5-1948

The Continuous Electrodeposition of Manganese

Joseph W. Joyce

Follow this and additional works at: http://digitalcommons.mtech.edu/bach_theses

Part of the Ceramic Materials Commons, Environmental Engineering Commons, Geology Commons, Geophysics and Seismology Commons, Metallurgy Commons, Other Engineering Commons, and the Other Materials Science and Engineering Commons

Recommended Citation

http://digitalcommons.mtech.edu/bach_theses/250

This Bachelors Thesis is brought to you for free and open access by the Student Scholarship at Digital Commons @ Montana Tech. It has been accepted for inclusion in Bachelors Theses and Reports, 1928 - 1970 by an authorized administrator of Digital Commons @ Montana Tech. For more information, please contact sjuskiewicz@mtech.edu.
THE CONTINUOUS ELECTRODEPOSITION
OF MANGANESE

by

JOSEPH W. JOYCE

A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of
the Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

MONTANA SCHOOL OF MINES
Butte, Montana
May, 1948
THE CONTINUOUS ELECTRODEPOSITION
OF MANGANESE

by

JOSEPH W. JOYCE

A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of
the Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

MONTANA SCHOOL OF MINES
Butte, Montana
May, 1948
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Scope and Importance of Investigations</td>
<td>4</td>
</tr>
<tr>
<td>Laboratory Apparatus and Procedures</td>
<td></td>
</tr>
<tr>
<td><strong>Apparatus List</strong></td>
<td>5</td>
</tr>
<tr>
<td><strong>Cell Construction</strong></td>
<td>5</td>
</tr>
<tr>
<td><strong>Electrodes</strong></td>
<td>9</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>9</td>
</tr>
<tr>
<td>Experimental Results and Discussion</td>
<td></td>
</tr>
<tr>
<td><strong>Generalities</strong></td>
<td>10</td>
</tr>
<tr>
<td><strong>Experimental Data and Results</strong></td>
<td>12</td>
</tr>
<tr>
<td><strong>Test 1</strong></td>
<td>14</td>
</tr>
<tr>
<td><strong>Test 2</strong></td>
<td>14</td>
</tr>
<tr>
<td><strong>Test 3</strong></td>
<td>15</td>
</tr>
<tr>
<td><strong>Test 4</strong></td>
<td>17</td>
</tr>
<tr>
<td><strong>Test 5 and 6</strong></td>
<td>17</td>
</tr>
<tr>
<td><strong>Test 7</strong></td>
<td>18</td>
</tr>
<tr>
<td><strong>Test 8</strong></td>
<td>19</td>
</tr>
<tr>
<td><strong>Test 9</strong></td>
<td>19</td>
</tr>
<tr>
<td>Conclusions</td>
<td>21</td>
</tr>
<tr>
<td>Recommendations</td>
<td>22</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>24</td>
</tr>
<tr>
<td>Bibliography</td>
<td>25</td>
</tr>
</tbody>
</table>

## PLATES

<table>
<thead>
<tr>
<th>Plate</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Components</td>
<td>8</td>
</tr>
<tr>
<td>Electrolytic Circuit Diagram</td>
<td>11</td>
</tr>
<tr>
<td>Electrolytic Apparatus</td>
<td>16</td>
</tr>
</tbody>
</table>
THE CONTINUOUS ELECTRODEPOSITION
OF MANGANESE

INTRODUCTION

Metallic manganese was discovered in 1774 but until its value in the steel industry was realized in 1856 it was of little importance. Many uses have been found recently for manganese but none that approaches the importance of its use in the steel industry.

The United States is the world's major consumer of manganese but a relatively minor producer. Our reserves of high grade ore are not sufficient in any way to meet our demand, however low grade ores are plentiful and promise a potential source of almost unlimited scope. Concentration of these ores to a high grade product has not been commercially successful in most cases, in competition with foreign ores.

In an effort to utilize these low grade ores an extensive research program has been in progress for the last thirty years. Until 1936 very little was accomplished in a practical sense. At that time S. M. Shelton, Associate Metallurgist, Electrometallurgical Section, Metallurgical Division, U. S. Bureau of Mines, published the results of his research on the electrowinning of manganese from aqueous sulphate solutions. Prior work had shown that it was possible to deposit a substantially pure metal by the electrolysis
of both fused salts and aqueous solutions. Concentrations, addition agents, impurities, current densities, electrode materials, hydrogen-ion concentrations, and electrolyte temperature all have a marked effect on the current efficiency, and the purity and texture of the deposit.

The earliest work began on manganese chloride solutions about 1854 and on aqueous sulphate solutions about the time of the first World War.

The basic principles of the electro deposition of manganese had been established by 1925 through the efforts of many investigators. These principles may be summarized as follows:8,9

(1) Manganese may be deposited from aqueous sulphate solutions.

(2) A high concentration of ammonium sulphate must be maintained.

(3) Deposition ceases if the sulfuric acid content exceeds 0.36 percent.

(4) A pH of 6.0 to 8 must be maintained and controlled by ammonia and sulfuric acid.

(5) Best results were obtained when catholyte and anolyte were separated by a diaphragm.

(6) The electrolytic potential of manganese in a normal manganese sulphate solution is 1.449 volts.

The United States Bureau of Mines established an Electrometallurgical Section of the Metallurgical Division in July of 1935 and under the supervision of S. M. Shelton attacked this problem as one of their first projects.
Shelton's objective was primarily to establish an emergency source of manganese in the event foreign supplies were cut off. The process developed was for the continuous deposition of manganese from aqueous solutions of manganese sulphate and chloride containing an excess, by normal weight, of an ammonium salt and maintaining the manganese concentration by additions of manganese carbonate. The cathodes were separated from the anodes by diaphragms, each catholyte compartment being fed separately. The Electro Manganese Corporation of Knoxville, Tennessee developed the process on a commercial scale and has been in production since 1939.

In 1940 Congress authorized the construction of a pilot-plant at Boulder City, Nevada to further the research in this field. A research laboratory maintained in conjunction with the pilot-plant, has made possible a considerable amount of advance in electrodeposition of manganese.2,7

J. H. Jacobs and associates at Boulder City have made several important improvements on Shelton's original process and applied their findings in the pilot-plant operation.5,6,7

The major changes adopted at the pilot-plant are:

1. purification by the addition of 0.4 grams of hydrogen sulphide per liter followed by removal of the precipitated impurities on a plate and frame filter.

2. the addition of 0.1 grams of iron per liter as copperas and subsequent aeration to precipitate colloidal sulphur, colloidal metallic sulphides and organic material.

3. the development and use of a perforated lead-silver-
arsenic anode which cut the formation of manganese dioxide from 25 percent to one percent of the weight of the deposited manganese.

(4) enclosing the anode in a diaphragm compartment making possible one catholyte and one feed and more accurate control of conditions.

SCOPE AND IMPORTANCE OF INVESTIGATIONS

The object of this research was to produce a workable electrolytic cell for the continuous deposition of manganese from aqueous sulphate solutions and determine the critical factors in its operation.

Manganese has become so vitally important to our national security and welfare that our low grade deposits must be commercially developed. Electrodeposition from leach solutions is possibly the answer for this development and if successfully accomplished could bring a new industry to this area.

The work has been based upon the Bureau of Mines research and pilot-plant operations as reported in the literature.
LABORATORY APPARATUS AND PROCEDURE

Apparatus List:

- 2 ampere A.C.-D.C. rectifier
- Ammeter
- Voltmeter
- Resistance box
- Pyrex cell, 10" x 6" x 4"
- Cathode, stainless steel (18-8)
- Anodes, Pb 98%, Ag 1%, As 1%, 40% void
- Hot plate
- Thermometer
- Feed bottle and ring stand

CELL CONSTRUCTION

The description of the operating cell used at Boulder City\textsuperscript{2,7} was the basis for the first attempts to build an experimental unit. The component parts as shown in figure 1 were (1) a rectangular glass cell (2) a false bottom (3) two canvas diaphragms and (4) an overflow siphon.

The false bottom of three-ply plywood was supported one inch above the bottom of the cell by four rubber stoppers and coated with an asphalt emulsion to prevent contact between the diaphragms and the false bottom and between the cell and false bottom using
the asphalt emulsion failed, probably due to the lack of mechanical strength of the emulsion. The common glass cell was broken and discarded in favor of pyrex glass.

The pyrex cell, used in all subsequent work, proved far more durable and satisfactory.

The second false bottom was constructed of one-eighth inch oak and again coated with asphalt emulsion. The diaphragm seal to the oak was made with asphalt and a hot asphalt seal attempted between the cell and false bottom but again failed after a short time.

The seal was finally effected with a reinforcing layer of melted piece of asphalt applied to the cell-false bottom junction.

Leaks in any of the seals allowed catholyte and anolyte to diffuse and since a considerable amount of time is necessary for the two solutions to reach equilibrium, the conditions favorable to deposition were destroyed and only an evolution of hydrogen could be obtained at the cathode. Close inspection revealed a very fine black coating assumed to be manganese dioxide, formed at the cathode.

The difficulties of sealing the diaphragm compartments were overcome by using a heavy coating of asphalt emulsion, allowing several days drying time and maintaining the same electrolyte levels in the two compartments. Further breaks in the seal at the false bottom-cell junction occurred however after a short time due to a very small warping of the oak and the brittleness of the piece of asphalt. This type of cell was then abandoned.
Shelton's early successful work was accomplished using individual cathode compartments rather than a common catholyte. Since the experimental cell had but one cathode, it was decided to redesign the cell along these lines.\textsuperscript{8,9}

The new cell was constructed using a rectangular canvas compartment three and one-half inches long, three inches wide and three inches deep with a sheet of one-eighth inch lead that hooked over the edge of the cell and lined the ends and bottom of the compartment to give it shape and hold it in place.

Two tests were run using this cell. In each case the deposit formed nicely for about four hours then began to redissolve and the catholyte became fouled. Careful examination revealed an excessive treeing at the edges of the cathode and they eventually fell off into the solution and started resolution. Part of the difficulty was traced to the fact that the lead lining of the compartment was a short distance from the anodes and a short distance from the cathode. The current, seeking the path of least resistance was apparently flowing from the anode to the lining and then to the cathode, concentrating the current at those edges of the cathode nearest the lining. The final cell used this same principle and a Lucite lining for the compartment as shown in figure 2.

The cell discharge was very difficult to regulate using the siphon and stop-cock due to the very small amount of feed. To overcome this difficulty a small hole was bored in the glass cell and the end of a small glass tube inserted and sealed to act as an overflow discharge. The final and most satisfactory cell is
Fig. 1. Components of original False-bottomed cell.

Fig. 2. Components of final test cell.
shown in Figure 2.

**ELECTRODES**

The anode most successful in pilot-plant work consisted of 98% Pb, 1% Ag and 1% As with 40% of the surface void.\(^5,6,7\)

To reproduce this anode the alloy was cast in a graphite mold then cut to four inches wide and six inches long. No rolls were available but the desired thickness was realized by machining the sheet to one-quarter on an inch. The sheet was then cut to give two anodes four inches by three inches by one-fourth inch.

The forty percent void was obtained by drilling seven-sixteenth inch holes through the anode. After drilling it was necessary to ream the underside of the hole and sand the anodes to a smooth finish.

The cathode used was sixteen gauge 18-8 stainless steel polished to a mirror finish and washed immediately before submerging in a strong soap solution.\(^6\)

**ELECTROLYTE**

The electrolyte in the circuit actually consists of the anolyte, the catholyte and the feed. All were aqueous solutions of chemically pure salts.

The anolyte and catholyte contain 13 grams per liter of manganese as manganese sulphate and one hundred thirty grams per liter of sulphuric acid.
The pH of the catholyte was 5.5 in the several samples measured with 5cc of concentrated ammonium hydroxide per liter necessary to provide a pH of 7.5. The practice of raising the pH of the catholyte was noted and the unused portion soon developed a light brown precipitate, making it unfit for use.

It was desired to strip about 20 grams per liter of manganese from the feed solution.5,6,7

EXPERIMENTAL RESULTS AND DISCUSSION

All experimental data has been compiled in Table 1 and the following discussion will refer directly to the results recorded.

Test number 1 was the only run made using the false-bottom cell on which data was available.

Tests number 2 and 3 were made using the lead lined compartment and the remainder were made using the Lucite lining for the cathode compartment.

GENERALITIES

The literature relating to the recent Bureau of Mines work stated that a current density of about forty-five amperes per square foot at the cathode and ninety amperes per square foot at the anode was optimum. Best control could be maintained at forty-eight amperes per square foot and was used in most of the tests.

The voltage rose immediately to 4.4 volts and after a film of manganese formed on the cathode dropped to about 4.2 volts.
Fig. 3. Schematic diagram of electrolytic apparatus.
<table>
<thead>
<tr>
<th>Test No.</th>
<th>C.D. Amps/ft.²</th>
<th>Rate of Feed cc/hr.</th>
<th>Catholyte pH Start</th>
<th>End</th>
<th>Time Hours</th>
<th>Deposit</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48</td>
<td>100</td>
<td>8.5</td>
<td>8.7</td>
<td>19</td>
<td>Granular, non-adherent</td>
<td>Catholyte fouled, NH₃ odor strong</td>
</tr>
<tr>
<td>2</td>
<td>48</td>
<td>100</td>
<td>7.6</td>
<td>8.7</td>
<td>19</td>
<td>Granular, burned</td>
<td>Lead diaphragm lining. Catholyte fouled, after 4 hours bright adherent deposit, NH₃ odor</td>
</tr>
<tr>
<td>3</td>
<td>55</td>
<td>100</td>
<td>7.5</td>
<td>8.7</td>
<td>4</td>
<td>Bright, but heavily treed</td>
<td>Catholyte fouled, NH₃ odor. Paraffin strips, short detected between lead lining and anode.</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>120</td>
<td>5.5</td>
<td>8.7</td>
<td>20</td>
<td>Fine-grained bright heavily treed</td>
<td>Lucite diaphragm lining. Paraffin strips, catholyte fouled, NH₃ odor</td>
</tr>
<tr>
<td>5</td>
<td>48</td>
<td>0</td>
<td></td>
<td></td>
<td>19</td>
<td>Bright adherent, trees in catholyte</td>
<td>Catholyte fouled, NH₃ odor cathode area 3/4 x 3/4 in. Feed stopped after 1/2 hrs.</td>
</tr>
<tr>
<td>6</td>
<td>48</td>
<td>100</td>
<td>assumed 5.5</td>
<td></td>
<td>19</td>
<td>Same as above</td>
<td>Catholyte fouled, NH₃ odor, 8 additional 1/2 in. holes in anode, treeing reduced.</td>
</tr>
<tr>
<td>7</td>
<td>48</td>
<td>220</td>
<td>assumed 8.7</td>
<td></td>
<td>2 hrs.</td>
<td>Bright, adherent</td>
<td>Catholyte clear, NH₃ odor</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4 hrs.</td>
<td></td>
<td>4 hrs.</td>
<td>One side burned</td>
<td>Catholyte fouled, strong NH₃ odor, 1/8 in. rubber strips</td>
</tr>
</tbody>
</table>
### TABLE I (cont'd)

#### EXPERIMENTAL DATA AND RESULTS

<table>
<thead>
<tr>
<th>Test No.</th>
<th>C.D. 2</th>
<th>Rate of Feed cc/hr.</th>
<th>Catholyte pH</th>
<th>Time Hours</th>
<th>Deposit</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>48</td>
<td>90</td>
<td>8.7</td>
<td>2</td>
<td>75% burned</td>
<td>Catholyte fouled, plain 1/8 in. lead anodes, NH₃ odor 1 hr., greatly increased MnO₂</td>
</tr>
<tr>
<td>9</td>
<td>48</td>
<td>50</td>
<td>8.3</td>
<td>5</td>
<td>Fine grained bright, adherent Wt. 3.652 gms.</td>
<td>Feed 20 cc/24 min., Catholyte clear</td>
</tr>
</tbody>
</table>
The voltage did not change noticeably when resolution began or as it progressed.

In tests 1, 2 and 3 the initial pH of the catholyte was increased as noted with ammonium hydroxide and thirty grams per liter of sulfuric acid was added to the anolyte to approximate operating conditions at the Boulder City pilot-plant.

TEST 1

The deposit began to form in about one hour but appeared quite dark. The catholyte began to show some signs of a leak in the diaphragm seal in about three hours. In nineteen hours electrolysis was stopped and the variables examined. The deposit was granular and non-adherent showing signs of resolution and with a major portion of the metal loose on the cell bottom. The catholyte was badly fouled with both a brown and a white precipitate assumed to be hydrous manganese dioxide and manganese hydroxide. A strong odor of ammonia was present indicating resolution of the metal and the accompanying formation of the precipitates.7

Further examination revealed a warping of the false bottom which had completely destroyed the seal between the cell and the false bottom.

TEST 2

The lead-lined cathode compartment cell was used for this test with the catholyte pH adjusted to 7.6 and twenty milliliters of
sulphuric acid per liter added to the anolyte.

After four hours the deposit appeared to be fine grained and bright but very heavily treed at the edges. Electrolysis was stopped after nineteen hours, the catholyte was fouled, the deposit burned and granular and a strong ammonia odor present.

TEST 3

Readjustment of cell components to provide for an overflow electrolyte discharge resulted in decreasing the cathode area submerged and consequently increased the current density considerably. This test was checked very closely in an effort to determine the cause of the excessive treeing.

The cell operated very well for about three and one-half hours. The cathode was raised from time to time to check the condition of the deposit. The deposit formed bright and adherent with a great many trees at the edges. The trees finally began to fall off the cathode into the electrolyte and redissolve and within fifteen minutes, the catholyte became fouled and a strong ammonia odor was detected. The cathode edges had been dipped in paraffin in an attempt to hold down the treeing but gas bubbles forming on the cathode peeled the strips away.

A check of the electrical circuit revealed a short circuit between the electrodes and the lead compartment lining. The anode to cathode distance was one and three-fourths inches through a relatively poor electrolyte conductor. The anode to lead lining
Fig. 4. Laboratory apparatus with cell in operation.
distance was less than one-half inch and the cathode to lining 
distance about three-eighths of an inch, apparently resulting in 
a concentration of current at the edges and an increase in the 
amount of treeing.

In each of the first three tests the pH had been raised 
initially and continued to rise to 8.7 at the time the ammonia 
odor was detectable. Since manganese hydroxide readily precipit-
ates at a high pH this practice was discontinued in an effort to 
reduce the final value.

**TEST 4**

The lead compartment lining was abandoned in favor of one made 
of Lucite to provide the necessary shape and rigidity for the 
compartment.

The current density was reduced to 45 amperes per square foot 
and the feed increased slightly to provide a more rapid solution 
flow through the cell. Paraffin strips were again used but with 
the same results as in test 3.

The results of test 4 were practically the same as in test 3.

**TEST 5 and 6**

Data compiled to this point indicated that if trees could 
be prevented the operation should proceed continuously. The area 
of the cathode was increased to allow an excess of one-eighth of 
an inch in all dimensions over the anode surface. It was believed
this would eliminate the treeing at the edges. The feed tip became plugged after about one and one-half hours but sufficient deposit was obtained to indicate treeing persisted along the lower edge. The anode had four seven-sixteenth inch holes to increase the anode current density, by using only three-quarters of an inch immersion of the anode it seemed likely that the diameter of the hole had become critical. The lower portion of the anodes in use was solid, the upper half contained the holes. Eight one-quarter inch holes were drilled in the bottom half of the anode for test 6, again using the large cathode.

Results were considerably better with treeing reduced to a great extent, and a bright close-grained deposit formed, however, the catholyte was again fouled and some particles of metal (presumably from treeing) were found in the bottom of the cell.

TEST 7

This test had two objects and was operated under close observation. First the cathode was stripped with one-eighth inch rubber tubing split lengthwise and slipped over the submerged edges of the cathode to eliminate the treeing at those areas. This was accomplished successfully, however a tendency to tree or peel was evident at the rubber-cathode junction. The feed was greatly increased to observe its effect on the cell operation. At the end of two hours a faint ammonia odor was detectable but no treeing had developed and a bright close-grained deposit was forming. The catholyte began to foul rather slowly and one side
of the cathode deposit began to dissolve and the deposit on both sides began to peel away from the bottom of the cathode.

**TEST 8**

Plain rolled-lead anodes one-eighth of an inch thick were installed in the cell and the feed reduced to ninety milliliters per hour. The increase in the formation of manganese dioxide at the anode was amazing and in about one hour ammonia was detectable from the cathode compartments. Electrolysis was stopped after two hours when the catholyte became fouled. The deposit formed had been about 75% dissolved.

**TEST 9**

A careful examination of the data collected in the first eight tests indicated a reduced rate of feed might be the answer to the problem. A feed of fifty milliliters per hour would maintain a concentration of thirteen grams per liter of manganese in the catholyte sixty percent current efficiency.

Increasing the size of the cathode and adding the rubber strips to the edges had almost filled the cross-section of the cathode compartment and stopped the free circulation of the electrolyte. Since the feed solution was introduced to only one side of the compartment, it seemed probable that most of the difficulties encountered in tests 6, 7 and 8 could be explained by the overfeeding of one half and the impoverishing of the other half of the cathode.
compartment.

The feed in test 9 was reduced to fifty milliliters per hour and fed intermittently, ten milliliters to each side of the cathode every twenty-four minutes. A slight burning of the deposit along the upper edge developed probably due to the fluctuating solution level.

After five hours of continuous operation, electrolysis was stopped. The cathode deposit was bright and fine grained and exhibited no treeing or nodules. The catholyte was clear and free from the odor of ammonia.

The deposited manganese stripped from the cathode readily upon flexing and, though very brittle, an estimated ninety-eight percent was recovered. The metal weighed 3.852 grams and represented a current efficiency of approximately fifty percent.
CONCLUSIONS

Metallic manganese can be continuously deposited from aqueous sulphate solutions within narrow limits of control.

The solution fed to the cell must be regulated to replace the manganese deposited on the basis of an anticipated current efficiency to prevent an increase in the manganese ion concentration in the catholyte. The hydrogen gas evolved at the cathode imparts a stirring action to the catholyte, however, the compartment must be large enough to allow free circulation.

A metallic deposit can be obtained only if the anolyte is prevented from diffusing or mixing with the catholyte.

Treeing at the cathode can be prevented by close control of the operating variables and by covering the cathode edges with suitable strips. Care should be exercised not to allow any individual void area of the anode to become a major portion of the surface.

Any material used in the cell construction with less resistivity than the electrolyte should be kept further from the electrodes than the distance from the anode to the cathode.
RECOMMENDATIONS

Recovery of manganese from the low grade Butte and Phillipsburg ores will undoubtedly attract future investigators. These recommendations are set forth in an effort to provide some assistance for them.

The cell used should be of the type first constructed for this work. I believe a successful cell could be built using Lucite for the false bottom. It is advantageous to be able to observe the interior of the cell in operation and since the electrolyte did not affect the Lucite in any way, it is possible that it could be used for all construction.

The catholyte compartment should be as large as possible and in any event contain a greater volume than the anolyte compartment. Jacobs and Woodman\(^5\) used a catholyte-anolyte ratio of 5.29 to 1 and the advantages of such a ratio are easily recognized.

Any cell to be operated continuously should be sufficiently large to require a substantial amount of feed solution. As the volume of feed required per unit of time is decreased, the difficulties encountered in providing a uniform flow multiply rapidly.

The cell should be equipped with an overflow discharge tube. Discharge by siphon must be regulated to correspond identically with the intake of feed and even a slight variation will give a fluctuating solution level and create trouble at the cathode.

The literature cited in the Bibliography covers all phases of the electrodeposition of manganese from aqueous sulphate solutions.
Future investigators should be warned, however, to carefully study the later reports before beginning any laboratory work. Many of the very important details are inferred or mentioned very briefly particularly if the information is negative.
ACKNOWLEDGEMENTS

The writer wishes to express his appreciation to Professor J. P. Spielman for his guidance and criticism, to Doctor K. N. McLeod and R. I. Smith for their valuable assistance, and to the faculty and staff of the Montana School of Mines for making this work possible.
BIBLIOGRAPHY

1) Dean, R. S., "Electrolytic Manganese and Its Potential Metallurgical Uses", Mining and Metallurgy, Feb., 1941

2) Dean, R. S., "Present Status of Electrolytic Manganese and Its Alloys", Metals Technology, June 1944


4) Hill, Fred J., "Electrodeposition of Manganese from Certain Aqueous Solutions", Montana School of Mines, Senior Thesis 1935


10) Sullaway, W. F., "Electrolytic Manganese from Aqueous Sodium Manganate Solutions", Montana School of Mines, Senior Thesis 1943

25
11) Thompson, L.L., "The Electrowinning of Manganese from Rhodochrosite", Montana School of Mines, M. S. Thesis 1941