Pilot plant study of producing battery active manganese dioxide by air oxidation of manganese carbonate
by Allen L Griggs

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Abstract:
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24 SCFH per pound of carbonate; Time *. one hour.

A run at these conditions should produce about two-thirds conversion to manganese dioxide.

•Typical batteries made with manganese dioxide produced in the pilot plant averaged 11 hours high
drain and 140 hours low drain. High drain tests on the manganese dioxide were found to be
independent of the pilot plant operating conditions but low drain tests were best with manganese
dioxide produced at between 425 C and 500 C.

The manganese dioxide from a number of runs was blended together to provide a twenty pound
sample which was sent to Ray-O-Vac Battery Company for analysis and evaluation. The drain tests on
this sample as reported by Ray-O-Vac were: High ________ Low ________ Three Month Delay
__________.

Since one hour proved to be sufficient time to obtain two-thirds conversion to manganese dioxide, a
continuous reactor might be more economical than the semi-batch type employed in this experiment,
and further work along that line appears to be warranted.
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A Thesis

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Approved:

[Signatures]

Head, Major Department

Chairman, Examining Committee

Dean, Graduate Division

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ABSTRACT

This thesis contains the results of a pilot plant study of a process by which battery-active manganese dioxide was produced by air oxidation of manganese carbonate made from Montana rhodochrosite ore.

The pilot plant was a semi-batch type apparatus patterned after an experimental reactor designed by Schilling (8), and utilizing a five pound charge of manganese carbonate. A series of runs was undertaken to determine the most efficient temperature and air rate to use, and a kinetic study was made to resolve the time variable.

The temperature range studied was from 400 C to 550 C, and air rates tried were 9, 18, and 24 standard cubic feet per hour per pound of carbonate. The time range investigated was from zero to six hours. The most efficient run conditions were found to be: Temperature, 475 C to 500 C; Air Rate, 24 SCPH per pound of carbonate; Time, one hour. A run at these conditions should produce about two-thirds conversion to manganese dioxide.

Typical batteries made with manganese dioxide produced in the pilot plant averaged 7 hours high drain and 140 hours low drain. High drain tests on the manganese dioxide were found to be independent of the pilot plant operating conditions, but low drain tests were best with manganese dioxide produced at between 425 C and 500 C.

The manganese dioxide from a number of runs was blended together to provide a twenty pound sample which was sent to Ray-O-Vac Battery Company for analysis and evaluation. The drain tests on this sample as reported by Ray-O-Vac were: High ________, Low ________, Three Month Delay ________.

Since one hour proved to be sufficient time to obtain two-thirds conversion to manganese dioxide, a continuous reactor might be more economical than the semi-batch type employed in this experiment, and further work along that line appears to be warranted.
INTRODUCTION

Montana has vast supplies of manganese in the Butte area, and low grade battery-active manganese dioxide at Philipsburg. For this reason, the Chemical Engineering Department at Montana State College has undertaken a series of research projects designed to develop an economically feasible method of producing high quality, battery-active manganese dioxide from these reserves.

Baughman (1) described a number of possible methods of accomplishing this. One of the methods which he felt had a reasonable chance for success involved the use of air to oxidize manganese carbonate, followed by acid leaching of the product to remove lower oxides and unreacted carbonate. Schilling (8) undertook to explore this method in detail, using manganese carbonate produced from a flotation concentrate of rhodochrosite ore ($\text{MnCO}_3$) donated by the Anaconda Company.

For his studies, Schilling designed a small experimental semi-batch type reactor. This reactor had three main parts; the preheater, reaction chamber, and scrubber. To operate the reactor the top seal and scrubber were removed and a charge of 150 grams of manganese carbonate was dumped into the reaction chamber. The top seal and scrubber were then replaced and as soon as the operating temperature had been attained, the air was turned on. The air passed through the preheater into the reaction chamber where it oxidized the carbonate to manganese dioxide and small amounts of lower oxides. The dust laden air then passed into the scrubber where it was scrubbed free of dust. The manganese dioxide produced was then leached with a ten percent sulfuric
acid solution to remove the unreacted carbonate and lower oxides. The manganese dioxide was washed, dried, and ground for two hours in a ball mill to prepare it for battery tests.

Schilling discovered that the oxidation yields and battery activity depended to a great extent upon the purity of the manganese carbonate, so he improved the ore purification process to a point where nearly iron-free carbonate with a minimum of foreign salt content was produced. Using this carbonate, he produced manganese dioxide which, when incorporated into batteries and tested, went 7.3 hours high drain, 125 hours low drain, and 99 hours three months delayed capacity, typically. Several samples even surpassed low drain specifications of 130 hours in addition to showing excellent high drains.

From this study it was apparent that good-quality manganese dioxide could be produced with this process. In order to better determine the feasibility of the process, it was decided to undertake a pilot plant study of it on a 15 to 1 scale up. This thesis discusses the results of the pilot plant study.
EXPERIMENTAL PROCEDURES

The questions which this research set out to answer were:

1. How does the yield efficiency of the pilot-plant compare with that of Schilling's experimental reactor?

2. Can manganese dioxide which surpasses both high and low-draw specifications as set by the Signal Corps (10) be produced with the pilot plant?

3. What are the most efficient operating conditions of the pilot plant?

This experiment was undertaken in the following manner. First, the pilot plant was constructed to utilize a five pound charge of manganese carbonate. Then a sizeable quantity of purified manganese carbonate was produced from the rhodochrosite ore donated by the Anaconda Company. After several test runs with the pilot plant, during which a number of minor defects were corrected, a series of runs was undertaken to resolve the temperature and air rate variables. A kinetic study was made to resolve the time variable.

The product from each run was leached with ten percent sulfuric acid solution to remove lower oxides and unreacted carbonate. The residue, which was manganese dioxide, was washed, dried, and ball milled to prepare it for battery tests. Finally, battery tests were conducted on a sample of manganese dioxide from each run. (See Figure 1 for Flow Diagram.)

The experiment was reported in this thesis in the following sequence.
1. A description of the manganese carbonate purification process.

2. A description of the pilot plant, and its operating characteristics.

3. The oxidation study and discussion of results.

4. The kinetic study and discussion of results.

5. The battery tests and results.

6. The final conclusions.

PURIFICATION OF MANGANESE CARBONATE

The starting material or source of manganese for this research was a flotation concentrate of rhodochrosite (MnCO₃) ore donated by the Anaconda Company. This ore was purified using the same process as Schilling used for his research with only minor variations in the process as he described it. The first step in the process was leaching this concentrate with 0.70 pounds of concentrated sulfuric acid (diluted to 100 grams per liter) per pound of ore containing 37 percent manganese. (See Figure 1 for Flow Diagram.)

\[
\text{MnCO}_3 \text{ (concentrate)} + \text{H}_2\text{SO}_4 \rightarrow \text{MnSO}_4 + \text{H}_2\text{O} + \text{CO}_2
\]

Leaching was continued for twenty-four hours with constant stirring. At the end of this time enough calcium carbonate was added to increase the pH to 5.5, and sodium carbonate was then added to bring the pH to 6.3, at which point manganese carbonate started to precipitate out of solution. Air was then sparged into the solution for a period of four days to oxidize the iron in solution to ferric hydroxide which pre-
cipitated out. The solution, which contained about ten percent manganese sulfate, was filtered with the insoluble material acting as a filter aid.

Manganese carbonate was precipitated by adding sodium carbonate solution:

\[
\text{MnSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{MnCO}_3 + \text{Na}_2\text{SO}_4
\]

The amount of sodium carbonate added was carefully controlled with the aid of a pH meter. As soon as the pH rose to 7.5, signifying that the endpoint of the manganese carbonate precipitation had been reached, the sodium carbonate flow was cut off to keep the salt content at a minimum. The manganese carbonate was washed by successive dilution and decantation at least ten times to insure good removal of sodium sulfate. Next, it was filtered, dried at 160°F for twenty-four hours in a tray drier, and ball milled for twenty minutes to break up the lumps of dried carbonate.

In all, seven batches of purified carbonate were prepared. The first three batches were produced only to gain experience in using the purification process. The carbonate produced in these first three batches had a definite reddish brown tinge which denoted incomplete iron removal. The last four batches produced a very light tan carbonate which was evidently relatively free of iron. These last four batches were combined and used as charge material for the pilot plant.

The particle size of this manganese carbonate was very small. A representative sample was chosen for screening and the entire sample passed through a 100-mesh standard sieve.
Figure 1
FLOW DIAGRAM: CARBONATE PURIFICATION AND OXIDATION PROCESS
PILOT PLANT FOR OXIDATION OF MANGANESE CARBONATE

The reactor (Figure 2) consisted of three main parts: the preheater, reaction chamber, and scrubber. Air was introduced into the preheater where it was heated to a specified temperature, and then passed into the reaction chamber where it oxidized a charge of manganese carbonate to manganese dioxide and small amounts of lower oxides. After passing through the reaction chamber, the air, which was laden with entrained dust particles, was passed through a water-filled scrubber which removed this dust. This reactor was patterned after Schilling's experimental air oxidation reactor, and was designed to take a five pound charge of manganese carbonate. This represented a scale-up of about 15 to 1 since Schilling's reactor utilized a 150 gram charge.

The reaction chamber and preheat sections were constructed of one-eighth inch stainless steel sheeting rolled and welded to form two cylinders four inches in diameter, and 48 and 18 inches long, respectively. A six-inch long stainless steel cylinder five inches in diameter was welded to the top of the reaction chamber to decrease losses due to dust entrainment. Mild steel welding-neck flanges were welded to both ends of the reaction chamber to serve as a means of attaching the scrubber and preheater to the reaction chamber.

The lower end of the preheater was sealed off by welding a circular stainless steel plate to it. A hole one inch in diameter was cut out of the center of the plate, and a length of black iron pipe was welded against the hole to serve as an entrance for air. The entire preheat
section was packed with stainless steel turnings which functioned as heat transfer media. Carbon Raschig Rings were first tried for this purpose but were discarded because they ignited at approximately 600 °C. A welding neck flange was welded to the top of the preheater, and the reaction chamber and preheater were bolted together. A disk of stainless steel filter screen (20x250 mesh) was placed between the flanges to serve as a support for the manganese carbonate and to disperse the air as it passed into the reaction chamber. Copper rings were used as gaskets.

A mild steel blind flange was used for a top seal for the reaction chamber. Two holes were drilled through the flange, and short lengths of pipe were welded against both holes. The center hole served as a passage for the air from the reaction chamber into the scrubber, and the offset hole was capped and used as a sampling and mixing port.

The scrubber was a 19 inch length of two and one-half inch iron pipe packed with fine copper turnings. An eight inch length of three-inch pipe was welded to the top of the smaller pipe to reduce water loss from entrainment. The top was capped and a piece of three-quarter-inch pipe was welded into the cap to serve as an exit for the air.

Heat was supplied to the reactor by eight strip heaters. Four 35-1/2-inch heaters were fastened against the sides of the reaction chamber by spot welds at one end, and bolts set into slots in the heaters at the other end. This way, the heaters were free to slide at one end as they expanded. The reaction chamber was round and the strip heaters, flat, so fine strands of copper wire were chinked in between the heaters and the
reactor to improve heat transfer. This wire was held in place with an alumina base cement with a relatively high heat transfer coefficient. The reaction bed heaters were placed with the lower end of the heaters approximately three inches above the lower flange. They had a capacity of 1500 watts each and were controlled by two 220 volt Variacs with two heaters wired in parallel to each Variac. The remaining four heaters were fastened to the sides of the preheater in the same manner as the others were fastened to the reaction chamber. These heaters were 17\(\frac{5}{8}\) inches long and had a capacity of 500 watts each. They were controlled by 110-volt Variacs, one Variac to each heater.

The entire heated portion of the reactor was covered with one and one-half to two inches of insulation, and this in turn was covered with a layer of aluminum foil to cut heat losses to a minimum.

The air flow rate in standard cubic feet per hour was measured with a rotameter. The temperatures in the reactor were measured by four thermocouples; one each on one upper and one lower strip heater, one in a thermowell placed in the bottom of the preheater and extending to within one inch of the screen partition, and one in a reaction bed thermowell. This latter thermowell could be moved up and down so that a longitudinal temperature profile of the reaction chamber could be measured.

The entire reactor was mounted on a pivot so that when a run was completed and the scrubber and top of the reactor could be removed and the reactor pivoted and dumped. Careful placement of the pivot on the heavy reactor resulted in a well balanced reactor which was quite easy to
It was found that one man could perform the loading and dumping operations at operating temperatures without a great deal of trouble.

Control of the reaction chamber temperature was found to be quite difficult. At least four hours were required to heat up the charge before a run could be started and there was a tendency to turn on the air before the manganese carbonate had attained the temperature specified in the run conditions. When this happened, as it did upon several occasions, the correct operating temperature sometimes could not be attained until as much as ninety minutes of reaction time had elapsed.

Air rate was impossible to keep constant since it depended on laboratory air pressure which varied constantly. This was not a great disadvantage because air flow rate above a certain minimum did not prove to be an important variable.

In general the reactor proved to be capable of performing the job it was designed for. Runs up to 550°C were made successfully although the preheater could not maintain a high output of air at that temperature. The limitations of the preheater did not seriously hamper reactor operation. The most serious flaw in the reactor's operating characteristics proved to be the existence of a longitudinal temperature gradient within the bed (Figure 3). This temperature gradient existed in spite of the fact that the air was preheated to the specified temperature of the run. At lower air velocities the temperature at the screen partition was often as much as 150°C lower than the upper portion of the bed. At higher air velocities this temperature difference was reduced to about 60°C. The
presence of aluminum foil on the outside of the reactor seemed to have very little effect on this "cold spot" in the bed. To reduce this temperature gradient still further, the strip heaters would have to be repositioned so they rested against the lower flange.

Because of the temperature gradient, all reaction bed temperature measurements were taken at a point twelve inches above the screen. This point was chosen because it indicated a fairly good average bed temperature.
PILOT PLANT FOR OXIDATION PROCESS
Figure 3
TYPICAL LONGITUDINAL TEMPERATURE GRADIENTS IN THE REACTION CHAMBER
AIR OXIDATION OF MANGANESE CARBONATE

The oxidation process was started by charging a five-pound batch of manganese carbonate into the hot reactor. The carbonate had to be heated inside the reactor for at least four hours to bring it up to the specified temperature of the run. When this temperature was approached, the air was turned on and the reaction proceeded. During the course of the run the bed was mixed at least once with a steel rod inserted into the bed through the mixing port in the top of the reaction chamber. After completing the run, the top was removed, and the reactor pivoted and dumped. Generally about three pounds of product was recovered from the reaction chamber. The loss of two pounds resulted from the evolution of carbon dioxide gas during the reaction and about one-half pound of partially oxidized carbonate being carried into the scrubber. The latter would be recoverable in a large scale apparatus so the actual weight loss would be caused solely by the evolution of carbon dioxide. This would amount to a loss of one-fourth pound per pound of manganese carbonate, assuming 100 percent conversion to manganese dioxide.

The lower oxides and unreacted carbonate were removed from the manganese dioxide by leaching the product with a ten percent sulfuric acid solution. Manganese dioxide reacts with concentrated sulfuric acid to form manganic sulfate, but it is insoluble in the dilute acid. The divalent manganese in the forms of manganous oxide and carbonate dissolved in the dilute acid with the formation of manganous sulfate.
Other oxides such as Mn$_2$O$_3$ and Mn$_3$O$_4$ reacted as follows:

\[
\begin{align*}
\text{Mn}_2\text{O}_3 + \text{H}_2\text{SO}_4 & \rightarrow \text{MnSO}_4 + \text{MnO}_2 + \text{H}_2\text{O} \\
\text{Mn}_3\text{O}_4 + 2\text{H}_2\text{SO}_4 & \rightarrow 2\text{MnSO}_4 + \text{MnO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

The weight percent manganese dioxide recoverable from the product was determined in the following manner. One thousand grams of the product was leached for two hours at boiling temperature with 5000 milliliters of ten percent sulfuric acid solution. The leach acid dissolved the lower oxides and unreacted carbonate, leaving manganese dioxide as residue. This residue was washed by successive dilution and decantation until addition of barium chloride to a sample of the wash water showed very little sulfate present. Then it was filtered, dried for 24 hours at 110°C, and weighed. This weight in grams divided by 10 was the weight percent of manganese dioxide in the sample. All "yield by leach" figures were obtained in this manner. It should be noted that the yield by leach is not the same as percent reacted because the former is a weight percent, not a mole percent, and the unreacted manganese is in a different form than the reacted manganese.

Five preliminary runs were undertaken in order to gain experience in operating the pilot plant, and to work out any defects in it. The carbonate used in these runs was from the first three batches. The first four of these five preliminary runs were characterized by poor reactor control and frequent equipment failure. As a result of this, the product showed incomplete oxidation, and likewise, poor yields. The fifth run was completed without incident, and showed a yield of
Since the pilot plant was designed as a scaled up version of an experimental reactor built by Schilling, it was desirable to compare its yield characteristics with those of the experimental reactor. Ten pounds of the manganese carbonate used by Schilling for certain of his runs were obtained for this purpose. It was decided to duplicate with the pilot plant the conditions of one of Schilling's runs. The conditions of this run were:

- Temperature: 475°C
- Time: 5 hours
- Pressure: Atmospheric
- Air Rate: 2.8 SCFH per 150 grams of carbonate

The resulting yield by leach of the experimental reactor was 71.5 weight percent. The duplication run with the pilot plant reactor resulted in a yield of 67.5 weight percent. Although this showed that the pilot plant was evidently slightly less efficient than the experimental reactor, the yield correlation between the two reactors was good. A second run was made using the same conditions with the exception that the air flow rate was boosted to six SCFH per 150 grams of carbonate. The reason for the author's interest in higher air flow rates was that higher air flow tended to reduce the longitudinal temperature gradient across the bed, thus giving more accurate temperature control. The resulting yield was only 60.6 percent. This low yield was not expected and was disappointing, although it did not
discourage the author's intention to use higher air flow rates in his oxidation study.

Schilling estimated the optimum conditions for his reactor to be:

- Temperature: 475°C
- Time: 7 hours
- Pressure: 3 atmospheres
- Air Rate: 5.4 SCFH per 150 grams of carbonate

A number of runs were undertaken with the pilot plant to determine if the above temperature, time, and volumetric air rate conditions would hold true for the pilot plant. The pilot plant and associated air flow and metering equipment were not designed to withstand pressure runs, so all the runs were made at atmospheric pressure. The carbonate used in these runs was from a supply made up of batches 4, 5, 6, and 7 mixed together thoroughly. The length of the pilot plant runs was set at six hours rather than the seven hours Schilling specified for his experimental reactor because it was apparent from his studies that the slight increase in the yield obtained in the seven hour runs did not appear to warrant the additional time required to obtain it. The time variable was to be resolved by undertaking a kinetic study, so this left only temperature and air flow rate to be resolved from these runs.

Figure 4 shows the plot of yield by leach versus temperature at two air flow rates. The temperature range investigated was from 400°C to 550°C, and the air rates were 91 and 121 SCFH. It can be seen that
the yield generally increased with the temperature although between 450°C and 500°C the temperature apparently had very little effect on yield. From this plot it would seem that an operating temperature of 550°C would result in the highest yields. This temperature proved to be somewhat beyond the recommended operating range of the pilot plant, however, and a lower temperature would be more desirable in this respect.

The different air flow rates showed no discernible effect upon yield. The higher air flow rate resulted in more positive temperature control, but the lower air flow rate would be more economical.
Figure 4
YIELD BY LEACH VERSUS TEMPERATURE

Air Rates: $X = 121$ SCFH
$\Theta = 91$ SCFH
KINETIC STUDY OF MANGANESE CARBONATE OXIDATION

In order to determine the optimum reaction time and possibly throw some light on the nature of the plot in Figure 4, a kinetic study was undertaken. However, before any successful kinetic study could be performed, there were a number of difficulties to be overcome. Foremost among these was the fact that the bed did not fluidize, and at lower air rates it mixed only negligibly. This would result in an uneven rate of oxidation throughout the bed, and samples removed from the bed at intervals might show poor correlation. In an attempt to observe the effect of air velocity on the bed, a partially oxidized charge was allowed to cool, the top of the reactor was removed, and with the aid of a flashlight the author peered down into the bed as air was being blown through it. At zero to 45 standard cubic feet of air per hour the bed expanded slightly. Then at 45 SCFH a channel appeared along the seam of the reactor. Between 45 and 121 SCFH the channel enlarged until at 121 SCFH the action of the air on the bed was so violent that new channels kept forming and collapsing, causing a noticeable amount of mixing. This high air rate also decreased the longitudinal temperature gradient down to about 60 degrees. It was decided to use this air rate in the kinetic study, and to mix the bed thoroughly with a steel rod before each sample was taken.

The other serious problem involved the analytical treatment of the samples. It was finally decided to analyze them by leaching them in the same manner as the previous runs were leached. This would give
yield by leach figure which was the weight percent of manganese dioxide recovered from the sample. In order to convert weight percent into mole percent it was necessary to assume that the weight fraction of each sample which dissolved in the leach had been one hundred percent unreacted manganese carbonate. This was very unlikely since there undoubtedly were lower oxides present in the sample. Therefore, the mole percentages obtained were at best only reasonable approximations.

The analyses were performed in the following manner. Five grams of the sample were leached at boiling temperature for two hours with three milliliters of sulfuric acid diluted to about 50 milliliters. The leach was then filtered and the residue dried for twenty-four hours in a tray drier. The weight of the dried product divided by the total sample weight gave the yield by leach.

Three runs were made using an air flow rate of 121 SCFH, at temperatures of 425°C, 475°C, and 500°C, respectively. A fourth run was made at 525°C with an air flow rate of 45 SCFH. Figure 5 shows the yield by leach versus time plot of the 425°C run. The data from this run followed a fairly respectable curve so it was decided to try to determine the order of the reaction from the curve. To begin with, all the weight percent yields were converted to mole percentages using the assumption that only manganese dioxide and manganese carbonate were present in the samples. Next, examination of the curve showed that it evidently approached a maximum of about 60 weight percent at infinite time. This was only an approximation since the reaction was not carried
to completion. This figure, which is equal to 66 mole percent, is apparently that percentage of the carbonate which was available to the reaction. Since this was a reaction involving a solid and a gas it seems probable that the completeness of the reaction was limited to that amount of the solid which was accessible to the gaseous phase, i.e., the molecules on or very close to the surface. Since the particle size of the carbonate was very small it was entirely possible that a majority of the manganese carbonate was accessible. Further creditability to this explanation of the limiting factor of the reaction comes from observation of the action of the hot leach acid on the product. The leach reaction was accompanied by the vigorous evolution of large quantities of gas which could only occur if the principal reaction involved the evolution of carbon dioxide from unreacted manganese carbonate.

Another possible albeit less likely explanation of this limiting factor is that there might exist the secondary reaction

$$2\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 + \frac{1}{2}\text{O}_2$$

If this reaction occurred at a high enough reaction rate, the manganese dioxide content in the product would be kept down even if the entire charge was oxidized. The pressure of the oxygen evolved in this reaction becomes equal to the pressure of oxygen in air at atmospheric pressure at about 450°C, so this reaction apparently does exist at temperatures above 450°C. The rate of this reaction was not known, however, and since the acid leach reaction with oxidation produced at temperatures above 450°C still was characterized by the evolution of
large quantities of gas, it seems probable that the rate of this re-
action at the operating temperature of the pilot plant was so slow as
to be unimportant.

Apparently no important chemical equilibria existed between dif-
ferent oxides or between the manganese carbonate and an oxide. Nearly
all of the reactions that take place during the oxidation involve the
evolution of gas which is lost from the system. These reactions go to
completion if given enough time. The single exception is the oxidation
of MnO to MnO$_2$. At 800°K the equilibrium constant for this latter re-
action is on the order of $10^3$, so it goes essentially to completion, also.

When testing for the order of the reaction, it was found that after
the first hour the reaction most accurately followed a first order
reaction curve as shown in Figure 6. The first order reaction rate
equation was

$$\log_e \frac{a}{a-x} = kt$$ (6)

where

- $a =$ percentage of the limiting reactant available
  for the reaction— in this case approximately
  66 mole percent.
- $x =$ percentage of the limiting reactant which has
  reacted.
- $k =$ reaction rate constant, hours$^{-1}$.
- $T =$ time, hours.
Two different reaction mechanisms were possible. Both of these mechanisms involved two reaction components—the solid and oxygen. The oxygen, after the initial rapid reaction, became present in excess, exerting a constant pressure of about 0.2 atmospheres. During this stage the reaction was apparently pseudo first order and the reaction rate constant, $k$, dependent upon the oxygen pressure.

The first of the two possible mechanisms involved the following single step reaction:

$$\text{MnCO}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{MnO}_2 + \text{CO}_2$$

This mechanism required that the manganese carbonate remain stable throughout the heating-up period before the air was turned on. The requirement could not be met completely because manganese carbonate decomposes to some extent upon being heated, with the evolution of carbon dioxide. At 327°C the carbon dioxide pressure exerted by this decomposition reaction is equal to one atmosphere. This led to the formulation of the second reaction mechanism which occurred in two steps.

$$\text{MnCO}_3 \rightarrow \text{MnO} + \text{CO}_2$$

$$\text{MnO} + \frac{1}{2} \text{O}_2 \rightarrow \text{MnO}_2$$

The first step would occur while the carbonate was being heated up to operating temperature. The second step would start when the air was turned on. It appears that the second step would follow a first order reaction only if the first step had gone to completion, resulting in an initial supply of manganous oxide and no more. Since the first step
is a decomposition reaction evolving a gas which is lost to the system. It seems probable that it would not be confined to 66 mole percent of the carbonate. Also, since the reaction of the product with the leach acid indicated that a quantity of unreacted carbonate had remained in the product, it would seem that the decomposition reaction was so slow as to render the second mechanism relatively unimportant. Most probably the actual oxidation was a combination of the two mechanisms with the first mechanism dominating the reaction.

Figure 7 shows the plot of yield by leach versus time for the 475°C run. It can be seen that there are two very distinct phases of the reaction. The first phase which occurred entirely within the first hour demonstrated a high reaction rate, and was evidently terminated when the readily available carbonate was used up. The second phase showed a very low reaction rate—3.4 weight percent over a period of five hours. Possibly this second phase could be explained as being controlled by what might be termed a diffusion process. In this process, the oxygen molecule would have to diffuse through a layer of manganese dioxide to come in contact with the unreacted manganese carbonate. Another possible explanation for the second phase might be that at the point where the second phase begins, essentially all of the remaining carbonate had been used up by competing reactions producing lower oxides of manganese. This second explanation is unlikely, however, in view of the fact that a first order reaction rate had been obtained. If this explanation were valid, a first order mechanism probably would
not have been obtained since simultaneous competing reactions would exist. The kinetic study at 475°C shows the practicability of using a continuous reactor to carry out the oxidation process rather than the semi-batch type that the author employed. Possibly a rotating kiln type of reactor, in which the preheated reactants were introduced either co-currently or counter-currently would prove satisfactory. At 475°C a residence time of one hour should be sufficient to obtain roughly two-thirds conversion to manganese dioxide, and at 500°C even less residence time should be necessary.

Unfortunately, the 500°C run (Figure 8) was characterized by poor temperature control during the first hour and a half. The air was turned on while the carbonate was still considerably cooler than the temperature specified in the conditions of the run. The carbonate did not attain 500°C until after ninety minutes of reaction time. For this reason the run was not entirely successful in that it failed to demonstrate the rapidity of the first stage of the reaction at 500°C. It did, however, result in the same type of reaction time curve as the 475°C run, thus confirming it.

These rate studies serve to shed some light on the nature of the yield versus temperature plot in Figure 4. Since all the runs were for a length of six hours, it can be seen from the kinetic study and Figure 4 that the reaction rate was not high enough to oxidize all the carbonate available to the reaction in the time allowed until the temperature of the runs was elevated to some point between 425°C and
The fourth run, (Figure 9) carried out at 525°C and an air rate of 45 SCFH was made for the purpose of observing the effect of a low air velocity on the high temperature reaction. Aside from the poor precision obtained in the samples, it can be seen that the first stage of the reaction wasn't complete until three hours of reaction time had elapsed. The first fifteen minutes demonstrated a very rapid reaction taking place, but after that the rate rapidly fell off. This could be explained by the fact that at the low air rate virtually no mixing was taking place in the bed, and there undoubtedly were areas in the bed where the air was not reaching the carbonate.
Figure 5
YIELD VERSUS TIME, 425°C
Figure 6
TEST FOR FIRST-ORDER REACTION, 425 °C RUN
Figure 7
YIELD VERSUS TIME, 475 °C
Figure 8
YIELD VERSUS TIME, 500 °C
Figure 9
YIELD VERSUS TIME, 525 °C
In order to determine the battery activity of the manganese dioxide produced, battery tests were made using manganese dioxide produced in each respective run. The batteries were made and tested according to Signal Corps Specification SCL-3117-D. The standard test cells were similar to commercial flashlight cells in appearance and principal components. The battery components, except for the manganese dioxide, were purchased from a commercial supplier. The most important part of a test cell was the bobbin made by compressing a mixture of manganese dioxide, acetylene black, ammonium chloride, and wetting solution or electrolyte of zinc and ammonium chlorides around a carbon rod. The amount of wetting solution used in the above mixture varied with the manganese dioxide and was sufficient to "insure proper tamping consistency". The bobbin was weighed, wrapped in gauze, and placed in a zinc can. A paste electrolyte solution was poured around the bobbin to form a conducting layer between the bobbin and the zinc can, and the battery was then sealed with wax.

Cells of this type were subjected to two standardized drain tests five days after they were made. The high drain test consisted of subjecting the battery to a continuous drain through a 16-2/3 ohm resistance, and noting the time required for the voltage to drop to 1.00 volts. Five and one-half hours was the Signal Corps specification. The cell was not dead at this time and would, in fact, regain much of its lost life if it was allowed to rest for a day or so. The low drain
test was similar to the high drain except that the cut-off voltage was 1.13 volts and the resistance was 166-2/3.ohms. Specification was 130 hours on the initial test. A delayed drain test in which batteries were subjected to a low drain test three months after fabrication was not carried out due to time considerations. Usually two cells from each batch of batteries were run on each test. According to Schilling, the expected lives of batteries subjected to high and low drain tests would be 20 hours and 200 hours, respectively, if the cell efficiencies were 100 percent. Actually, the observed lives of typical batteries fabricated during this experiment were 7 hours and 140 hours, respectively.

Before the manganese dioxide could be used in the fabrication of batteries, it had to be ball milled. Moore (5) postulated that reproducible results with chemically synthesized manganese dioxide could best be obtained by milling 100 to 300 grams of manganese dioxide with five pounds of ceramic balls for two hours in a 2.5 gallon mill revolving at 70 RPM. This should be followed by screening to minus 100 mesh.

Larger samples involving pound quantities obviously could not be ground in the above manner. Moore's treatment of larger quantities consisted of increasing the ball load to ten pounds and adding manganese dioxide until the mill was approximately half full. After six hours grinding time, approximately 80 percent would pass through a 100-mesh standard sieve. Moore made no specific mention of the battery
activity of the dioxide ground in the manner so the author felt that it was necessary to explore the matter further.

Table I lists a number of preliminary ball milling runs undertaken by the author and the results of these runs. Although no conclusive grinding study was made, these preliminary runs indicate the necessity of such a study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ball Wt lbs</th>
<th>MnO$_2$ Wt gms</th>
<th>Ball:MnO$_2$ Wt ratio</th>
<th>Grinding Time, Hrs</th>
<th>Apparent Density</th>
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</thead>
<tbody>
<tr>
<td>PP-5</td>
<td>5</td>
<td>500</td>
<td>4.5:1</td>
<td>2</td>
<td>9.0</td>
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<td>PP-5b</td>
<td>5</td>
<td>300</td>
<td>4.5:1</td>
<td>6</td>
<td>12.1</td>
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<tr>
<td>PP-6</td>
<td>5</td>
<td>250</td>
<td>9.1:1</td>
<td>2</td>
<td>10.5</td>
</tr>
<tr>
<td>PP-6-8</td>
<td>15</td>
<td>500</td>
<td>13.6:1</td>
<td>8</td>
<td>12.1</td>
</tr>
<tr>
<td>PP-7-2</td>
<td>7.5</td>
<td>100</td>
<td>34.1:1</td>
<td>2</td>
<td>12.8</td>
</tr>
<tr>
<td>PP-7-8</td>
<td>15</td>
<td>500</td>
<td>13.6:1</td>
<td>8</td>
<td>12.4</td>
</tr>
</tbody>
</table>

Runs PP-5, PP-6, and PP-7 were each made with different carbonates and different run conditions so the only true comparisons that can be made are between samples of the same run; i.e., between PP-5 and PP-5b. It can be noted, however, that high drain seems to increase with grinding time, regardless of ball:manganese dioxide weight ratios. On the other hand, low drain appears to pass through an optimum and then decrease with increased grinding time and weight ratio. It is emphasized that these observations are by no means conclusive, and are based on the results of a very rudimentary preliminary study.

All 100 gram samples used for battery tests were ground with five to seven and one-half pounds of balls for two hours. Larger quantities
were ground for eight hours using fifteen pounds of balls and 500 grams of manganese dioxide. All samples were screened to minus 100 mesh after grinding.

The results of the drain tests on batteries made with manganese dioxide from each pilot plant run are listed in Table II. Unfortunately, all of the later sets of batteries were made using contaminated acetylene black in the bobbins. These later batteries exhibited a noticeably reduced high drain, but the low drains appeared to be unaffected by the contamination.

The results of the drain tests on batteries made with manganese dioxide from each pilot plant run are listed in Table II. Unfortunately, all of the later sets of batteries were made using contaminated acetylene black in the bobbins. These later batteries exhibited a noticeably reduced high drain, but the low drains appeared to be unaffected by the contamination.

<table>
<thead>
<tr>
<th>Run</th>
<th>Carbonate Batch</th>
<th>Temp. °C</th>
<th>Air Rate SCFH</th>
<th>Drain Tests</th>
<th>Bobbins gms</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-6</td>
<td>4,5,6,7</td>
<td>450</td>
<td>121</td>
<td>7.2</td>
<td>143.5</td>
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<tr>
<td>PP-7</td>
<td>Schilling's</td>
<td>475</td>
<td>.45</td>
<td>6.7</td>
<td>138.5</td>
</tr>
<tr>
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<td>Schilling's</td>
<td>475</td>
<td>91</td>
<td>6.7</td>
<td>146.5</td>
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<tr>
<td>PP-9</td>
<td>4,5,6,7</td>
<td>500</td>
<td>91</td>
<td>7.0</td>
<td>141.5</td>
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<tr>
<td>PP-10</td>
<td>4,5,6,7</td>
<td>550</td>
<td>91</td>
<td>7.2</td>
<td>132.5</td>
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<tr>
<td>PP-11</td>
<td>4,5,6,7</td>
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<td>91</td>
<td>7.0</td>
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<td>.91</td>
<td>6.2</td>
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<tr>
<td>PP-13#</td>
<td>4,5,6,7</td>
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<td>91</td>
<td>6.0</td>
<td>143.5</td>
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<td>PP-14#</td>
<td>4,5,6,7</td>
<td>425</td>
<td>121</td>
<td>6.2</td>
<td>141.5</td>
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</table>

# contaminated carbon black in bobbins

From observation of the high drain tests it is apparent that run conditions had no visible effect upon them. Low drains, however, apparently tend to drop off at 400°C and again at 550°C, but remain fairly constant at temperatures in between. Figure 10 shows a plot of low drain versus temperature for runs made from carbonate 4,5,6,7.
Figure 10
LOW DRAIN VERSUS TEMPERATURE
One further correlation can be obtained. The run made with Schilling's carbonate with the purpose of duplicating one of his runs showed high and low drain tests of 6.7 and 138 hours, respectively. Schilling's drain tests were 7.6 and 128 hours, respectively. Comparison of the two runs shows a trend to higher low drains and lower high drains with pilot plant manganese dioxide.

A twenty-pound sample of battery-active manganese dioxide was prepared by combining the leached and ground dioxide from all the runs from PP-5 to PP-18. This sample was sent to Ray-O-Vac Battery Company for analysis and evaluation. The results of the drain tests are:

<table>
<thead>
<tr>
<th>Montana State College</th>
<th>Ray-O-Vac</th>
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<tr>
<td>High</td>
<td>6.8 hours</td>
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<tr>
<td>Low</td>
<td>120 hours</td>
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CONCLUSIONS

The pilot plant as described in this thesis proved to be satisfactory in performing the carbonate oxidation process. Its greatest fault seemed to be the lack of accurate temperature control due to the existence of a large longitudinal temperature gradient across the bed. This could be reduced by repositioning the heaters so that they rested against the lower flange of the reaction chamber.

Representing a 15 to 1 scale up of Schilling's experimental reactor, the pilot plant gave comparable albeit slightly lower percentage yields of manganese dioxide. Batteries made from the dioxide produced with the pilot plant showed good drain characteristics with both high and low drain specifications, as set by the Signal Corps, being surpassed. Typical batteries fabricated during this experiment averaged 7 hours high drain and 140 hours low drain, whereas 5.5 hours and 130 hours are Signal Corps specifications. High drains appeared to be unaffected by run conditions. Low drains, however, appeared to drop off at 400°C and 550°C with the best tests being exhibited by batteries made with manganese dioxide produced at between 425°C and 500°C.

Grinding time and ball:MnO₂ weight ratios were found to have a very pronounced effect on battery activity. Although no grinding study was undertaken it can be seen from Table I that such a study is to be desired.

The best estimate of run conditions which would be compatible with both good yields and battery quality is:
Temperature 475°C to 500°C
Time 1 hour
Air Rate .24 SCFH per pound of carbonate

The kinetic study shows that one hour should be sufficient to complete the first stage of the reaction at the air rate and temperature specified, thus producing a product requiring about one-third recycle. Due to the extremely slow rate of the second stage it would not appear to be economical to carry the reaction past the first stage.

In view of the shortened reaction time, it would seem that a continuous reactor could perform the oxidation process more economically than the semi-batch type used.
LITERATURE CITED AND CONSULTED


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


(10) U. S. Army Signal Corps, Manganese Dioxide, Synthetic, SCL-3117-D. March 18, 1952, Fort Monmouth, New Jersey.
<table>
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<th>Run</th>
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<th>Temperature</th>
<th>Yield by Leach</th>
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<tr>
<td>PP-12</td>
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<td>450</td>
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Yield versus Temperature Data for Figure 4
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Kinetic Data for Figures 5 and 6.
TABLE V

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<th>Sample Wt. mg</th>
<th>Residue Wt. mg</th>
<th>Yield Wt.%</th>
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Kinetic Data for Figure 7.
### TABLE VI

<table>
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<th>Residue Wt. mg.</th>
<th>Yield Wt. %</th>
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Kinetic Data for Figure 8.
## TABLE VII

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<th>Residue Wt. mg.</th>
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Kinetic Data for Figure 9.
Griggs, A. L.

Pilot plant study of producing heavy...