



The air oxidation of manganese carbonate to battery active manganese dioxide in a rotary kiln
by John P Humphrey

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
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Abstract:

This thesis contains the results of an experimental investigation into the feasibility of producing battery active manganese dioxide by air oxidation of manganese carbonate in a rotary kiln. The manganese carbonate was made from a rhodochrosite ore concentrate.

The variables studied were retention time and maximum kiln temperature. The manganese dioxide produced was tested for high and low drain capacity as described in Signal Corps Specifications SCL-3117-D Regression equations describing the effect of temperature and retention time on yield and low drain capacity are given. The high drain capacity was found to be independent of retention time and temperature. On the basis of the low drain capacity regression equation, it was determined that operating at temperatures from 10000F to 14000F and at retention times of 45 minutes to 75 minutes will produce manganese dioxide which will exceed Signal Corps specifications.

THE AIR OXIDATION OF MANGANESE CARBONATE TO BATTERY
ACTIVE MANGANESE DIOXIDE IN A ROTARY KILN

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A thesis submitted to the Graduate Faculty in partial
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Chemical Engineering

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VITA

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ABSTRACT

This thesis contains the results of an experimental investigation into the feasibility of producing battery active manganese dioxide by air oxidation of manganese carbonate in a rotary kiln. The manganese carbonate was made from a rhodochrosite ore concentrate.

The variables studied were retention time and maximum kiln temperature. The manganese dioxide produced was tested for high and low drain capacity as described in Signal Corps Specifications SCL-3117-D.

Regression equations describing the effect of temperature and retention time on yield and low drain capacity are given. The high drain capacity was found to be independent of retention time and temperature. On the basis of the low drain capacity regression equation, it was determined that operating at temperatures from 1000°F to 1400°F and at retention times of 45 minutes to 75 minutes will produce manganese dioxide which will exceed Signal Corps specifications.

INTRODUCTION

In 1800 an Italian physicist, Alessandro Volta, discovered that when a copper plate was separated from a zinc plate by an acid soaked cloth, an electrical force was generated between the copper and zinc. This was the invention of the first true battery. Since Volta's invention, there have been many primary cells developed, but probably the most important of these (in quantity produced) has been the battery introduced in 1868 by Georges Leclanche⁹ (9) (10) (12).

The Leclanche⁹ battery - the common dry cell, or flashlight battery as we know it today - is composed of a zinc anode, a carbon cathode surrounded by a mixture of manganese dioxide, carbon black, and ammonium chloride, and an ammonium chloride - zinc chloride paste electrolyte.

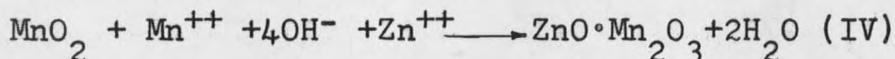
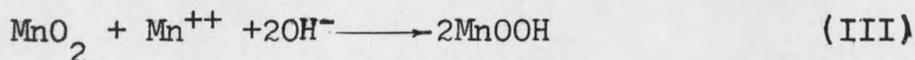
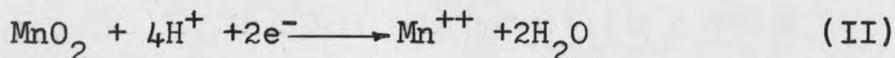
The exact chemical reactions which take place in the cell during discharge are still being debated, but it is certain that by some irreversible reaction, zinc goes into solution at the anode giving up electrons which travel through an exterior circuit to the cathode. For many years it was assumed that the manganese dioxide in the cathode mix acted as a depolarizer, i.e., reacted with hydrogen formed at the cathode, but now it is fairly certain that no hydrogen is produced. However, manganese dioxide is still referred to as a depolarizer. The more recent evidence seems to

indicate (5):

At the anode,



and at the cathode,



As can be seen from the above reactions, the amount of manganese dioxide in a cell is very important, and in a Leclanche' battery manganese dioxide is the limiting reactant. However, there are many other factors which influence a battery's capacity, i.e., available electrical energy.

Early in the history of the battery industry, it was recognized that there are two types of manganese dioxide; one which is battery active, i.e., will produce electrical energy, and one which is not. It was not until the advent of the electron microscope and X-ray diffraction equipment that a difference between the two was discovered. For manganese dioxide to be battery active, it must have an amorphous structure, and be of the proper crystalline

phase.

To date, there have been as many as six crystalline phases of manganese dioxide identified, of which the three most common naturally occurring phases are α - MnO_2 (cryptomelane), β - MnO_2 (pyrolusite), and γ - MnO_2 (ramsdellite). The γ - MnO_2 has been found to be the active phase in both natural and synthetic manganese dioxide. There is one other battery active phase which appears quite frequently in synthetic manganese dioxide, ρ - MnO_2 , but it is thought that this is only poorly crystallized γ - MnO_2 , because both appear in a continuous spectrum of mixtures. While the proper crystalline phase is necessary for battery activity, it is not sufficient to insure it.

The chemical purity of manganese dioxide plays an important role in battery activity. The material must be high in manganese dioxide, in comparison to the other oxides of manganese (MnO , Mn_2O_3 and Mn_3O_4), and low in other metals, especially in copper and nickel. There have been many attempts in the past to correlate the above properties, as well as many others, and battery capacity. However, the only real way of measuring how a sample of manganese dioxide will function in a cell seems to be put it in one and try it.

Currently the chief source of battery grade manganese dioxide is the naturally occurring material in Ghana (Gold Coast of Africa). However, there are two other important deposits; one in Russian Caucasus and the other in the Philipsburg area of Montana. The Montana ore was used quite extensively during World War I, but this material is a relatively poor grade depolarizer, and its use has been almost discontinued.

During the last five years the amount of battery active manganese dioxide being used in the United States has decreased (Table I).

TABLE I
TONS OF MANGANESE DIOXIDE CONSUMED BY THE BATTERY INDUSTRY
IN THE UNITED STATES-1956 to 1960.

	Year				
	1956(16)	1957(17)	1958(18)	1959(19)	1960(20)
Imported	30,853	28,702	24,447	24,637	22,930
Domestic	1,510	1,400	2,157	4,097	4,285
Total	32,363	30,102	26,604	28,734	27,215

This can probably be attributed to two major factors, the first being the new demand for smaller and smaller dry cells, which require less manganese dioxide, and the second being that there are several other types of dry cell batteries replacing a small percentage of the Leclanche^o market. However, most of these batteries are much more expensive than the Leclanche^o battery. There is also a third

factor which may be influencing the amount of manganese dioxide used in the United States and that is the import of cheaper flashlight batteries from other countries. These sell for about half of what a battery produced in this country will cost, and generally speaking, are much lower in quality (8). Regardless of the decrease in manganese dioxide consumption, we find the Leclanche^o cell in a wide number of applications ranging from flashlights to a whole host of childrens^o battery-powered toys. The Leclanche^o cell will be used for many years to come because of its versatility, economy and popularity with the general public.

Because manganese dioxide is a vital raw material and because it is difficult to obtain during time of war, each World War has resulted in greater activity in trying to synthesize it. During World War II, with the aid of the Army Signal Corps, several firms started manufacturing battery active manganese dioxide by an electrolytic process. This material is far superior to natural ore (Table II), and there are several plants operating even today (26). However, even though electrolytic manganese dioxide is an excellent depolarizer, a plant for its manufacture requires a large capital investment and uses vast quantities of strategically located electric power. Therefore, from June 1951 to June

1954, the Army Signal Corps sponsored at Montana State College an investigation into the chemical synthesis of battery grade manganese dioxide (3). From 1954 to 1955 research was carried on under various sponsors and from 1955 to date under the sponsorship of the Montana State Engineering Experiment Station (11, 24, 25).

TABLE II

A COMPARISON OF NATURAL BATTERY ACTIVE MnO_2 AND ELECTROLYTIC

	MnO_2	
	<u>High Drain*</u>	<u>Low Drain**</u>
Gold Coast (25)	3.7	80
Philipsburg (25)	4.2	82
Electrolytic (15)	Not reported	147

*Time required for an "A" size dry cell to discharge to 1.0 volts through a 16 2/3 ohm resistor.

**Time required for an "A" size dry cell to discharge to 1.13 volts through a 166 2/3 ohm resistor.

Mr. Fred Baughman described in his thesis (2), a process where battery grade manganese dioxide could be made by the air oxidation of manganese carbonate, followed by an acid leach to remove the lower oxides of manganese. Schilling (25) chose to do a more thorough study of this reaction in a small batch-type fluid bed reactor, and concluded that the conversion of manganese carbonate to manganese dioxide was a function of carbonate purity, reactor temperature, reactor pressure, air rate through

the bed, and reaction time. Even though he decided not to design his experiments for the study of battery quality, he did conclude that a good depolarizer could be made by the air oxidation of manganese carbonate in a fluid bed reactor.

Griggs (11) followed up Schilling's research by constructing a pilot plant size batch-type reactor. However, Griggs experienced considerable difficulty with temperature control because the bed would not fluidize, except at fairly high air velocities. Again, Griggs did not design his experiments for the study of the battery quality, but he concluded, also, that good battery active manganese dioxide could be made in this fashion.

Because manganese carbonate does not fluidize well and because of the batch-type operation in the fluid bed experiments, it was decided to study the air oxidation of manganese carbonate in a more continuous piece of equipment—a small stainless steel rotary kiln. This research was carried out under the auspices of the Montana State Engineering Experiment Station.

HYPOTHESES

The questions which this research set out to answer were:

- (1) Can a high quality battery active manganese dioxide be made in a gas fired, stainless steel rotary kiln?
- (2) How do the variables retention time and temperature in a rotary kiln effect the quality of the depolarizer, and the percent manganese dioxide in the kiln discharge?
- (3) If operating conditions effect the quality of the depolarizer, what operating conditions will give a material which will meet or exceed Army Signal Corps specifications for battery active manganese dioxide (29)?
- (4) Does the quality of the manganese dioxide pass through a maximum?

EXPERIMENTAL PROCEDURES

The experimental procedures used in this research are presented in the following order:

1. Discussion of a typical synthesis of battery active manganese dioxide.
2. Description and operation of the rotary kiln used for oxidizing manganese carbonate to manganese dioxide.

A Typical Synthesis

The first step in the synthesis of battery active manganese dioxide was the manufacture of manganese carbonate. The starting material was a floated rhodochrosite (MnCO_3) concentrate ore donated by the Anaconda Company (see Figure 8 for a flow diagram). First the ore was leached with 0.70 pounds of technical grade sulfuric acid, diluted to 100 grams per liter, per pound of ore. The ore contains about thirty-five percent manganese and the above acid-ore ratio is approximately the amount required to react with the manganese. However, the acid is in slight excess.



After the ore had leached for twenty-four hours with constant stirring, the pH of the resulting slurry was adjusted to six with calcium carbonate and sodium carbonate.

Calcium carbonate will lower the pH to about 5.5, then it is necessary to add a small amount of sodium carbonate to attain a pH of six. Sodium carbonate alone could be used for this pH adjustment, but calcium carbonate was used first, because it is cheaper. The calcium carbonate requirement for this step was about 0.2 pounds per pound of ore, and the sodium carbonate requirement about 0.02 pounds per pound of ore.

Next, air was sparged into the slurry for the purpose of oxidizing any iron which was in solution to ferric hydroxide, which precipitates. This step in the production of manganese carbonate was very slow and on occasion required fourteen days to oxidize all of the iron. The slurry was then filtered with the solids acting as a filter-aid. The resulting filtrate - approximately ten percent manganese sulfate - is a very clear pink solution, and if it becomes cloudy upon standing three or four hours, there is still considerable iron in solution.

Next, the manganese sulfate filtrate was treated with sodium carbonate solution to precipitate manganese carbonate.



The manganese carbonate was then washed by successive dilution and decantation until no sulfate ion was

evidenced when barium chloride was added to a sample of the wash water.

After precipitation and washing, the manganese carbonate was filtered, dried in a cabinet drier at 160°F for twenty-four to forty-eight hours, and ball milled for fifteen or twenty minutes to break up any lumps.

In all, fourteen separate batches of manganese carbonate were prepared (numbered c-1 through c-14). The first eleven of these were prepared in thirty-two gallon polyethylene barrels and only twenty-five pounds of ore could be leached at any one time. During the preparation of these batches, considerable difficulty was had with iron removal. The air used for oxidation was blown into the solution from the laboratory's air supply and dispersed by a small $\frac{1}{4}$ H.P. mixer. As mentioned earlier, sometimes the oxidation required fourteen days. However, batches c-12 and 13 were prepared in a 100 gallon redwood tank. This made it possible to leach 120 pounds of ore, thus greatly increasing the amount of carbonate made per batch. During the preparation of these batches, it was discovered that if a $\frac{1}{3}$ H.P. Lightning mixer was used to stir the slurry, and if it was set so that a large whirlpool was formed, the mixer pulled enough air from the room into the slurry to oxidize the iron in twenty-four hours, thus

greatly speeding up the iron oxidation step. Batch c-14 was produced in a 250 gallon redwood tank, requiring 180 pounds of ore, and by using the same Lightning mixer, iron oxidation took only twenty-four hours.

Filtration of the slurry after iron oxidation was also a little troublesome for the first few batches of manganese carbonate. Originally the filtration was done in ten inch Buchner funnels with four liter suction flasks, but after considerable experimenting, a Sperry Filter Press in the unit operations lab was successfully used for this operation. In place of cloth, a heavy industrial filter paper was used between the plates and frames of the press. Unfortunately, it was impossible to obtain accurate yield data on the manganese carbonate preparations because of large losses during filtering and washing. However it is felt that some loss is unavoidable and that this problem should be studied in detail.

Of the fourteen batches of carbonate made, c-1,2,3,4 and 5 were blended together and used in the "shake-down" runs of the rotary kiln (see page 18), as were batches c-6,7,8 and 9. Batches c-10,11,12 and 13 were blended together and were used for runs HG-3 through HG-34 (page 33). Part of batch c-14 was used to make run HG-35. A qualitative spectrographic analysis of these blends of carbonates (Table III) was made so that it could be compared

with the carbonate analysis reported by Schilling (25), and they compared reasonable well, considering that his type of analysis is accurate to only the nearest factor of ten.

TABLE III

QUALITATIVE SPECTROGRAPHIC ANALYSIS OF CARBONATES - PERCENT

CARBONATE

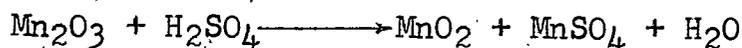
used in runs	c-1,2,3,4,5 Shake-down	c-6,7,8,9 Shake-down	c-10,11,12,13 HG-3 through 34	c-14 HG-35
Calcium	0.5	0.5	0.5	0.5
Zinc	0.1	0.1	0.1	0.1
Silicon	0.05	0.05	0.05	0.01
Iron	0.05	0.05	0.05	0.05
Sodium	0.01	0.01	0.01	0.01
Lead	0.01	0.01	0.01	0.05
Nickel	0.005	0.005	0.005	0.005
Aluminum	0.001	0.005	0.001	0.001
Chromium	0.001	0.001	0.001	0.001

Titanium, Molybdenum, Vanadium, Copper, and Strontium - only a trace found in all carbonates analyzed.

Potassium, Tungsten, Barium - none found in carbonates analyzed.

After the manganese carbonate had been dried and ball milled, it was oxidized in the rotary kiln described on page 18. A small portion of the discharge was set aside for available oxygen analysis and from 400 to 1000 grams (depending on the amount recovered from the kiln) was leached with one gram of technical grade sulfuric acid, diluted to 100 grams per liter, per gram of discharge. This step was to remove any unreacted carbonate and the lower oxides of

manganese.



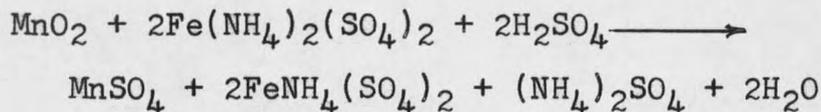
One gram of sulfuric acid was used for every gram of discharge because this would be approximately the amount of sulfuric acid required to leach the discharge had it all been Mn_3O_4 . However, the acid was in slight excess. The acid was diluted because MnO_2 is soluble in concentrated sulfuric acid while it is not in dilute sulfuric acid.

After the discharge had leached for two hours at boiling temperature, the remaining residue, manganese dioxide, was washed with water by successive dilution and decantation. Washing was continued until a sample of the wash water showed no sulfate ion upon the addition of barium chloride. Next, the manganese dioxide was filtered and dried at 110°C for 24 hours.

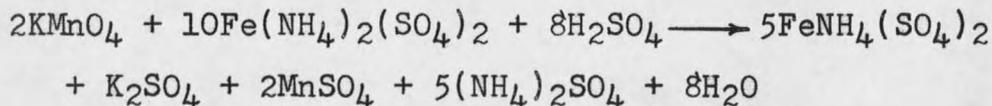
While yield from acid leaching, the weight of dried manganese dioxide compared to the weight of the material leached, would have been a good measure of the manganese dioxide in the kiln discharge, it was not used. This figure was very much subject to error because of material losses during washing and filtering. Therefore, an available oxygen analysis was used to measure the amount

of manganese dioxide in the discharge, and this analysis gave the yield figures reported in this thesis.

The available oxygen analysis was carried out in the following manner (for a more detailed description see page 82 of the appendix). A small sample of the discharge was placed in a beaker containing exactly 50 milliliters of a prepared ferrous ammonium sulfate - sulfuric acid solution and heated until the sample dissolved. Since there was a large excess of sulfuric acid, it was assumed that any $MnCO_3$, Mn_2O_3 and Mn_3O_4 reacted according to the reactions given on page 14. This left only manganese dioxide to react with the ferrous ammonium sulfate.



Next, the excess ferrous ammonium sulfate was titrated with potassium permanganate, as was 50 milliliters of blank ferrous ammonium sulfate solution.



By knowing the normality of the potassium permanganate, the percent manganese dioxide in the sample was calculated from:

$$\%MnO_2 = \frac{4.35 (C_2 - C_1) N_k}{W}$$

where C_2 = milliliters of $KMnO_4$ required to titrate the blank $Fe(NH_4)_2(SO_4)_2$ solution.

C_1 = milliliters of $KMnO_4$ required to titrate the excess $Fe(NH_4)_2(SO_4)_2$ in the beaker containing the sample.

and

W = weight of the sample in grams.

Two available oxygen analyses were made on each run in the kiln.

After the manganese dioxide from the acid leach had been washed and dried, it was ground for two and one-half hours in a 3.5 gallon ceramic ball mill containing approximately 5 pounds of ceramic balls. Next the dioxide was screened and the material passing through a standard 100 mesh sieve was fabricated into size "A" dry cell batteries (a detailed description of battery fabrication is given in the appendix). These batteries were made and tested according to Signal Corps specifications SCL-3117-D(29). These batteries were very similar to commercial flashlight batteries at least in principal components. The battery components, except for the manganese dioxide, were purchased from a commercial supplier.

Each cell was comprised of a zinc can, a paste electrolyte and a manganese dioxide bobbin. The bobbin was

made by compressing a mixture of manganese dioxide, ammonium chloride, acetylene black, and wetting solution around a carbon rod. The amount of wetting solution varied with the manganese dioxide, but enough was added to insure proper tamping consistency of the mixture. The bobbins were weighed, wrapped in gauze, tied with cotton thread, placed in the zinc can, paste electrolyte poured in, and then sealed with wax. A set of eight batteries was made for each sample of manganese dioxide.

The batteries were submitted to two standard tests five days after fabrication. The high drain test consisted of draining the battery through a $16 \frac{2}{3}$ ohm resistor and noting the time required to reach 1.0 volts. Five and one-half hours was the Signal Corps specification. The low drain test was very similar, except the resistance was $166 \frac{2}{3}$ ohms and the cut-off voltage was 1.13 volts. Specification was 130 hours. Two batteries from each set were used for high drain tests and two for low drain tests. Delayed capacity tests (see page 93 of the appendix) were not run because of the lack of proper battery storage facilities.

In summary, a typical experiment consisted of making manganese carbonate, oxidizing the carbonate in a rotary kiln, leaching the kiln discharge, washing, drying and milling the leached product, making a set of batteries and subjecting them to high and low drain battery tests.

THE ROTARY KILN FOR THE OXIDATION OF MANGANESE CARBONATE

The rotary kiln used in this research (Figures 1, 2, 3, 4, and 5) consisted of four main parts; the rotating tube, the feed mechanism and stack, the burner and control, and the support frame.

The rotating tube (Figures 2, 3, and 4) consisted of two five foot concentric pipes. The inner pipe was 8 inches in diameter and was made by rolling 1/8 inch 309 stainless steel. The outer pipe was made from fourteen inch mild steel pipe and served as an insulating jacket. The annular space between the two pipes was filled with vermiculite insulation. The drums on which the tube rolled were made from two four inch pieces of sixteen inch mild steel pipe, which were turned down to approximately fifteen inches. The drive for the tube consisted of a 1/3 H.P. motor coupled to a variable speed hydraulic transmission which was in turn hooked to a series of sprockets and chains.

The temperature of the rotary kiln was measured in three places (10 inches, 30 inches and 58 inches from the burner end) with thermocouples. The thermocouple wells were 3 inch pieces of 3/8 inch stainless steel pipe, which passed through the insulating jacket and insulation, and were welded on the outside of the 8 inch diameter tube. All kiln temperatures were measured through the wall of the inner tube.

Because the thermocouples for measuring kiln temperature were an integral part of the rotating tube, it was necessary to devise sliding contacts for them. This was done by mounting six copper rings (two for each thermocouple) on the outside of the insulating jacket and contact was made with each ring by a stationary spring loaded carbon brush (indicated in Figure 4). Two of the thermocouples on the tube were connected through sliding contacts to a multiple point switch which in turn was connected to a pyrometer. The thermocouple nearest the burner end of the kiln was connected through a sliding contact to a recorder controller (Figure 1). This thermocouple was approximately at the hottest point in the kiln and was used as the control point. Figure 6 shows typical temperature profiles at each control temperature.

The stack and feed mechanism (Figures 3 and 5) was all constructed of stainless steel. The stack was made of a piece of four inch 302 stainless pipe with an eight inch expansion chamber on top. Originally it was hoped that the dust going up the stack could be collected electrostatically. This is the purpose of the six inch sewer tile on top of the expansion chamber. The tile acted as an electric insulator. However, because of the high gas velocities through the expansion chamber, it was impossible

to collect the dust in this fashion. Later, a damper was placed in the tile, and this cut down considerably on the dust leaving the unit. This damper did not seem to restrict the flow of combustion gases going up the stack very much. The temperature profile along the kiln tube was essentially the same when the damper was one-fourth open as it was when it was full open. So the damper was set about one-fourth open throughout the research.

The feed mechanism (Figure 5) consisted of a feed hopper and an auger. The hopper was made from 302 stainless steel and the auger was cut from a piece of 5/8 inch 304 stainless rod. The manganese carbonate being fed to the kiln was conveyed from the feed hopper by the auger through a 5/8 inch (I.D.) stainless steel tube, slid down the inside of another 5/8 inch tube, which passed down the center of the stack, and then fell into the kiln at a point about 58 inches from the burner end of the kiln. The drive mechanism for the feed auger consisted of a 1/4 H.P. electric motor coupled by a V-belt to a variable speed hydraulic transmission, which was in turn connected to a pulley on the auger by a V-belt.

The frame supporting the rotary kiln, the stack and feed mechanism and all of the necessary drive equipment (Figures 2 and 3) was made of two-by-six lumber. On each side of the head end (the end opposite the burner end)

of the frame was a screw jack for changing the pitch of the kiln.

Heat was supplied to the kiln by burning natural gas with a small gas burner (Denver Fire Clay Burner Number 781) and the kiln temperature - ten inches from the burner end - was controlled by a Minneapolis Honeywell pneumatic recorder controller (Model Number Y152P13P-96-(17)).

In the course of this research from fifteen to twenty preliminary runs were attempted. Many of these were not completed because of operating difficulties which usually resulted in major changes in the kiln design. Therefore no valuable data was obtained from these runs but they did give experience in operating a small rotary kiln, a better kiln design, and, finally, the kiln just described. These runs served two other purposes. They showed that the air oxidation of manganese carbonate to battery active manganese dioxide in a rotary kiln was possible and they served to give some insight into the range of the operating variables (retention time and kiln temperature) that should be studied.

As mentioned earlier the kiln's temperature was controlled ten inches from the burner end. This was the hottest point in the tube (or very near it) and since the crystalline phase of manganese carbonate can change with

temperature (27), it is important to control the maximum temperature the material in the kiln encounters.

The actual retention time, the time the reacting material is in the kiln, is very difficult to measure, as each particle of material moving down the tube looks just like the other. Therefore, retention time was defined according to an empirical relationship determined by Sullivan, Maier, and Ralston (23) (28).

$$R = \frac{0.19L}{NDS}$$

where

R = retention time in minutes

L = length of the kiln in feet

N = rate of rotation in r.p.m.

D = diameter of the kiln tube in feet

S = slope of the kiln in feet per foot of kiln length

This equation has two advantages. It made it possible to obtain a reproducible retention time and any retention time set on this small unit could be obtained on a large unit.

Since the length and diameter of the kiln were fixed, this left retention time dependent only upon the speed of rotation (N) and the slope (S) of the kiln. The speed of rotation of the kiln could be reasonably varied only

over a small range - one to four revolutions per minute. It was decided therefore to set the rate of rotation at two r.p.m. This is well in the range of operation of larger kilns and seemed to give ample bed mixing. This left retention time only a function of the kiln's slope (S).

Considerable difficulty was encountered during shake-down runs with material hanging up in the tube. The reacting material seemed to get sticky which probably explains to some extent why the manganese carbonate did not fluidize well in the fluid bed experiments (11) (25), and would hang up on the inside of the kiln. However, if enough material was fed to the kiln, a fixed bed would build up and then material would be discharged. This bed build-up cut down on the diameter of the kiln. So, a stainless steel spring-mounted scraper was placed the full length of the kiln tube. The ends of this scraper can be seen in Figures 2 and 3. This scraper kept the kiln diameter nearly constant over the length of the tube and provided extra mixing for the reacting material.

Probably at this point a description should be made of how a typical run in the kiln was carried out. First, the retention time was set by adjusting the incline of the kiln with the screw jacks. Next, the kiln drive was turned on and the rate of rotation was checked with a

stop watch. The rate of rotation could be changed by adjusting the variable speed hydraulic transmission in the kiln drive mechanism. However once the rate of rotation was set, it rarely had to be adjusted. The burner was then lighted and the kiln was brought up to the desired control temperature by the manual controls on the recorder controller. After the kiln had reached the desired temperature, the controller was switched to automatic control. When the kiln temperature had lined out, the feed (manganese carbonate) was started into the kiln.

The feed rate to the kiln was set at thirty revolutions per minute of the feed auger and was later measured at 2.4 ± 0.1 pounds of manganese carbonate per hour. As determined by Sullivan, Maier and Ralston (28), retention time did not depend upon the feed rate to the kiln. Of course, this assumes that the kiln is fed at a reasonable rate. Therefore, the feed rate used was rather arbitrary.

After the feed was started, the kiln was allowed to run for a period of time equal to the retention time and then the discharge was collected until the hopper ran out of feed. The amount of feed used per run was either five or ten pounds depending on the retention time. Next, this material was leached and ground as described earlier.

