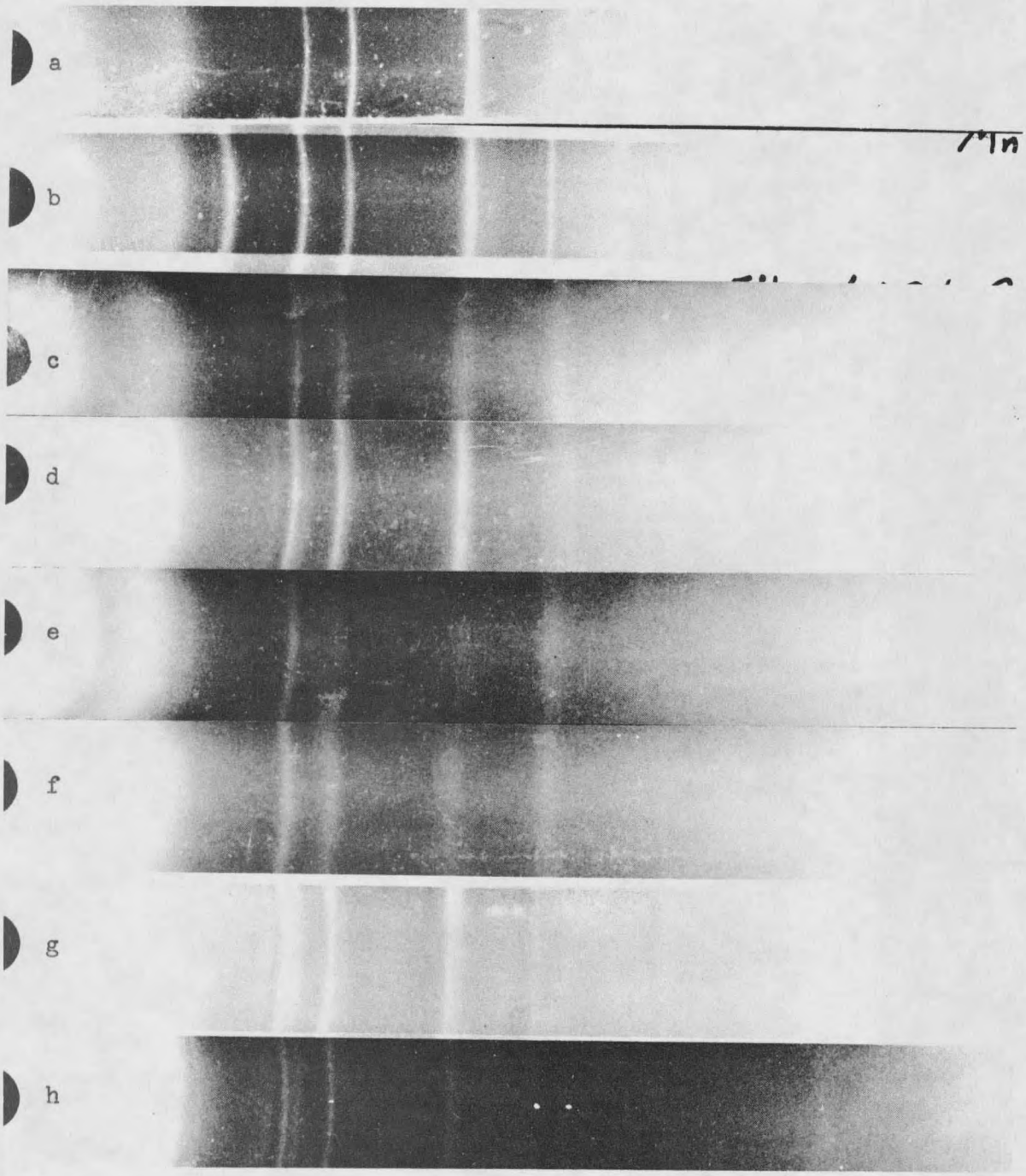

Figure 10 X-Ray Diffractions of MnO_2. a, electrolytic MnO_2; b, MC1-19; c, MC1-35; d, MC1-28; e, MC1-31; f, MC1-32; g, KS-1; h, MC1-58.

the diffraction pattern of the pressure chlorination along with the pattern of sample MCl-10, which was prepared by the low temperature, 24 hour reaction period at atmospheric pressure. The similarity is striking; both samples are in the gamma rho structural range.

At this point, two additional exploratory runs were made to determine the proper concentration of manganese hydroxide for the pressure oxidation. A slurry of twice the concentration of previous runs and a filter cake of manganese hydroxide were the feed materials for the two pressure runs. The viscous slurries were difficult to agitate and the oxidation proceeded slowly and incompletely.

The low permeability of the concentrated manganese hydroxide gels to the chlorine even at 25 psig was not anticipated, but it demonstrated the need of good agitation for successful completion of the oxidation in a short period of time. Another case illustrating the critical nature of agitation is the reaction MCl-4a, a scale-up of MCl-4 to approximately 10 gallons in a Saran-lined round bottom reaction vessel. The agitation was insufficient to keep all the manganese hydroxide in suspension. That which settled out in the bottom of the reaction vessel survived a 16-hour interval in contact with the reaction liquor which was at a pH of 1.8. Contamination by the $Mn(OH)_2$ can only be resolved by removing it with dilute acid.

Conditions for the pressure reactions were again chosen as a matter of expediency in acquiring equipment and simplicity of operation. Chlorine pressure was chosen as 15 psig, largely because the process was visualized as a counter current chlorination in a column type reactor; the

head of reaction liquor which would correspond to 15 psig at the chlorine inlet would be about thirty feet. The manganese hydroxide concentration was kept at the 2 mols per 3.5 liter level used in the atmospheric oxidations because adequate agitation of a slurry of this concentration was possible. Since the atmospheric oxidation runs showed a high reaction temperature to be undesirable and that temperatures of 40°C and lower were satisfactory, the reactants were charged to the reaction vessel at a temperature which with the exothermic heat of reaction would result in a final reaction temperature less than 40°C. The average temperature of all pressure runs was close to 30°C.

The first runs were made by placing the reagents in a sealed 4-liter suction flask and admitting chlorine while the vessel was agitated by a mechanical shaking device. The reaction was deemed complete when the chlorine rotameter showed no more flow. The results were encouraging; the better runs are illustrated by MC1-28, which had the following properties:

Sample	O_2 as $\%MnO_2$	%Mn	gm/in^3 Density	Drain Tests high	low	3 mo.
MC1-28	89.8	60.8	13.8	7.2	137	133
MC1-27	88.0	59.0	13.4	6.4	144	108

Some samples prepared by this technique were contaminated by flakes of unreacted manganese hydroxide which were observed to remain in the corners of the reactor where agitation was poor. In an effort to eliminate the contamination, the reactor was modified by adding a corrosion resistant Vanton pump which circulated the reaction contents at a rate of 3-4 liters per minute. This system was successful in producing a rather uniformly

good product, MC1-27 being a typical example. A difference between the atmospheric and pressure chlorination product should be noted. The pressure product consistently required more wetting solution to get the proper tamping consistency in the battery fabrication. The bobbin weights averaged less than 9.0 grams, as compared to the 9.5 to 10.0 gram bobbins of the atmospheric product. The latter MnO_2 required 20 to 30% less wetting agent than the pressure product, thus resulting in a higher percentage of MnO_2 in the bobbin in addition to the heavier bobbin. Despite the lower concentration in the bobbin, the pressure product gave at least as good drain tests as the atmospheric product.

The success of the relatively short contact time pressure chlorination of manganese hydroxide slurries batchwise led to the construction and operation of a continuous counter current chlorination apparatus which allowed continuous production of MnO_2 at a rate of 50 grams per hour, with a contact time of 20 minutes. A schematic diagram of the continuous reactor is shown in Figure 11.

The best results with the 50% per pass reaction when run in the continuous reactor were with run CR-I-1. The physical properties and chemical analyses are similar to those of the batch reactions and the drain tests of 6.6 hours high drain, 134 hours low drain, and 114 hours at three months, about equal to the better batch results. Operating difficulties for the apparatus were those characteristic of the small scale of the equipment, plugging of the $\frac{1}{4}$" take-off lines, and erratic performance of the bellows pump. Larger take-off lines and better agitation in the feed reservoir alleviated the difficulties, and satisfactory operation was then

obtained. Optimum reaction conditions for continuous reaction were not determined since the scope of the project did not allow 24-hour operation for extended periods.

In continuous column reaction systems, a smooth conversion profile should be maintained; in other words, agitation which is sufficient to break up the manganese hydroxide gel particles and prevent by-passing of these unreacted particles to the exit stream. Contamination of the product by manganese hydroxide was eliminated by an agitation level of 1/40 horsepower per gallon of reactants.

Tank type reactors in series should not be overlooked as a reaction media. Additional work on the physical chemistry of chemically prepared MnO_2 depolarizers may show that optimum crystal size is of the order of 1 micron or greater, whereas the manganese hydroxide chlorination without nucleation leads to a predominance of sub micron (nominally .1 to .2 micron) crystals. Knowledge of the crystal habit and its effect on battery life, stability, cell potential and other depolarizer characteristics is likely to be developed only after commercial application of the process; the reason being that enough data are at hand to guide production of a product which exceeds the requirements of the Signal Corps for synthetic military grade depolarizer.

The nucleation inherent in a stirred tank type reaction system opens some interesting avenues for the researcher interested in optimums rather than a "specification grade" product.

The data to this point demonstrate the feasibility of (1) a 50% conversion per pass process featuring a 100% ultimate yield on all reagents,

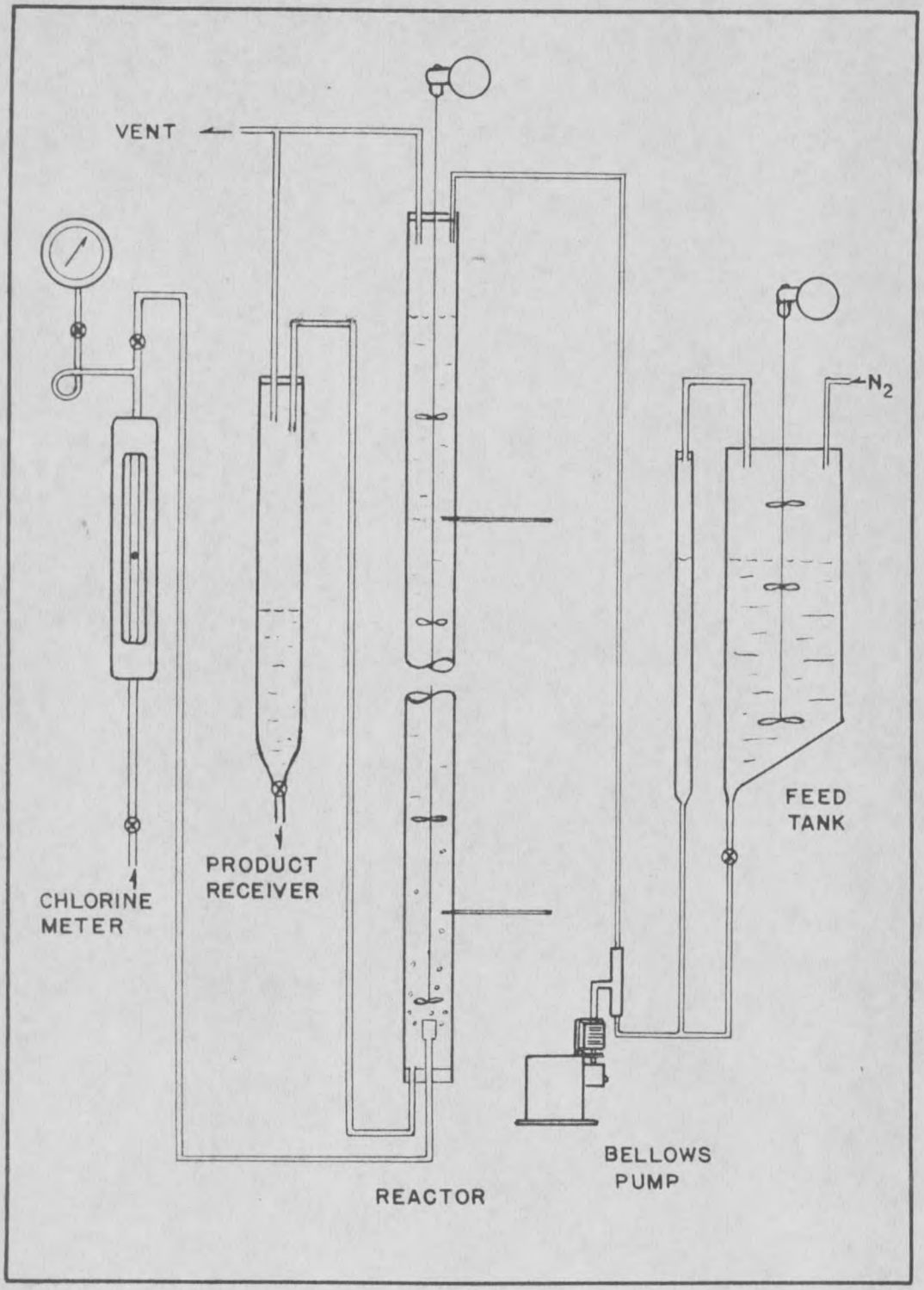

FIG. 11 CONTINUOUS REACTOR

and good product quality without added activation steps, and (2) a 100% conversion per pass process which requires an acid leach and solution of 5-10% of the manganese as an activation step with an ultimate yield on all reagents of about 85%.

In an effort to discover alternate routes to a 100% conversion, high yield process which did not require an activation treatment, other oxidation procedures were attempted.

Several reactions were run in which the caustic-to-manganese ratio was 2:1 to 4:1 and the resulting manganese hydroxide slurry with various amounts of free caustic was chlorinated in the batch 4-liter pressure reactor.

The data of Table III illustrate the effect of caustic ratio on conversion and product quality.

Table III

Sample	mol NaOH / mol Mn	Conversion	O_2 as $\%MnO_2$	%Mn	Drain Tests		
					High	Low	3 Mo.
MC1-28	2	57	89.8	60.8	7.2	137	133
MC1-29	2.9	80	86.7	59.1	8.6	120	109
MC1-30	3.5	86	83.8	55.3	6.9	125	106
MC1-31	3.75	89	82.2	59.3	6.7	115	84
MC1-7	4.0	100	83.4	58.0	1.4	118	12
MC1-31a	---	---	88.5	60.6	6.8	109	110

Results indicate that the activity of the MnO_2 decreases as the conversion increases and especially affected is the storage life, which deteriorates to a negligible value at 100% conversion. In addition, X-ray diffraction analyses show that the 100% conversion material of MC1-31 may contain the undesirable epsilon phase as indicated by the diffraction patterns of Figure 10e.

These patterns do not indicate that epsilon phase MnO_2 is inherent to a 100% conversion process, for, as will be brought out in a later section, the presence of certain impurity ions may effectively catalyze the formation of gamma phase MnO_2. Regardless of phase, the fact remains that no 100% conversion run of the type where all the caustic was added to the manganese and subsequently chlorinated has produced a depolarizer which will pass the Signal Corps specification for synthetic MnO_2, nor has any sample of this type retained a significant percent of its initial activity after three months' storage. Some improvement in the initial drain tests was accomplished by digesting the product in 100 gram per liter H_2SO_4 at the boiling point for one hour. The effects of the leach are marginal, although the stability, physical, and chemical properties are enhanced.

Continuous counterflow chlorination with high conversions of the manganese was attempted in the runs CR-IV, V, and VI. Selected samples from these runs are listed in Table IV.

Table IV

Sample	Conversion	O_2 as $\%MnO_2$	%Mn	Drain Tests		
				High	Low	3 Mo.
CR-IV-1[a]	94	89.6	59.8	7.6	143	106
CR-V-1[a]	100	89.6	59.4	7.0	140	69
CR-V-2[a]	100	89.2	59.7	6.7	149	77
CR-V-3[a]	100	79.9	56.3	5.8	128	87
CR-VI-1[a]	100	85.5	57.1	7.4	146	119
CR-VIII-1	100	78.1	54.0	6.2	90	0

Operating difficulties in these runs were principally due to the foaming tendencies in the column reactor and a somewhat more critical trouble, the tendency for the feed to change caustic ratio due to manganese hydroxide settling. The changing caustic ratio resulted in per-

manganate formation. Permanganate formation occurred from another source also; when air was allowed to contact the manganese hydroxide feed, some was oxidized by the following reaction sequence:

XVI. $2Mn(OH)_2 + \frac{1}{2}O_2 \longrightarrow Mn_2O_3 \cdot H_2O + H_2O$

The air oxidation upsets the ratio of caustic to divalent manganese, resulting in an excess of oxidant when all the manganese is in the tetravalent state, thereby resulting in $NaMnO_4$. The air oxidation was eliminated by blanketing the agitated closed feed storage vessel with nitrogen.

The runs produced a product like CR-VIII-1, which shows a high degree of hydration, though only a moderate amount of divalent manganese. When the hydrated product was heated in the presence of 100 gram per liter H_2SO_4, a change in the degree of hydration was noted when the temperature attained 65-70°C or higher. The subscript, a, associated with the first five samples of Table IV, indicate an acid digestion. The low temperature (33°C) leach of CR-V-3^a was not effective in reducing the hydration, while samples CR-V-1^a and CR-V-2^a, which were digested at 95°C, were improved considerably. A few percent of the divalent manganese is removed in the leach so that the object of 100% conversion in the oxidation step is not realized. The results of the continuous high conversion runs are not encouraging for two reasons: the highly hydrated product requires an acid digestion for activation and the delayed capacity after three months is rather poor. The unleached products corroded the zinc battery cans after two months' storage, indicating occlusion of an oxidant more active than MnO_2, perhaps sodium chlorate. The X-ray diffraction patterns of samples CR-IV-1^a, CR-V-1^a, and CR-VI-1^a show the MnO_2 to be of the gamma-rho

structure with fairly poor crystallization or extremely fine particles. The very diffuse nature of the pattern of CR-VI-1[a] compared to CR-V-1[a] may be indicative of the effects of the reaction variable. The contact time of CR-V-1[a] was 50 minutes while that of CR-VI-1[a] was half that value, 25 minutes. The caustic-to-manganese ratio was 3.75 mols/mol, and the temperature ranged from 30° to 40°C over the 8 foot length of the reactor, for the runs CR-V, CR-VI, and CR-VIII. The caustic ratio of CR-IV-1[a] was 3.5 to mols per mol, thus accounting for the incomplete conversion for this run.

It is conceivable that the high conversion process is a feasible means of producing a very active depolarizer. The poor stability may be remedied by a more thorough study of the acid digestion. An instance where this sort of stabilizing treatment was successful has been reported (4).

A corrosive product was prepared by the oxidation of acidic $MnSO_4$ by $NaClO_3$ at elevated temperatures. The product, when unleached, corroded the cells badly and storage life was negligible. When the MnO_2 was digested in successive portions of boiling 150 gram per liter H_2SO_4, the delayed capacity improved to the point where the product could pass the Signal Corps specification.

The high initial battery activity, coupled with the high conversion of the CR-IV, V, and VI series makes them worth further consideration. It is questionable whether the critical control necessary for successful operation of the high conversion process, together with the need for an activation acid leach of the product is an advantage over the 50% conversion process.

Only one reagent addition method was discovered which allowed 100% conversion of the manganese, 100%+ ultimate yield of caustic and chlorine (based on the electronic requirements of 4 mols NaOH and 1 mol Cl_2 per mol MnO_2). This method was the constant pH oxidation of $MnSO_4$ solutions by chlorine. The pH was held at the desired level by addition of 10% NaOH as the reaction proceeded.

The first reaction of this nature was MCl-16, where a caustic ratio of 4:1 was used, and the pH was held at 6.5 to 7.0. As the base is added at this pH, it is apparent that the oxidation proceeds via manganese hydroxide, since the hydroxide particles are clearly evident. The reaction proceeds fairly slowly even initially, because of the low solubility of chlorine at atmospheric pressure and the reaction temperature of 25°C. The reaction could be followed to a degree by the observed deflection sensitivity of the pH meter as a function of amount of caustic added, much the same as a potentiometric titration endpoint is determined. The addition of relatively large volumes of base initially causes a small pH change, due to the buffering action of the insoluble weak base $Mn(OH)_2$, whereas near the endpoint of the reaction, little or no Mn^{++} is present to react with the added base, and the addition of but a few drops of the NaOH causes a large change in the pH. The difficulty in using this potentiometric method is that as a normal procedure, the sample is over-titrated, and the endpoint determined from the maximum rate of change of electrode potential with reagent addition. Overtitration with caustic in the case under discussion results in the reaction of the product to form permanganate.

Table V shows the physical, chemical, and depolarizer properties of the constant pH series:

Table V

Sample	Caustic Ratio	Reaction pH	O_2 as $\%MnO_2$	%Mn	Density	Drain Tests High	Low	3 Mo.
MC1-18	4	4.5	83.0	57.2	8.4	0	6	0
MC1-18a	---	---	90.4	59.4	11.3	4.4	134	78
MC1-19	3.6	3.-4.	86.8	57.4	10.6	5.2	116	58
MC1-16	4	6.-7.	92.4	63.1	12.2	6.0	122	13
MC1-17	3.6	6 - 7	93.0	64.6	14.0	6.1	123	123

In all runs the 3.6:1 caustic-to-manganese ratio is most effective. The product of MC1-18 was very corrosive, so a portion was digested with 100 gm per liter H_2SO_4 at 95°C for 2 hours. The leached portion (-18a) was upgraded considerably although the delayed capacity remains unsatisfactory. It is interesting to note that X-ray diffraction analysis of 18 and 18a shows the acid leach effected the phase shift from gamma to rho; however, this minor structure shift does not account for the observed difference in activity. Electron micrographs show a much better crystal development in the constant pH type of oxidation. The ultimate particles appear to be predominately in the .5 to 1 micron size range, whereas .02 to .2 micron size particles are generally obtained by the manganese hydroxide chlorination.

Reduction of the caustic ratio in MC1-19 yielded a product of much better initial drain tests, although it, too, shows poor storageability. It is interesting to note that at the low pH of MC1-18 no permanganate formed, although the product was the low density, highly hydrated product characteristic of Volhard MnO_2. Permanganate was formed in MC1-16 at a

pH of 6-7 during the addition of the last 130 ml of base. The caustic ratio corresponding to the permanganate free endpoint is approximately 3.7 or about 92% of the theoretically required caustic. MCl-17 was run at the neutral point, with a caustic ratio of 3.6. The product contained all the manganese for 100% conversion and the initial and delayed capacity were satisfactory so that no subsequent leach was necessary. The delayed capacity maintenenace of MCl-17, even after two years' storage under the low humidity Montana State College storage conditions, was 19 hours, which compares with a high grade electrolytic sample which had retained 25 hours low drain capacity after 2 years under the same storage conditions. Figure 12 shows the delayed capacity of several chemical MnO_2 samples compared with electrolytic MnO_2 performance.

X-ray diffraction patterns of 17, 16, and 19 show a distorted beta-gamma structure while 18 and 18a are gamma and rho. The battery tests of MCl-17 and MCl-19 are much better than the predominate beta diffraction lines would indicate. Many battery tests of pure beta MnO_2 with good particle morphology show that the best drain tests obtainable are about 2.5 hours high drain, and 70 hour low drain; tests which are far below those of MCl-17 and -19.

The high conversion and yield obtainable by this procedure and the fact that the product approaches closely Signal Corps synthetic specifications, without the need for acid digestion or other activation, makes the method noteworthy. The constant pH oxidation viewed from the point of view of adaptability to a continuous process is not especially attractive. Control by pH electrodes is feasible, though the electrode life in

the Cl_2 saturated solution at any appreciable pressure is rather short, judging from the number of electrode failures occuring in the 120 hours of constant pH operation. Even though a usable pH controlling device is devised, a simple method of maintaining the reaction stoichiometry in a flow process is not immediately apparent.

A procedure which allowed the high manganese conversion to a good quality product without an acid leach was a modification of the 50% per pass manganese hydroxide oxidation. The reaction was run by chlorination of a manganese hydroxide slurry to the usual endpoint of pH 2. Caustic was then added to precipitate the remaining manganese as $Mn(OH)_2$ and the chlorination continued to a pH of 2.0. The procedure was repeated so that the theoretical overall manganese conversion would be 87.5%. The actual conversion was 89%. A typical product of this procedure is MCl-14, which is considerably better than Gold Coast ore, but not up to the activity required by SCl-3117-D. The trend of decreasing density with increasing conversion applies to this procedure since the apparent density of all samples prepared by this method were of the order of 9 to 9.5 grams per cubic inch as opposed to the 50% conversion product which usually has a density of 12 to 14 grams per cubic inch.

Several runs of the sequential caustic addition method outlined above were made in the 4-liter pressure chlorination apparatus. The only improvement resulting from the pressure chlorination was in the high drain performance. The properties of MCl-38 are listed in Tables IX and X and illustrate the type product obtained by this method. The high hydration and low density of the product are characteristic. A portion of MCl-38

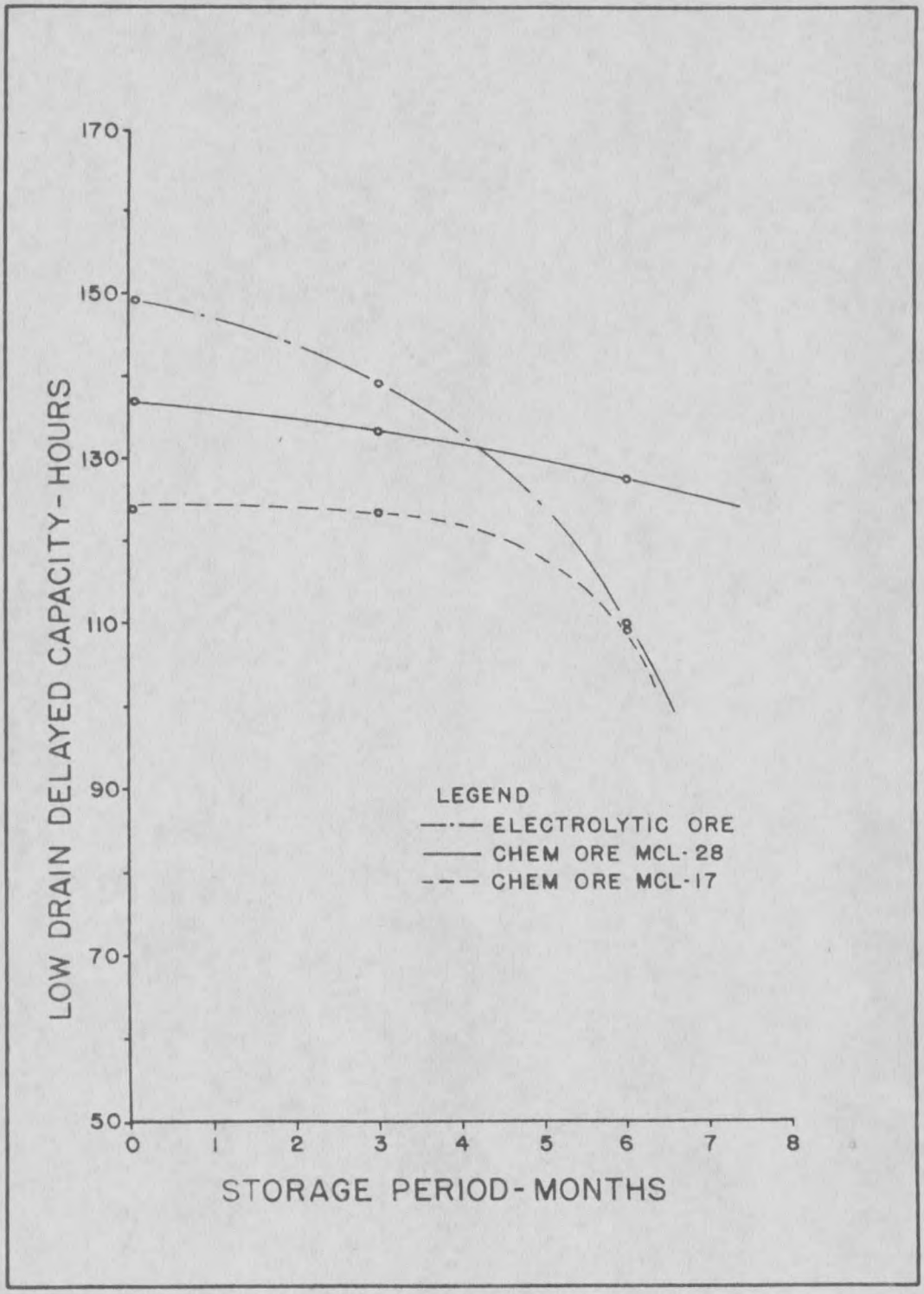

FIG 12 DRAIN LIFE VS. STORAGE TIME

was digested with 100 gram per liter H_2SO_4 at 95°C for one hour and designated MCl-38a. The acid digestion improves the chemical and physical properties and gives a specification grade product although the stability after three months' storage is questionable. The sequential caustic addition method seems to be the equivalent of the runs like MCl-31, where all the caustic is added at the start and the chlorination allowed to proceed to the endpoint without interruption. No micro-optical data on the products made by the sequential 50% conversion technique is available; however, the manner in which the sample was upgraded by the acid digestion would indicate a predominance of a stable crystalline phase, and the high order of activity would suggest the gamma-rho structural range.

Another approach to the utilization of chlorine and caustic to obtain battery active MnO_2 from $MnSO_4$ is the use of sodium hypochlorite. Sodium hypochlorite may be prepared directly by electrolysis of brine or by chlorination of cold dilute caustic colutions. Solutions containing 20% NaOCl and three grams per liter of free NaOH are stable at room temperature, but even dilute solutions with no excess caustic tend to decompose with the evolution of oxygen. The silver-platinum metal electrode couple was successfully used in determination of chlorination endpoints in preparation of sodium hypochlorite by adding chlorine to caustic solutions. Electrode potentials were correlated with free caustic determinations and available chlorine analyses so that NaOCl solutions of accurately known composition could be prepared.

Sodium hypochlorite reacts with $MnSO_4$ in several ways depending on the pH of the solution. In acidic solution the reaction is essentially

as follows:

$$\text{XVII.}\quad 2NaOCl + MnSO_4 \xrightarrow{pH < 7} Na_2SO_4 + MnO_2 + Cl_2 \uparrow$$

$$2(Cl^{+1} \xrightarrow{+1e} Cl^{0})$$
$$Mn^{+2} \xrightarrow{-2e} Mn^{+4}$$

However, if the pH is held in the basic range, no chlorine is evolved and the reaction is represented by this sequence:

$$\text{XVIII.}\quad NaOCl + 2NaOH + MnSO_4 \longrightarrow Na_2SO_4 + MnO_2 + NaCl + H_2O$$

$$Cl(+1) \xrightarrow{\pm 2e} Cl(-1)$$
$$Mn^{+2} \longrightarrow Mn^{+4}$$

Of the two reactions, the second seems to be of most interest since the preparation of the oxidant may be controlled closely, and the oxidant addition to $MnSO_4$ with high conversion of manganese and no recycle streams appears to be practical.

Oxidant addition to manganese sulfate solutions was accomplished under a variety of reaction conditions. Of most interest was the evaluation of product quality as a function of conversion. No significant difference is noted in the reaction product up to the caustic ratio of 3.75 mol per mol of manganese. The oxidant was of constant mol ratio; that is, the mol ratio of NaOH:NaOCl:NaCl remained constant at 2:1:1 for all runs, but the amount of this oxidant used in each reaction was changed. Table VI shows the chemical, physical, and drain test data for typical runs of the hypochlorite evaluation.

Table VI

Sample	Caustic ratio	Conversion	O_2 as $\%MnO_2$	%Mn	Gm/in^3 density	Drain Tests High	Low	3 Mo.
MC1-20	3.0	81	89.6	60.4	12.6	4.0	139	45
MC1-21	3.25	86	89.5	59.5	12.4	3.4	134	49
MC1-22	3.75	96	91.4	59.6	10.0	3.7	121	100
MC1-23	4.0	100	82.8	53.6	7.6	0.0	6	0
MC1-22a	---	---	94.9	58.8	12.8	3.9	152	49
MC1-24	3.5	94	91.6	62.3	11.3	4.0	88	47
MC1-25	3.5	92	84.6	60.7	9.4	1.0	100	97

The four to one caustic ratio is again noted to be conducive to permanganate formation, hydration of the product, and poor drain tests. No method produced a satisfactory depolarizer, although the X-ray diffraction showed essentially single phase rho manganese dioxide and the better samples had high MnO_2 content. The uniformly poor delayed capacity of samples is not explained by the data. A careful spectrographic and chemical analysis of the samples, together with micro-optical examination of the bobbins after extended storage may show that absorbed ions catalyze crytomelane formation in the presence of the battery electrolyte. Samples 24 and 25 show that no improvement in the drain characteristics results from high or low reaction temperature. The relatively low MnO_2 content of the low-temperature oxidation, MC1-25, may suggest that the oxidation mechanism may be the oxidation of $Mn(OH)_2$ via these routes:

XIX. $MnSO_4 + 2NaOH \overset{k_1}{\rightleftharpoons} Mn(OH)_2$

XX. $Mn(OH)_2 + NaOCl \xrightarrow{k_2} NaCl + H_2O + MnO_2$

Reaction XIX is known to go to completion almost instantaneously, while in MC1-25, the presence of 9% of divalent manganese indicates that reaction XX has slowed significantly due to the lower temperature, thus

producing a product contaminated with $Mn(OH)_2$. It should be mentioned that $Mn(OH)_2$ is rapidly converted to manganite by atmospheric oxygen during the drying of the MnO_2 filter cake.

Other preparations were made utilizing the basic hypochlorite oxidizer with varied free caustic to hypochlorite ratio, but the results were no more encouraging than those of Table VI. The data for all hypochlorite oxidations indicate that a product of desirable chemical, crystalline, and initial drain capacity may be produced at conversions of 95+% and ultimate yields of close to 100%. Further treatment, such as acid digestion at elevated temperature, improves the initial low drain tests, but the delayed capacity is not enhanced when the acid used is 100 gram per liter H_2SO_4.

Other hypochlorite reactions evaluated included:

XXI. $2NaOCl + MnSO_4 \longrightarrow MnO_2 + Na_2SO_4 + Cl_2$

in which the hypochlorite was added to the $MnSO_4$. The mechanism here is apparently ionic, since the reaction remains at or near pH 4, which is below the point of precipitation of appreciable amounts of $Mn(OH)_2$. The results of this type oxidation are not encouraging enough to warrant further study, since a much better depolarizer is obtained without the evolution of chlorine according to the procedure of the previous section.

The addition of NaOCl solutions to strongly acidic (H_2SO_4) solutions of $MnSO_4$ yields MnO_2 of good battery quality (5). Conversions are reported to decrease as the acid concentration increases until at 300 grams per liter H_2SO_4, no MnO_2 is obtained. The micro-optical, physical, and chemical properties of this MnO_2 prepared by reaction of equi-molar ratios

of NaOCl and $MnSO_4$ in boiling 100 gram per liter H_2SO_4 indicated a specification grade material. Delayed capacity of this material is not reported. Yield figures indicate the acidic reaction follows reaction XXI.

The next effort was toward evaluating the impurity effects arising from the use of commercial reagents. Manganese Incorporated of Henderson, Nevada made available a technical grade $MnSO_4$ which contained the impurities Mg, Si, Na, Al, Ca, Fe, K, Cu, Ni, and Ti. These materials were present principally as sulfates. Table XII lists analyses of typical technical $MnSO_4$ samples, and Table XIII shows the spectrographic analyses of a technical grade sample together with the analysis of the same sample after a copper purification and pH adjustment.

The 50% conversion manganese hydroxide chlorination reaction was chosen to evaluate the technical grade $MnSO_4$ since this reaction sequence was fairly foolproof and reproducably produced MnO_2 of high purity and good activity and stability from chemically pure $MnSO_4$. Table VII lists several runs made with impure $MnSO_4$ and corresponding runs with CP $MnSO_4$.

Table VII

Sample	Mn Source	O_2 as $\%MnO_2$	%Mn	Density	Bobbins	Drain Tests		
						High	Low	3 Mos.
MC1-9	MS-4	80.7	60.8	10.3	9.4	5.6	78	60
MC1-8	MS-4	78.2	60.1	9.7	8.9	2.4	65	14
MC1-3	CP	92.2	62.2	12.5	9.5	6.5	118	112
MC1-28	CP	89.8	60.8	13.8	9.3	7.1	136	133
MC1-34	MS-6	82.2	58.0	12.3	9.0	7.3	112	98
MC1-36	MS-5	84.6	56.6	12.9	9.0	8.0	125	98
MC1-32	MS-6	81.4	58.0	8.3	8.3	1.5	99	48
MC1-33	CP	84.6	58.2	10.7	8.8	4.7	114	106
MC1-33a	---	91.1	60.0	13.4	9.2	6.9	139	---
MC1-32a	---	85.9	58.0	14.1	9.6	7.0	133	---

Samples MCl-8 and MCl-9 show that the impurities are detrimental since a poorly oxidized product is obtained. Since the pressure chlorination technique was shown to be superior to the atmospheric chlorination, no further runs like MCl-8 and -9 were attempted. The improvement in drain tests of MCl-34 over MCl-8 and -9 is due to the pressure chlorination. The amount of lower oxides in MCl-34 is decreased by a factor of two over the atmospheric chlorination runs. The improvement is not great enough to yield a specification grade product, however, as does the CP counterpart, MCl-28. The results showed that a purification of the technical grade $MnSO_4$ was necessary. A simple technique was tried first since it involved no expensive reagent or adverse treatment conditions. The treatment was to contact the impure $MnSO_4$ solution with an excess of iron in order to precipitate copper, and follow by a pH adjustment with $CaCO_3$ and air oxidation to precipitate the iron as $Fe(OH)_3$.

The reason for the copper removal was based on the known catalytic activity of copper in decomposing hypochlorite to form oxygen and chloride ion. The first technical grade runs showed a high percentage of lower oxides even though the same pH endpoint was attained as was reached in the CP runs. The presence of these oxides could arise from the presence of oxygen because oxygen rapidly oxidizes $Mn(OH)_2$ not to the tetravalent oxide, but the tervalent oxide, manganite. The improved oxidation obtained by increasing the partial pressure of Cl_2 in the pressure chlorinations would fit in with this rationalization.

Sample MCl-36 was prepared from a purified or copper-free $MnSO_4$ solution having the analysis shown in Table XIII. The purification

effectively reduced the copper and aluminum content but did not affect the other impurities greatly. The initial drain tests and chemical properties of MC1-36 are but slightly under the SCL-3117-D specification. The delayed capacity of MC1-36 after one year was 94 hours, or about equivalent to the better electrolytic or CP chemical ore.

The X-ray diffraction patterns of MnO_2 made from the CP and the technical grade $MnSO_4$ by similar processing shows the predominance of gamma patterns in the technical grade product, while the CP products are rho or gamma-rho. These patterns are shown in Figure 10. The distinction between gamma and rho or gamma-rho structures is not important in itself since all of the structures appear to be equally desirable depolarizers; however, the fact that the undesirable epsilon phase occurs in MC1-31, made from CP $MnSO_4$, and does not occur in the technical grade duplicate, MC1-32, has considerable importance. Identification of the impurity which causes this phenomenon would be an interesting project.

Runs 33 and 32 show again that the impurities of 32 cause a lower MnO_2 content and poorer drain tests when the conversion is increased to 90+% by using a 3.75:1 NaOH:Mn ratio. These samples were leached at 95°C with 100 gram per liter H_2SO_4 and have the properties listed under the designation 33a and 32a. Considerable improvement in the properties is noted, even though the chemical composition of the samples is not greatly altered.

The results show that an acceptable depolarizer can be prepared from $MnSO_4$ containing Al, Mg, Si, Fe, and Ca. Copper is considered detrimental possibly from its activity in decomposition of hypochlorite to form chlo-

ride ion and oxygen.

Several large batches of MnO_2 were prepared so that more extensive investigation on leaching, grinding, sizing, blending, etc. could be made. The reaction chosen was the chlorination of 3.5 mol NaOH per mol $MnSO_4$ slurries. This particular mode of operation is not considered an optimum of the process variables studies, but was chosen because it is economical in time, cost of construction, and in operation.

The process begins with the $MnSO_4$ preparation. Commercial manganese carbonate was dissolved with H_2SO_4 and the iron precipitated by simultaneous pH adjustment and air oxidation to the ferric state. The filtered $MnSO_4$ solution was reacted with technical grade caustic prepared by solution of the 76% Na_2O flake in tap water. The process water used for all solutions, washing, etc., contained 180 ppm hardness as $CaCO_3$. The agitated $Mn(OH)_2$ slurry was oxidized by sparging Cl_2 as fast as the reaction would allow; this rate depended on the amount of free caustic present, agitation, and temperature in that order of importance. Reaction pH was the critieria for terminating the chlorine addition. The oxidation product was washed by the slurry-decantation method and was leached with dilute H_2SO_4 to remove lower oxides and unreacted $Mn(OH)_2$. The leached product was washed to a sulfate-free endpoint, filtered and dried at 160°F in a circulating air, steam-heated oven. Grinding in a 2.5 gallon ball mill and screening -100 mesh completed the treatment.

This general procedure was successfully employed to prepare 25 pound samples of MnO_2 which had sufficient activity to pass the SCL-3117-D specification for synthetic MnO_2. Properties of several samples are tabulated

below in Table VIII:

Table VIII.

Sample	O_2 as $\%MnO_2$	%Mn	Density	Bobbins	Drain Tests		
					High	Low	3 Mo.
PR-I-1	89.2	58.9	12.0	9.1	7.5	127	116
PR-II-1	91.6	58.7	9.1	8.9	6.0	92	---
PR-II-2	91.6	58.7	11.3	9.3	5.5	112	115
PR-II-3	91.6	58.7	15.4	9.8	7.0	124	103
PR-III-1	89.0	60.9	10.3	9.1	2.8	95	84
PR-III-2	89.0	60.9	11.3	9.1	7.3	113	93
PR-III-3	89.0	60.9	14.2	9.5	8.8	126	---
PR-V-2	89.6	59.8	14.3	10.0	5.2	140	---
PR-VI-1	84.8	56.6	13.7	9.4	7.0	134	---

The results of the runs are encouraging although most did not produce specification grade MnO_2. The better samples contain high percentages of Mn and MnO_2, good density, and are of the rho phase with fair particle morphology. Stability after three months' storage is good, as the three month tests indicate.

In reviewing the scaled up operations, the only serious difficulty occurred in the chlorination step. Very low yields were obtained in all runs because of non-equilibrium conditions in the oxidation step. The agitation in the tank reactor used was not sufficient to allow complete conversion of the $Mn(OH)_2$ and serious contamination of the product occurred. The product quality was not impaired since an acid leach effectively removed the unconverted $Mn(OH)_2$, but the necessity for good agitation is again demonstrated. The level of agitation used in these runs was about .01 horsepower per gallon of reaction mixture.

The runs PR-II-1, 2, and 3 and PR-III-1, 2, and 3 show the importance of the grinding technique to the physical properties and battery activity

of the chemical battery ore. The relation of battery performance to grinding time is presented graphically in Figures 13 and 14. Figures 15, 16, 17, and Figures 18 and 19 are electron micrographs of the PR-II and PR-III samples which were ground successively for two-hour periods. The electron micrographs clearly indicate the distortion of the bladed morphology until finally, aggregates of the fractured particles are grouped into larger anhedral particles several microns in diameter. Figure 20 shows the X-ray diffraction patterns of PR-II-1, 2, and 3, and reveals that no change in crystal structure occurs during the grinding. The highest density, heaviest bobbins and best high and low drain tests are obtained with the large anhedral aggregates shown in Figure 17 and Figure 19. The implication from the grinding study is that a precipitation technique which produces anhedral micron size particles would be desirable. On the other hand, the use of grinding to upgrade a low density but otherwise satisfactory depolarizer is a demonstrated fact.

After preparing many hundreds of samples of chemical battery ore, relating apparent density, particle size and distribution, bobbin weight, and battery life as a function of grinding or ball milling treatment, the only usable postulate seems to be a very inexact one: regardless of method of preparation, a two-hour ball milling period followed by screening to -100 mesh seems to be the most reproducible sample preparation technique. This system has served as long as the sample size was held to 100-300 grams, the ball charge was five pounds, and the 2.5 gallon mill was rotated at 70 r.p.m. When the large samples (10-30 pounds) were processed, the grinding procedure had to be changed to a more practical ball and

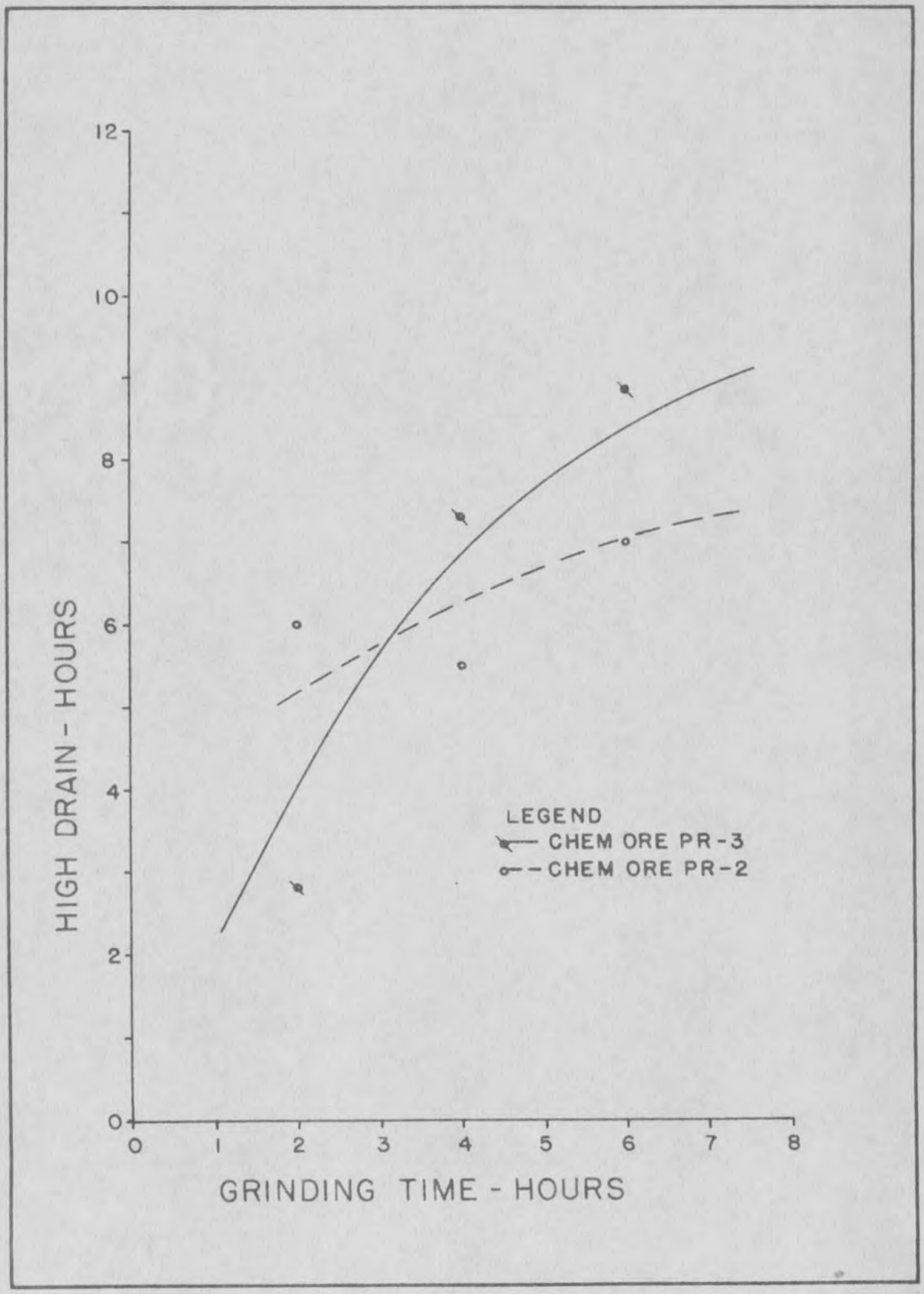

FIG. 13 DRAIN LIFE VS. GRINDING TIME

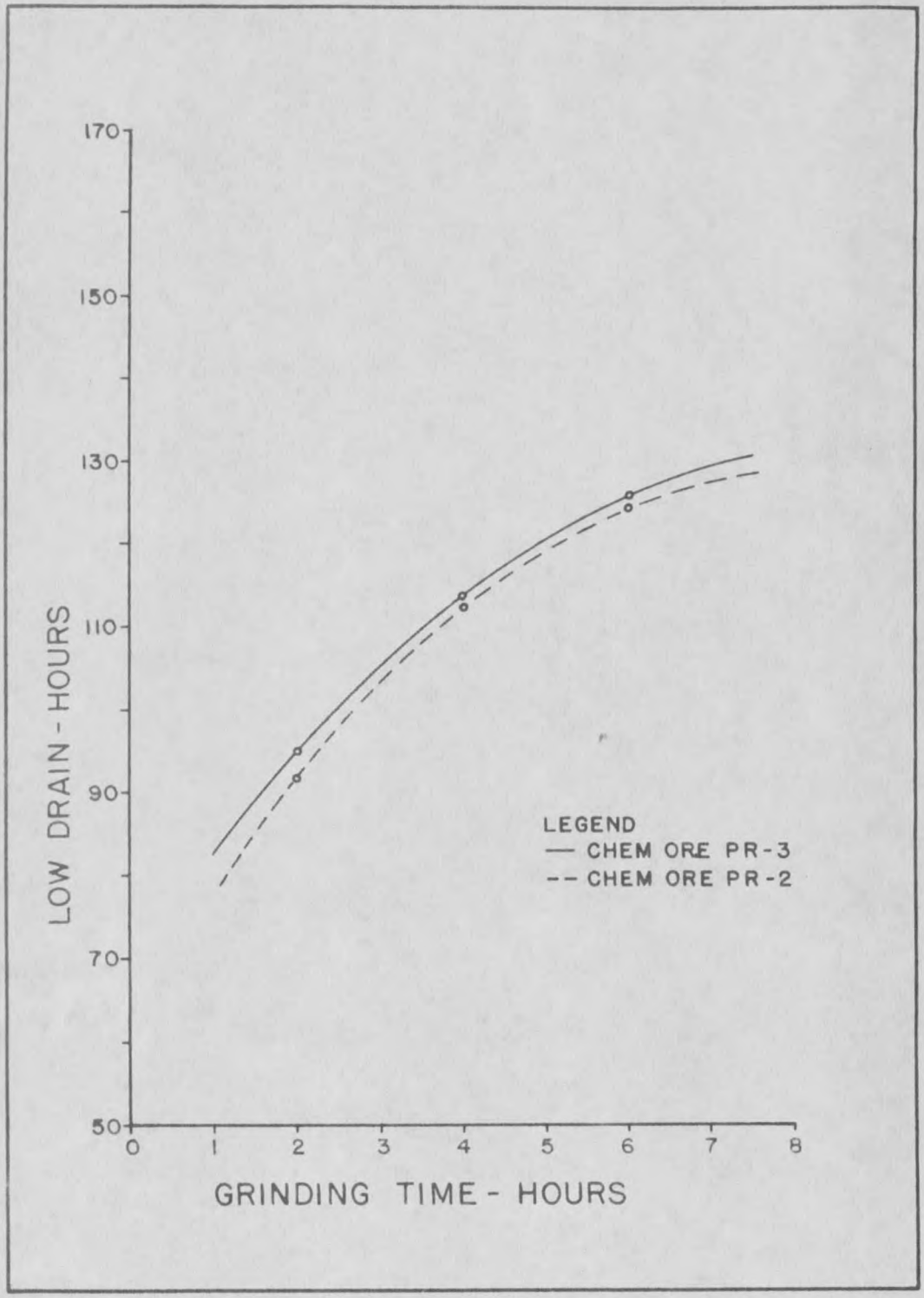

FIG 14 DRAIN LIFE VS. GRINDING TIME

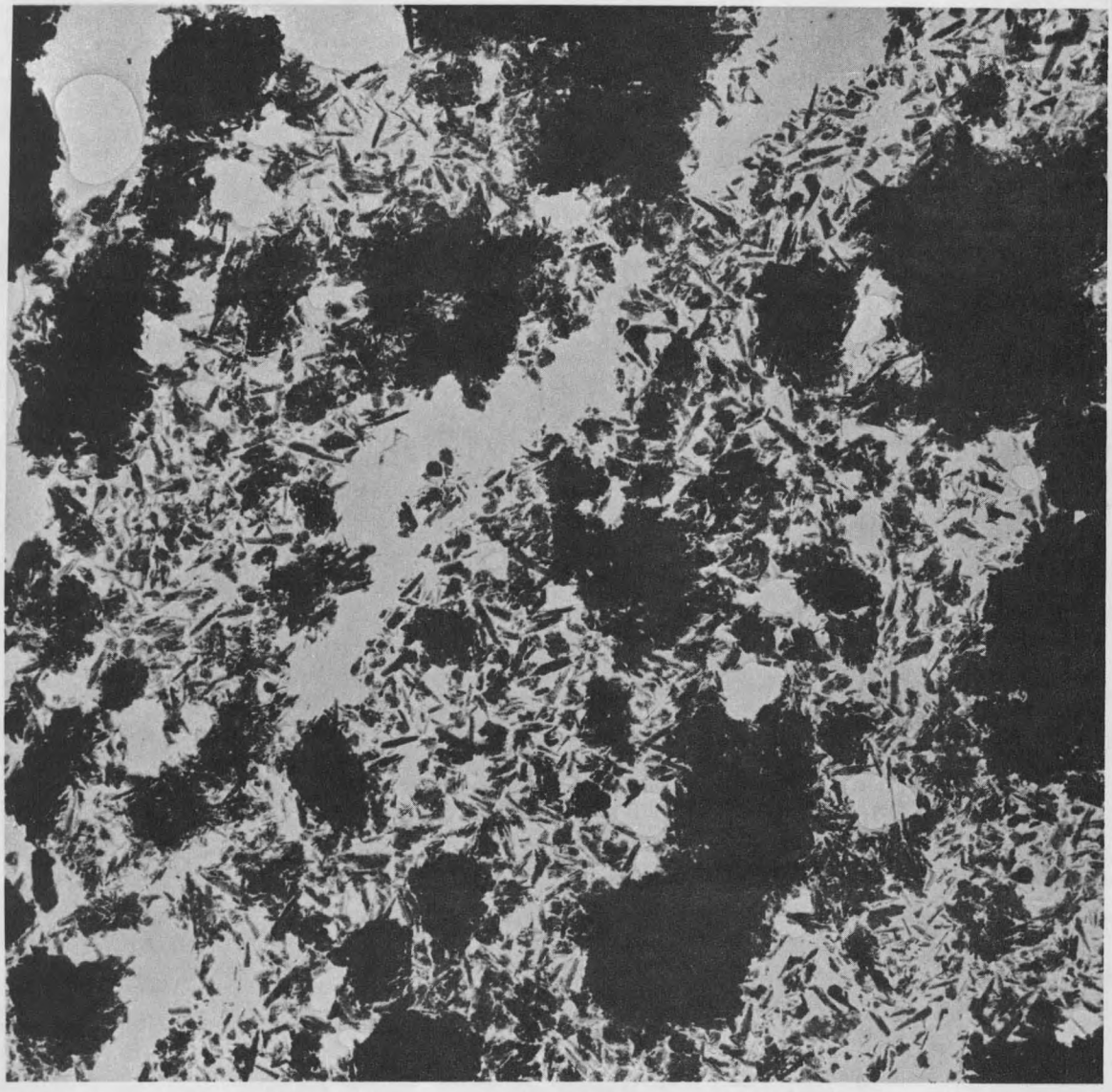

Figure 15 Electron Micrograph of PR-II-1

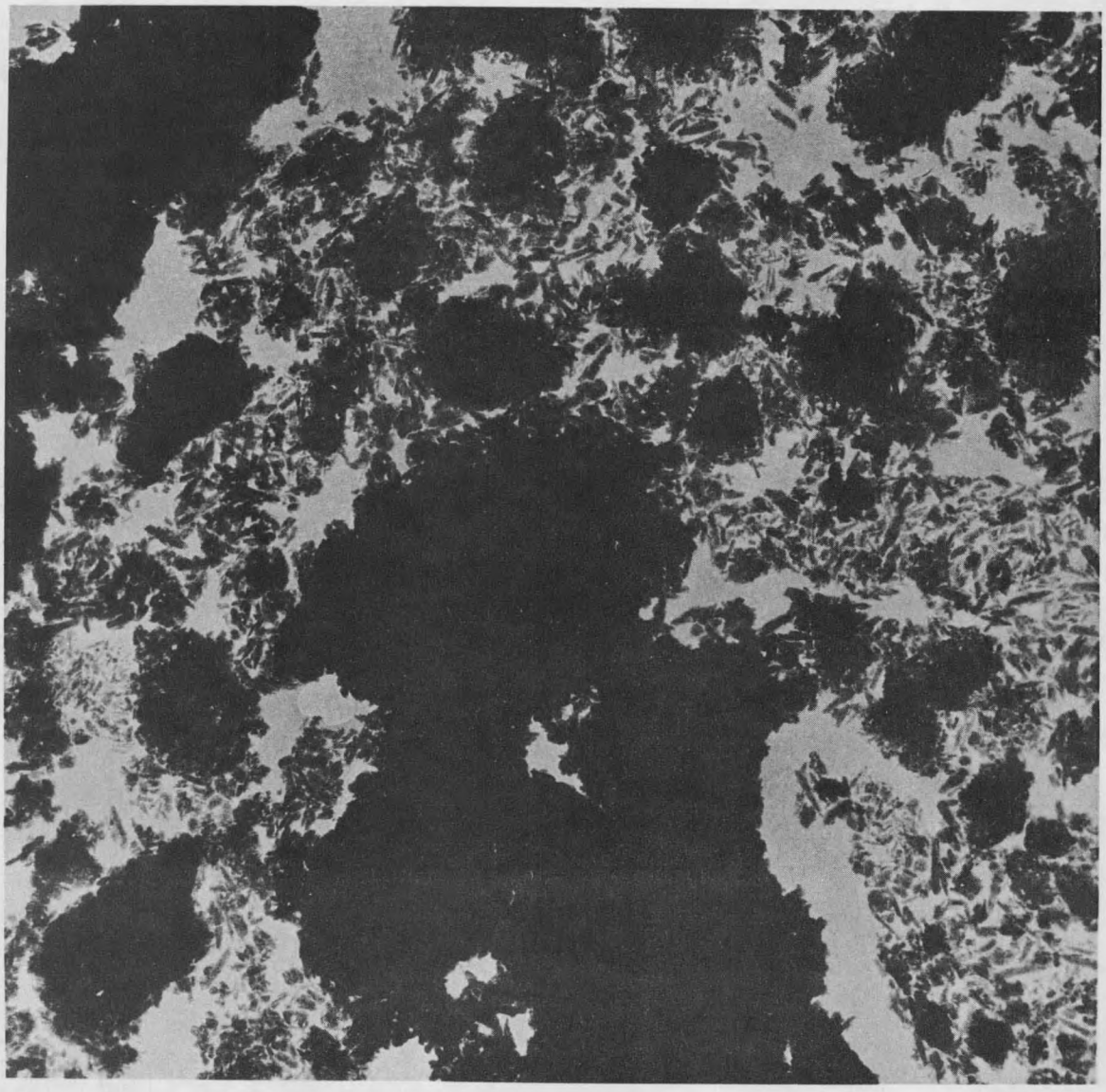

Figure 16 Electron Micrograph of PR-II-2

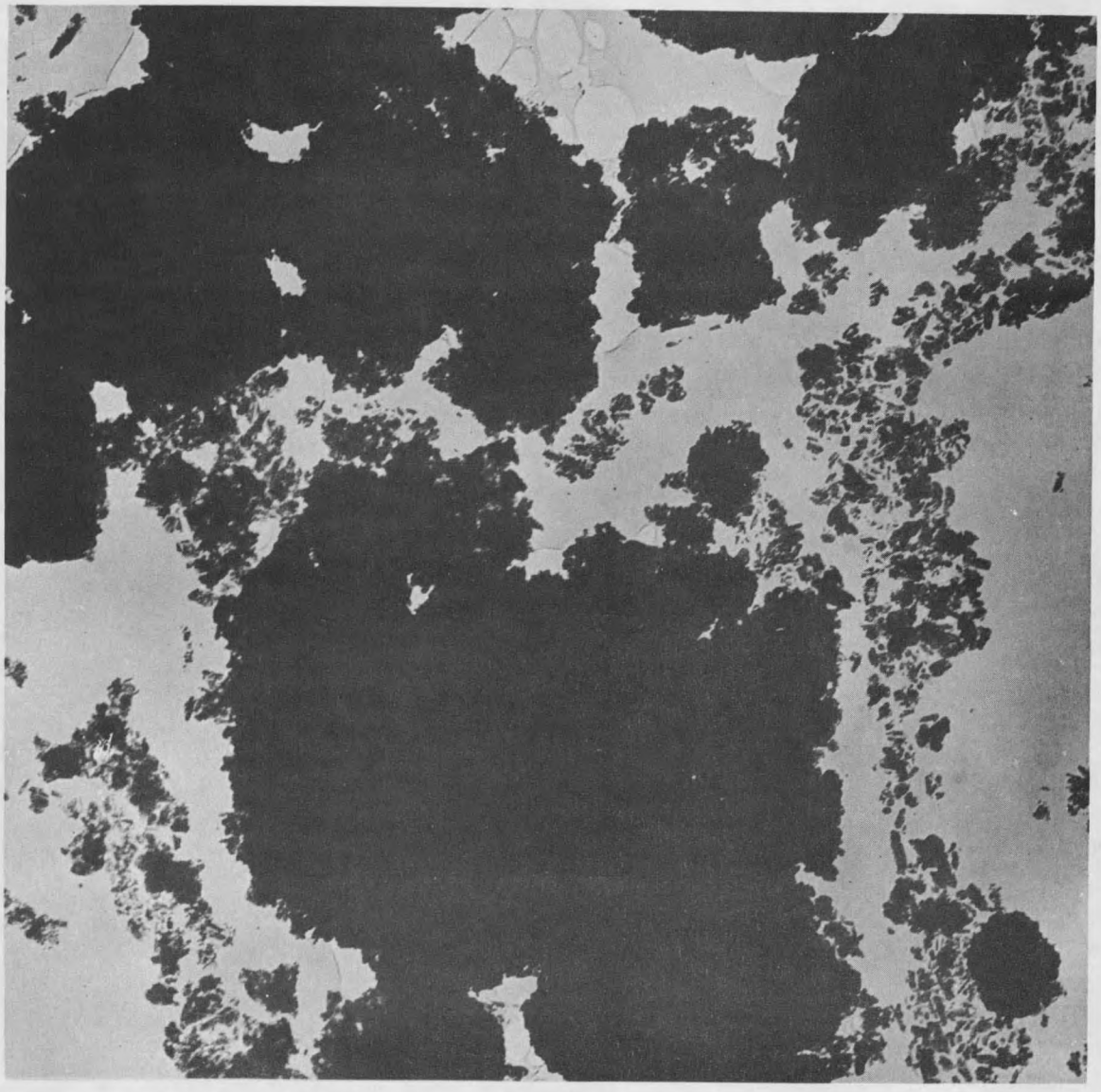

Figure 17 Electron Micrograph of PR-II-3

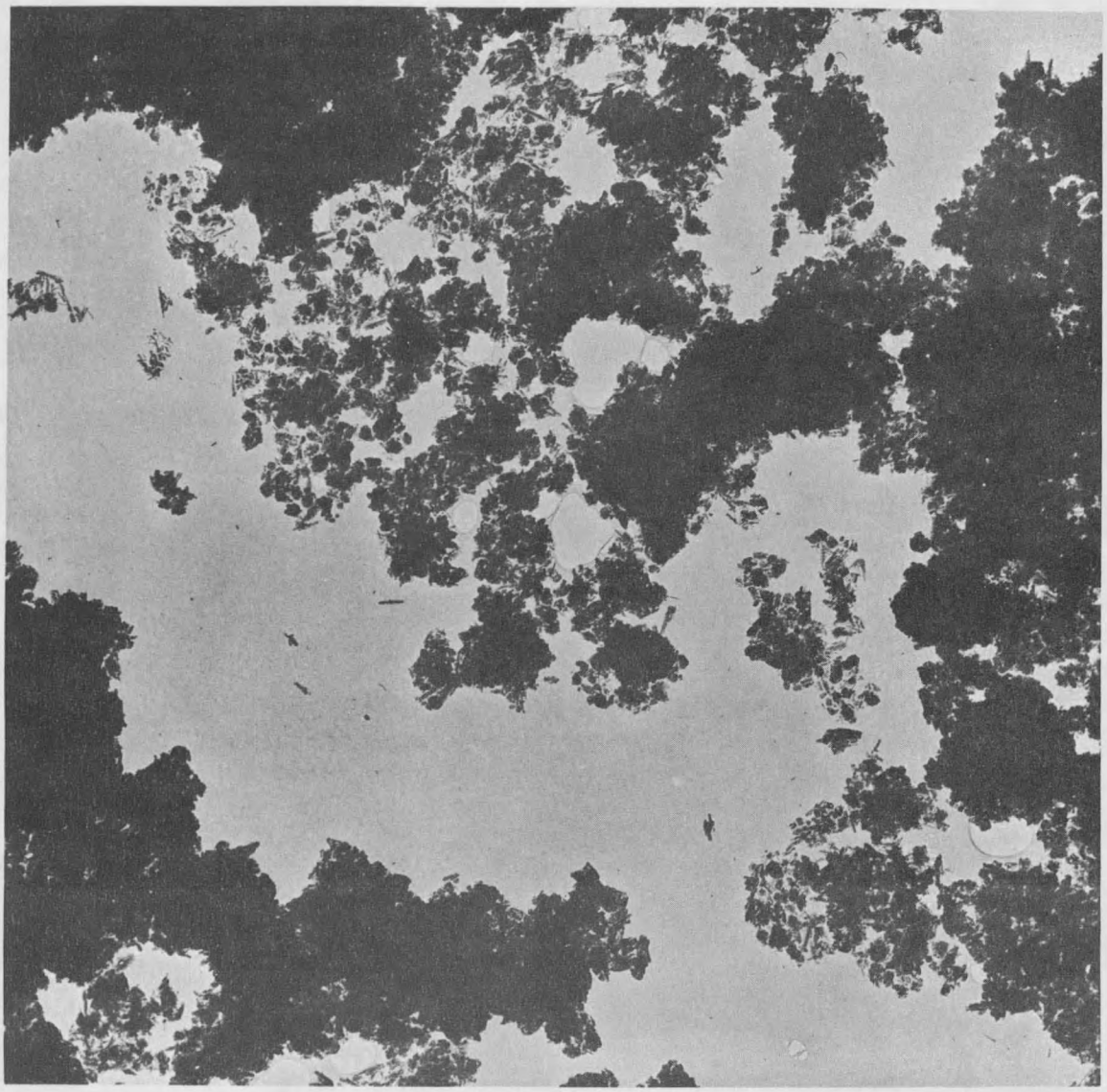

Figure 18 Electron Micrograph of PR-III-1

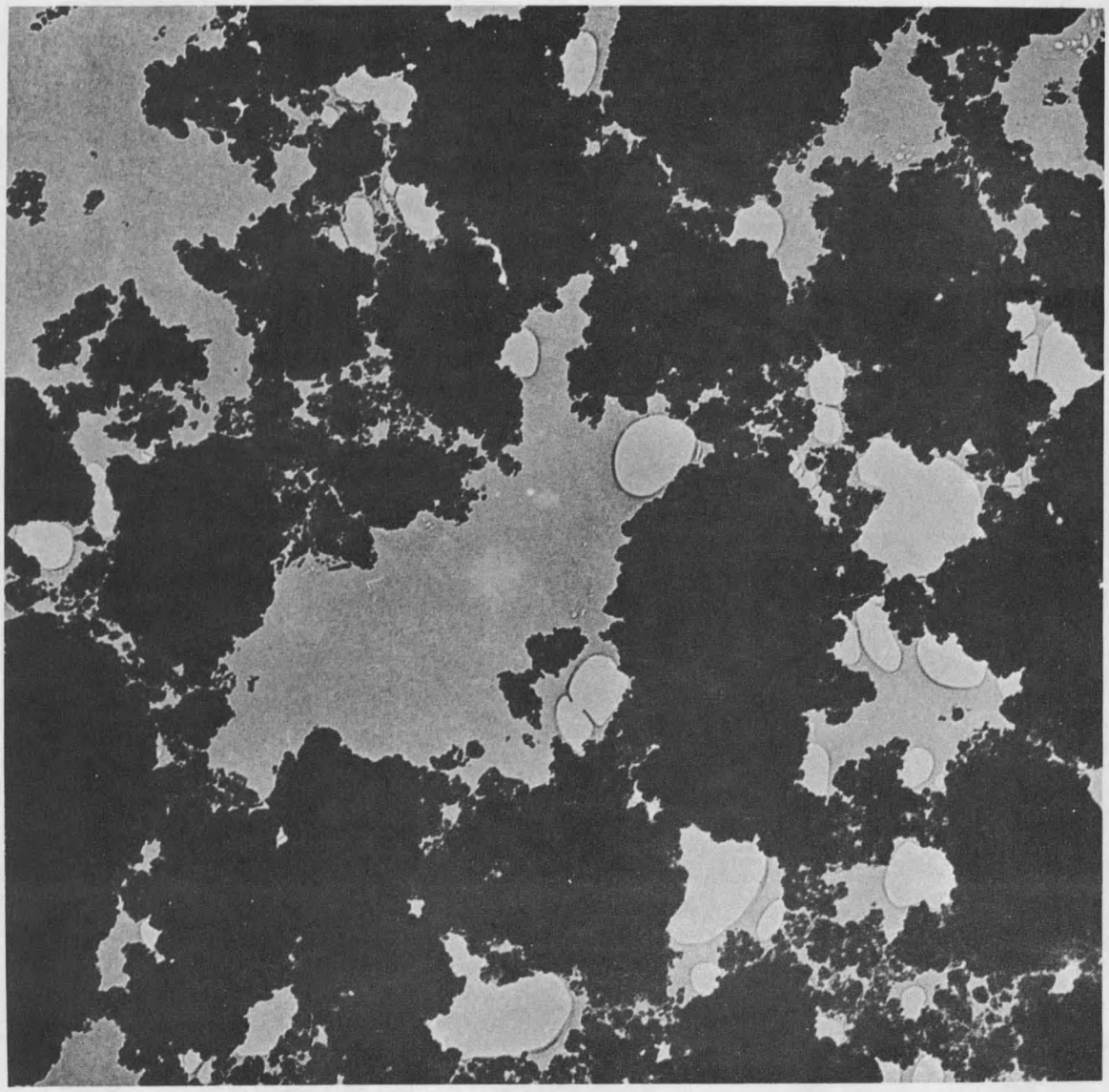

Figure 19 Electron Micrograph of PR-III-3

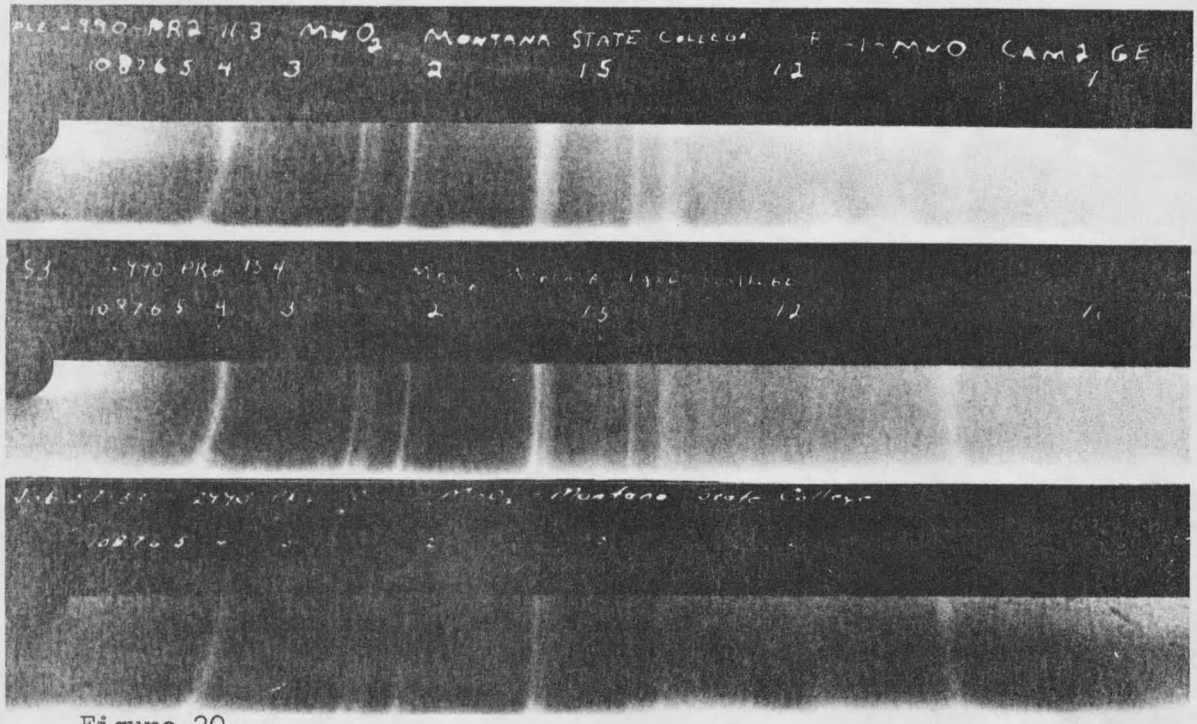

Figure 20.

sample load. The ball load was increased to 10 pounds and the sample charge added to fill the mill approximately half full. This procedure allowed about 80% recovery of -100 mesh MnO_2 after a six-hour grind.

The construction materials used for the reactors, leach vessels, and wash tanks were wood, fibre glass reinforced polyester, and a molding compound made of a room-temperature curing epoxy-poly amide resin. These materials were generally satisfactory, having withstood repeated runs where conditions were alternately highly alkaline, acidic with solutions saturated with chlorine, and strongly acidic with H_2SO_4 at the boiling point. The leach conditions were a bit drastic for the polyester and small pinholes developed in the tank lining. However, the lay-up procedure used on this tank was questionable. The epoxy resin was satisfactory at all conditions, and in addition, was found to be a very ef-

fective corrosion resistant coating for the iron parts of a small oliver rotary filter, and a plate and frame press. A polyester resin coated marine plywood 1000 gallon wash tank was satisfactory in all respects.

Polyethylene was an excellent material as regards chemical resistance; however, the low softening point of the low density polyethylene was undesirable for the high temperature operations, such as preparing the caustic solutions from 76% flake or the acid leaching step mentioned previously. Saran tubing was successfully used for transferring the reagents to the various process vessels.

Operating characteristics of the pilot runs are not considered indicative of commercial operation. The runs never really got out of the shakedown stage since continual modification was made to make the units functional and few investigations were made which would indicate processing optimums. The chlorination step has been cited as an example of reactor inefficiency which could be easily rectified by a variety of commercial reaction systems, including turbine agitated tank or column reactors operated at super atmospheric chlorine pressure.

A further purpose of the large sample preparation was to study the blending characteristics of the chemical MnO_2 when mixed with natural ore from the Gold Coast. Figure 21 shows the battery life versus blend composition for PR-I and Gold Coast blends. The curve shows that a mutual upgrading occurs. The shape of this curve is rather unexpected, but has been verified by other researchers in the chemical MnO_2 field. The reason for the curvature probably is attributed to an increase in MnO_2 concentration in the bobbins due to better tamping qualities of the mix. Data on

the electrolytic-Gold Coast blends indicate these materials blend to give an essentially linear battery life versus composition relationship. Comparison of the curves of Figure 21 show that a given battery activity can be arrived at with lower concentrations of the chemical MnO_2 over almost the entire concentration range, even though the pure electrolytic ore is superior to the pure chemical ore in this instance. It is easy to conclude that the chemical ore has an economic advantage over the electrolytic ore in upgrading Gold Coast blends. As an example, calculations based on current market quotations of $140 per ton for Gold Coast ore and $600 per ton for electrolytic and chemical ore show that the total depolarizer cost in fabricating batteries meeting SCL-3117-D specifications is reduced by as much as 33% when the chemical ore is used instead of electrolytic ore in the Gold Coast blends. More data on the chemical ore blends are necessary to reveal the maximum potential in upgrading Gold Coast ore. Blends utilizing chemical ore like that obtained in the 50% conversion pressure chlorination which had activity comparable to the electrolytic ore should be evaluated.

The technical feasibility of the caustic-chlorine oxidation of manganese sulfate has been demonstrated. The better techniques result in good yields of a depolarizer which will satisfy the Signal Corps specification for synthetic manganese dioxide, SCL-3117-D.

A review of the economics of one oxidation procedure will demonstrate the commercial feasibility of the process. The 50% conversion process was chosen for its simplicity of operation and its demonstrated ability to produce a specification grade depolarizer.

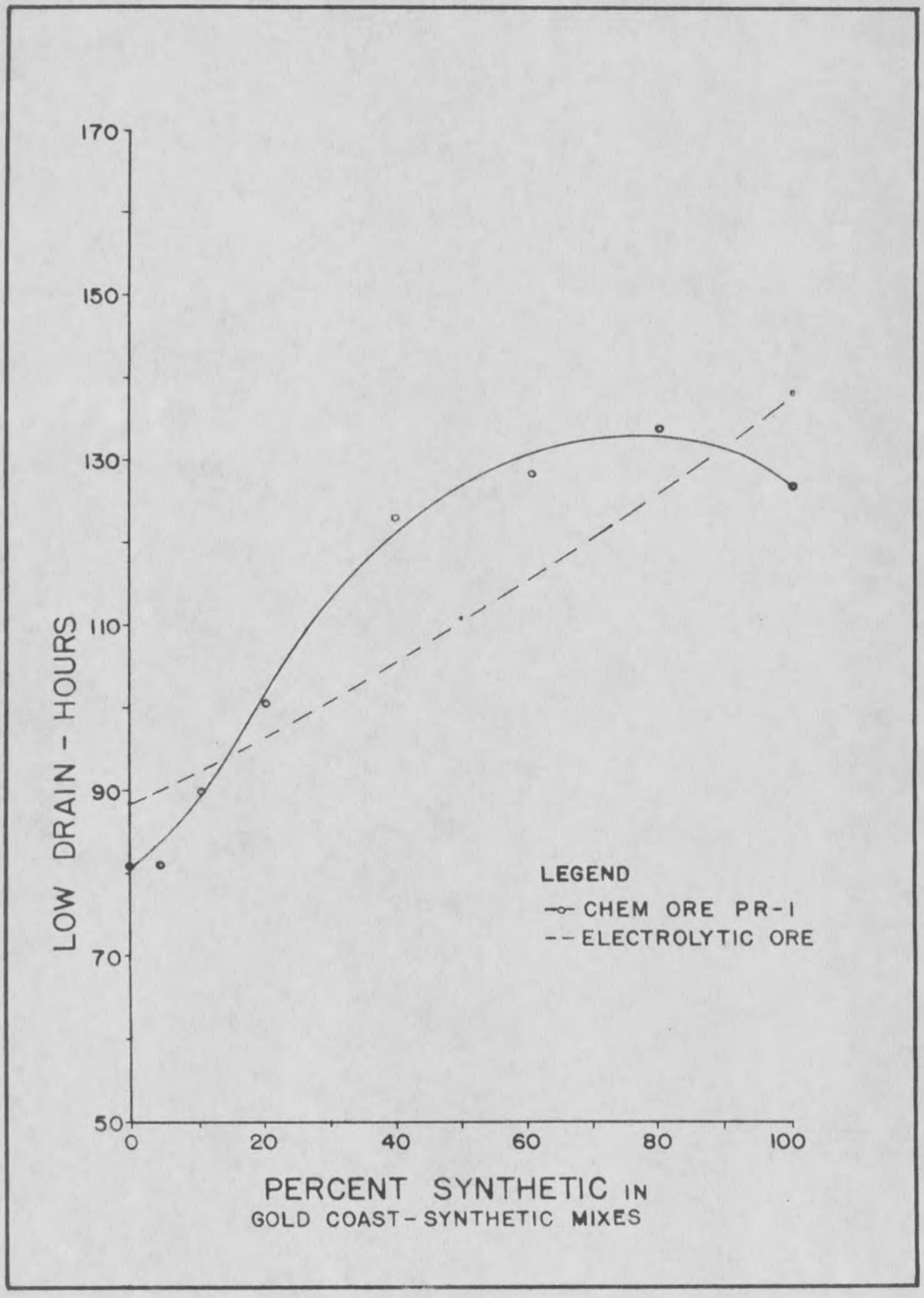

FIG. 21 DRAIN LIFE VS. COMPOSITION

The operations necessary to commercial production are similar to those used in the bench-scale operation:

1. Ore leach to produce neutral $MnSO_4$.
2. Purification of $MnSO_4$ to remove iron and heavy metals.
3. Caustic addition to form $Mn(OH)_2$
4. Chlorination
5. Product separation and recycle of unconverted manganese
6. Washing, drying, grinding of product
7. Quality determination, blending, packaging

A flow sheet showing the basic equipment necessary for this type of operation is shown in Figure 22. A list of equipment and facilities necessary for the operation are listed in Table XIV. The sizing of process equipment is only approximate. The estimated prices for the equipment are rule of thumb estimates in the case of the filters, but are based on current quotations from equipment manufacturers for the majority of items.

A rather large general expense item was entered to allow for neglected items. The sum of equipment expenses and capital requirements for startup and running for 90 days amounts to nearly $1,000,000.

A continuation of Table XIV shows a breakdown of reagent costs based on daily plant requirements and are calculated from current published market prices. A final accounting of yearly expenses and income results in a net return after taxes of $250,000. This net represents a 28% return on the investment.

The process would be considerably more attractive to a chlorine caustic producer since the daily cost for these items is over half of the total raw materials cost.

The calculations are rather idealized, but are considered to indicate that the 50% conversion process can be scaled to 10 tons per day with a capital requirement of less than $1,000,000, and will return more than 20% per year of the invested capital.

SUMMARY

1. Manganese dioxide prepared by the chlorine oxidation of manganese hydroxide will pass Signal Corps specification SCL-3117-D for initial drain tests when the following conditions are observed:

A. the reagents Cl_2 and NaOH are of standard commercial purity, technical grade, or better.

B. the manganese sulfate used in preparing the manganese hydroxide has less than 1% Mg, .5% Si, .1% Al, .1% Ca, .1% Fe, .1% K, .001% Cu, .001% Ni.

C. the NaOH to $MnSO_4$ mol ratio is 2:1 or alternately, if it is no greater than 3.75:1 provided the product is digested with dilute H_2SO_4 at a temperature greater than 65°C for sufficient time to remove the lower oxides and decrease the hydration.

D. the reaction temperature is maintained at 45°C or less.

E. the agitation is sufficient to keep the $Mn(OH)_2$ dispersed and available for reaction.

F. the reaction time is long enough to obtain a product containing 92-95% of the manganese in the tetravalent oxidation state.

G. the product is dried to less than three percent free moisture at a temperature of 110°C or lower.

H. the dried product is ball milled for long enough to assure the highest possible concentration in the battery bobbin, or until further milling shows no improvement in battery

tests.

2. Manganese dioxide of rho or gamm-rho crystalline phase can be prepared by addition of a basic sodium hypochlorite solution to pure $MnSO_4$ solutions when:

A. the oxidant is added to the $MnSO_4$ solution.

B. the oxidant composition has the molar ratio NaOH:NaOCl: NaCl of 2:1:1.

C. the mol ratio of sodium in the oxidant to manganese is less than 3.75:1 or otherwise maintained at a level which prevents the formation of permanganate.

D. the temperature is approximately 35°C.

3. A distorted beta-gamma phase of MnO_2 of excellent battery quality and stability is produced by the chlorination of pure manganese sulfate with the simultaneous addition of dilute NaOH to maintain the reaction pH at a constant value when:

A. the NaOH to manganese mol ratio is below the value where permanganate formation occurs, or about 3.75 mols NaOH per 1 mol Mn.

B. the reaction temperature is 25°C.

C. the pH is held at 6.0 to 7.5.

4. Analysis of MnO_2 samples prepared as in 1 show that impurities present in the $MnSO_4$ to the extent of 1% Al, 1% Mg, .5% Si, .1% Ca, .1% k, .05% Fe, and .01% Cu consistently causes formation of gamma phase MnO_2, while C. P. $MnSO_4$ produces rho or gamma-rho phase MnO_2.

5. The use of $MnSO_4$ having the impurities cited in 4 results in:

A. contamination of the product with divalent manganese.

B. high degree of hydration of the product roughly proportional to the MnO content.

6. Dilute sulfuric acid leaching at elevated temperatures activates the product made as in 4 when:

A. the sulfuric acid concentration is 150 grams per liter or less.

B. the leach temperature is greater than $65^{o}C$.

C. the MnO content is reduced to the range of 0-6%.

7. Blends of manganese dioxide prepared as in 1 and Gold Coast MnO_2 exhibit a mutual upgrading effect; that is, mixtures show higher battery tests than would be predicted by linear interpolation between the drain tests of the pure components.

8. The Leclanche cell depolarizer reaction with a depolarizer prepared as in 1 appears to be sequential when discharged continuously through 167 ohms resistance. The primary depolarizer reaction is the reduction of MnO_2 to Mn_2O_3 occurring over the output voltage range of 1.75 to .90 volts and a secondary reaction of the Mn_2O_3 to Mn_3O_4 over the voltage range of .8 to .1 volts.

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TABLE IX

ANALYTICAL DATA

Sample	% O_2 as MnO_2	% Mn	% H_2O	pH	Density gm/in^3
MC1-1	78.0	56.0	6.5	9.3	12.5
MC1-1[a]	95.5	61.4	3.8	6.2	12.2
MC1-2	91.2	63.3	0.0	6.4	11.9
MC1-3	92.2	62.2	2.8	6.5	12.5
MC1-4	92.2	59.2	0.8	4.3	13.8
MC1-5	89.6	61.1	1.3	4.4	14.2
MC1-6	92.1	60.2	2.2	4.8	12.8
MC1-7	83.4	58.0	7.4	5.3	11.8
MC1-8	78.2	60.1	4.3	6.2	9.7
MC1-8a	88.4	58.4	4.6	6.2	13.3
MC1-9	80.7	60.8	1.5	4.4	10.3
MC1-10	90.2	60.6	2.8	6.5	11.0
MC1-11	91.3	58.5	2.3	6.3	10.4
MC1-12	93.6	60.0	2.0	5.8	10.4
MC1-13	91.5	59.8	3.3	5.6	10.4
MC1-14	90.1	58.1	3.3	5.7	9.3
MC1-15	90.0	58.3	3.2	5.8	9.7
MC1-16	92.4	63.1	2.3	7.0	12.2
MC1-17	93.0	64.6	1.6	5.9	14.0

TABLE IX (Cont'd)

Sample	% O_2 as MnO_2	% Mn	% H_2O	pH	Density gm/in^3
MC1-18	83.0	57.2	3.3	7.8	8.4
MC1-18[a]	90.4	59.4	0.8	7.0	11.3
MC1-19	86.8	57.4	1.7	7.2	10.6
MC1-20	89.6	60.4	1.0	6.6	12.6
MC1-21	89.5	59.5	1.5	7.4	12.4
MC1-22	91.4	59.6	1.6	7.3	10.0
MC1-22[a]	94.9	57.8	0.7	6.7	12.8
MC1-23	82.3	54.4	1.4	8.6	7.6
MC1-24	91.6	62.3	1.6	7.8	11.3
MC1-25	84.6	60.7	2.1	7.6	9.4
MC1-26	84.6	58.7	3.4	6.7	11.8
MC1-27	88.0	59.0	3.2	6.8	13.4
MC1-28	89.8	60.8	3.0	5.8	13.8
MC1-29	86.7	59.1	2.6	5.9	11.8
MC1-30	83.8	55.3	4.1	6.1	12.7
MC1-31	82.2	59.1	4.8	7.0	12.0
MC1-31[a]	88.5	60.6	3.4	6.3	12.9
MC1-32	81.4	58.0	3.7	6.2	8.3
MC1-32[a]	85.9	58.0	3.7	6.0	14.1

TABLE IX (Cont'd)

Sample	% O_2 as MnO_2	% Mn	% H_2O	pH	Density gm/in^3
MC1-33	84.6	58.2	5.8	6.7	10.7
MC1-33[a]	91.9	60.0	3.2	6.4	13.4
MC1-34	82.2	58.0	3.4	6.1	12.3
MC1-35	83.0	57.8	3.5	5.7	10.7
MC1-36	84.6	56.6	5.1	5.6	12.9
MC1-37	75.0	56.4	6.4	6.4	12.9
MC1-38	82.0	57.3	6.0	7.0	10.0
MC1-38[a]	85.0	57.8	4.3	6.7	12.7
CR-I-1	90.8	61.9	2.5	6.1	13.4
CR-II,III-1[a]	91.1	61.6	3.2	5.9	15.6
CR-IV-1[a]	89.6	59.8	2.6	5.9	15.5
CR-V-1[a]	89.6	59.4	2.3	6.1	16.6
CR-V-2[a]	89.2	59.7	3.6	5.1	14.6
CR-V-3[a]	79.9	56.3	4.3	6.3	14.5
CR-VI-1[a]	85.5	57.1	2.9	6.2	14.5
CR-VI-2[a]	86.5	58.8	3.0	6.0	13.9
CR-VII	88.2	60.1	1.2	8.0	10.1
CR-VIII-1	78.1	54.0	6.4	6.1	13.0
PR-I-1[a]	89.3	58.9	2.9	6.0	12.0

TABLE IX (Cont'd)

Sample	% O_2 as MnO_2	% Mn	% H_2O	pH	Density gm/in^3
PR-II-1	91.6	58.7	1.9	6.1	9.1
PR-II-2	91.6	58.7	1.9	6.1	11.3
PR-II-3	91.6	58.7	1.9	6.1	15.4
PR-III-1	89.0	60.9	2.8	6.4	10.3
PR-III-2	89.0	60.9	2.8	6.4	11.3
PR-III-3	89.0	60.9	2.8	6.4	14.2
PR-V-2	89.6	59.8	1.4	6.0	14.3
PR-VI-1	84.8	56.6	2.4	6.2	13.7

TABLE X

DRAIN TEST DATA

Sample	Bobbin Wt grams	High Drain (5 day test) hrs	Low Drain (5 day test) hrs	Low Drain (3-month test) hrs
MC1-1	9.4	2.5	84	84
MC1-1[a]	9.6	4.5	153	128
MC1-2	9.7	5.6	117	104
MC1-3	9.5	6.5	118	109
MC1-4	9.1	7.2	133	119
MC1-5	9.3	7.6	140	104
MC1-6	9.4	5.5	129	112
MC1-7	9.2	1.4	118	12
MC1-8	8.9	2.4	65	14
MC1-8[a]	9.1	5.6	129	---
MC1-9	9.4	5.6	78	60
MC1-10	9.8	5.2	119	105
MC1-11	10.4	4.2	106	52
MC1-12	9.8	2.9	91	68
MC1-13	9.9	5.3	123	108
MC1-14	9.5	4.3	106	94
MC1-15	9.0	7.8	129	109
MC1-16	9.8	6.0	122	13
MC1-17	9.9	6.2	123	123

TABLE X (Cont'd)

Sample	Bobbin Wt grams	High Drain (5 day test) hrs	Low Drain (5 day test) hrs	Low Drain (3-month test) hrs
MC1-18	8.6	0.0	6	0
MC1-18[a]	9.7	4.4	134	78
MC1-19	9.4	5.2	116	58
MC1-20	11.1	4.0	139	45
MC1-21	9.9	3.4	134	49
MC1-22	8.8	3.7	121	100
MC1-22[a]	9.8	3.9	152	49
MC1-23	7.9	0.0	6	0
MC1-24	9.9	4.0	88	47
MC1-25	8.8	1.0	100	97
MC1-26	9.0	6.6	140	108
MC1-27	8.9	6.4	144	108
MC1-28	9.3	7.2	137	133
MC1-29	8.9	8.6	120	109
MC1-30	9.3	6.9	126	106
MC1-31	8.9	6.7	115	85
MC1-31[a]	9.9	6.8	109	110
MC1-32	8.3	1.5	99	48
MC1-32[a]	9.6	7.0	133	---

TABLE X (Cont'd)

Sample	Bobbin Wt grams	High Drain (5 day test) hrs	Low Drain (5 day test) hrs	Low Drain (3-month test) hrs
MC1-33	8.8	4.7	114	106
MC1-33[a]	9.2	6.9	139	---
MC1-34	9.0	7.3	112	98
MC1-35	8.9	8.9	111	72
MC1-36	9.0	8.0	125	98
MC1-37	8.8	6.4	111	81
MC1-38	8.7	6.5	113	75
MC1-38[a]	9.6	6.2	134	75
CR-I-1	9.6	6.6	134	114
CR-II,III-1[a]	9.9	7.4	150	112
CR-IV-1[a]	9.7	7.6	143	106
CR-V-1[a]	9.7	7.0	140	69
CR-V-2[a]	9.7	6.7	149	77
CR-V-3[a]	9.4	5.8	128	87
CR-VI-1[a]	9.8	7.4	146	119
CR-VI-2[a]	9.5	6.6	134	106
CR-VIII-1	9.5	6.2	90	0
PR-I-1[a]	9.1	7.5	127	116

TABLE X (Cont'd)

Sample	Bobbin Wt grams	High Drain (5 day test) hrs	Low Drain (5 day test) hrs	Low Drain (3-month test) hrs
PR-II-1	8.9	6.0	92	---
PR-II-2	9.3	5.5	112	115
PR-II-3	9.8	7.0	124	103
PR-III-1	9.1	2.8	95	84
PR-III-2	9.1	7.3	113	93
PR-III-3	9.5	8.8	126	---
PR-V-2	10.0	5.2	140	---
PR-VI-1	9.4	7.0	134	---

TABLE XI

METHODS OF PREPARATION OF SAMPLES

Sample	Preparation
MCl-1	A solution of 310 grams of NaOH in 3 liters water was chlorinated and a solution of 308 grams C.P. $MnSO_4 \cdot H_2O$ in .6 liters of water added dropwise over a 5 hour period. The average reaction temperature was 29°C and the total reaction time was 22 hours.
MCl-1[a]	Eighty grams of MCl-1 was acid leached with 27 ml of concentrated HCl in one liter of water at 85°C for two hours.
MCl-2	A solution of 338 grams of C.P. $MnSO_4 \cdot H_2O$ in three liters of water was reacted with 160 grams of NaOH dissolved in .5 liter of water to form two mols of $Mn(OH)_2$ in 3.5 liters of solution. The resulting slurry was chlorinated for 24 hours at 25°C to a final pH of 1.8. The reaction mixture was then heated to 65°C for two hours.
MCl-3	A solution of 338 grams of C.P. $MnSO_4 \cdot H_2O$ in three liters of water was reacted with 160 grams of NaOH dissolved in .5 liter of water to form two mols of $Mn(OH)_2$ in 315 liters of solution. The resulting slurry was chlorinated for 24 hours at 25°C to a final pH of 1.8. The reaction mixture was then heated to 65°C for two hours.
MCl-4	A solution of 338 grams of C.P. $MnSO_4 \cdot H_2O$ in 5.5 liters of water was reacted with 160 grams of NaOH dissolved in .5 liter of water to form two mols of $Mn(OH)_2$ in 6 liters of solution. The resulting slurry was chlorinated for 24 hours at 0°C to a final pH of 1.8. The reaction mixture was then heated to 65°C for two hours.
MCl-5	A solution of 338 grams of C.P. $MnSO_4 \cdot H_2O$ in three liters of water was reacted with 160 grams of NaOH dissolved in .5 liter of water to form two mols of $Mn(OH)_2$ in 3.5 liters of solution. The resulting slurry was chlorinated for 24 hours at 2°C to a final pH of 1.8. The reaction mixture was then heated to 65°C for two hours.
MCl-6	A solution of 338 grams of C.P. $MnSO_4 \cdot H_2O$ in three liters of water was reacted with 160 grams of NaOH dissolved in .5 liter of water to form two mols of $Mn(OH)_2$ in 3.5 liters of solution. The resulting slurry was chlorinated for 24 hours at 20°C to a final pH of 1.8. The reaction mixture was then heated to 65°C for two hours.

TABLE XI (Cont'd)

Sample	Preparation
MC1-7	A solution of 338 grams of C.P. $MnSO_4 \cdot H_2O$ in three liters of water was reacted with 320 grams of NaOH dissolved in .5 liter of water to form two mols of $Mn(OH)_2$ in 3.5 liters of solution. The resulting slurry was chlorinated for 24 hours at 5°C to a final pH of 1.8. The reaction mixture was then heated to 65°C for two hours.
MC1-8	A duplicate of MC1-6, except that the manganese sulfate was of the composition of MS-4, Table XII.
MC1-8[a]	Forty-two grams of MC1-8 was leached with 100 ml of 100 gram per liter H_2SO_4 for two hours at 95°C.
MC1-9	A duplicate of MC1-8. The average reaction temperature was 27°C.
MC1-10	Two mols of C.P. $MnSO_4$ dissolved in 2 liters water was reacted with 160 grams of NaOH in one liter of solution. The resulting $Mn(OH)_2$ slurry was chlorinated for 24 hours at 3°C.
MC1-11	The reaction effluent of MC1-10 was reacted with sufficient NaOH to bring the pH to 10. The resulting $Mn(OH)_2$ slurry was chlorinated for 48 hours at 0°C.
MC1-12	Four mols of $MnSO_4$ in 4 liters of water was reacted with eight mols of NaOH in 2 liters of water. The resulting $Mn(OH)_2$ slurry was chlorinated for 24 hours at 20°C.
MC1-13	The reaction effluent of MC1-12 was reacted with 160 grams of NaOH in .5 liters of water. The resulting $Mn(OH)_2$ slurry was chlorinated for 24 hours at 20°C.
MC1-14	Four mols of $MnSO_4$ in 4 liters of water was reacted with eight mols of NaOH in 2 liters of water. The resulting $Mn(OH)_2$ slurry was chlorinated for 24 hours at 20°C. One hundred sixty grams of NaOH in .5 liter of water was added to precipitate the manganese as $Mn(OH)_2$. The resulting $MnO_2 \cdot Mn(OH)_2$ slurry was chlorinated for 24 hours at 20°C. The procedure was repeated with 80 grams of NaOH in .250 liter of water and the slurry again chlorinated for 24 hours at 20°C.

TABLE XI (Cont'd)

Sample	Preparation
MCl-15	A duplicate of MCl-12, except that the product was ball milled instead of mortar ground.
MCl-16	Three liters of a solution containing 2 mols $MnSO_4$ was chlorinated at an average temperature of 23°C. A caustic solution consisting of 320 grams NaOH in 3 liters H_2O was added slowly to maintain a constant pH of 6.5 to 7.0. Total chlorination time was 28 hours, although the reaction was run over a 5-day time interval.
MCl-17	Three liters of solution containing 2 mols $MnSO_4$ was chlorinated at an average temperature of 27°C. A caustic solution consisting of 320 grams NaOH in 3 liters H_2O was added slowly to maintain a constant pH of 6.8 to 7.0. Total chlorination time was about 20 hours although the reaction was run over a 5-day interval. All but 330 grams of the NaOH solution was added.
MCl-18	Three liters of a solution containing 2 mols $MnSO_4$ was chlorinated at an average temperature of 20°C. A caustic solution consisting of 320 grams NaOH in 3 liters H_2O was added slowly to maintain a constant pH of 4.0 to 5.0. Total chlorination time was 35½ hours although the reaction was run over a 7½-day time interval.
MCl-18[a]	One hundred grams of MCl-9 was leached with 120 ml of 95 gram per liter H_2SO_4 for two hours at 95°C.
MCl-19	One and one-half liters of solution containing one mol C.P. $MnSO_4$ was chlorinated at a rate of two liters per hour and at an average temperature of 25°C. A caustic solution consisting of 144 grams NaOH in 1.3 liters H_2O was added slowly to maintain the pH in the range 4.0 to 5.0. Total reaction time was 16.8 hours.
MCl-20	A solution containing 480 grams of NaOH in four liters of water was chlorinated until the molar composition was 2NaOH:1NaOCl:1NaCl. One half of this solution was added dropwise to 1.5 liters of solution containing 338 grams of C.P. $MnSO_4 \cdot H_2O$ over a three-hour period. Total reaction time was eight hours and the average temperature was 27°C.

TABLE XI (Cont'd)

Sample	Preparation
MCl-21	The procedure of MCl-20 was used except the ratio of caustic to manganese was increased. Five hundred and twenty grams of NaOH in four liters of water was chlorinated to a NaOH:NaOCl:NaCl ratio of 2:1:1, and one half of this oxidant was used as in MCl-20.
MCl-22	The procedure of MCl-21 was followed except that the NaOH used was 600 grams in four liters.
MCl-22[a]	One hundred grams of MCl-22 was acid leached with 100 ml of 100 gram per liter H_2SO_4.
MCl-23	The procedure of MCl-21 was followed except that the NaOH used was 640 grams in 4 liters of water.
MCl-24	The procedure of MCl-21 was followed except that the NaOH used was 280 grams in 2 liters of water. The reaction temperature was 90-95°C and the final pH was 4.5.
MCl-25	The procedure of MCl-24 was followed except the reaction temperature was 7°C and the final pH was 4.0.
MCl-26	Two mols of C.P. $MnSO_4$ in 2 liters of water was reacted with four mols of NaOH in 1.5 liters of water. The resulting $Mn(OH)_2$ slurry was placed in a mechanically agitated 4-liter suction flask. The flask was sealed, evacuated, and chlorine admitted at 5 psig. The reaction time was 3.7 hours and the average temperature was 25°C. The time for zero chlorine flow was 3.2 hours.
MCl-27	The procedure of MCl-26 was followed except that the chlorine pressure was 15 psig and the reaction time was 1.7 hours. The time for zero chlorine flow was 1.2 hours.
MCl-28	A duplicate of MCl-27 except the reaction time was 2.5 hours.
MCl-29	Two mols of C.P. $MnSO_4$ in 2 liters of water was reacted with 5 3/4 mols of NaOH in 1.5 liters of water to form 2 mols of $Mn(OH)_2$ and 1 3/4 mol of free NaOH in 3.5 liters of slurry. The resulting $Mn(OH)_2$ was chlorinated in the pressure chlorination apparatus for 3.5 hours at 25°C.

TABLE XI (Cont'd)

Sample	Preparation
MCl-30	The same procedure of MCl-29 was followed except that the amount of NaOH used was 7 mols in 1.5 liters of water.
MCl-31	The same procedure of MCl-30 was used except the amount of NaOH used was 7.5 mols in 1.5 liters of water. The average reaction temperature was 22°C.
MCl-31[a]	Sixty-nine grams of MCl-31 was acid leached with 200 ml of 100 gram per liter H_2SO_4 at 85°C for 1 hour.
MCl-32	The procedure of MCl-31 was followed except that the $MnSO_4$ was not C.P. but was prepared as in MS-6, Table XII.
MCl-32[a]	Fifty grams of MCl-32 was acid leached with 150 ml of 100 gram per liter H_2SO_4 at 95°C for 1 hour.
MCl-33	A duplicate of MCl-31 except the average temperature was 33°C.
MCl-33[a]	Fifty grams of MCl-33 was acid leached with 150 ml of 100 gram per liter H_2SO_4 at 95°C for 1 hour.
MCl-34	Two mols of technical $MnSO_4$ prepared as in MS-6, Table XII, was diluted to 2 liters and reacted with 4 mols of NaOH in 1.5 liters of water. The resulting slurry was chlorinated at 15 psig for 2.5 hours at an average temperature of 33°C.
MCl-35	A duplicate of MCl-34 except that the average temperature was 23°C.
MCl-36	A duplicate of MCl-35 except that the source of $MnSO_4$ was MS-5, prepared as in Table XII.
MCl-37	A duplicate of MCl-35 except that the source of $MnSO_4$ was MS-4, prepared as in Table XII.
MCl-38	Two mols of C.P. $MnSO_4$ in 2 liters of water was reacted with 7.5 mols of NaOH in 1.5 liters of water. The resulting $Mn(OH)_2$ slurry was chlorinated at 15 psig for 2.5 hours. The average temperature was 29°C.

Table XI (Cont'd)

Sample	Preparation
MC1-38[a]	Ninety grams of MC1-38 was acid leached with 200 ml of 100 gram per liter H_2SO_4 at 95°C for 1 hour.
CR-I-1	Continuous counter current chlorination of $Mn(OH)_2$ was carried out in an 8 foot, 2 inch I.D. glass reactor shown schematically in Figure 11. The $Mn(OH)_2$ feed was prepared by reacting 2 mols of C.P. $MnSO_4$ with 4 mols of NaOH to form 2 mols of $Mn(OH)_2$ in 4 liters of slurry. The average temperature was 27°C, and the conversion of manganese in the feed was 55%.
CR-II, III-1[a]	The same procedure as CR-I was followed except for the contact time, which was 1 hour. $Mn(OH)_2$ contaminated these products due to foaming in the reaction section. The products of both runs were combined and acid leached with 100 gram per liter H_2SO_4 at 85°C for 1 hour.
CR-IV	The procedure of CR-I was followed. The feed was prepared by reacting 4 mols of C.P. $MnSO_4$ with 14 mols of NaOH to form 8 liters of $Mn(OH)_2$ slurry. The contact time was 1.7 hours, the average temperature was 35°C and the conversion was 95%.
CR-IV-1[a]	One hundred grams of the product from this reaction was acid leached with 100 gram per liter H_2SO_4 at 95°C for 1 hour.
CR-V	A duplicate of CR-IV except the contact time was 1 hour.
CR-V-1[a]	A 100 gram sample of CR-V was acid leached with 100 gram per liter H_2SO_4 at 95°C for 1 hour.
CR-V-2[a]	A duplicate of CR-V-1[a].
CR-V-3[a]	A duplicate of CR-V-1[a] except that the leach temperature was 33°C.
CR-VI-1	A duplicate of CR-IV except that the contact time was .5 hours.
CR-VI-1[a]	A duplicate of CR-V-1[a].

Table XI (Cont'd)

Sample	Preparation
CR-VI-2	A duplicate of CR-VI-1 except the NaOH was increased. Four mols of C.P. $MnSO_4$ was reacted with 15 mols of NaOH to form 4 mols of $Mn(OH)_2$ and 7 mols of free NaOH in 8 liters of slurry. The slurry was treated as in CR-VI-1.
CR-VI-2[a]	A duplicate of CR-V-1[a].
CR-VII	A duplicate of CR-VI-2 except that the contact time was 1 hour.
CR-VIII-1	A duplicate of CR-I except that the $MnSO_4$ used was prepared as in MS-6, Table XII.
PR-I	100 pounds of $MnSO_4$ prepared as in MS-7, Table XII, was diluted to 10% $MnSO_4$ and reacted with 28 pounds of NaOH to form 45 gallons of $Mn(OH)_2$ slurry. The slurry was chlorinated until the pH reached 3.0 at an average temperature of 33°C.
PR-I-1[a]	The product of PR-I was acid leached with 100 gram per liter H_2SO_4 at 80°C for three hours.
PR-II	The procedure of PR-I was followed except the quantities were all doubled, and the manganese sulfate was purified of iron according to the procedure outlined in Table XII, MS-8. The product was acid leached with 100 gram per liter H_2SO_4 at 80-90°C for three hours.
PR-II-1	The product of PR-II was ground in a ball mill for two hours. A portion was screened -100 mesh and designated PR-II-1.
PR-II-2	The same procedure as PR-II-1 was followed except that the grinding was continued for an additional two hours.
PR-II-3	The same procedure as PR-II-2 except the grinding was continued for an additional two hours.
PR-III	Six hundred pounds of 10% $MnSO_4$ prepared as in Table XII, MS-8, was reacted with 32 pounds of NaOH to yield 90 gallons of $Mn(OH)_2$ slurry. The slurry was chlorinated for 12 hours until the pH reached 2.5. The product was acid leached with 50 gram per liter H_2SO_4 for 2 hours at 80-90°C.

Table XI (Cont'd)

Sample	Preparation
PR-III-1	The grinding procedure used in PR-II-1 was duplicated.
PR-III-2	The grinding procedure used in PR-II-2 was duplicated.
PR-III-3	The grinding procedure used in PR-II-3 was duplicated.
PR-IV	The same procedure used in PR-I was followed except that the $MnSO_4$ was C.P. grade and the quantities were reduced by half. The product was acid leached with 100 gram per liter H_2SO_4 for 2.5 hours at 85-90°C.
PR-V	Six hundred pounds of 10% $MnSO_4$ prepared as in Table XII, MS-9, was reacted with 56 pounds of NaOH to give 90 gallons of $Mn(OH)_2$ slurry. The slurry was chlorinated for 14 hours to a pH of 4. The product was acid leached with 50 gram per liter H_2SO_4 for 2 hours at 80-90°C. Due to excessive $Mn(OH)_2$ contamination, two successive leaches with 5 gram per liter acid were necessary for the pH of the leach solution to remain less than 2.
PR-V-2	A five pound portion of PR-V was ball milled for six hours and screened -100 mesh.
PR-VI-1	Seven hundred fifty pounds of 10% $MnSO_4$ prepared as in Table XII, MS-8, was reacted with 70 pounds of NaOH to give 115 gallons of $Mn(OH)_2$ slurry. The slurry was chlorinated for 10 hours until the pH reached 3.5. The product was acid leached with 100 gram per liter H_2SO_4 for 1 hour at 90°C.

Table XII

MANGANESE SULFATE PREPARATION

A lead fume by-product from Manganese, Incorporated which assayed at 28% Mn, 26% Pb, 32% H_2O was contacted with 66° Be H_2SO_4 in the weight ratio 100:35. The acidic mixture was heated with intermittent stirring for thirty minutes over a temperature range of 60-100°C. The solution was cooled and diluted with water to yield an acidic solution containing Mn, Fe, Al, Mg, Cu, Ca, and some colloidal SiO_2. The free acid was neutralized with lime and solutions with a pH of 3 - 5 were obtained. Typical solution compositions were as follows:

Sample	Mn(g/l)	Fe(g/l)	Cu(g/l)	pH
MS-1	36	.8	.2	1.
MS-2	39	.6	.1	3.6
MS-3	37	.3	.15	4.2
MS-4	67	.7	.26	4.3
MS-5	69	.8	.02	5.7
MS-6	68	.2	.2	4.3
MS-7	228	1.1	--	4.4
MS-8	74	.2	--	4.5
MS-9	74	.2	--	5.9

Manganese sulfate made from the lead fume is reported above as MS-1 through MS-6, inclusively.

The manganese sulfate of MS-7 and -8 was prepared from $MnCO_3$ obtained from Manganese Chemicals Corporation of Riverton, Minnesota. The $MnCO_3$ was prepared by the ammonium carbonate process and contains ammonium carbonate as a major impurity although iron is also present. This $MnCO_3$ contains 46% manganese. The manganese was dissolved by adding stoichiometric amounts of H_2SO_4 to the slurried $MnCO_3$. No purification of MS-7

Table XII (Cont'd)

was attempted and when the concentrated solution was diluted to 10% for use in reaction PR-1, $Fe(OH)_3$ precipitated, but was not removed. MS-9 was a duplication of MS-7 except that $CaCO_3$ was added and air sparged in to complete precipitation of iron. The purified $MnSO_4$ solution was filtered through a plate and frame press with Filteraid precoated dacron cloths. The $MnSO_4$ of MS-9 was prepared by dissolving technical grade $MnSO_4$ obtained from the Carus Chemical Company. This $MnSO_4$ assayed 81% $MnSO_4$ with about 10% $(NH_4)_2SO_4$ as the major impurity.

Table XIII

SPECTROGRAPHIC ANALYSIS OF $MnSO_4$

Component	Impure $MnSO_4$ MS-6 %	Purified $MnSO_4$ MS-5 %
Aluminum	1	0.1
Magnesium	1	1
Silicon	0.5	0.5
Sodium	0.5	0.5
Calcium	0.1	0.1
Potassium	0.1	0.1
Iron	0.05	0.1
Copper	0.01	0.001
Nickel	0.001	0.001
Titanium	0.001	0.001
Chromium	None found	None found
Cobalt	None found	None found
Barium	None found	None found

Table XIV

ECONOMIC SURVEY OF MANGANESE DIOXIDE PLANT

PLANT COST

	Item	NO. & CAPACITY	EST. PRICE -$-
1.	Outside storage	200 tons	1,000
2.	Jaw crusher	50 tons/day	2,800
3.	Ball mill	50 tons/day	3,000
4.	Fine ore bin	350 tons	1,000
5.	Leach tanks & accessories	2 - 15,000 gal.	6,000
6.	Thickeners	3 - 10' x 7'	4,000
7.	Cu removal tank	1 - 10,000 gal.	1,000
8.	Fe containing $MnSO_4$ storage tank	1 x 40,000 gal.	2,000
9.	Fe removal tank	1 x 20,000 gal.	1,200
10.	Oliver vacuum rotary filter	800 ft^2	40,000
11.	Purified $MnSO_4$ storage	2 x 60,000 gal.	5,600
12.	$Mn(OH)_2$ tank	1 x 20,000 gal.	2,200
13.	50% NaOH syn.	1 x 10,000 gal.	2,000
14.	50% NaOH storage	1 x 10,000 gal.	2,000
15.	Chlorinator	1 x 1,000 gal.	14,700
16.	Cl_2 storage	1 x 2,000 gal.	2,000
17.	Product thickeners	3 x 24' x 10'	10,500
18.	Oliver vacuum rotary filter	800 ft^2	50,000
19.	Product storage tank	1 x 20,000 gal.	2,200
20.	Dryer grind size	Combination unit	25,000
21.	Package & storage	20,000#/day	6,000
22.	Sulfuric acid (98%) storage	2,000 gal.	2,400
23.	Pumps	17	3,400
24.	Instruments		10,000
	TOTAL		$200,800
	Total equipment		$200,000
	Transmission equipment (10%)		20,000
	Piping (4%) and wiring (5%)		18,000
	Special piping (15%)		30,000
	Installation of equipment (21%)		42,000
	Freight on machinery at (5%)		10,000
	Engineering 10% total		45,000
	Building		25,000
	General expense (50%)		100,000
	TOTAL PLANT		$490,000
	Operating Capital (total daily raw materials and fixed costs x 100 days)		405,000
	TOTAL CAPITAL REQUIREMENT		$895,000

Table XIV (Cont'd)

Income: 20,000# MnO_2 at $0.30/#		$ 6,000
Daily Reagent Costs:		
Mn: based on product assay of 60% Mn, 12,000# at $.045/#		$ 545
H_2SO_4: 120% of theoretical to make $MnSO_4$, 26,200# at $.025/#		655
NaOH: 92% of theoretical, 32,100# at $.041/#		1,315
Cl_2: 100% of theoretical based on product assay of 92% MnO_2, 15,000# at $.047/#		705
$CaCO_3$: 6,000# at $.01/#		60
	TOTAL RAW MATERIALS	$ 3,280
Daily Fixed Costs:		
Freight on product and selling expense at $.01/# product		$ 200
Insurance and property taxes at 5%		70
Depreciation at 20% per year		280
Payroll - 18 people		360
Payroll taxes at 2%		10
Maintenance		50
Heat and power		250
	TOTAL FIXED COSTS	$ 1,220
Sum of daily raw materials and fixed costs		$ 4,500
Daily Net Before Taxes:		
$6,000 - $4,500		$ 1,500
Taxes at 52%		780
	Daily net after taxes	$ 720
	Yearly net after taxes (350 operating days/yr)	$252,000

Return on Investment:

$$\frac{252,000}{895,000} \times 100 = 28\%$$

Table XV

EXCERPTS - SCL-3117-D SPECIFICATION

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

Available oxygen as % MnO_2	85% min.
Total manganese as % Mn	58% min.
Absorbed moisture as % H_2O	3% max.
Iron as % Fe (soluble HCl)	0.3% max.
Silicon as % SiO_2	0.5% max.
Total alkali and alkaline Earth Metals	1.0% max.
Total Heavy Metals (other than Fe, Pb)	0.3% max.
Lead as % Pb	0.2% max.
pH	4.0 - 8.0

3.3.1 The synthetic manganese dioxide shall have an apparent density between 20-30 grams per cubic inch.

3.4 Particle Size. The synthetic manganese dioxide shall be of such size that at least 65 percent of the material shall pass through a U. S. Standard Sieve #200 (see 4.2) and at least 90 percent through a U. S. Standard Sieve #100.

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

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

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

Table XV (Cont'd)

d	I
4.00	5
2.45	7
2.14	7
1.65	10
1.40	5
1.06	3

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

a. High Drain Test . . . . . 5.50 hours

b. Low Drain Test . . . . . 130 hours

4.3.8 Determination of pH. A sample of dried ore (approx. 1 gram) is accurately weighed into a 250 ml Erlenmeyer flask and exactly 100 times the weight of distilled water is added. The outside wall of the flask is then marked at this level. The contents of the flask are boiled actively for 15 minutes, the water lost by evaporation is replaced and the mixture is again brought to boiling. The flasks are fitted with tubes containing ascarite and cooled to room temperature in a water bath. The contents are transferred to a suitable beaker and the pH is then determined on the slurry be means of a pH meter after stirring the mixture to obtain a uniform suspension.

4.3.9 Determination of Apparent Density. A Scott volumeter is used for this determination. The original sample of manganese dioxide is quartered several times but not ground or dried. The resulting material is poured from a 4-oz. bottle into the brass funnel which directs the manganese dioxide into a baffle box containing glass plates. These glass plates regulate the fall of the manganese dioxide. A funnel at the bottom directs the material into a one-inch brass cube. Enough material is used so that the cube is filled just to overflowing. A flat steel edge is used to level the material at the top of the one-inch cube and to remove any excess without packing the manganese dioxide. The material plus the cube is weighed and the weight of the empty cube is subtracted from the total weight. The resulting value is reported as the apparent density in grams per cubic inch.

4.3.10 Analyses for Alkali, Alkaline Earth, Heavy Metals (other than iron and lead). Analyses for impurities shall be performed by spectrographic methods. Chemical composition is determined semi-quantitatively by emission spectroscopy in the visible and ultra-violet. The

Table XV (Cont'd)

samples are burned to completion in a d-c arc and the resultant spectrum is photographed. A specially selected spectrum line of each of the various constituent elements is measured for intensity and compared with the intensity of the manganese internal standard line. These data are used with previously established working curves to determine the percentages of elements present.

4.4 Crystallographic and Micro-Structural Analyses.

4.4.1 Electron Microscopy. The samples shall be prepared for examination in the electron microscope as follows: Approximately 0.2 gram of the sample, in fine powder form, is moistened with 4 to 6 drops of butyl acetate (reagent grade) on a flat glass plate, and slurried for approximately 3 minutes under the blade of a stainless steel spatula at moderate pressure. The sample is then mixed with 2 drops of a 2 percent solution of parlodion in butyl acetate, slurried for complete dispersion, and cast on clean distilled water. A portion of the film thus formed is selected and mounted in the microscope by the usual techniques. Photographs shall be taken of five representative fields.

4.4.2 Electron Diffraction. Electron diffraction patterns are obtained by the transmission method on dense samples supported on the parlodion film; the film is prepared as previously described in 4.4.1.

4.4.3 X-Ray Diffraction. X-Ray diffraction patterns are obtained by the usual techniques, using either a Debye powder camera or a Geiger counter X-Ray spectrometer. The use of filtered FeK alpha radiation in a Debye powder camera having a dispersion of 1 degree of 20 mm of film is recommended, with an exposure of 6 to 12 hours in order to bring out the gamma MnO_2 pattern.

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

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

80% MnO_2
8% Carbon Black
12% NH_4Cl

(b) The dry mix is ball-milled for 20 minutes in a 1.25 gallon porcelain jar to assure uniformity.

(c) The following wetting solution shall be used:

Table XV (Cont'd)

5.8% NH_4Cl
8.6% $ZNCl_2$
85.6% H_2O

(d) Between 65 and 125 ml of wetting solution shall be uniformly mixed with 500 grams of dry mix in order to insure proper tamping consistency.

(e) The "A" cell bobbin shall have the following dimensions:

Height . . . . . 1.375 inches
Diameter . . . . . 0.492 inches

(f) The "A" cell bobbin shall weigh between 9.5 and 10.5 grams when made as previously described.

(g) Each bobbin shall be hand wrapped in battery cloth and tied with cotton thread.

(h) The following paste formulation shall be used:

(1) Solution: 23.7% NH_4Cl
22.3% $ZnCl_2$
0.1% $HgCl_2$
53.9% H_2O

(2) Starch and Flour Mixture: 74.7% cornstarch
25.3% flour

(3) Cold Setting Paste: 50 ml of solution of 10.7 grams of flour and starch mixture.

(4) Quantity used: Approximately 2.5 ml of cold setting paste per cell.

4.5.2 Cell Aging Period. Fabricated cells shall undergo a 10-day stand period at 70°F and 50% R. H. prior to being screened and assigned for capacity tests. Cell screening consists of measuring open circuit voltage and flash current of each cell. Cells within ± 0.01 volts of the average voltage and within ± 0.5 ampere of the average current value are acceptable for test purposes. (The above limits are tentatively set).

4.6 Capacity Tests.

Table XV (Cont'd)

4.6.1 Fifteen (15) each dry cells, size "A", prepared as described in 4.5.1, shall be used for each of the initial capacity tests *1 as follows:

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

*1 - Inasmuch as an evaluation of each sample is required in not more than 1 month's time, the evaluation must of necessity be based upon initial capacity tests only. However, in order to prove each evaluation, sufficient dry cells are made from each sample, as previously described in 4.5.1 and 4.6.1, and set aside for delayed capacity tests after storage periods of 3, 6, 12, 18 and 24 months at a temperature of 70 F. It is also desired to have a capacity maintenance of 85% after a storage period of 1 year at a temperature of +70°F and 50% R. H.

Table XVI

NATURAL AND SYNTHETIC MANGANESE DIOXIDE BLENDS

Blend					Drain Tests	
Type	%	Type	Code	%	High - hrs	Low - hrs
Gold Coast	100	Chemical	PR-I-1a	0	4.2	82
" "	95	"	"	5	4.5	82
" "	90	"	"	10	4.5	91
" "	80	"	"	20	5.3	101
" "	60	"	"	40	5.7	124
" "	40	"	"	60	6.0	128
" "	20	"	"	80	6.2	134
" "	0	"	"	100	7.5	127
" "*	100	Electrolytic				
			PR-841(4)	0	4.4	88
" "*	50	"	"	50	6.1	105
" "*	0	"	"	100	7.0	138

* Lot No. P-49-112