Battery active manganese dioxide by air oxidation of manganese carbonate
by Fred P Schilling

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

Abstract:
This report contains the results of an experimental investigation of the feasibility of producing a battery active manganese dioxide by the air oxidation of manganese carbonate made from a Montana rhodochro- Site ore " The effect on the yield of manganese dioxide of, the reaction variables of temperature, time, pressure and linear air rate was investiga-ted using an experimental design of the "method of steepest ascent" type. The maximum observed yield was 70.5 percent available oxygen content occurring at the reaction conditions of 4757deg;C, 5hours, 3 atmosphere pressure, and 8 feet per minute linear air velocity. Linear regression equations were estimated for a correlation between yield and iron and sodium content' of the manganese carbonate. Iron did not show any corre-lation with yield ; however, the presence of sodium was found to depress yield with the effect being more pronounced at 400° C. than at 450°C Inferences regarding an effect of the reaction variables of temper-ature, time, pressure, and air rate on battery quality were not made.

It was found that a high sodium and iron analysis of the carbonate was associated with poor low drain and delayed capacity of the resulting manganese dioxides. The effect of iron and sodium on high drain was less pronounced.

The effect of wetting solution, carbon ratio, and leach acid concentration was investigated as a factorial type of experiment. Within the region investigated, 100 grams per liter leach acid concentration, 10-1 manganese dioxide to carbon ratio, and 15.0 milliliters of vetting solu- tion per 40 grams of manganese dioxide were shown to give the best results .

Typical battery drain tests for manganese dioxide made according to the conditions found best were 7.3 hours high drain,125 hours low drain, and 99 hours three months delayed capacity. The best set of batteries had 7-7 hours' high drain, l46 hours low drain and 117 hours delayed capacity.

Based on these experiments a proposed flowsheet for a commercial plant, assumed to be located at Butte, Montana, and utilizing rhodochro-site ore, sulfuric acid from Anaconda and sodium carbonate from Wyoming, was prepared.

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ABSTRACT

This report contains the results of an experimental investigation of the feasibility of producing a battery active manganese dioxide by the air oxidation of manganese carbonate made from a Montana rhodochrosite ore.

The effect on the yield of manganese dioxide of the reaction variables of temperature, time, pressure, and linear air rate was investigated using an experimental design of the "method of steepest ascent" type. The maximum observed yield was 70.5 percent available oxygen content occurring at the reaction conditions of 475° C., 5 hours, 3 atmospheres pressure, and 8 feet per minute linear air velocity. Linear regression equations were estimated for a correlation between yield and iron and sodium content of the manganese carbonate. Iron did not show any correlation with yield; however, the presence of sodium was found to depress yield with the effect being more pronounced at 400° C. than at 450° C.

Inferences regarding an effect of the reaction variables of temperature, time, pressure, and air rate on battery quality were not made. It was found that a high sodium and iron analysis of the carbonate was associated with poor low drain and delayed capacity of the resulting manganese dioxides. The effect of iron and sodium on high drain was less pronounced.

The effect of wetting solution, carbon ratio, and leach acid concentration was investigated as a factorial type of experiment. Within the region investigated, 100 grams per liter leach acid concentration, 10 - 1 manganese dioxide to carbon ratio, and 15.0 milliliters of wetting solution per 40 grams of manganese dioxide were shown to give the best results.

Typical battery drain tests for manganese dioxide made according to the conditions found best were 7.3 hours high drain, 125 hours low drain, and 99 hours three months delayed capacity. The best set of batteries had 7.7 hours high drain, 146 hours low drain and 117 hours delayed capacity.

Based on these experiments a proposed flowsheet for a commercial plant, assumed to be located at Butte, Montana, and utilizing rhodochrosite ore, sulfuric acid from Anaconda and sodium carbonate from Wyoming, was prepared.

INTRODUCTION

From the multitude of primary cells that have been developed, the type introduced by George Leclanché in 1868 has proved to be the most popular in terms of quantity produced. Beginning about 1900 the Leclanche type of dry cell was marketed chiefly for use as a flashlight battery. In the sixty years since then research has improved the cell considerably, the basic ingredients of the battery remaining unchanged. The technique of manufacture and the shape of the battery have undergone considerable change and the quality of the components has been improved such that battery life has increased by about fivefold.

If a dry cell is defined as a primary source of electric power that can be used in any attitude, i.e., electrolyte will not spill, numerous types are currently being used, including rechargeable as well as the more common non-rechargeable cells. A list of some of the names or classes of dry cells being made or in development at this time are: Leclanché type, including standard zinc anodes, magnesium anodes, and aluminum anodes; Lelande type; mercuric oxide and other alkaline cells including alkaline manganese dioxide types; nickel-cadmium rechargeable; thermal cells; gas activated cells; silicon or "solar" cells; and the "atomic" batteries.

Most of these batteries were developed for specific applications and have specific advantages over the Leclanché cell. In the currently popular missile industry Leclanché cells have been virtually replaced by special purpose batteries, exemplified by the silicon cell or solar battery used in the Vanguard satellite. The rechargeable nickel-cadmium battery is gaining popularity in the commercial market due to development of simple compact rectifiers that can be included in the battery package. Mercury cells are used extensively in electronic applications because of their excellent stability and relatively constant output voltage. Alkaline cells, in general, are popular because of their excellent shelf life, high capacity, and perfect seal.

Regardless of the great variety of cells, the Leclanché type continues to be widely used. It can attribute its wide use to versatility, availability, economy, dependability, and a long history of use by the public.

The basic ingredients of a Leclanché cell are a zinc anode, a carbon cathode in contact with a mixture of manganese dioxide, acetylene black and ammonium chloride, and an electrolyte of ammonium and zinc chlorides. The exact cell reactions have not been established. In general, the cell produces current through an irreversible reaction resulting in zinc from the anode going into solution with the release of two electrons which travel through an external circuit to the carbon cathode where a reaction takes place resulting in the reduction of manganese. From a consideration of the end products, reactions such as the following have been postulated.

I. $Zn + 2\ MnO_2 + 2\ NH_4Cl \rightarrow ZnCl_2 \cdot 2\ NH_3 + Mn_2O_3 \cdot H_2O$

II. $4\ Zn + 8\ MnO_2 + 8\ H_2O + ZnCl_2 \rightarrow 4\ Mn_2O_3 \cdot H_2O + ZnCl_2 \cdot 4\ Zn(OH)_2$

The particular reaction that occurs depends on the condition of the cell, the load on the cell, and the relative concentration of ammonium and zinc chlorides. One fact, at least during the first stage of discharge, is that the tetravalent manganese (MnO_2) is reduced to trivalent manganese (Mn_2O_3) and this reaction imposes a limit on cell capacity.

The term "depolarizer" as applied to manganese dioxide needs some explanation. In wet cells, it was sometimes found that hydrogen gas which formed at the cathode inhibited the reaction. This phenomenon was called polarization. In dry cells it was postulated that hydrogen was released at the carbon electrode and that the function of the manganese dioxide was to react with the hydrogen formed. Since hydrogen has not been detected in a cell, the reaction of manganese dioxide can not be with hydrogen. Thus, manganese dioxide is not a depolarizer in the sense of removing hydrogen. Cell reactions are postulated without the formation of hydrogen.

For a given cell, the limiting reactant is the manganese dioxide depolarizer. The capacity of the cell is not only limited by the quantity of manganese dioxide available for reaction, but also by the "activity" of the manganese dioxide. Activity is related to the rate of reaction and is determined by the crystal phase, particle morphology, and chemical composition.

As many as six different phase types of MnO_2 have been classified--of which the three most commonly found in nature are α-MnO_2 or cryptomelane, β-MnO_2 or pyrolusite, and γ-MnO_2 or ramsdillite. The γ-MnO_2

has been shown to be the active phase of natural manganese dioxide. Active synthetic manganese dioxides frequently occur as ρ-MnO_2 or γ-MnO_2 where ρ is believed to be a poorly crystallized variation of γ-MnO_2 and the two occur in a continuous spectrum of mixtures. Other oxides of manganese are Mn_2O_3 (two phases), Mn_3O_4, and MnO. Proper phase type is a necessary requirement for good depolarizer, but not sufficient.

Electron microscope studies have shown that the best physical structure is one that is described as discrystalline of small size and large surface area (8). The chemical composition requires a high percentage of dioxide (compared to lower oxides) and lack of impurities, especially metal ions such as nickel and copper and to a smaller extent, iron. Attempts to correlate depolarizer activity quantitatively with the preceding and other measurable quantities have not been successful. The only test which has consistently proved to be a true indication of the battery activity of manganese dioxide is its performance in a dry cell. Fabrication and testing of cells is discussed under experimental procedures.

The chief supply of depolarizer has been from natural deposits--initially from the Russian Caucasus, still the largest source, from the Philipsburg area of Montana during World War I, and currently from Ghana (Gold Coast of Africa). Each war has encouraged the effort to synthesize a manganese dioxide rather than to depend on natural sources. Research on synthetics has shown that their chief advantage was for heavy duty or high drain loads, but synthetics have usually shown less overall gain for intermittent or low drain duty and suffered most from poor or erratic stability (shelf life). During World War II, with the encouragement of the Signal Corps, several concerns started making an electrolytic manganese dioxide which was much superior to natural ores. Considerable electrolytic manganese dioxide is still being produced by these manufacturers for heavy duty batteries.

At Montana State College, since 1951, research has been directed toward the development of a chemical synthesis for high grade manganese dioxide. Although the supply of natural depolarizer from Ghana is currently stable and the electrolytic processes are supplying present demands for high grade depolarizer, it is anticipated that the supply situation could change drastically. Electrolytic processes involve large investments and use strategically required power. A chemical process is expected to be more versatile and more economical. Under several sponsors, a variety of chemical processes have been studied at Montana State College (1) plus, of course, a great number elsewhere. A review of the possible processes showed one which seemed promising and adaptable to the criteria of a Montana location--economical, versatile, and using chemicals and ore readily available in this area. In Mr. Fred Baughman's thesis (1) he described the production of a battery active manganese dioxide by the oxidation of manganese carbonate with air followed by acid leaching.

It was decided to do a more thorough investigation of air oxidation as a process for making a good quality depolarizer in an economical manner. It was assumed for this study that the starting ore would be rhodochrosite ($MnCO_3$) concentrated by flotation of which a large sample was obtained at the courtesy of the Anaconda Company. Other ores could be used with appropriate variation in the ore treatment (14). In addition it was assumed that sulfuric acid would be available from Anaconda, sodium carbonate from Wyoming, and the necessary plant site, water, power, etc., could be made available in the Butte, Montana, area. For reasons of economy it was endeavored to avoid unusual equipment and to keep the handling of corrosive solutions to a minimum. This research was carried out under the auspices of the Montana State Engineering Experiment Station.

EXPERIMENTAL PROCEDURES

The questions which this research set out to answer were:

1. Can air oxidation of manganese carbonate be used to make good quality battery active manganese dioxide?

2. Can a Montana ore, a technical grade of chemicals, and a steel reactor be used and still give good quality depolarizer?

3. What are the necessary operating conditions for the above?

The experimental procedures and results are presented in the following order:

1. A discussion of the typical steps in a synthesis, i.e., a discussion of the flow sheet.

2. A description of the apparatus used.

3. A discussion of the initial exploratory runs to establish the general feasibility and operating variables.

4. A discussion of experiments to study the variables affecting yield.

5. A discussion of the effect of the process variables on depolarizer quality.

6. A discussion of miscellaneous runs and observations, including a group of battery tests to study blending of synthetic material and natural ore from Philipsburg, Montana.

7. Summary of results.

Except for the initial exploratory runs, the experiments were designed from statistical considerations (experimental design) and the results are presented accordingly. A brief, simplified discussion of some of the mathematical aspects and the rationale of the designs is included in the appendix.

The starting material or source of manganese for this research was a flotation concentrate of rhodochrosite ($MnCO_3$) ore donated by the Anaconda Company. The first step in the process was the leaching of this concentrate with 0.75 pounds of concentrated technical grade sulfuric acid, diluted to 100 grams per liter, per pound of ore containing 37 percent manganese. (See Figure 2 for Flow Diagram.)

$$MnCO_3 \text{ (ore)} + H_2SO_4 \rightarrow MnSO_4 + H_2O + CO_2\uparrow$$

Leaching was continued for twenty-four hours with constant stirring, followed by the addition of enough calcium carbonate to raise the pH to 5.5. Air was then sparged into the solution for a period of one to three days to oxidize the iron in solution to ferric hydroxide. The addition of a small quantity of manganese dioxide would probably have been a more efficient method of oxidizing the iron. This solution containing about 10 percent manganese sulfate was easily filtered with the insoluble material from the ore leach acting as a filter aid.

Manganese carbonate was precipitated by adding sodium carbonate solution.

$$MnSO_4 + Na_2CO_3 \rightarrow MnCO_3\downarrow + Na_2SO_4$$

The carbonate was washed by successive dilution and decantation until little sodium sulfate was evidenced by the addition of barium chloride.

After as many as ten decantations, the sodium concentration in the carbonate was still fairly high due, presumably, to occluded salts in the manganese carbonate precipitate. The carbonate was then filtered, dried at 160° F. for twenty-four hours in a tray drier, and ball milled for ten minutes to break up the dried carbonate. The results of qualitative spectrographic analyses of different batches of carbonate are contained in Table XV.

The next step was the air oxidation of 150 grams of carbonate in a small stainless steel reactor described on page 21.

$$MnCO_3 + \text{Air} \rightarrow \text{Mixture } (MnO_2 + Mn_2O_3 + MnO + MnCO_3) + CO_2 \uparrow$$

A sample of the product was taken for oxygen analysis and the remainder leached with 1360 grams of 100 g./l. sulfuric acid for one-half hour at boiling temperature. Leaching dissolved the lower oxides of manganese and unreacted carbonate leaving the manganese dioxide as a residue. This quantity of acid was selected since it was approximately the quantity needed to leach the incoming ore, assuming that the acid would be recycled to the ore leach so that manganese would not be lost in this step. The manganese dioxide was washed by successive decantation, filtered, dried at 110° C. for 12 hours, and ball milled for two hours. The weight of the dried product compared to the weight of the material leached produced the "yield from leach" figures used in this report.

The overall yield of manganese dioxide would be 100 percent except for unavoidable losses in ore leaching, filtering, washing, etc. Losses do not occur as a direct result of poor oxidation. This step does determine the amount of recycle, however, and thus the size of reactor and head end equipment.

The true measure of the reaction efficiency was the percent of manganese that did not require recycle. The yield by acid leach approximated this value but was not precise since the soluble manganese was in a different form from the insoluble manganese dioxide. Percent available oxygen, a measure of the relative amount of ferrous ammonium sulfate oxidized by a sample of dioxide compared to the amount that would have oxidized if the sample had been pure dioxide, was proportional to the amount of manganese that did not recycle. The material balance, Figure 1, is considered typical and gives the relation between recycle, acid leach yield, and percent available oxygen. It can be seen that acid leach yield was a better measure of recycle than available oxygen; however, in this report available oxygen was used to measure reaction efficiency as it was an easier figure to obtain and was less subject to error. During acid leaching the material had to be handled several times with the corresponding chances for loss, which, in several cases, occurred during decantation.

The leached, dried, and ground manganese dioxide, screened to minus 100 mesh, was then used to fabricate batteries. These 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 given two standardized drain tests five days after they were made and a repeat of the low drain test three months later. 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 and delayed tests were similar except that the cut-off voltage was 1.13 volts and resistance was 166 2/3 ohms. Specification was 130 hours on the initial test. There was no specification for delayed capacity. A drain test of 85 percent of the initial test was considered good delayed capacity.

Usually two cells from each batch of batteries were run on each of these tests (six cells used in all).

As a measure of the efficiency of the cell a simple calculation may be made of the completeness of the cell reaction assuming a reaction in which tetravalent manganese is reduced to trivalent manganese. For a nine gram bobbin having a 1.5 gram carbon rod and 7.5 grams of a mixture of 50 grams of manganese dioxide of 90 percent available oxygen content with 5 grams of carbon, 7.5 grams of ammonium chloride and 15.0 grams of wetting solution, the manganese dioxide for reaction was 4.65 grams.

$$\frac{4.65\text{ g.}}{87\text{ g./equiv.}} \text{ X } \frac{96{,}494\text{ amp. sec./equiv.}}{3600\text{ sec./hr.}} = 1.44\text{ amp. hrs. capacity.}$$

Assuming an average of 1.3 volts potential drop across the 16 2/3 ohm resistance, the expected high drain capacity would be

$$1.44\text{ amp. hrs. X } \frac{16\ 2/3\text{ ohms}}{1.3\text{ volts}} = 20\text{ hours high drain}$$

where 7 hours was typical. For low drain the expected capacity would be $1.44 \text{ X } \frac{166\ 2/3}{1.3} = 200$ hours low drain where 120 hours was typical.

In summary, then, a typical experiment consisted of making manganese carbonate from rhodochrosite ore, oxidizing this carbonate, leaching the oxidized product, washing, drying and grinding the leach product, making a set of batteries and subsequently testing these batteries for high drain, low drain, and delayed capacities.

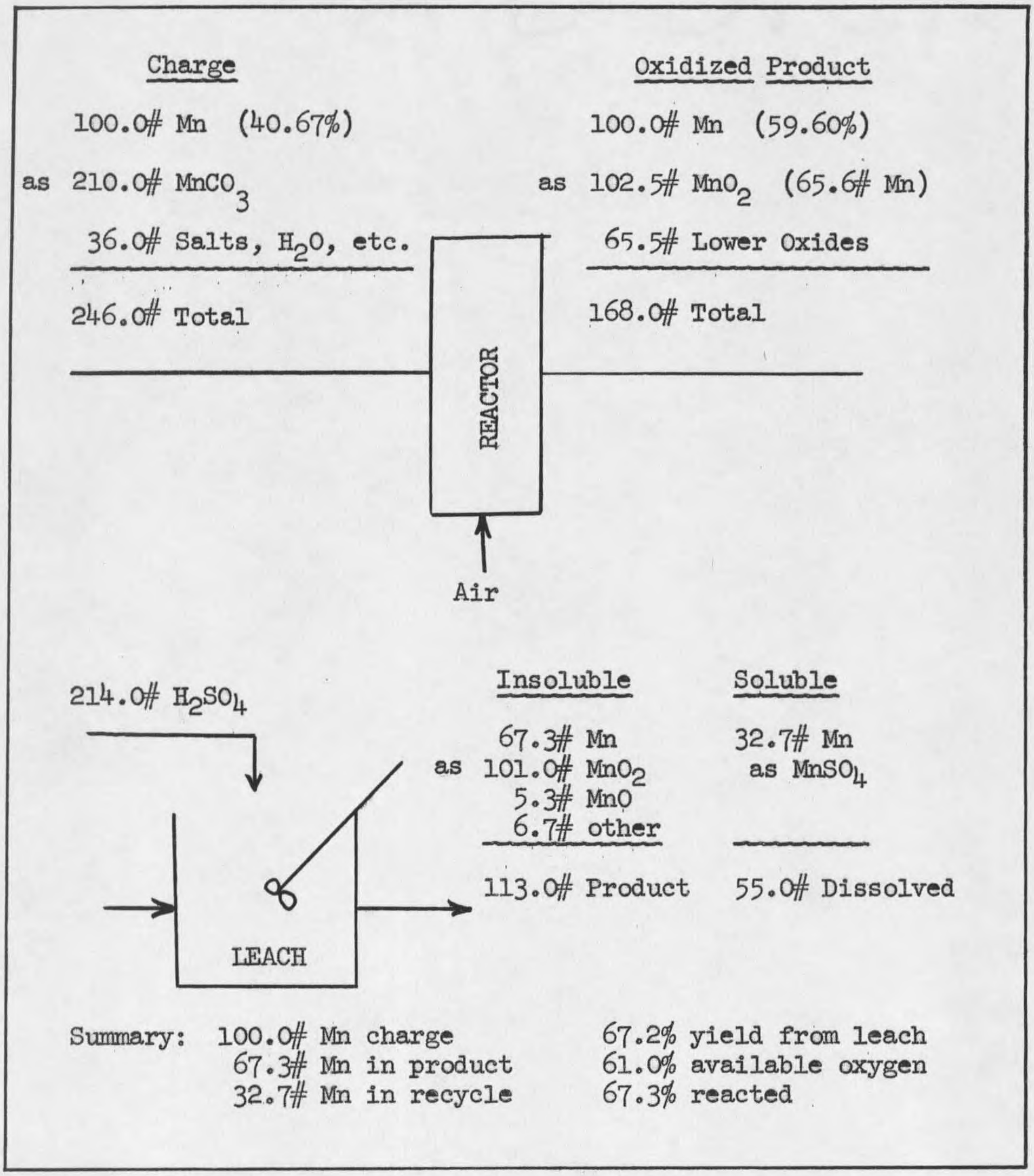

Figure 1

REACTOR and LEACHING

MATERIAL BALANCE

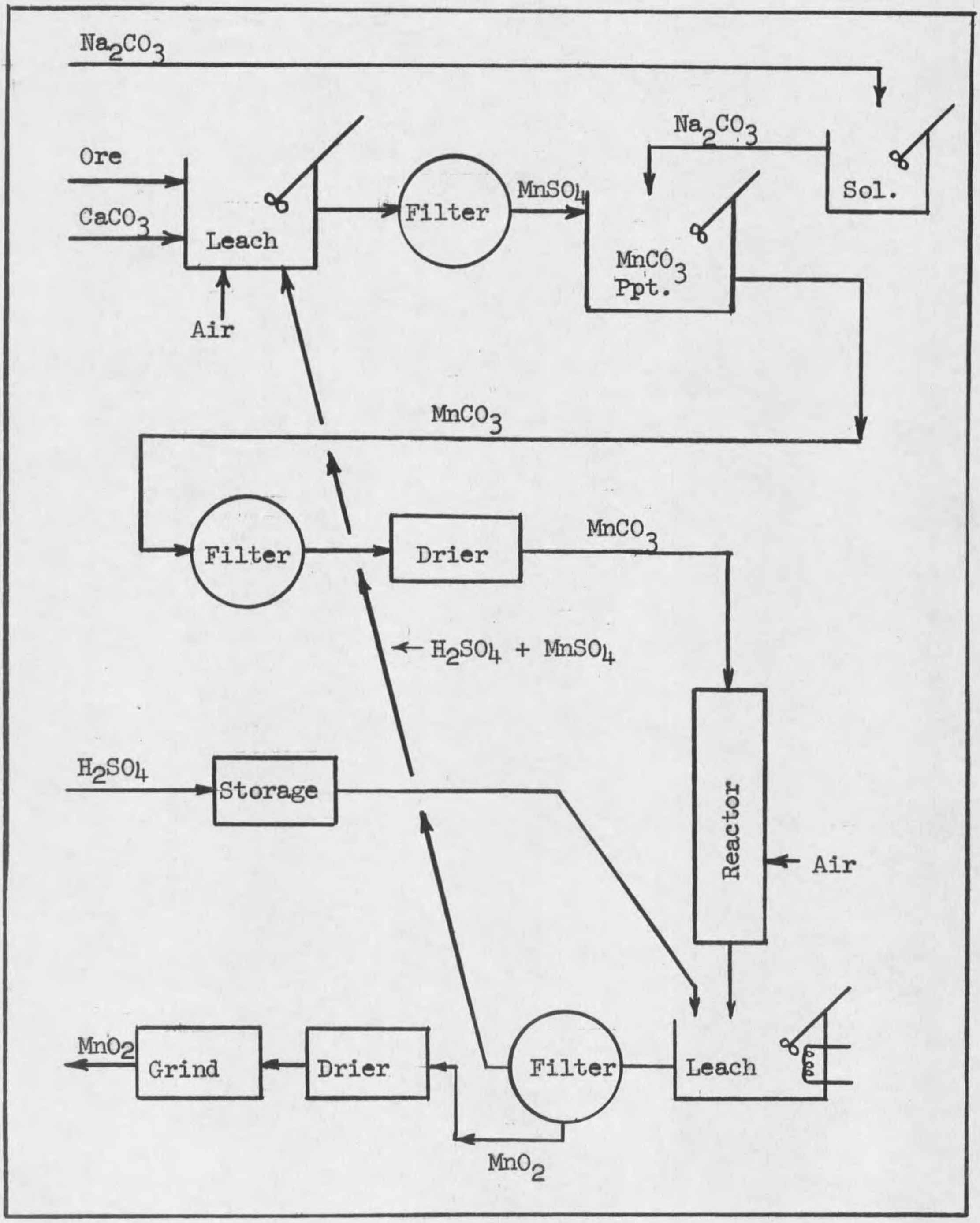

Figure 2

FLOW DIAGRAM

APPARATUS

The reactor (Figure 3) was made from a four foot length of stainless steel pipe wrapped with heating coils of nichrome wire in ceramic beads. Inside the reactor, one foot from the bottom, was a fine mesh stainless steel screen used to support the carbonate and disperse the air. A six inch length of two-inch black iron pipe was used at the top for dust de-entrainment and a two-inch pipe union was used for a top seal. The whole reactor was mounted on a pivot so that it could be tipped upside down for unloading. Air from the 60 psig. laboratory supply entered the bottom of the reactor via a pressure regulator to control reactor pressure and left the reactor via a water scrubber to remove dust, a needle valve to control air rate, and a wet test meter to measure total air volume. In the case of atmospheric pressure runs, air rate was controlled by a needle valve preceding the reactor. The air velocity was calculated in feet per minute based on the free reactor cross section and the actual reaction temperature and pressure. The conversion from linear air rate to standard cubic feet of air per hour was

$$\text{SCFH.} = \frac{84\ P \times A}{T}$$

where T = temperature in degrees Kelvin

P = pressure in atmospheres

A = air rate in feet per minute

Reactor pressure was expressed in atmospheres at the elevation of Bozeman, Montana--approximately 12.5 pounds per square inch.

The control of temperature was found to be difficult. Power was supplied to three separate heating coils through three 120 volt variacs. The lower foot of the reactor, the air preheat section, was heated with one coil, the middle two feet or reaction zone by a second coil, and the top section by a third coil. Temperature was measured by two thermocouples, one fixed three inches below the screen separating the air preheat section and the reaction section, and the other entering from the top projected down into the reaction section. The thermocouple entering from the top could be moved up and down so that a longitudinal temperature cross section of the reaction zone could be measured. Two examples of temperature cross sections are shown in Figure 4. With the difference in temperature between runs being 25° C., the variation along the carbonate bed was a good proportion of the temperature difference between runs. So that one run could be compared with another, the temperature in the reaction zone was always measured six inches from the bottom of the reaction zone. In this way, the temperature readings could be reproduced from one run to another.

This variation in temperature along the reaction zone also demonstrated that the carbonate did not fluidize.

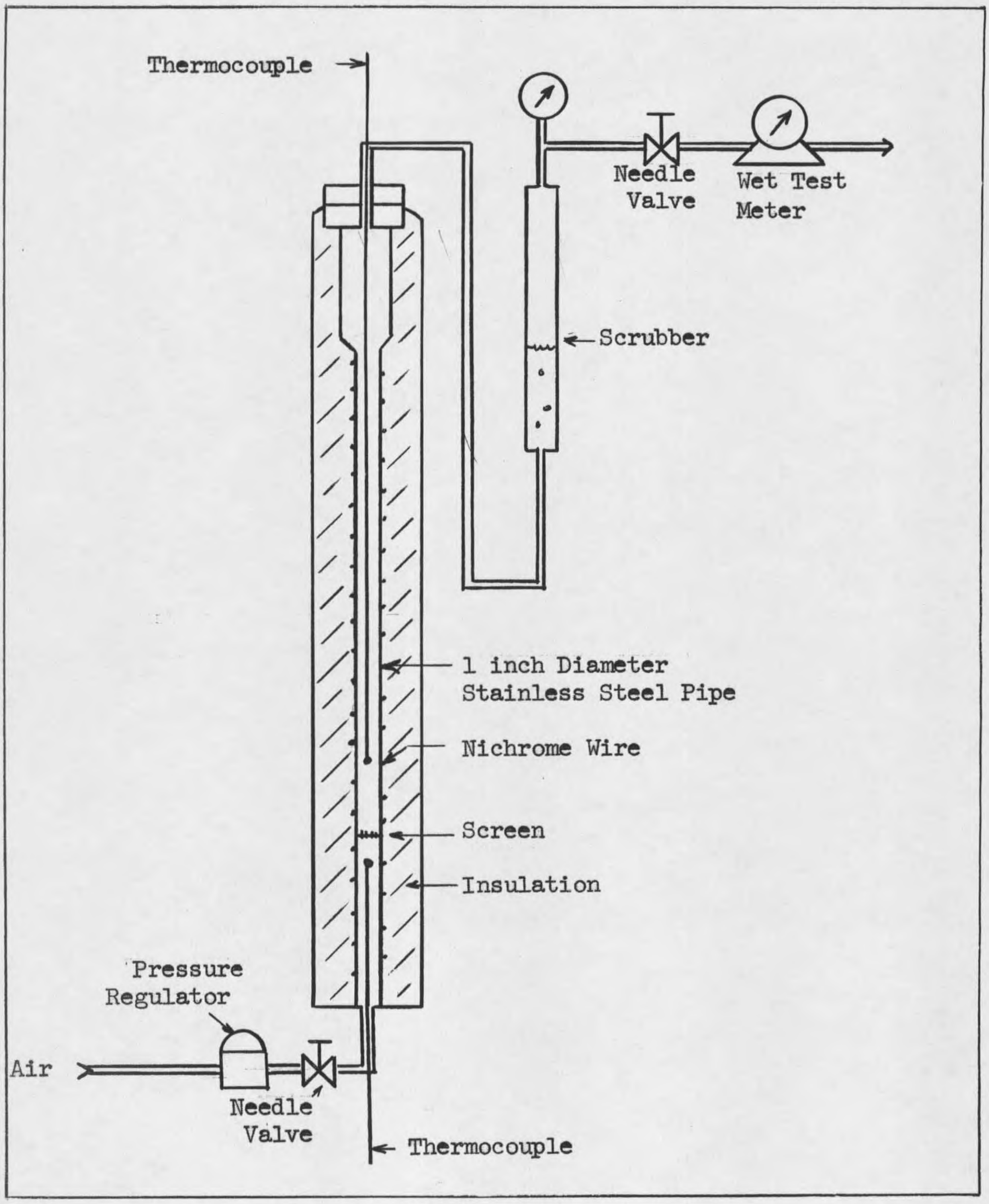

Figure 3

REACTOR

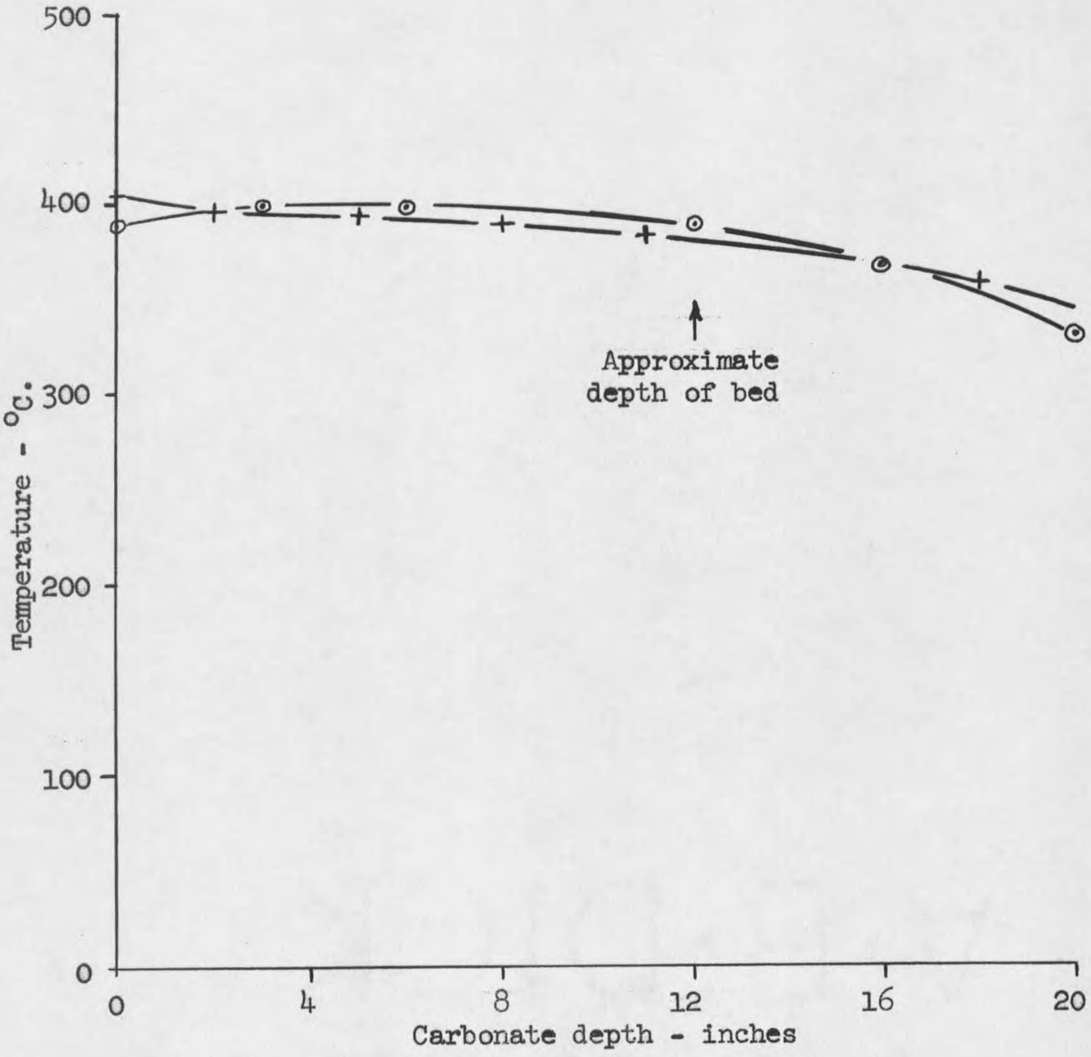

Figure 4

TYPICAL LONGITUDINAL TEMPERATURE

CROSS SECTIONS OF REACTOR

PRELIMINARY RUNS

In order to establish the general feasibility of the anticipated synthesis of manganese dioxide, and to give some indication of the variables which effect the process, a group of preliminary runs were made. The first runs consisted of oxidizing chemically pure manganese carbonate in a quartz reactor. Essentially, the reactor was a 5/8 inch diameter quartz tube, two feet long, wrapped with nichrome wire for heating, and having a porous glass plate part way up the tube to disperse the air through the carbonate. After some experimentation it was found that 300° C. and two standard cubic feet of air per hour were reasonable operating conditions. About twenty 16-hour runs were made at these conditions with 55 grams of chemically pure manganese carbonate per run. Half of the product from these runs was leached and drain tests were made on batteries from both the leached and unleached material (samples A04 and A04L of Table II). High drain capacity was 5.3 hours for unleached and 7.1 hours for leached material, corresponding low drain capacities were 106 and 124 hours and delayed capacities were 75 and 127 hours. This manganese dioxide was also used in blends with Philipsburg ore (page 79). These first few runs were encouraging from both the quality and the yield standpoint and had shown that air oxidation in this type of reactor was possible.

Acid leaching was shown to be important to remove the lower oxides of manganese as well as unreacted carbonate. Although the reactor was designed for a fluidized bed, it was apparent from watching a reaction that the carbonate did not fluidize. Channelling occurred to the extent that no mixing was evident. The carbonate was porous and all parts eventually oxidized to a fairly uniform composition, resulting in good conversion (80 percent yield from the acid leach).

Due to the encouraging results with the quartz tube reactor, a larger, stainless steel reactor (Figure 3) was built which had better temperature control, air rate control, and the ability to be run under pressure. The first question posed by the use of a steel reactor, other than the question of whether or not it would work, was whether or not reaction in a steel reactor would have a deleterious effect on the quality of the manganese dioxide. The anticipated source of trouble would have been caused by corrosion of the reactor resulting in the contamination of the product with metals--nickel being the most serious possible contaminant.

The first few runs in the steel reactor were made with chemically pure carbonate identical to that used in run A04L and at similar conditions except that 30 psig. air pressure was used. The data from these runs are contained in Tables I and II. Runs 1 and 3 showed similar conversion, and initial drain tests that were only slightly poorer than A04L. The delayed capacity turned out to be much poorer for reasons which, in the light of subsequent runs, could not be attributed to the reactor. Run 2 had a low yield due to poor control of the reactor temperature, which was common during the first few runs until some experience had been gained in the operation of the reactor.

More than twenty preliminary runs (Tables I - IV) were made with the steel reactor to test the reactor, gain an idea of the effect of the process variables, and to observe the effect of using various carbonates. The range of investigation was from 300° C. to 500° C. for temperature, 0 to 30 psig. pressure, 6 to 48 hours reaction time, 2.4 to 7.2 standard cubic feet per hour air rate, and three different carbonates, but there was no distinct design to these runs.

The carbonates used were a chemically pure carbonate and two (ANA-1 and ANA-2) made from rhodochrosite ore. Qualitative spectrographic analyses of these carbonates are included in Table XV. ANA-1 was high in iron, sodium, calcium, and magnesium compared with C.P. and with ANA-2. In ANA-2 iron removal was improved by sparging air into the solution for a longer time with better mixing and the sodium content was reduced by adding the sodium carbonate as a solution, not as a solid. The greatest difference noted between C.P. carbonate and synthesized carbonate was in the yield of manganese dioxide at a given set of reaction conditions.

These preliminary runs had demonstrated that:

1. Air oxidation had a reasonable chance for success.

2. A steel reactor was not unusually detrimental to the manganese dioxide.

3. Temperature had a distinct effect on yield. (Runs 4 and 5, Table I).

4. Reaction time, pressure, and air rate had a less pronounced effect on yield.

5. Charge size was not important in range tried (Table IV). The first runs, 19 and 24, to test this, seemed to show an effect which the others did not confirm.

6. Yield varied with the different carbonates.

7. Drain tests from runs on synthesized manganese carbonate in which enough material was made to make batteries were, in general, poorer than C.P. but not discouragingly so.

Since yield was found to vary most, and since batteries could not be made if the yield was poor, the variables affecting yield were studied first in the endeavor to raise yield up to a value near that observed for chemically pure carbonate. As yield was studied, batteries were made from the dioxide produced so that the effect of these variables on battery quality was also observed, but the experiments were designed primarily to study yield.

Table I

YIELD DATA - PRELIMINARY RUNS 1 - 18

Run	Temperature °C.	Time hrs.	Pressure atmos.	Air Rate ft./min.	Charge Material	Yield From Leach percent
A04	300	--	1.0	--	C.P.	80
1	300	6	3.4	4	C.P.	80
2	300	6	3.4	4	C.P.	47
3	300	6	3.4	8	C.P.	77
4	300	6	1.0	13	ANA-1	17
5	400	6	1.0	15	-1	43
8	400	18	1.0	15	-1	43
9	400	12	3.4	14	-1	--
10	500	6	3.4	14	-1	57
11	400	16	3.4	14	-1	52
12	400	6	1.0	15	-1	48
13	400	--	1.0	15	C.P.	--
14	400	6	1.0	15	C.P.	42
15	300	48	3.4	12	ANA-1	21
16	300	6	1.0	4	ANA-2	36
17	300	6	3.4	12	-2	30
18	300	24	3.4	12	-2	30

Table II

DRAIN TESTS - PRELIMINARY RUNS 1 - 18

Run	Temperature °C.	Carbonate	Wetting Solution ml.	Bobbin Weight g.	High Drain hrs.	Low Drain hrs.	Delayed Capacity hrs.
A04	300	C.P.	20.0	9.4	5.3	107	77
A04L	300	C.P.	17.1	9.6	7.2	125	127
1	300	C.P.	15.7	9.0	6.0	116	44
3	300	C.P.	16.7	9.0	6.3	113	100
9	400	ANA-1	16.7	9.1	6.4	115	70
10	500	ANA-1	13.5	9.4	4.3	52	0
5+12	400	ANA-1	16.8	9.1	6.6	111	106

Table III

EFFECT OF LEACHING ON DRAIN TESTS

Run	Comment	High Drain hrs.	Low Drain hrs.	Delayed Capacity hrs.
A04	Unleached	5.3	106	75
	Leached	7.1	124	127
6	Unleached	1.4	50	25
	Unleached	3.5	66	28
	Leached	6.4	116	70

Table IV

EFFECT OF CHARGE SIZE

Run	Charge Weight	Yield by Leach	Wetting Solution	Bobbin Weight	High Drain	Low Drain	Delayed Capacity
21	200	63.0	14.6	9.2	7.1	120	88
31*	150	61.0	22.6	8.3	5.0	89	67
23	200	50.5	17.4	9.1	6.5	116	64
33**	150	48.4	15.8	9.2	6.4	106	65
24***	200	40.6	15.8	9.2	7.1	120	90
19	150	56.0					

* Drain tests are for a mixture from runs 31 and 43 which differ in air rate and in carbonate.

** Drain tests from mixture of 33 and 44.

*** Runs 24 and 19 combined for making batteries.

EFFECT OF REACTION VARIABLES ON YIELD - RUNS 31 - 50

The effect on yield of the four independent reaction variables of temperature, time, pressure, and air rate was studied. The experimental design was of the "method of steepest ascent" type first discussed in detail by Box and Wilson (4). Essentially, Box and Wilson outlined a systematic approach to the problem of empirically establishing the location of a set of operating conditions that give a maximum or optimum yield. A brief discussion of the method applied to this problem is contained in the appendix, the reading of which may assist in following the material in this section.

Based on the results of the preliminary runs and experimental convenience, the levels of the factors listed below were selected for study.

Levels of Factors

	-1	0	+1	Unit
Temperature	350° C.	375° C.	400° C.	25° C.
Time	4 hours	6 hours	8 hours	2 hours
Pressure	2 atmos.	2.5 atmos.	3 atmos.	0.5 atmos.
Air Rate	12 ft./min.	15 ft./min.	18 ft./min.	3 ft./min.

A complete 2^4 factorial of the high and low levels of these factors plus four runs at the center point--twenty runs in all--were made. The runs were divided into blocks of ten each. Each block of ten runs, assuming a linear response, would have had the same mean and thus differences in block means could have been attributed to changes that occurred as the runs progressed.

Carbonate for these runs was being made in batches of approximately 8 pounds at a rate of one batch per week. When the runs started, batches 2, 3, and 4 were mixed and used for the first block. Batches 5 and 6 were completed and added to the other for the remainder of the runs (block two). Every batch of carbonate was made in the same manner; therefore, it was expected that each would be the same and no change in the results would occur because of adding the carbonate from batches 5 and 6. However, the carbonate from batches 5 and 6 was added between blocks of runs so that any effect due to this change in carbonate could be detected. Unfortunately, or possibly fortunately, the change in carbonate was found to have considerable effect.

The results of these twenty runs is given in Table V, expressed as percent yield from the acid leach and as percent available oxygen content. The average ratio of oxygen analysis to leach was 0.89 ± .12. Since this ratio was fairly constant, the two methods of measuring yield led to similar conclusions, and it was decided that available oxygen content, believed to be more reliable, would be used for the analysis of the results. The estimated regression equation for percent oxygen was found to be:

$$Y = 45.97 + 6.23 B_i + 8.43 X_T + 1.78 X_\theta + 0.74 X_P - 0.96 X_A$$

or in terms of the factors themselves, the estimated regression equation would be:

$$Y = 45.97 + 6.23\,B_i + 8.43\left[\frac{T - 375}{25}\right] + 1.78\left[\frac{\theta - 6}{2}\right]$$

$$+\,0.74\left[\frac{P - 2.5}{0.5}\right] - 0.96\left[\frac{A - 15}{3}\right]$$

From the analysis of variance (Table VI) several conclusions regarding the estimated regression equation were made. Since the mean square attributable to blocks was large, there was apparently a definite effect on yield due to the carbonate change from block one to block two (12.5 percentage points change). The estimate of error mean square from the four center points and the mean square for lack of fit were similar, indicating that a linear regression adequately described the results. The estimate of the standard deviation of the regression coefficients was 1.20, which was as large or larger than three of the coefficients. This would mean, in a test of significance, that there was no evidence that these coefficients were different from zero. They were the best estimates available, however, and for lack of evidence that they were zero, were used.

To give an idea of the relative effect of the various factors, the estimated change in their level which would result in a one percentage point change (say from 46 to 47 percent) in available oxygen content of the product within the experimental region was:

ΔT = 3.0° C. or + 0.118 units
$\Delta \Theta$ = 1.1 hours or + 0.562 units
ΔP = 0.7 atmospheres or + 1.35 units
ΔA = 3.1 feet per min. or - 1.04 units

That is, a 3.0° C. change in temperature was found to change yield as much as 1.1 hours change in reaction time. These runs showed that temperature was the most important variable, as expected, with time, pressure, and air rate having a lesser effect. Increases in temperature, time, and pressure increased yield; however, the lower air rate seemed to have been better.

The difference between the two blocks of runs was not anticipated and was undesirable, but pointed out the necessity of studying carbonate synthesis. The average yield from block one was 12.46 percentage points (39.74 vs. 52.19 percent oxygen) lower than block two. As block one was run first, some difference could be due to improved technique, changes in the equipment or such, but the most likely difference was in the change in carbonate as previously mentioned. Unfortunately, the carbonates were mixed before the effect was observed and thus little information about the differences in carbonate was available.

Additional experiments were conducted in which carbonate synthesis was varied (page 46). In order to preserve continuity of the discussion of temperature, time, pressure, and air rate, further discussion of carbonates is deferred. Since the results were adequately described by a linear model, it was concluded that an optimum did not lie within the region studied. To have contained an optimum the yield surface would have been curved, resulting in a poor fit for a linear equation. From the regression equation the path of steepest ascent was calculated as follows.

Temperature	Time	Pressure	Air Rate	Est. Yield
375	6.00	2.50	15.00	52.2
400	6.42	2.54	14.66	59.5
425	6.84	2.59	14.62	66.8
450	7.27	2.63	13.98	74.1
475	7.68	2.68	13.64	81.4

Considering the estimated yields along the path, it is obvious that the path of ascent can not be extrapolated much beyond the region of the experiment or it would lead to an absurd conclusion. Within the region this path was the best route to follow into a new region of experimentation. In this experiment, the estimated path of steepest ascent has been biased due to the disproportionately large effect of temperature, since the calculation of the steepest path assumed that all variables were of equal importance.

This first set of runs indicated a need for a second set of runs in a region of expected higher yield having a center point selected along the path of steepest ascent. In the first set of runs the estimated coefficients of air rate and pressure had been small in comparison to error which could have been because the effects were actually small or the range of variation was too small (which amounts to the same thing), or that the range of variation was near the optimum where the effects were tapering off. Consequently, the ranges of pressure and air rate were increased so that these factors would have a better chance of showing an effect. The range of temperature was kept the same since a tapering off for this factor was anticipated and the range of time was kept the same, since at higher temperature the time effect was expected to be comparable with the others. The conditions selected for the new set of runs were

	-1	0	+1	Unit
Temperature	425° C.	450° C.	475° C.	25° C.
Time	5 hours	7 hours	9 hours	2 hours
Pressure	1 atmos.	2 atmos.	3 atmos.	1 atmos.
Air Rate	8 ft./min.	16 ft./min.	24 ft./min.	8 ft./min.

Table V

YIELD DATA

Yield - Percent Oxygen - Runs 31 - 50

		Temperature					
		350° C.		375° C.		400° C.	
Air Rate ft./min.	Pressure atmos.	Time-hours		Time		Time	
		4	8	6	6	4	8
12	2.0	23.7	46.4*			57.5*	47.8
18		41.4*	36.3			49.6	53.3*
15	2.5			46.2	53.6*		
15				58.0*	37.6		
12	3.0	30.1	48.2*			62.2*	53.7
18		39.6*	28.8			43.6	61.7*

Yield - Acid Leach - Runs 31 - 50

		Temperature					
		350° C.		375° C.		400° C.	
Air Rate ft./min.	Pressure atmos.	Time		Time		Time	
		4	8	6	6	4	8
12	2.0	26.7	51.0*			63.5*	53.6
18		46.7*	39.0			54.5	65.0*
15	2.5			51.0	64.0*		
15				60.2*	41.0		
12	3.0	33.2	54.0*			67.0*	61.0
18		51.2*	32.4			48.4	67.5*

*Runs in Block II

Table VI

ANALYSIS OF VARIANCE

PERCENT AVAILABLE OXYGEN - RUNS 31 - 50

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square
Blocks (Carbonate)	775.0	1	775.0
Due to Regression	1211.6	4	302.9
Lack of Fit	221.9	12	18.5
Error	46.7	2	23.3
TOTAL	2255.2	19	

Estimated standard deviation of a regression coefficient =

$$\sqrt{\frac{23.33}{16}} = 1.20$$

Table VII

SUMMARY OF YIELD DATA FROM RUNS 31 - 50

		Percent Oxygen	Standard Deviation	Yield from Leach	Standard Deviation
Temperature	350° C.	36.8	1.70	41.8	1.89
	400° C.	53.7	"	60.1	"
Time	4 hrs.	43.5	1.70	48.9	1.89
	8 hrs.	47.0	"	52.9	"
Pressure	2.0 atmos.	44.5	1.70	50.0	1.89
	3.0 atmos.	46.0	"	51.8	"
Air Rate	12 ft./min.	45.2	1.70	51.3	1.89
	18 ft./min.	44.3	"	50.6	"
Center Points		48.9		54.1	
Block I		39.7		44.1	
Block II		51.2		59.2	
TOTAL		46.0		51.6	

EFFECT OF REACTION VARIABLES ON YIELD - RUNS 61 - 70

The second set of runs was similar to the first set except that a half replication of the 2^4 factorial was run instead of the full factorial. This cut the number of runs in half, saving considerable time, but reduced the chance of determining the actual effects of the variables. The results for these runs are given in Table VIII, presented as percent available oxygen and as yield from acid leach. The mean of the runs was increased to 60.3 percent oxygen compared to 46.0 percent in the first set. The highest yield was 70.5 percent, where 90 percent would correspond, approximately, to complete conversion. The estimated regression equation was

$$Y = 60.3 + 2.78\,X_T - 0.35\,X_\theta + 4.58\,X_P + 3.55\,X_A$$

or

$$Y = 60.3 + 2.78\left[\frac{T - 450}{25}\right] - 0.35\left[\frac{\theta - 7}{2}\right] + 4.58\left[\frac{P - 2}{1}\right] + 3.55\left[\frac{A - 16}{8}\right]$$

The estimated standard error of the regression coefficients was 0.67 compared to 1.20 for the previous estimate where four runs were made at the center point instead of two at the center. An analysis of variance (Table XIX) revealed that the degree of fit was not significant. A comparison of error mean square and lack of fit indicates that a linear model did not adequately describe the data. Since a linear equation did not fit the results, the proper procedure would have been to finish the other half of the factorial and again test for linearity.

If the data still failed to fit a linear regression, one would assume that the response surface was curved and make additional runs so that the response could be described in terms of a quadratic regression equation from which an estimate could be made as to the location of the optimum conditions.

It was believed that the second group (runs 61 - 70) was in a region of maximum yield, but the additional runs to show this were not made. This conclusion about the region was based on the observation that the effect of time was to increase yield for the lower temperature but to decrease yield at the upper temperature, while the overall effect of temperature was reduced from that of the previous runs. In general, higher air rate was better for low pressure, but had no effect at high pressure. High pressure seems to have been better. It was postulated that a region was being approached such that there was an optimum time for a given temperature provided the product of air rate and pressure, which determines the total quantity of air, were above a certain minimum. There was some indication that it might be better to use a high pressure and a low air rate. The conclusion was that above an air rate and pressure product of 24, corresponding to about 2.8 standard cubic feet of air per hour per 150 grams of carbonate charge, an optimum time existed for a given temperature. An upper limit for temperature or pressure was not indicated. The best yield in the range studied was 70.5 percent oxygen content. Runs to confirm the above postulate were not made since it was more important to investigate carbonate synthesis and the quality of the manganese dioxide being produced.

These experiments showed that one may reasonably expect to produce manganese dioxide having 65 to 70 percent available oxygen from carbonate similar to sample ANA-6. Without further runs, the best estimate of the proper conditions was

Temperature	475° C.
Time	7 hours
Pressure	3 atmos.
Air Rate	16 ft./min.

Table VIII

YIELD DATA

Yield - Percent Oxygen - Runs 61 - 70

		Temperature					
		425° C.		450° C.		475° C.	
		Time		Time		Time	
Air Rate ft./min.	Pressure atmos.	5	9	7	7	5	9
8	1.0	45.4	--			--	49.6
24		--	61.0			64.7	--
16	2.0			--	60.3		
16				63.0	--		
8	3.0	--	60.5			70.5	--
24		62.3	--			--	66.5

Yield - Acid Leach - Runs 61 - 70

		Temperature					
		425° C.		450° C.		475° C.	
		Time		Time		Time	
Air Rate ft./min.	Pressure atmos.	5	9	7	7	5	9
8	1.0	49.3	--			--	54.5
24		--	70.2			71.5	--
16	2.0			--	65.3		
16				70.5	--		
8	3.0	--	68.2			79.2	--
24		67.2	--			--	74.4

Table IX

ANALYSIS OF VARIANCE

PERCENT AVAILABLE OXYGEN - RUNS 61 - 70

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square
Due to Regression	330.85	4	82.71
Lack of Fit	177.80	4	44.45
Error	3.65	1	3.65
TOTAL	512.30	9	

Estimated standard deviation of a regression coefficient =

$$\sqrt{\frac{3.65}{8}} = 0.67$$

Table X

SUMMARY OF YIELD DATA FROM RUNS 61 - 70

		Percent Oxygen*	Yield from Leach
Temperature	425° C.	57.3	63.7
	475° C.	62.8	69.9
Time	5 hrs.	60.7	66.8
	9 hrs.	59.5	66.7
Pressure	1 atmos.	55.2	61.3
	3 atmos.	65.0	72.3
Air Rate	8 ft./min.	56.5	61.6
	24 ft./min.	63.6	72.0
Center Points		61.6	67.9
TOTAL		60.3	66.3

* An estimate of standard error is not included since it would have to be based on one degree of freedom.

CARBONATE RUNS

During the preliminary runs and runs 31 - 50, it was observed that the carbonate had considerable influence on the results. Chemically pure carbonate readily reacted at 300° C., whereas none of the carbonates synthesized in the laboratory reacted as well at temperatures less than 475° C. Also, ANA-1 was much poorer than the others and a mixture of batches 2, 3, and 4 reacted less readily than a mixture containing batches 2 through 6. Samples of C.P., ANA-1, a mixture of ANA-2 and 4, ANA-5, and ANA-6 were given a qualitative spectrographic examination to see if the difference between carbonates could be detected. The results of these analyses are given in Table XV. In fairness to the chemical manufacturer, it should be mentioned that the C.P. manganese carbonate had been ball milled by a previous graduate student on this project, which accounts for the relatively high impurities such as silicon. A comparison of the C.P. carbonate with the others showed a lower analysis of calcium, magnesium, and sodium, similar amounts of copper, lead and zinc, and lower iron than all but ANA-5. From these analyses a few trends were suspected. As sodium, calcium, and magnesium analysis went up, yield went down. Also, but less definite, there was a tendency for yield to go down as iron analysis went up. The impurities which seemed most interesting to study further were iron and sodium.

To study the effect of carbonate synthesis, four additional samples of carbonate were made with varying amounts of impurities.

Ore was leached in the usual manner and iron was removed from half the manganese sulfate. The two sulfate solutions were further divided in half and manganese carbonate precipitated. One batch from each was filtered without washing and the other washed several times to remove sodium sulfate. The four samples then represented two with high iron content and two with high sodium content. One sample with high sodium also had high iron and the other sample with high sodium had low iron. The spectrographic analysis of these carbonates is presented in Table XV and a quantitative analysis for sodium and iron in Table XIV. The spectrographic analysis showed all samples to be the same, which was not unreasonable since the accuracy of such an analysis is generally considered to be within a factor of 10 and should only be used for trace elements. The quantitative analysis confirmed the general levels of the impurities that were desired. Sodium content reflected poor washing and indicated the general presence of salts, and iron content reflected the efficiency of iron removal. Iron removal was not as efficient as in the previous batches due to the fact that the stirrer failed and iron was precipitated without mixing. The difference in sodium content between batches was not as large as expected considering the amount of dilution during the successive decantations, indicating that sodium salts were occluded with the manganese carbonate precipitate. It was also observed that the physical properties of these carbonates varied, especially in regard to color and fluidity or fluffiness. A correlation of these physical properties with yield was not attempted, but it is quite likely that the main difference between carbonates was in their structure.

Six runs were made with each of the carbonates and with the same carbonate used in runs 41 - 50 and 61 - 70. Three runs were made at 400° C. and three at 450° C., all with 6 hours reaction time, 3 atmos. pressure, and 18 ft./min. air rate. The experiment was initially considered and analyzed as a completely randomized design with five treatments (carbonates) and three replicates, where the two temperatures were considered separate experiments. The results of the runs are contained in Table XI and the analysis of the variance in Table XII. A brief discussion of the rationale of this experiment is contained in the appendix.

Individual comparisons were also made between ANA-6 (the standard) and the others, between 7 and 8 vs. 9 and 10 (high iron vs. low iron), 7 and 9 vs. 8 and 10 (high sodium vs. low sodium), and between 7 and 10 vs. 8 and 9 (the interaction for a factorial design). Note that this was not strictly a factorial design because the levels of sodium and iron could not be controlled precisely. By the analysis of variance it was shown that a significant difference existed for carbonates and all comparisons except one. The conclusion that there was a difference between carbonates can not be questioned, nor that ANA-6 was better than the average of the others; but note that ANA-8 was also as good or better than ANA-6, while the others tended to be much poorer. The high value of ANA-8 resulted in the other comparisons being significant. The apparent conclusion was that high iron was better and low sodium was better. These conclusions did not seem rational. The individual comparisons were made on an "a priori" basis assuming that just two levels of iron and sodium--high and low--would be present. The quantitative analysis made after this analysis of variance showed that the assumption of high and low levels was only partially correct. After the iron and sodium analyses were made and it was apparent that sodium and iron varied considerably, it was decided to try to correlate yield with the iron and sodium content. Linear regression equations were estimated for yield as a function of iron and sodium as follows:

$$Y_{400^\circ\ C.} = 82.6 - 1.6\ (Fe) - 54.9\ (Na)$$

$$Y_{450^\circ\ C.} = 70.6 + 2.3\ (Fe) - 29.1\ (Na)$$

An analysis of variance of these results is presented in Table XIII along with the appropriate "F" ratios to test the hypothesis that the true regression coefficients were zero. It was found that the hypothesis could be rejected at the 95 percent confidence level. Thus, a significant proportion of the variation in yield was associated with the analysis of carbonate, sodium being the only variable of importance for a range of sodium from 0.41 to 0.93 percent. Although the correlation was significant, it was not exceptionally good, i.e., ANA-10 had the poorest yield with a sodium content in the middle of the range. A slight extrapolation of the equation at 400° C. to a sodium analysis of 1.5 percent would mean zero yield and extrapolation to zero sodium would give around 80 percent yield.

These equations give an indication of the large effect associated with sodium, but would be poor to use for predicting results. Essentially, it has been shown that poorer yields are associated with higher sodium analysis and that iron content does not have a significant effect on yield. Actually it was unlikely that the presence of sodium was in itself the prime cause of poor conversion. It is more logical to assume that sodium was associated with the general level of the salt content of the carbonate which had an effect on the carbonate such that the rate of reaction was reduced. Such an assumption was supported by the general effect of temperature which was to raise yield for the poorer carbonates, but not for the better carbonates.

In addition, the effect of temperature noted in these runs was considered to be further confirmation of the trend observed during runs 61 - 70 in which a leveling off of yield was noted. The yield for ANA-6 at 400° C. was 61.8 compared to 58.7 percent for appropriate runs from 31 - 50. At 450° C. the yield was 61.6 percent which was identical with that of the center points of runs 61 - 70.

Table XI

YIELD DATA FROM CARBONATE STUDY

Temperature	Carbonate	Oxygen Analysis Replicates			Average	Yield from Leach
		1	2	3		
400° C.	ANA-6	59.6	64.1	63.0	62.2	60.5
	ANA-7	32.2	38.5 38.1*	31.6 31.2	34.1	42.5
	ANA-8	63.3	62.9 63.2	63.4	63.2	75.5
	ANA-9	33.5	35.0 34.7	35.7	34.7	39.0
	ANA-10	29.7 29.1	26.4 27.2	34.7 37.4	30.7	37.5
450° C.	ANA-6	61.2 63.2	63.2	60.5	61.6	72.2
	ANA-7	52.8	51.6	56.5	53.6	64.2
	ANA-8	61.4	61.1	63.0	61.8	77.0
	ANA-9	41.2 40.0	47.8	42.6	43.8	50.0
	ANA-10	50.1	53.3	46.0	49.8	58.0

* Lower numbers are duplicate analytical determinations of the same sample.

Table XII

ANALYSIS OF VARIANCE

EFFECT OF CARBONATE ON YIELD

Source of Variation	Degrees of Freedom	Mean Squares		Expected Mean Squares
		400°C.	450°C.	
Carbonates	4	778.7*	174.5*	$\sigma^2_{\alpha\beta} + \frac{3}{4} \sum \beta^2$
Comparisons:				
6 vs. others	1	1108.5*	209.8*	$\sigma^2_{\alpha\beta} + \frac{3}{20} (4\beta_1 - \beta_2 - \beta_3 - \beta_4 - \beta_5)^2$
7 + 8 vs. 9 + 10	1	750.5*	356.4*	$\sigma^2_{\alpha\beta} + \frac{3}{4} (\beta_2 + \beta_3 - \beta_4 - \beta_5)^2$
7 + 9 vs. 8 + 10	1	480.0*	149.8*	$\sigma^2_{\alpha\beta} + \frac{3}{4} (\beta_2 + \beta_4 - \beta_3 - \beta_5)^2$
7 + 10 vs. 8 + 9	1	811.8*	3.9	$\sigma^2_{\alpha\beta} + \frac{3}{4} (\beta_2 + \beta_5 - \beta_3 - \beta_4)^2$
Error	10	4.8	7.0	$\sigma^2_{\alpha\beta}$
TOTAL	14			

* Significant at 95 percent confidence level.

Table XIII

ANALYSIS OF VARIANCE - REGRESSION EQUATIONS

EFFECT OF CARBONATE ON YIELD

Source of Variation	Sum of Squares		D.F.	Mean Squares	
	400° C.	450° C.		400° C.	450° C.
Due to Regression	1794	508	2	897*	254*
Lack of Fit	1420	282	12	118	24
TOTAL	32.4	790	14		

"F" RATIOS

400° C.	7.6
450° C.	10.6
$F_{.05}(2, 12)$	3.88

* Significant at 95 percent confidence level.

Table XIV

SUMMARY OF YIELDS FROM CARBONATE STUDY

Carbonate	Analysis		Average Oxygen Analysis	
	Iron	Sodium	400°C.	450°C.
ANA-6	0.30	0.51	62.2	61.6
ANA-7	1.90	0.83	34.1	53.6
ANA-8	1.58	0.41	63.2	61.8
ANA-9	0.68	0.93	34.7	43.8
ANA-10	0.81	0.59	30.7	49.8

Estimated Standard Deviation of Average Oxygen

Analysis = 1.90

Table XV

QUALITATIVE SPECTROGRAPHIC ANALYSIS OF CARBONATES - PERCENT

	Carbonate								
	C.P.	ANA-1	ANA-2, 3, 4	ANA-5	ANA-6	ANA-7	ANA-8	ANA-9	ANA-10
Used in Runs	1,2,3, 13, 14	4-12, 15	21-40	*	*	**	**	**	**
Calcium	0.010	I	0.500	0.100	0.100	0.100	0.100	0.100	0.100
Magnesium	0.010	I	I	0.500	0.500	0.500	0.050	I	0.500
Silicon	I	I	1.000	1.000	0.500	0.500	0.500	0.500	0.500
Iron	0.005	0.500	0.005	0.001	0.050	0.500	0.500	0.500	0.500
Copper	0.005	0.005	0.001	0.001	0.005	0.005	0.005	0.005	0.005
Lead	0.005	0.001	0.001	0.005	0.005	0.005	0.005	0.005	0.005
Zinc	0	0.100	0.050	--	0.050	0.100	0.100	0.100	0.100
Sodium	0	0.500	0.100	0.010	0.100	0.100	0.100	0.500	0.100

Aluminum 0.500, Potassium 0.100, Nickel 0, Titanium 0.001, Strontium 0.050, Molybdenum 0--for all carbonates analyzed.

I Intermediate concentration.

* Carbonate batches 2, 3, 4, 5, and 6 mixed and used for runs 41 on.

** Used for study of carbonate variables.

DRAIN TESTS FROM RUNS 31 - 50

The discussion of drain tests, except for the preliminary runs, has been left until the discussion of yield had been covered. However, as manganese dioxide was produced, batteries were made and tested. In the set of runs 31 - 50, the yields were generally too low for making a set of batteries from each run; consequently, the product from two runs was combined to make enough dioxide for batteries. As pointed out previously, the runs were made in two different blocks arranged as shown by Table V, where the starred values are from block two and the unstarred are from block one. Note that for each starred run an unstarred run differs only in the air rate. The blocks were set up in this manner since it was expected that air rate was the least likely to affect the quality where phase type would be the most important variable for a given starting material. Thus, product from two runs differing only in air rate could be combined for making batteries. Drain tests on these batteries gave a comparison of reaction temperature, time, and pressure averaged over air rate and blocks. Data from these battery tests are presented in Table XVI.

Before discussing these tests, and their shortcomings, there is one point the author would like to make. The runs from which these batteries were made were designed to study yield and not quality. Considerable information about quality was learned, but not as much as if the runs had been designed to study quality.

The experiment was analyzed as a 2^3 factorial of temperature, pressure, and time with subsampling since two batteries were tested from each set. The analyses of variance for the three different drain tests are included in Table XVII. Since there was no provision for replication, an estimate of error (variation between sets of batteries with the same treatment) was not available.

Tests of significance are, therefore, not possible. The analysis of variance shows, however, that for all three drain tests (high, low, and delay) the largest source of variation was attributable to temperature, with lower temperature being an advantage. A consideration of the data of Table XVI shows one variable that has not been considered that may have contributed to this result. When making a battery, the quantity of wetting solution added to the manganese dioxide was arbitrary. Note that wetting solution varied from 15.7 ml. to 23.0 ml. and that the two batteries with poorest drain tests contained the most wetting solution. The reaction conditions for these batteries were 400° C., 4 hours, and 2 atmos. pressure, and 400° C., 8 hours, and 3 atmos. pressure. If wetting solution did contribute to the poor drain tests then the effect would have been cancelled out for time and pressure, but not for temperature, forcing the variance due to temperature to increase. Figure 5 was prepared to illustrate the effect of wetting solution on drain tests.

Little correlation between wetting solution and drain tests was shown, tending to confirm that the higher temperature runs produced poorer depolarizer. The large variation in wetting solution casts doubt on the validity of a temperature effect, but at the same time one should not assume that high wetting solution leads to poor battery drain tests. Since wetting solution was added until "proper" tamping consistency was obtained, it follows as logically that poor manganese dioxide requires more wetting solution as that more wetting solution causes poorer battery drain tests. Undoubtedly, an optimum wetting solution occurs for each dioxide.

The results of these drain tests are summarized in Table XVIII. For all runs, the average drains were 6.2 hours high drain, 104 hours low drain, and 68 hours delayed capacity. The best batteries gave 7.3 hours high drain, 114 hours low drain, and 75 hours delayed capacity and were made from dioxide produced at 375° C., 6 hours reaction time, and 2.5 atmos. pressure. Thus, high drain was, in general, good but low drain and delayed capacity were poor.

When the batteries were stored for delay capacity tests, two cells from each set were stored in the open, as is usually done, and one cell in a sealed polyethylene bag to prevent loss of moisture. The average drain tests of the two stored in the open and the one stored in polyethylene are shown below.

										Ave.
Stored in open	67	75	66	88	81	75	66	65	53	71
Stored in polyethylene	104	101	108	95	104	94	83	0	84	97

With the exception of one battery which corroded out, all batteries stored in polyethylene gave better drain tests.

Table XVI

DRAIN TEST DATA

High Drain Tests - Runs 31 - 50

	Temperature					
	350° C.		375° C.		400° C.	
	Time		Time		Time	
Pressure atmos.	4	8	6	6	4	8
2.0	7.1	6.5			5.8	5.1
	6.9	6.3			5.8	5.3
2.5			7.0	7.4		
			6.5	7.2		
3.0	6.8	7.0			6.0	5.7
	6.5	7.0			6.8	4.3

Low Drain Tests - Runs 31 - 50

	Temperature					
	350° C.		375° C.		400° C.	
	Time		Time		Time	
Pressure atmos.	4	8	6	6	4	8
2.0	112	114			102	99
	118	120			107	89
2.5			110	112		
			112	116		
3.0	113	99			99	85
	109	99			112	93

Table XVI (cont'd)

DRAIN TEST DATA

Delayed Capacity Tests - Runs 31 - 50

	Temperature					
	350° C.		375° C.		400° C.	
Pressure atmos.	Time 4	8	Time 6	6	Time 4	8
2.0	63 71	66 66			53 78	49 56
2.5			91 71	91 58		
3.0	80 71	92 85			68 63	67 60

Wetting Solution and Bobbin Weights Corresponding to Above Tables

18.4 8.8	17.0 9.0			23.0 8.3	15.9 8.3
		15.7 9.1	19.9 8.7		
16.0 9.0	19.9 8.7			15.8 9.2	22.6 8.3

Table XVII

ANALYSIS OF VARIANCE

DRAIN TESTS FROM RUNS 31 - 50

Source of Variation	Degrees of Freedom	Mean Squares		
		High Drain	Low Drain	Delayed Capacity
Treatments	7	1.19	197.3	215.6
Temperature	1	5.41	600.3	625.0
Time	1	1.26	342.3	2.3
Pressure	1	0.10	169.0	441.0
T x Θ Interaction	1	0.77	72.3	182.2
T x P "	1	0.01	81.0	100.0
P x Θ "	1	0.01	100.0	155.7
T x Θ x P "	1	0.76	16.0	2.8
Between sets of batteries		(no estimate)		
Between batteries of same set	8	0.18	27.9	58.9
TOTAL	15			

SUMMARY OF RESULTS

DRAIN TESTS RUNS 31 - 50

		High Drain Average	Low Drain Average	Delayed Capacity Average
All Batteries		6.2	104	68
Temperature	350° C.	6.8	110	74
	400° C.	5.6	99	62
Time	4 hrs.	6.4	109	68
	8 hrs.	5.9	100	68
Pressure	2.0 atmos.	6.1	108	63
	3.0 atmos.	6.1	101	73
Center Point		7.0	114	78
Best Set		7.3	114	75

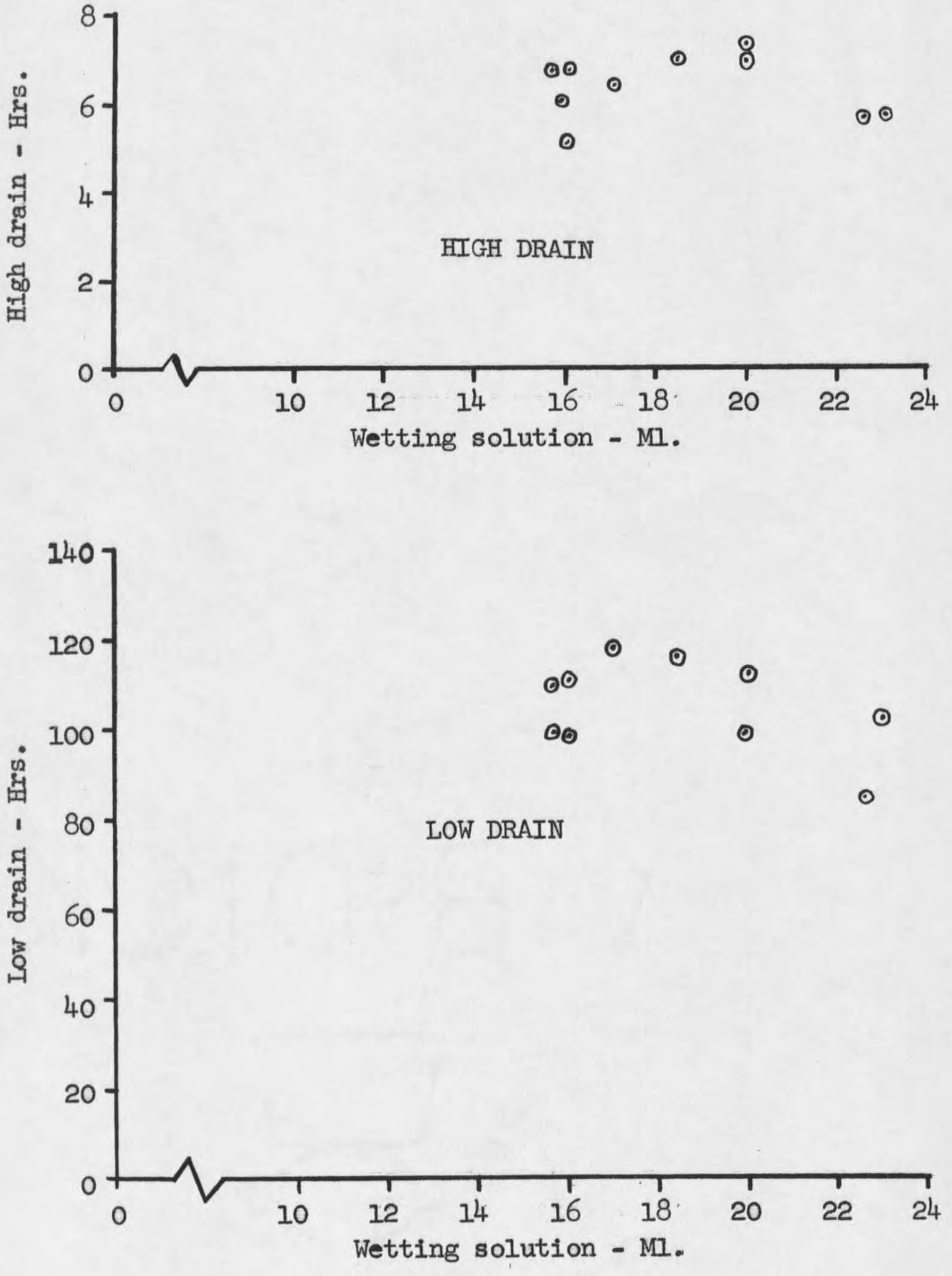

Figure 5

EFFECT OF WETTING SOLUTION ON DRAIN TESTS

WETTING SOLUTION

Following the initial drain tests on these batteries from runs 31 - 50, a set of experiments was run to study the effect of wetting solution on drain tests. Also, the possibility of increasing low drain capacity by using a more concentrated acid leach or a higher ratio of manganese dioxide to acetylene black (hope to increase bobbin weight) was investigated. The experiment consisted of making 2 kilograms of manganese dioxide in 16 runs at 400° C., 3 atmos. pressure, and an air rate of approximately 18 ft./min. Reaction time varied between 5 hours and 14 hours as the reactor was run continuously making three batches per day. The carbonate was the same as used for the second block of runs 31 - 50 and runs 61 - 70. The product from these runs was divided and half was leached with 100 g./l. acid for one-half hour and the other was leached with 150 g./l. acid. Batteries were then made using 15.0, 17.5, and 20.0 ml. of wetting solution per 40 grams of manganese dioxide and manganese dioxide to carbon ratios of 10 - 1 and 12 - 1. The basic experiment was thus a 2 x 2 x 3 factorial. Each treatment combination was used twice and two batteries from each set were used for each drain test. The layout of the experiment and the results are contained in Table XIX. The analysis of the variance of this data is contained in Table XX.

From the analysis of variance, certain factors were seen to have had significant effects (starred mean squares) as follows:

1. WETTING SOLUTION: Had a significant effect on low drain and delayed capacity, but not on high drain. From the summary (Table XXI) it was apparent that the lower quantity of wetting solution was better with the possibility of an optimum at 17.5 ml. for low drain. A slight increase in high drain was noted as wetting solution decreased.

2. LEACHING: Had significant effect only on high drain and the 100 g./l. acid concentration was superior.

3. CARBON RATIO: Had an effect on high drain and low drain with the 10 - 1 ratio being superior.

4. INTERACTIONS: Two interactions were important; namely, L x K for high drain and W x L for delayed capacity. These interactions were illustrated by Figure 6 and Figure 7.

From Figure 6 it was observed that the effect of wetting solution depended on the acid leaching, i.e., the shape of the curve for 150 g./l. leach was different from the shape of the curve for 100 g./l. For comparison the low drain results were also plotted as an example of insignificant interaction. Figure 7 is self-explanatory.

The best conditions were at the lower level of wetting solution, 100 g./l. leach and 10 - 1 carbon ratio. Wetting solution did not seem to be as important in this range as was anticipated when the experiment was designed. The two best sets of batteries occurred at 15.0 ml. wetting solution, 100 g./l. leach, and 10 - 1 carbon ratio. Their average drain tests were:

High drain	7.6	±	0.5	hours
Low drain	118	±	4.0	hours
Delayed Capacity	114	±	6.0	hours

The estimates of error that could be made from this experiment were also of interest. As shown in the summary, the estimate of standard deviation for batteries of the same set was 0.114 hours, 3.26 hours, and 7.92 hours for high, low and delayed tests, respectively. Table XXV gives a summary of the estimates of variance between batteries of the same set from all experiments in this report. The variances were relatively homogeneous with a higher variance for delayed capacity than for low drains. This experiment gave the only good estimate for the variance of different sets of batteries from the same manganese dioxide, as shown in Table XX. If this was a good estimate of variance for all cases, it could be used to test for significance in the other experiments. This estimate did not apply to other experiments, however, because it was for batteries very much alike, i.e., made from the same manganese dioxide and having the same quantity of wetting solution, whereas the other experiments compared batteries made from manganese dioxide that was only made in the same way and did not necessarily have the same wetting solution. For instance, in the drain tests from runs 31 - 50, the "error" would be made up of differences between batteries of the same set, differences between sets of batteries made from the same manganese dioxide, and differences between sets of batteries made from manganese dioxide that was made similarly. The experiment itself contained an estimate of variance from the first source, the experiment on wetting solution gave an estimate of the variance from the second source but no estimate was available for the third source of variation.

Table XIX

DRAIN TEST DATA

EFFECT OF WETTING SOLUTION, CARBON RATIO, AND ACID LEACHING

Leach Conc. g./l.	Carbon Ratio	Wetting Solution ml.	Bobbin Weight g.	High Drain hrs.		Low Drain hrs.		Delayed Capacity hrs.	
100	10-1	20.0	8.6	7.1	7.3	110	108	89	80
		17.5	8.7	7.4	7.4	125	126	110	101
		15.0	8.7	7.3	7.3	115	117	119	118
		20.0	8.7	7.3	7.3	110	117	94	95
		17.5	8.8	7.1	7.1	111	108	74	90
		15.0	8.4	8.0	7.8	120	120	111	116
	12-1	20.0	8.6	6.5	5.8	106	106	100	90
		17.5	8.9	7.6	7.8	110	106	94	101
		15.0	9.2	5.8	5.8	114	114	113	110
		20.0	8.7	7.7	7.5	103	103	92	83
		14.5	8.8	7.0	7.2	125	122	100	99
		15.0	8.8	7.7	7.8	125	119	106	112
150	10-1	20.0	8.6	7.3	7.0	122	122	105	105
		17.5	8.7	7.5	7.5	120	118	89	86
		15.0	8.5	7.2	7.3	120	120	82	96
		20.0	8.4	6.7	6.6	115	122	94	99
		17.5	8.9	6.3	6.5	126	117	95	91
		15.0	8.7	7.4	7.6	114	116	94	105
	12-1	20.0	8.6	4.3	3.8	94	102	100	68
		17.5	8.8	6.6	6.8	124	124	96	94
		15.0	8.9	6.1	5.1	103	115	100	96
		20.0	8.7	2.0	4.0	100	100	93	118
		17.5	9.0	4.5	4.5	114	114	97	81
		15.0	9.0	6.5	6.0	110	116	100	100

Table XX

ANALYSIS OF VARIANCE

EFFECT OF WETTING SOLUTION, CARBON RATIO, AND LEACHING ON BATTERY DRAIN TESTS

Source of Variation	Degrees of Freedom	Mean Squares		
		High Drain	Low Drain	Delayed Capacity
Wetting Solution	2	2.9	390.1*	649.8*
Leaching	1	15.8*	1.3	266.0
Carbon Ratio	1	17.4*	468.7*	0.5
W x L Interaction	2	1.7	51.6	570.3*
W x K "	2	1.6	183.3	0.1
L x K "	1	8.8*	140.2	60.8
W x L x K "	2	1.5	56.3	89.6
Between sets of batteries	12	1.2	64.1	121.6
Between cells from same set	24	0.1	10.6	62.8

* Significant at 95 percent confidence level.

Table XXI

SUMMARY OF RESULTS

EFFECT OF WETTING SOLUTION, CARBON RATIO, AND LEACHING

		High Drain Average	Low Drain Average	Delayed Capacity Average
All Batteries		6.62	114.3	97.5
Wetting Solution	20.0 ml.	6.14	108.8*	94.1*
	14.5 ml.	6.80	118.1*	93.6*
	15.0 ml.	6.91	116.1*	104.9*
Leach	100 g./l.	7.19*	114.2	99.9
	150 g./l.	6.04*	114.5	95.1
Carbon Ratio	10-1	7.22*	117.5*	97.4
	12-1	6.02*	111.2*	97.6

ESTIMATES OF STANDARD DEVIATION

	High Drain	Low Drain	Delayed Capacity
Batteries of same set	0.114 hrs.	3.26 hrs.	7.92 hrs.
Sets of batteries based on average of two batteries from same set	0.78 hrs.	5.66 hrs.	7.80 hrs.

* Comparisons that were shown to be statistically significant.

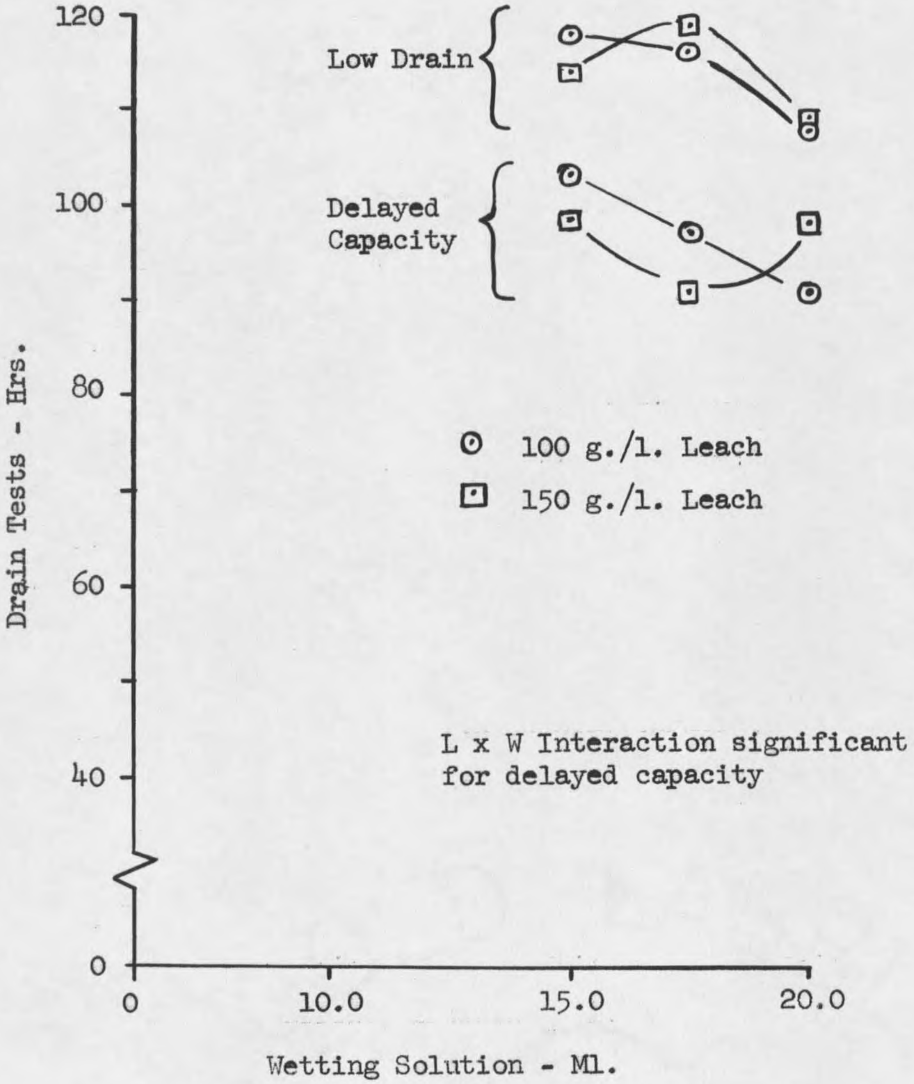

Figure 6

EFFECT OF WETTING SOLUTION

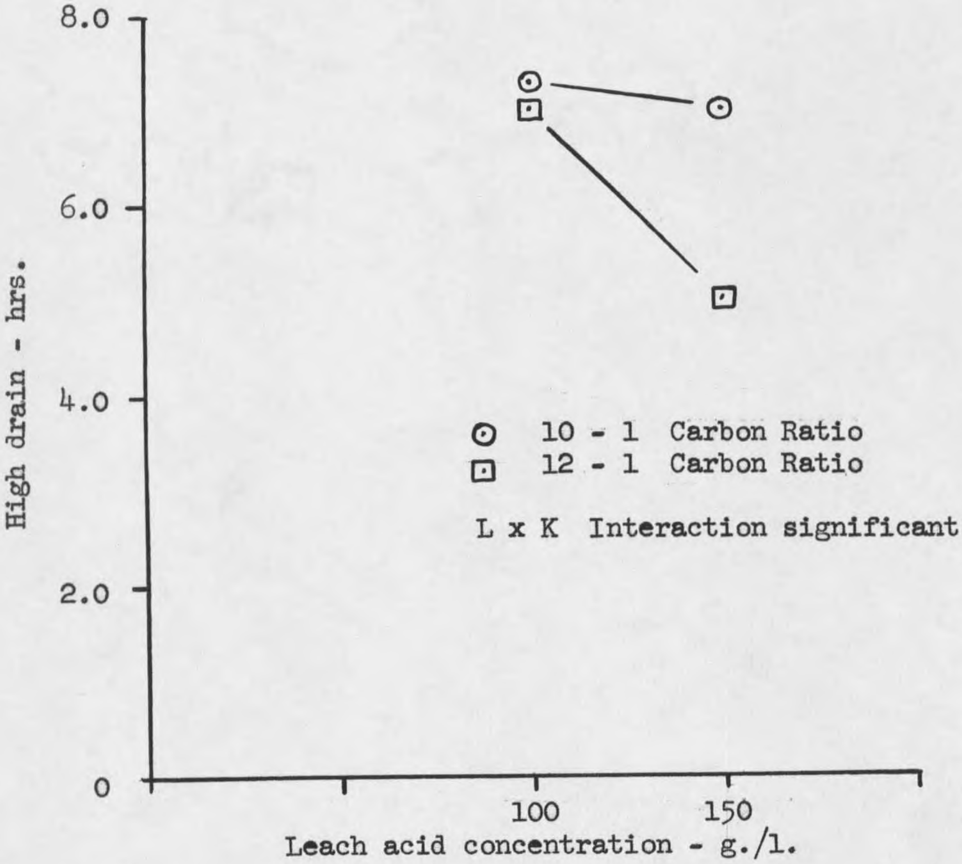

Figure 7

CARBON RATIO - LEACH INTERACTION

DRAIN TESTS FROM CARBONATE STUDY

A set of batteries was made from each batch of manganese dioxide made during the study of the effect of carbonate composition on yield. The results of drain tests on these batteries are presented in Table XXII. The results were analyzed by estimating a linear regression equation correlating iron and sodium analysis with drain tests.

$$Y_{\text{high } 400^\circ \text{ C.}} = 7.07 + 1.60\,(\text{Na}) - 0.81\,(\text{Fe})^{*}$$

$$Y_{\text{high } 450^\circ \text{ C.}} = 7.81 - 0.81\,(\text{Na}) - 0.26\,(\text{Fe})$$

$$Y_{\text{low } 400^\circ \text{ C.}} = 146.0 - 5.6\,(\text{Na}) - 23.5\,(\text{Fe})^{*}$$

$$Y_{\text{low } 450^\circ \text{ C.}} = 140.7 - 33.2\,(\text{Na}) - 6.2\,(\text{Fe})^{*}$$

$$Y_{\text{delay } 400^\circ \text{ C.}} = 126.1 - 25.2\,(\text{Na}) - 8.8\,(\text{Fe})$$

$$Y_{\text{delay } 450^\circ \text{ C.}} = 128.0 - 31.2\,(\text{Na}) - 16.8\,(\text{Fe})^{*}$$

Drain tests are in hours and iron and sodium in percent.

The analysis of variance of the results is presented in Table XXIII along with the appropriate "F" ratio to test whether the variation due to linear effects was significant in relation to the interactions and error. For the low drain tests a significant proportion of the variation in drain tests could be correlated with the iron and sodium content of the carbonate used to make the manganese dioxide. For delayed capacity the effect of iron and sodium was about

---

* Regression equations that were found to be significant.

the same as with low drain, however, the correlation was not as good since only one of the regression equations was significant. High drain was affected less by the quality of the carbonate with an increase in iron also tending to reduce drain capacity. The effect of sodium varied showing a positive effect for the dioxide made at 400° C. and a negative effect for that made at 450° C.

Whether these impurities were the direct cause of the poor drain tests was, of course, not established but it was shown that poor drain tests were associated with high iron and sodium analysis of the carbonate and were thus to be avoided. Averaged over these carbonates high drain was 7.1 hours with a range of 6.5 to 8.3 hours, low drain was 115 hours with a range of 98 to 146 hours and delayed capacity was 95 hours with a range of 68 to 117 hours. The best set of batteries had 7.7 hours high drain, 146 hours low drain and 117 hours delayed capacity.

Table XXII

EFFECT OF CARBONATE ON DRAIN TESTS

Carbonate	Analysis		Wetting Solution		High Drain		Low Drain		Delayed Capacity	
	Iron	Sodium			400°C.	450°C.	400°C.	450°C.	400°C.	450°C.
ANA-6	0.30%	0.51%	12.8	15.0	7.7*	7.0	146	134	117	105
ANA-7	1.90	0.83	15.7	16.2	6.6	6.5	98	110	85	68
ANA-8	1.58	0.41	15.8	14.8	6.9	7.1	112	111	114	90
ANA-9	0.68	0.93	16.5	13.0	8.3	6.9	129	99	113	90
ANA-10	0.81	0.59	14.1	17.6	6.8	7.5	103	108	72	96
AVERAGE					7.3	7.0	118	112	100	90

* High drain and low drain test averages were for three batteries, delayed capacity test averages were for two batteries.

Table XXIII

ANALYSIS OF VARIANCE - REGRESSION EQUATIONS

EFFECT OF CARBONATES ON DRAIN TESTS

Source of Variation		Degrees of Freedom	Mean Squares 400°C.	Mean Squares 450°C.
High Drain	Due to Regression	2	2.30*	0.40
	Lack of Fit	12	0.40	0.18
Low Drain	Due to Regression	2	1482*	445*
	Lack of Fit	12	283	101
Delayed Capacity	Due to Regression	2	277	729*
	Lack of Fit	7	740	67

"F" Ratios

High Drain	400° C.	5.77
	450° C.	2.25
Low Drain	400° C.	5.23
	450° C.	4.38
Delayed Capacity	400° C.	0.374
	450° C.	10.9

$F_{.05}(2, 12) = 3.88$

$F_{.05}(2, 7) = 4.74$

* Significant at 95 percent confidence level.

DRAIN TESTS FROM RUNS 61 - 70

With the higher yields of runs 61 - 70, it was possible to make a set of batteries for each run. The results of these drain tests are shown in Table XXIV. Two sets of batteries from runs 69 and 70 are missing due to, it is believed, an error in weighing the quantity of acetylene black and ammonium chloride mixed with the manganese dioxide. The error was first suspected while making batteries when the bobbin weights were abnormally high. Drain tests showed zero life. Because of these missing observations statistical analysis of the data was not attempted. In general, the battery quality was superior to that found in runs 31 - 50 and in the experiment on wetting solution. It seemed to follow the general tendency for good yield to result in good depolarizer. There was no evidence that high temperature was harmful to battery quality. All the batteries met Signal Corps high drain specification and all except two came within five hours of the low drain specification. Delayed capacity was fair, being on the average 79 percent of initial low drain capacity.

The average drain tests were 7.3 hours high drain, 125 hours low drain, and 99 hours delayed capacity with a high set of 7.4 hours high drain, 133 hours low drain, and 112 hours delayed capacity after three months storage in the open. The runs 61 - 70 were considered the closest to being typical of the overall results to be expected. The manganese carbonate, although the best made, was a mixture of five large batches made before it was evident that carbonate purity was so critical and the reaction conditions were in the range expected to contain an optimum yield of manganese dioxide.

Table XXIV

DRAIN TEST DATA RUNS 61 - 70

Temperature	Time	Pressure	Air Rate	Wetting Solution	Bobbin Weight	High Drain Average	Low Drain Average	Delayed Capacity Average
425	5	1	8	20.0	8.9	6.7	112	--
425	5	3	24	16.2	9.2	7.3	130	94
425	9	1	24	15.0	9.0	7.6	125	108
425	9	3	8	15.0	9.2	7.4	129	117
450	7	2	16	15.0	9.1	7.4	133	112
450	7	2	16	16.2	9.3	7.2	128	74
475	5	1	24	13.8	9.3	7.6	128	88
475	5	3	8	--	--	--	--	--
475	9	1	8	16.6	9.2	6.9	119	106
475	9	3	24	--	--	--	--	--
	AVERAGE					7.3	125	99

Table XXV

SUMMARY OF VARIANCE ESTIMATES

Experiment	Sample Size	Variance Between Batteries of Same Set		
		High Drain	Low Drain	Delayed Capacity
Runs 31 - 50	10 sets 2 per set	0.18	27.9	58.9
Wetting Solution	24 sets 2 per set	0.10	10.6	62.8
Carbonate	10 sets 3 per set	0.19	89.9	174.2
Runs 61 - 70	8 sets 2 per set	0.03	3.8	112.1

BLENDING

Part of the manganese dioxide made from chemically pure carbonate in the quartz reactor during the preliminary runs was used for blends with a sample of Philipsburg ore. Batteries were made from mixtures of the leached and unleached synthetic manganese dioxide and natural ore and mixtures of leached synthetic and leached natural ore (Table XXVI). Sample P-1 was Philipsburg ore ball milled to minus 100 mesh, PL-2 and PL-3 were samples leached with sulfuric acid with PL-3 also being ball milled before leaching as well as after leaching. Table XXVII contains the results of drain tests with these samples and with a sample of ore from the Gold Coast. From these tests it was apparent that leaching helped high drain of the Philipsburg ore, but did not affect low drain or delayed capacity to any extent. From the data on mixtures of these ores it was observed that a small quantity of a superior grade of depolarizer had a tendency to upgrade the high and low drain capacity of the batteries more than would be expected from a linear addition of their individual drain capacities. Delayed capacity, however, was depressed.

Table XXVI

BLENDS OF PHILIPSBURG ORE AND CHEMICALLY SYNTHESIZED MANGANESE DIOXIDE

Mixture		Wetting Solution	Bobbin Weight	High Drain		Low Drain		Delayed Capacity	
Percent	Percent	ml.	g.	Hours	Percent Gain	Hours	Percent Gain	Hours	Percent Gain
P-1	AO4								
100	0	14.3	9.6	3.7		80		67	
90	10	11.8	9.5	4.0	+3.8	92	+12.1	50	-26.4
80	20	12.1	9.8	4.0	-1.0	93	+ 8.9	60	-12.8
50	50	14.0	9.2	4.3	-3.9	101	+ 8.0	62	-11.9
0	100	20.0	9.4	5.2		107		76	
P-1	AO4-L								
100	0	14.3	9.6	3.7		80		67	
90	10	12.7	9.7	4.1	-1.2	93	+10.0	60	-17.8
80	20	12.1	9.7	4.5	+2.3	104	+18.2	58	-26.6
50	50	14.4	9.3	5.0	-8.3	108	+ 5.4	58	-40.2
0	100	17.1	9.6	7.2		125		127	
PL-3	AO4-L								
100	0	12.4	9.9	4.9		88		67	
90	10	12.3	9.8	5.6	+9.2	94	+ 2.5	60	-17.8
80	20	14.4	9.7	5.5	+2.6	94	- 0.4	70	-11.6
50	50	15.4	9.5	5.5	-9.1	108	+ 1.4	64	-34.0
0	100		9.6	7.2		125		127	

Table XXVII

DRAIN TESTS OF PHILIPSBURG AND GOLD COAST ORES

Sample	Wetting Solution	Bobbin Weight	High Drain	Low Drain	Delayed Capacity
P-1	14.3	9.6	3.7	80	67
	12.5	9.5	3.6	85	50
PL-2	13.1	9.9	4.8	92	76
PL-3	12.4	9.9	4.9	88	67
	12.5	9.4	4.4	89	60
Gold Coast	13.5	10.0	4.2	82	65

SUMMARY

Battery active manganese dioxide was synthesized from rhodochrosite ore by a process of leaching the ore with sulfuric acid, removing iron, reprecipitating the manganese as carbonate, drying, oxidizing the carbonate with air at elevated temperatures, and leaching the oxidized product with dilute sulfuric acid at the boiling point to remove lower oxides of manganese. Technical grade chemicals were used in the process and the oxidation reaction was accomplished in a steel reactor.

For a manganese carbonate having approximately 41.0 percent manganese, 0.30 percent iron, 0.51 percent sodium, and minor quantities of copper, lead, and zinc, the percent conversion to manganese dioxide as measured by available oxygen analysis was found, on the basis of twenty runs, to be adequately described by the regression equation

$$Y = 52.2 + 8.43\left[\frac{T - 375}{25}\right] + 1.78\left[\frac{\Theta - 6}{2}\right] + .74\left[\frac{P - 2.5}{.5}\right] - .96\left[\frac{A - 15}{3}\right]$$

where T = Reaction temperature in the range $375 \pm 25^{\circ}$ C.

Θ = Reaction time in the range 6 ± 2 hours.

P = Reaction pressure in the range $2.5 \pm .5$ atmospheres pressure at the elevation of Montana State College (12.5 pounds per square inch absolute).

A = Linear air rate in the range 15 ± 3 feet per minute.

The preceding equation accounted for a significant proportion of the variation in the yields. The standard deviation of the regression coefficients was estimated to be 1.20.

Drain tests on batteries made from the manganese dioxide produced under the above conditions had an average high drain of 6.2 hours, average low drain of 104 hours, and average three months delayed capacity of 68 hours; with the best set having a high drain of 7.3 hours, low drain of 114 hours, and three months delayed capacity of 75 hours. Due to the lack of replication, inferences regarding the effect of the reaction variables of time, temperature, pressure, and air rate could not be made.

With the same carbonate, but in the range:

Temperature = 450° ± 25° C.
Time = 7 ± 2 hours
Pressure = 2.0 ± 1.0 atmospheres
Air Rate = 16 ± 8 feet per minute

the estimated regression equation for percent available oxygen content on the basis of ten runs was

$$Y = 60.3 + 2.78\left[\frac{T - 450}{25}\right] - .35\left[\frac{\Theta - 7}{2}\right] + 4.58\left[\frac{P - 2}{1}\right] + 3.55\left[\frac{A - 16}{8}\right] .$$

This equation, however, did not account for a significant proportion of the variation in yields. It was believed that a region of maximum yield had been approached. The maximum yield observed was 70.5 percent available oxygen requiring approximately 20 percent recycle and occurred at reaction conditions of 475° C., 5 hours, 3 atmospheres, and 8 feet per minute air rate.

Drain tests of batteries made from manganese dioxide produced under the above conditions had a mean high drain of 7.3 hours, low drain of 125 hours, and three months delayed capacity of 99 hours; with the best set having a high drain of 7.4 hours, low drain of 133 hours, and delayed capacity of 112 hours. Again, inferences regarding an effect, or lack of effect, of reaction variables could not be made.

On the basis of five carbonates analyzed for iron and sodium, the percent available oxygen for runs at 400 or 450° C., 6 hours reaction time, 3 atmospheres pressure, and 18 feet per minute air rate was found to be correlated with iron and sodium as

$$Y_{400^\circ\ C.} = 82.61 - 1.59\ (Fe) - 54.98\ (Na) \quad \text{and}$$

$$Y_{450^\circ\ C.} = 70.58 + 2.33\ (Fe) - 29.05\ (Na) \quad \text{for sodium}$$

analysis between 0.51 and 0.93 percent and iron analysis between 0.30 and 1.90 percent.

Drain tests for batteries made from the manganese dioxide produced from the above carbonates were analyzed by estimating linear regression equations. It was found that an increase in iron content reduced drain capacity in all cases and that an increase in sodium content reduced low and delayed capacity. The effect of sodium on high drain was positive in one case (400° C.) and negative in the other (450° C.). For batteries made from the lowest level of iron (same carbonate as used previously) average drain tests were 7.3 hours high drain, 140 hours low drain, and 111 hours delayed capacity.

Although a correlation between sodium analysis of the carbonate and yield and drain tests was shown, it was suspected that sodium was not in itself detrimental but was only a symptom of the real cause of the poor results. The true cause may be more closely related to other properties of the carbonate such as crystal structure.

The effect of the variables of wetting solution, carbon ratio, and acid concentration during leaching were studied in the range

Wetting solution = 15.0, 17.5, and 20.0 milliliters per 40 grams of manganese dioxide,
Carbon ratio = 10 - 1 and 12 - 1 manganese dioxide to carbon,
Leaching = 100 and 150 grams per liter acid concentration.

A significant effect of wetting solution was found on low drain and delayed capacity with the lower quantity of wetting solution being better. A leach concentration of 100 grams per liter acid was found to be significantly better for high drain tests. A carbon ratio of 10 - 1 was significantly better for high and low drain. Interaction between leaching and carbon ratio was found for high drain and between leaching and wetting solution for low drain. The better conditions were 15.0 ml. wetting solution, 10 - 1 carbon ratio, and 100 g./l.

leach acid concentration. At these conditions for an average of two sets of batteries high drain was 7.60 ± .55 hours, low drain 118 ± 4.0 hours, and delayed capacity 116 ± 5.5 hours.

Mixtures of manganese dioxide made from C.P. carbonate and a good grade of natural ore from Philipsburg, Montana, showed in general that adding a small percentage of synthetic manganese dioxide resulted in an upgrading of high and low drain tests, but depression of delayed capacity from what would be anticipated by a linear addition of their individual capacities. High drain capacity was increased for the natural ore by an acid leaching but little improvement in low or delayed capacity was noted.

Of the 59 sets of batteries made during this investigation, the average capacities were 6.6 hours high drain, 113 hours low drain and 91 hours delayed capacity. The best single set had 7.7 hours high drain, 146 hours low drain and 117 hours delayed capacity. For a series of eight sets made from the better carbonate and under reaction conditions in the region of anticipated optimum yield of manganese dioxide (runs 61 - 70) the average high drain was 7.3 hours, low drain 125 hours and delayed capacity of 99 hours. A commercial process is predicted to be able to produce manganese dioxide of at least the above quality.

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APPENDIX

ATTAINMENT OF OPTIMUM CONDITIONS (4)

The following is a simplified discussion of the ideas underlying the Box method as used in this report to find the maximum yield of manganese dioxide. It was assumed that the yield could be expressed as a function of the reaction variables.

$$Y = f(X_T, X_\theta, X_P, X_A)$$

where X_T, X_θ, X_P, and X_A are levels of temperature, time, pressure and air rate. It was also assumed that the levels of the variables could be controlled exactly at any selected value within the experimental region and that the observed values for a given set of conditions would be normally distributed.

The problem of optimization was, with the smallest number of experiments, to locate a point in the region for which yield was maximum. The method of procedure chosen required that the error be small in comparison to the effect of the various factors and that the results of one set of runs could be evaluated before a second set of runs was made. The response to varying sets of reaction conditions was visualized as defining some type of response surface. In the surface considered for this experiment a five dimensional space was necessary.

To visualize five dimensions is impossible; therefore, the experiment will be discussed in terms of a three dimensional space, the concepts of which can be generalized to more dimensions. In particular, the experiment will be discussed in terms of a mountain. The problem of finding a maximum yield is the same problem as trying to find the top of a mountain by measuring altitudes at different points. One procedure would be to measure the altitude at a number of points and select the highest to be the mountain peak. If enough points were taken over a wide enough area, the answer would be close.

Another method, analogous to the one used in this report, would be to lay out a grid of equally spaced points along north-south and east-west lines covering an area large enough that it is sure to contain the whole mountain. Now the altitudes of four corners of one of the squares are measured. It is unlikely that the peak occurs at any one of these points; however, one can tell from these points the direction in which the hill is steepest, i.e., going north the rise might be 50 feet for a given horizontal distance and going east the rise might be 100 feet for a given horizontal distance, thus, the steepest part of the section would be in a direction somewhat east of north east. Naturally the mountain is not smooth and it is only necessary that the local roughness (ϵ) be small in comparison with the general slope (effect of a factor). Before measuring the altitudes of another set of points, one would move in the direction of steepest ascent for a distance which is believed reasonable in the light of the rate of climb and the expected height of the mountain. A new set of four points is selected and the analysis repeated.

Eventually this method defeats itself when a section is reached where it is impossible to tell which direction is up. This would occur, presumably, near the top where the points are straddling the ridge or where the mountain starts to flatten out. Whatever the shape of the summit, it is presumed that the observed heights will cease to indicate a rising plane. This method does not exclude the possibility of climbing a false peak, but the possibility of a double peak is not too great for a chemical process. Also, it is possible that the peak lies outside the experimental region so that yield continues to increase up to the experimental limit of a particular variable. Near the summit the size of the section observed could be reduced or more points could be taken so that the shape could be determined with more precision. The main merit of this method is that it is systematic and will guarantee with a predetermined probability the eventual location of the maximum within a region of arbitrary small size provided a sufficient number of experiments are made and the experimental error is sufficiently small.

The adaptation of these ideas to an actual experiment consists of selecting an experimental region and making enough runs in this region that an estimate can be made of the coefficients of a linear regression equation of the type

$$Y = \beta_0 + \beta_1 X_T + \beta_2 X_\theta + \beta_3 X_P + \beta_4 X_A + \epsilon$$

where

β_i = regression coefficients

X_T = level of temperature

X_Θ = level of time

X_P = level of pressure

X_A = level of air rate

ϵ = a normally distributed random variable having a mean of 0 and variance σ^2. All ϵ's are assumed to be mutually independent.

Two levels of each factor were selected and all possible combinations of these levels were run--a 2^4 factorial--giving more points than absolutely necessary for estimating a linear regression equation, but it was expected that experimental error would be large thereby making extra points necessary for increased accuracy. One set of conditions typical of the center point of the experimental region was run several times so that an estimate could be made of the experimental error. From the observed yields, a regression equation was estimated using the method of least squares. By an analysis of variance the validity of assuming a linear regression was tested. If the regression equation accounted for a significant proportion of the variation in the observed results, it would be concluded that the region investigated did not contain a maximum. From the regression equation the path of steepest ascent was calculated. This path was given by the gradient

$$\text{del } Y = \beta_1 \vec{x}_T + \beta_2 \vec{x}_\Theta + \beta_3 \vec{x}_P + \beta_4 \vec{x}_A$$

where $\vec{x}_T$ represents a unit vector in the direction of increasing temperature. Another set of runs was then made with the center along the path of steepest ascent.

As pointed out in the mountain analogy, this approach eventually failed when a region was reached in which a linear model would no longer adequately describe the results. When this occurred, additional points were to be selected and runs made so that a quadratic equation of the type

$$\begin{aligned} Y = {} & \beta_0 + \beta_1 X_T + \beta_{11} X_T^2 + \beta_2 X_\theta + \beta_{22} X_\theta^2 + \beta_{12} X_T X_\theta + \beta_3 X_P + \beta_{33} X_P^2 \\ & + \beta_{13} X_T X_P + \beta_{23} X_\theta X_P + \beta_4 X_A + \beta_{44} X_A^2 + \beta_{14} X_T X_A + \beta_{24} X_\theta X_A \\ & + \beta_{34} X_P X_A + \epsilon \end{aligned}$$

could be estimated. From this equation the maximum could be determined by the calculus technique of solving for the points where the partial derivatives are zero. In addition, the quadratic regression equation could be used to describe the shape of the response surface in the region near the summit.

Analysis of Variance

The analyses of variance used in several parts of the report all have a very similar conceptual background. Some aspects of the basic type (Table XII), characterized by that used in the experiment for analyzing the differences between carbonates, will be discussed briefly.

In the carbonate experiment runs were made with five different carbonates and the yields for these runs were used to compare the carbonates. For this experiment a population or set of yields was assumed which would represent the results of all possible runs. Certain parameters of this population were defined and the experiment was thought to be a method of estimating these parameters. The population was defined as having

$\bar{y}$ = the mean or average yield of the population.

$\bar{y}_{\cdot\beta}$ = the mean of all possible runs with a given carbonate.

$y_{\alpha\beta}$ = one particular yield associated with the "α" run with the "β" carbonate.

α = subscript denoting the particular run with a given carbonate $\alpha = 1, \ldots, P$ where P is assumed to be infinitely large.

β = subscript denoting the particular carbonate $\beta = 1, \ldots, B = 5$ (five carbonates were all that were of interest).

The following identity relating the above quantities

$$y_{\alpha\beta} = \bar{y} + (\bar{y}_{\cdot\beta} - \bar{y}) + (y_{\alpha\beta} - \bar{y}_{\cdot\beta})$$

shows that yield may be considered to be equal to the population mean plus an average effect of the "β" carbonate (mean of all runs with that carbonate minus population mean) plus a random variation due to the deviation of an individual run with "β" carbonate from the average of all runs with the "β" carbonate. The above relation may also be written

$$y_{\alpha\beta} = \bar{y} + \beta_{\beta} + \epsilon_{\alpha\beta}$$

where β_{β} = carbonate effect.

$\epsilon_{\alpha\beta}$ = a random variable assumed to be normally distributed with a mean of 0 and variance of $\sigma^2_{\alpha\beta}$. $\epsilon_{\alpha\beta}$ are N.I.D. $(0, \sigma^2_{\alpha\beta})$.

The population was further characterized in terms of sums of squares by rewriting the equation as

$$(y_{\alpha\beta} - \bar{y}) = (\bar{y}_{\cdot\beta} - \bar{y}) + (y_{\alpha\beta} - \bar{y}_{\cdot\beta})$$

and squaring both sides and summing over all P runs for each "β" carbonate giving

$$\sum_{\alpha\beta} (y_{\alpha\beta} - \bar{y})^2 = P \sum_{\beta} (y_{\cdot\beta} - \bar{y})^2 + \sum_{\alpha\beta} (y_{\alpha\beta} - \bar{y}_{\cdot\beta})^2$$

where the cross product term from squaring can be shown to be equal to zero. The total sum of squares (left side) was equal to the sum of squares of deviations of the mean yield for a given carbonate from population mean plus a sum of squares of deviations of individual yields from the average yield with that carbonate. These sums are referred to as total sum of squares, sum of squares due to carbonates, and error sum of squares.

Variance components of the population are defined to be

$$\sigma^2_{\alpha\beta} = \frac{1}{B(P - 1)} \sum_{\alpha\beta} (y_{\alpha\beta} - \bar{y}_{\cdot\beta})^2$$

$$= \frac{1}{B(P - 1)} \sum_{\alpha\beta} (\epsilon_{\alpha\beta})^2$$

$$\sigma^2_{\beta} = \frac{1}{B - 1} \sum_{\beta} (\bar{y}_{\cdot\beta} - \bar{y})^2$$

$$= \frac{1}{B - 1} \sum_{\beta} (\beta_\beta)^2 .$$

Note that $\sigma^2_{\alpha\beta}$ may be thought of as the variance of a normal population while σ^2_{β} is defined as the sum of squares of the effects associated with the carbonates.

With the assumed population defined, the experiment was then visualized as a method of sampling a given number of elements from the population such that $p = 3$ of the P elements from each of the $b = 5$ carbonates were observed. The observed value, x_{ij}, corresponding to the i^{th} run with the j^{th} carbonate was one of the $y_{\alpha\beta}$ population elements where i corresponds to α and j corresponds to β. There were $b \times p = 15$ observed values randomly selected from the $B \times P$ $(\rightarrow \infty)$ assumed population values $y_{\alpha\beta}$. A sample model was defined as

$$x_{ij} \;\overline{=}\; x + (\bar{x}_{\cdot j} - \bar{x}) + (x_{ij} - \bar{x}_{\cdot j})$$

from which the following sums of squares may be calculated.

$$\sum_{ij} (x_{ij} - \bar{x})^2 = 3\sum_{j} (x_{\cdot j} - \bar{x})^2 + \sum_{ij} (x_{ij} - \bar{x}_{\cdot j})^2$$

This ability to partition sums of squares is basic in analysis of variance and is analogous to the problem in mechanics of finding moments of inertia using the parallel axis theorem. The next step, and the critical one, is to relate the observed results to the assumed population model. The relations vary with the model. For the carbonate experiment it can be shown that

$$\bar{x} \qquad \text{estimates} \qquad \bar{y} \, ,$$

$$\frac{3}{5-1} \sum_{j} (\bar{x}_{\cdot j} - \bar{x})^2 \qquad \text{estimates} \qquad \sigma^2_{\alpha\beta} + \frac{3}{4} \sum \beta^2_{\beta} \, ,$$

and that

$$\frac{1}{5(3-1)} \sum (x_{ij} - \bar{x}_{\cdot j})^2 \qquad \text{estimates} \qquad \sigma^2_{\alpha\beta}$$

These results are best summarized in an analysis of variance table showing sums of squares, degrees of freedom, and mean squares attributable to each of the different sources of variation. Mean squares are the sum of squares divided by degrees of freedom, where the degrees of freedom are such that the mean square is an unbiased estimate of the population variance component given in the column for expected mean squares. In general, the analysis of variance is used for testing hypotheses regarding the population and estimating variance components of the population. The most common hypothesis is that the treatment (carbonate) effects are zero.

$$H: \beta_1 = \beta_2 = \beta_3 = \beta_4 = \beta_5 = 0$$

which is the same as the hypothesis

$$H: \sigma^2_\beta = 0$$

assuming σ^2_β is zero, then the mean square attributable to carbonates and mean square for error are both estimates of $\sigma^2_{\alpha\beta}$ (Table XII). The ratio of the two estimates of $\sigma^2_{\alpha\beta}$ is distributed as "F" and bounds on the probability of any given "F" ratio may be determined from available tables from which a decision may be made as to whether to reject or fail to reject that σ^2_β is zero--a decision as to whether there is or is not an effect due to carbonate in proportion to experimental error. From the estimates of variance components, the standard errors may be estimated, of which the most useful is the standard error of a treatment mean ($S.E. = \sqrt{\sigma^2_{\alpha\beta}} / n$) where n is the number of observations making up the mean.

The differences between various experiments and the resulting analyses of variance is due to the population model assumed. The basic processes of defining the model, partitioning the sums of squares, and using the observed values to estimate population parameters remain the same.

Individual Comparisons

Individual comparisons, such as done for carbonates, depend on a further partitioning of the sums of squares of the treatments. For the particular case of the carbonates it can be shown algebraically that the sum of squares attributable to carbonates

$$3\sum_{\beta}(y_{\cdot\beta}-\bar{y})^2 = 3\sum_{\beta}(\beta_\beta)^2 = 3\left[\beta_1^2+\beta_2^2+\beta_3^2+\beta_4^2+\beta_5^2\right]$$

$$= \frac{3}{20}\left[4\beta_1-(\beta_2+\beta_3+\beta_4+\beta_5)\right]^2 + \frac{3}{4}\left[\beta_2+\beta_3-\beta_4-\beta_5\right]^2$$

$$+ \frac{3}{4}\left[\beta_2+\beta_4-\beta_3-\beta_5\right]^2 + \frac{3}{4}\left[\beta_2+\beta_5-\beta_3-\beta_4\right]^2$$

where the quantities on the right represent meaningful comparisons. For example, the quantity

$$\frac{3}{20}\left[4\beta_1-(\beta_2+\beta_3+\beta_4+\beta_5)\right]^2$$

is the square of the difference between the effect β_1 and the average of the other effects. For the observed effects $B_1, \ldots, B_5$ it is possible to show that

$$\frac{3}{20}\left[4B_1-(B_2+B_3+B_4+B_5)\right]^2 \qquad \text{estimates}$$

$$\sigma_{\alpha\beta}^2 + \frac{3}{20}\left[4\beta_1+(\beta_2+\beta_3+\beta_4+\beta_5)\right]^2$$

Thus, an assumption that

$$\beta_1 = \frac{\beta_2 + \beta_3 + \beta_4 + \beta_5}{4}$$

would mean that the mean square for this comparison and mean square for error are both estimates of $\sigma^2_{\alpha\beta}$ and tests of the hypotheses follow exactly as before.

Factorial Designs

A factorial experiment is essentially the same as the completely randomized design except that the "treatments" are made up of different combinations of the levels of the factors. For example, in the experiment on wetting solution there were the three factors of wetting solution, carbon ratio, and leach acid concentration with three levels of wetting solution and two levels of the others--a 3 x 2 x 2 factorial giving 12 treatment combinations. Each treatment was replicated once and two batteries were tested from each set. The population model was assumed to be

$$y = \bar{y} + W_{\alpha_1} + K_{\alpha_2} + (W \times K)_{\alpha_1\alpha_2} + L_{\alpha_3} + (W \times L)_{\alpha_1\alpha_3}$$

$$(K \times L)_{\alpha_2\alpha_3} + (W \times K \times L)_{\alpha_1\alpha_2\alpha_3} + \epsilon_{\alpha_1\alpha_2\alpha_3\beta} + \delta_{\alpha_1\alpha_2\alpha_3\beta\gamma}$$

where

ϵ is a random variation due to differences between sets of batteries.

δ is a random variation due to differences between batteries of the same set.

W, K, L, are the first order effects of the variables.

(W x K), etc. are interaction effects.

$\alpha_1 = 1, 2,$ or 3

$\alpha_2 = 1$ or 2

$\alpha_3 = 1$ or 2

$\beta = 1, \ldots, P$

$\gamma = 1, \ldots, S$

Variance components are defined for each source of variation such as

$$\sigma_s^2 = \frac{1}{12\,P(S-1)} \sum_{\alpha_1\alpha_2\alpha_3\beta\gamma} (\delta)^2 \qquad \text{(variance associated with } \delta\text{)}$$

$$\sigma_e^2 = \frac{1}{12(P-1)} \sum_{\alpha_1\alpha_2\alpha_3\beta} (\epsilon)^2$$

From the experimental data estimates are made of each of the population parameters.