A Study of the Possible Use of Aluminum as a Reducing Agent for Manganese Chloride

William J. Borzick

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A STUDY OF THE POSSIBLE USE OF ALUMINUM AS A REDUCING AGENT FOR MANGANESE CHLORIDE

A Thesis Presented to the Faculty of the Department of Metallurgy at Montana School of Mines

In Partial Fulfillment of the Requirements for the Degree Bachelor of Science in Metallurgical Engineering

By William J. Borzick

May 1957
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ACKNOWLEDGEMENTS

The author of this report is very grateful to those who have helped him throughout the investigation.

Mr. Ruggles, of the Chemistry Department was very helpful in supplying some of the reagents and doing work on the glass in the pumping system.

Mr. Smith took all of the pictures in the report and assisted in many other ways.

All of the assay work was done by Mr. C. J. Bartsean of the Montana Bureau of Mines and Geology.

The author is especially indebted to Dr. Shih for his encouragement, and guidance in both the experimental work and the writing of the report. Without his help, the writing of this report would have been much more difficult.
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CHAPTER I

THE PROBLEM

Aluminum has been used as a reducing agent for various reactions, the best known of which is the thermit reaction, which is defined in the "Metals Handbook" as:

An exothermic, self-propagating process in which finely divided aluminum powder is used to reduce metal oxides to free metals by direct oxidation of aluminum to aluminum oxide, with accompanying reduction of the less stable metal oxide. (1-15)

Of the desirable properties that aluminum possess as a reducing agent, some of the more important are as follows: The oxide of aluminum has a high free energy of formation; the heat of formation of aluminum oxide is usually so large that no additional heat is required after the reaction is once started; large amounts of other metal oxides can be reduced with comparatively small amounts of aluminum, because aluminum has a low atomic weight and forms a trivalent oxide.

Most of the above advantages for the thermit processes could be applied to the reduction of chlorides of other metals with aluminum. In addition, aluminum chloride is a vapor at the reaction temperature, and can be easily removed from the reaction zone of the furnace.

Under reduced pressures, many of the metal chlorides have boiling points that are easily obtained in most furnaces, and so in many cases, the excess of reactant can be removed by sublimation. If several zones or chambers are present in the system, the condensate can be kept separate from each other by careful temperature control. Ideally, the process
would consist of a preliminary heating to remove mechanically held water and water of hydration, further heating to initiate the reaction, and finally, further heating to remove excess of reactants.

The presence of water of hydration presents a problem of possible hydrolysis of the reactants or the products. However, since most of the water of hydration is given up at temperatures below the reaction temperature, and is usually the first vapor removed, the possibility of hydrolysis is minimized.

Another problem is the oxidation of the products formed, by oxygen in the air. These two points presented the most difficulty throughout the investigation.

For these two reasons, the system was kept under reduced pressures and constant pumping. Any gaseous products formed would be readily removed from the reaction zone of the furnace. Reactions with gases in the air would be greatly reduced, since the residual air is at a greatly reduced pressure.

The free energy of any reaction of the type

\[ bB + cC \leftrightarrow dD + eE \]

is given by the following formula:

\[ \Delta G = \Delta G^\circ + RT \ln \frac{AD^d \cdot AE^e}{AB^b \cdot AC^c} \]

where \( b, c, d, \) and \( e \) are the number of moles of reactants \( B \) and \( C \), respectively, and \( d \) and \( e \) are the number of moles of products \( D \) and \( E \) respectively, \( A \) is the activity, \( \Delta G^\circ \) is the standard free energy of the reaction, \( G \) is the free energy of the reaction, \( R \) is the gas constant in cal per degree, and \( T \) is the temperature in degrees Kelvin.
If all of the products and reactants are in their standard states, i.e., unit activities, $\Delta G = \Delta G^\circ$. Figures 1 and 2 are graphs of standard free energies of formation for metal chlorides as a function of temperature. (4-864)

From these graphs, the $\Delta G^\circ$ term is negative for any reaction of a metal chloride with aluminum if the curve for aluminum chloride is below that of the metal chloride on the graph. This is true because if one equation on the graph is subtracted from another, the chlorine will cancel out, and the result will be a replacement reaction.

If B, C, and D are in their standard states, and E is a gas, then the free energy of the reaction is given approximately by the formula

$$\Delta G = \Delta G^\circ + RT \ln P_E \, ^\circ$$

where $P$ is the partial pressure of the gaseous product. It is in this form that the reaction for a metal chloride fits, since $AlCl_3$ is a gas at the reaction temperature. At reduced pressures, the $RT \ln P_E \, ^\circ$ term is negative and decreases the free energy of the reaction.

Even though by the above standards a reaction is favorable, the actual conditions necessary to cause it to go at a reasonable rate, and the extent to which it will go can not be told from this type of data.

It is the purpose of this investigation to examine a reaction of this type to determine its feasibility for use in the reduction of a metal from its chloride at reduced pressures.

The first chloride selected for study was cuprous chloride, but after several preliminary runs, it was abandoned in favor of a chloride that would react less violently. The second chloride tried, and selected for further study was manganese chloride. An examination of the phase
Fig. 1—Standard free energies of formation for metal chlorides as a function of temperature. ΔG° between +5000 and −90,000 cal.
Standard free energies of formation for metal chlorides as a function of temperature, $\Delta G^\circ$ between $-90,000$ and $-160,000$ cal.
diagram of the Cu - Mn system indicated only very limited solid solubilities. Since the reduction of manganese oxide with aluminum has been successfully performed, the alloying effect does not appear to restrict the process.
CHAPTER II

SURVEY OF THE LITERATURE

Although no published work on the actual reduction of a chloride with aluminum has been found, the possibilities were suggested by both Kellog (4) and Pidgeon (8) in recent publications.

I. METAL CHLORIDES IN GENERAL

A very good summary of the metal chlorides is given by Herbert H. Kellog in his article, "Thermodynamic Relationships in Chlorine Metallurgy" (4). The report, based on data which are scattered throughout the literature, presents a concise review of the subject. In addition to the data for the reduction of metal chlorides, this article also gives thermodynamic data for the chlorination of metal oxides, and on other thermodynamic relationships in chlorine metallurgy.

II. MANGANESE CHLORIDE

Apparently the most stable condition of MnCl₂ at room temperature is the tetrahydrate, MnCl₂.4H₂O, but the water of hydration can be easily removed by heating to a temperature above 198°C.

...W. Muller-Erbsbach observed that the dihydrate loses one of its moles of water more readily than the other; P. Kulznelzoff that it loses water at 170°C, and when allowed to stand exposed to air for a couple of months, it forms the tetrahydrate. These results show that there are three well defined hydrates of manganese chloride, with defined transition temperatures: (7-350,351)

\[
\begin{align*}
\text{MnCl}_2\cdot6\text{H}_2\text{O} & \xrightarrow{-20°C} \text{MnCl}_2\cdot4\text{H}_2\text{O} & 58.089°C & \xrightarrow{198°C} \text{MnCl}_2 \\
\end{align*}
\]
The low temperature at which the water is given up is desirable, because when the chloride is heated in water vapor, according to F. Kulhmann, HCl and manganese tritiatetrate are formed. (7-357)

The melting point and boiling point of MnCl₂ as given in the 36th edition of the Chemical Rubber Publishing Company "Handbook of Physics and Chemistry" are 650°C and 1150°C respectively.

In a recent progress report (5), R. R. MacMillan and T. L. Turner suggested the method of chlorinating a complex manganese ore. They also discussed the hydrolysis of MnCl₂ which they employed to convert the MnCl₂ to manganese oxide.

III ALUMINUM CHLORIDE

Since the gaseous nature of AlCl₃ at the reaction temperature is one of the important properties for use in this reaction, some of the data on the boiling point of the compound was studied.

...According to J. von Liebig, anhydrous aluminum chloride boils between 180° and 185°, and G. Friedel and J. M. Crafts found the B.P. to be 167.8° at 0.33 atm. press.; 171.1° at 0.41 atm. Press.; 175.7° at 0.57 atm. press... (6-316)

IV MANGANESE

Since the removal of excess reactants could possibly be carried out more conveniently by leaching than by subliming, the action of Mn in the possible leach solutions was sought.

H. V. Regnault said that finely divided manganese kept under water at ordinary temperatures slowly liberates H₂, but if heat is applied, even below 100°, the evolution of gas is rapid and a yellowish brown powder is formed which becomes dark brown on exposure to air...
O. Prelinger found that Mn gives off $H_2$ when it is heated with a soln. of NaOH; but A. N. Camplee observed no perceptible action when Mn is boiled with a conc. soln. of soda lye or potash lye. (7-186, 187)

V VACUUM TECHNOLOGY

Although comparatively little work has been done on vacuum reduction of metal chlorides, much work has been done recently on reduction of metal oxides (8) and sulfide (9), and on vacuum equipment for melting and casting some of the more active metals.

With increasing study of vacuum techniques and equipment, the cost of installations should tend to decrease, while the quality should increase. A summary of the position of the vacuum system as a useful tool is given as follows:

The past fifteen years has witnessed an amazing growth in the use of vacuum as a processing tool. Classic concepts relating to design of vacuum systems, materials of construction, fabricating methods, size evacuating rates, and ultimate pressures have bowed to this rapidly advancing technology. The engineer has inherited the task of designing from the experimental physicist. The carefully built up, fragile systems of glass, rubber and perhaps some brass, have given way to the precision and durability of steel, teflon and stainless steel. Large systems are now measured in thousands of cubic feet rather than in a few liters. Production of low pressures is now accomplished quickly and routinely. (2-1)
CHAPTER III

EXPERIMENTAL

For the vacuum reduction of manganese chloride, the materials, equipment and procedures described in the following sections were used.

I MATERIALS

The manganese chloride used was Mereck, chemically pure grade. It had hydrated to the extent that it contained 25 per cent water of hydration. It was found, therefore, to contain 0.327 per cent manganese.

The aluminum reducing agent was produced by the Metal Disintegrating company, and was found to contain 99.8 per cent aluminum.

II EQUIPMENT USED

Three major components make up the equipment used in these experiments. They are the pumping assembly, the furnace assembly, and the charge container.

A. The Pumping System

All of the parts of the pumping system, as designed by Dr. Shih, are mounted conveniently on a portable wooden stand. Figure 3 is a picture and diagramatic sketch of the system.

The pump and motor, which are on the lower part of the stand, make up the main part of the system. The pump, made by the Welsh Manufacturing Company, is a Duo-Seal model, and has a free air capacity of 21 liter per min. According to the manufacturer, when it is in operation at the
optimum speed of from 400 to 475 RPM, the pump is capable of producing
a pressure of .0001 mm of Hg.

The original 1/3 HP motor burned out and was replaced with a
Westinghouse 1/4 HP, 1725 RPM, 120v, 5.5 amp, 60 cycle motor. This
motor operated the pump within the optimum speed given by the manufacturer
of from 400 to 475 RPM.

The pump is connected to the glass system on the upper portion of
the stand by a short length of rubber tubing. The glass system consists
of various valves, a manometer, and appropriate tubing. The lower three-
way valve is employed so that the furnace system can be connected to
either the pumping system or the atmosphere. The second three-way valve
is employed so that the pumping system can be connected to either of two
furnace systems. The third valve is a two-way valve to the manometer.

Ground glass fittings are employed to connect the furnace system
to the pumping system.
LEGEND

A. TWO WAY VALVE TO MANOMETER
B. MANOMETER
C. THREE WAY VALVE TO FURNACE SYSTEM
D. THREE WAY VALVE TO ATMOSPHERE OR GAS
E. STAND
F. MOTOR
G. PUMP

FIGURE 3
PUMPING SYSTEM
B. The Furnace System

The furnace used for the process is a horizontal resistance furnace made by the Electric Heating Apparatus Company. It was used with a Superior Electric Company powerstat. The powerstat has a 0 to 130 v range. The furnace is 13 in. long, has an outside diameter of 7 in., and an inside diameter of 1½ in. At 110 v, the furnace draws a current of 2.55 amp. A fused silica tube, 36 in. long and 1 in. in diameter was used as the refractory material for the furnace. The tube was sealed at both ends with rubber stoppers.

A section of glass tubing forced through a one-hole stopper on the right end of the tube connects the tube to the vacuum system by way of a flask, which serves as a trap to collect any condensate that escapes the tube.

A chromel-alumel thermocouple, forced through the stopper on the other end and connected to a Bristol temperature indicator, graduated in 20°F intervals is employed for temperature control. All of the rubber-glass and glass-glass junctions in the system were coated with vacuum grease, and as far as can be told by the manometer and the high voltage coil are vacuum tight.

Cooling coils were used on the tube to try to hold all of the condensates in the tube proper. Figure 5 is a picture of the furnace system.
FIGURE 4
CHARGE CONTAINER
(Actual Size)

FIGURE 5
FURNACE SYSTEM
C. The Charge Container

Much time was spent during the earlier part of the investigation in trying to obtain a suitable container for the charge. The first container tried was simply a refractory combustion boat that was filled with the charge and set into the furnace. However, during the reaction, much of the product spilled over the sides and was difficult to recover.

The next container tried was a smaller fused silica tube inside the main reaction tube. Although this was somewhat better, there was still a considerable loss of product. At this point, the samples were compressed in a steel cylinder, by forcing a rod into the cylinder with a hydraulic jack and thereby compressing the charge into cylindrical pellets. The die that was used was one normally used for mounting metal specimens in the metallographic laboratory and the pellets thus made were too large for the small tube. Before they were charged, the pellets had to be broken, and part of the sample was lost as a fine powder.

A small tap and die, having a \( \frac{3}{4} \) in. diameter was then constructed, with the idea that compressed pellets of the proper size would cut down on mechanical loss of sample, be easier to handle, promote better contact of the reactants, and be easier to recover quantitatively.

Before each sample was compressed, the reactants were ground together in a small mortar. A portion of the charge was then compressed in the small tap and die, so that several pellets were made from each prepared charge.

Mechanical loss was somewhat cut down by using the small compressed samples in the fused silica container, but it was not completely eliminated.
The final container decided upon was an aludum thimble with a glass wool plug. This would permit the vapors to escape, while holding the solid particles for weighing. This container was not entirely suitable, since some contamination of the sample was noted. However, it did give a good indication of weight loss.

III EXPERIMENTAL PROCEDURE

For each run, the charge was compressed in the die described earlier in the paper, and placed in the container. The thimble was placed in the tube with the end of the thermocouple approximately \( \frac{1}{2} \) in. up from the bottom of the thimble. Both ends of the tube were coated with vacuum grease and sealed with the rubber stoppers. After the vacuum pump was started, and the tube was evacuated, the furnace was turned on, and the tube was heated to the desired temperature for the desired time. The pump was used only intermittently during the cooling period, since the motor was not capable of long continued use. All products in the thimble were recovered, reground, and sent for assay.

IV DATA

The data obtained in these experiments is listed on the following pages.

Run 1.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Assay</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time: 1 hr</td>
<td>Mn 37.3%</td>
<td>% of Mn reduced</td>
</tr>
<tr>
<td>Temp: 750°F</td>
<td>Cl 48.5%</td>
<td>% of reduced Mn reoxidized</td>
</tr>
<tr>
<td>Ratio: 9.45:1</td>
<td>Al 12.3</td>
<td></td>
</tr>
</tbody>
</table>
### Conditions

**Run 2.**

**Assay**

- Mn: 44.9
- Cl: 39.9
- Al: 11.6

**Results**

- % of Mn reduced: 31.4
- % of reduced Mn reoxidized: 0.0

### Conditions

**Run 3.**

**Assay**

- Mn: 46.7
- Cl: 39.0
- Al: 12.9

**Results**

- % of Mn reduced: 35.3
- % of reduced Mn reoxidized: 0.0

### Conditions

**Run 3A**

**Assay**

- Mn: 45.3
- Cl: 40.8
- Al: 6.4

**Results**

- % of Mn reduced: 30.0
- % of reduced Mn reoxidized: 0.0

### Conditions

**Run 4.**

**Assay**

- Mn: 66.8
- Cl: 20.6
- Al: 8.9

**Results**

- % of Mn reduced: 76.0
- % of reduced Mn reoxidized: 0.0

### Conditions

**Run 5.**

**Assay**

- Mn: 81.4
- Cl: 1.7
- Al: 4.2

**Results**

- % of Mn reduced: 78.5
- % of reduced Mn reoxidized: 33.9

### Conditions

**Run 6.**

**Assay**

- Mn: 78.4
- Cl: 0.8
- Al: 8.6

**Results**

- % of Mn reduced: 97.7
- % of reduced Mn reoxidized: 7.2
<table>
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<th></th>
<th></th>
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<th></th>
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<tr>
<td>Time: 1 hr</td>
<td>Assay</td>
<td>Assay</td>
<td>Assay</td>
<td>Assay</td>
<td>Assay</td>
<td>Assay</td>
</tr>
<tr>
<td>Temp: 1400°F</td>
<td>Mn 61.3</td>
<td>Mn 80.1</td>
<td>Mn 83.6</td>
<td>Mn 82.2</td>
<td>Mn 86.2</td>
<td>Mn 62.4</td>
</tr>
<tr>
<td>Ratio: 9.45:1</td>
<td>Cl 2.4</td>
<td>Cl 0.2</td>
<td>Cl 1.2</td>
<td>Cl 1.5</td>
<td>Cl 0.4</td>
<td>Cl 29.2</td>
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<tr>
<td>MnCl₂ heated prior to run.</td>
<td>Al 4.2</td>
<td>Al 7.9</td>
<td>Al 4.1</td>
<td>Al 3.8</td>
<td>Al 5.3</td>
<td>Al 5.9</td>
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<td>Results</td>
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<tr>
<td>% of Mn reduced</td>
<td>97.7</td>
<td>99.8</td>
<td>98.8</td>
<td>99.4</td>
<td>99.7</td>
<td>63.8</td>
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<tr>
<td>% of reduced Mn reoxidized</td>
<td>25.2</td>
<td>12.5</td>
<td>21.5</td>
<td>28.9</td>
<td>11.7</td>
<td>0.0</td>
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</table>
Run 13

Assay

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<tr>
<td>Mn</td>
<td>79.4</td>
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<td>Cl</td>
<td>0.2</td>
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<tr>
<td>Al</td>
<td>4.2</td>
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</tbody>
</table>

Results

- % of Mn reduced: 99.8
- % of reduced Mn reoxidized: 38.7

Run 14

Assay

<table>
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<tr>
<th>Element</th>
<th>Assay</th>
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<tbody>
<tr>
<td>Mn</td>
<td>84.3</td>
</tr>
<tr>
<td>Cl</td>
<td>1.7</td>
</tr>
<tr>
<td>Al</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Results

- % of Mn reduced: 98.4
- % of reduced Mn reoxidized: 16.3

Conditions

Run 13
- Time: 1 hr
- Temp: 1250°F
- Ratio: 10.5:1
- Product leached with NaOH soln

Conditions

Run 14
- Time: 30 min at 500
- 30 min at 1250
- 30 min at 1650
- Ratio: 10.5:1
CHAPTER IV

DISCUSSION OF RESULTS

In all of the experiments performed, the first condensate noted outside of the furnace zone was water, which condensed primarily in the cooling coil zone. The second condensate noted was aluminum chloride, which deposited between the cooling coil and the furnace, and extended slightly into the cooling coil zone. Where the aluminum chloride came into contact with the water, it reacted according to the following reaction:

\[ 2\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{HCl} \]

The aluminum oxide was in the form of a fine smoke and covered the remainder of the tube, and extended into the trap. Figure 6 is a picture and sketch of the tube after a reaction has occurred.

---

A. \( \text{Al}_2\text{O}_3 \)
B. \( \text{AlCl}_3 \)
C. Furnace Zone
D. \( \text{MgCl}_2 \)

FIGURE 6

TUBE AFTER REACTION
From the previously listed data, the entire content of the products were not explained by the summation of the Mn, Cl and Al contents. This indicates that some other element or elements are present in the product. The possibilities include oxygen from the hydrolysis of MnCl₂, nitrogen from the air, and oxygen from the air.

The nitride of aluminum is one possible explanation, but it is only formed from nitrogen gas in the presence of sodium carbonate. If it were formed, it would hydrolyze in water and give off ammonia. When the products were leached with water in one run, no odor of ammonia was noticed.

If the contamination was a result of the hydrolysis, it would have been evident in run 1, which took place at 750°F. In this run, the summation of Mn, Cl, and Al in the products was 98.2%. This would indicate that the hydrolysis does not explain the contamination in the larger amounts in subsequent runs. Also, in the first run, the ratio of Mn to Cl was nearly exactly the same as that of MnCl₂. This indicates that the contamination was in the form of an aluminum compound.

From these considerations, it appears that the contamination is oxygen from residual oxygen in the tube, or from leakage in the tube.

The motor used with the pump was not capable of driving it over large periods of time. For this reason, the pump was kept running only during the heating and earlier part of the cooling stages. After the tube had cooled, the drop in pressure was visible on the manometer.

Thermodynamic considerations show that aluminum oxide is much more stable than manganese oxide at all temperatures. If manganese oxide was formed in the presence of elemental aluminum, it would be reduced by
aluminum, so if any oxide was present, the most favorable oxide would be aluminum oxide. If more oxide was present than was in the aluminum oxide, it would be as manganese oxide.

The series of runs from 1 to 8 were designed to show the effect of temperature on the per cent reduction of MnCl₂. The reaction can be written as follows:

$$\text{MnCl}_2 + \frac{2}{3} \text{Al} \rightarrow \text{Mn} + \frac{2}{3} \text{AlCl}_3$$

From figure 1, the standard free energy of formation is favorable at temperatures above 500°C. However, by decreasing the pressure, the free energy of the reaction can be made to be negative even though the standard free energy is positive.

At 750°F (400°C), the standard free energy of the reaction is 0 from figure 1, but by decreasing the pressure, the $$RT \ln P \frac{\text{AlCl}_3}{2/3}$$ term is negative. However, at 1 hr time, the reduction had not occurred at all. At all temperatures above 400°C, the reaction is favorable for all of the pressures used.

Figure 7 is a graph of the per cent reduction of the manganese chloride as a function of temperature, with the time constant at 1 hr and the ratio constant at 9.45 to 1, which is nearly the exact stiochemical ratio. The curve levels off at approximately 1300°F.

The reoxidation of the Mn varied widely from run to run, indicating that the tightness of the vacuum varied from run to run.

Washing the product with NaOH apparently increased the amount of oxidation, as did washing with water.
FIGURE 7.
Per Cent Reduction of MnCl₂
vs
Temperature °F
CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

From the experiments performed, it appears that the reaction does go to near completion, at temperatures above 1300°F, but a better vacuum system is needed.

In order to explain the oxidation, better vacuum equipment would be needed. A vacuum gage would indicate accurately what pressures were obtained at each run and if leakage is present in the system.

A diffusion pump would aid in obtaining very low pressures and thus eliminate most of the residual oxygen.

A better motor on the pump would allow the pump to run continuously with no danger of ruining the motor, and would aid in keeping the pressures constant throughout the runs.

By melting the manganese, any oxides present would form a slag which would be easily removed. A vacuum furnace capable of withstanding these higher temperatures would also aid in the study of this reaction.

From figures 1 and 2, many other metallic chloride can be reduced with aluminum. These present a series of problems for future study. With the favorable properties that aluminum has as a reducing agent, much use should be made of it in this way, in the future.


