



Electrolytic synthesis of battery-grade manganese dioxide
by George E Lohse

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University
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Abstract:

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ELECTROLYTIC SYNTHESIS OF
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GEORGE E. LOHSE

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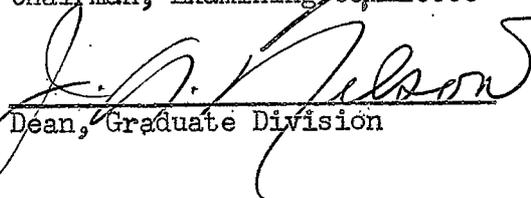
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Chairman, Examining Committee



Dean, Graduate Division

Bozeman, Montana
September, 1952

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ABSTRACT

This paper describes the semi-pilot plant production of battery active manganese dioxide from Montana manganese ores.

The operations included crushing and grinding the ores; leaching them with sulfuric acid; removal of impurities, filtration, and electrolysis of the solution, and stripping the electrodes of the product.

Iron, the chief impurity, was removed by making use of the selective solubility of ferric and manganous ions in dilute solutions of pH equal to 6.0.

Filtration was accomplished on a plate and frame press but a large volume of filter aid was required.

Electrolysis was performed in a 25 gallon plastic-coated steel tank using AGR graphite anodes and chemical lead cathodes.

Anode stripping of manganese dioxide was easily accomplished by baking the electrodes in an oven at 115°C, then scraping to free the product.

Battery tests of the manganese dioxide produced from these operations compare favorably with the U.S. Army Signal Corps Specification. The product and specification values are respectively 138 hours and 130 hours for low drain tests of size "A" cells through 166 2/3 ohms, and 5.25 hours and 5.5 hours for high drain test of size "A" cells through 16 2/3 ohms.

INTRODUCTION

The use of naturally occurring forms of manganese dioxide in dry cells has been described by Phalen in 1919 (4). The exact physical structure of battery-active manganese dioxide and the manner in which its depolarizing action proceeds is not generally known. There is therefore no direct method of evaluating battery activity other than by actual test in a dry cell.

Manganese dioxide occurs naturally in various physical phases most of which are not sufficiently battery active. The form most suited for dry cells as determined by electron micrographs of proven samples is that known as "gamma," which is represented by anhedral (amorphous) particles and clusters. Electron diffraction patterns of the "gamma" phase give characteristic lines which lack fineness, another indication of amorphous structure.

Of the world's known deposits of manganese dioxide that from the African Gold coast provides the principal source of MnO_2 of good battery-activity for the United States. A small deposit of battery-active manganese ore has been found in this country at Phillipsburg, Montana, but its quality renders it hardly competitive with the imported product. In the event of extreme emergency and the uncertainty of the African supply in wartime, military and domestic needs require the use of domestic ore as a source for the production of manganese dioxide.

Prior to this investigation work has been done in detail both at this institution (3) and at the Georgia Institute of Technology (1) regarding the electrolytic synthesis of battery grade manganese dioxide on a laboratory scale. In these reports are listed full information on the effects of con-

centrations of solution, current density, cell voltage, types and sizes of electrodes, and impurities on the nature and activity of manganese dioxide produced.

Experiments by the Western Electrochemical Company (5) and the Tennessee Corporation (6) have shown that battery grade manganese dioxide can be produced continuously by electrolysis with good current efficiency, providing the proper conditions are employed. The former has produced one ton per day of material which met U. S. Army Signal Corps Specifications (7). Conditions used compare closely with those reported by Magnuson (3).

Montana ores are of two types, pyrolusite and rhodochrosite. The chief impurities of each are silica and iron, the latter being the more detrimental and the harder to remove. The amount of iron in some cases is as high as eight percent. Data have not been reported on the removal of iron of such a high concentration from a manganous solution without loss of manganese. In every case where experimenters have produced "gamma" phase manganese dioxide by electrolysis, all have obtained battery life long enough to meet Signal Corps Specifications. The presence of iron in manganese dioxide apparently has no effect on the phase produced but counteracts the slight acidity of the battery once it is made. As a result the depolarizing action of manganese dioxide ceases in the neutral or basic medium and battery life terminates.

The reason for this investigation was to develop a stepwise series of operations for the processing of raw ore, through leaching, filtering, and electrolyzing to obtain specification material; a procedure that can easily be copied for a large industrial operation for Montana ores.

METHODS

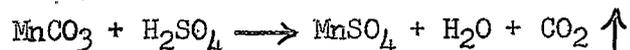
Processing of Ore

Rhodo-chrosite and pyrolusite ores were initially reduced in a jaw crusher to particle sizes ranging up to one-half inch in diameter. The ores were further reduced in a pulverizer to sizes no larger than one-eighth inch, and then ground in a ball mill to pass a 40-mesh screen. At that point rhodo-chrosite ore (manganese carbonate) was ready for leaching. Pyrolusite (inactive oxide of manganese) however required roasting, preferably to manganous oxide, before leaching was possible.

Leaching

Ores were leached with 10 N technical grade sulfuric acid in a twenty-five gallon tank which was coated with asphaltum paint to resist the action of the acid on the metal. Agitation was intermittent and was accomplished with a one-third horsepower mixer (1700 R.P.M.) using a wooden impeller. Abrasion by the ore on the sides of the tank eventually removed the asphaltum and allowed the acid to attack the metal surface. To prevent such action a rubber coating to resist abrasion should be used.

The extraction of rhodo-chrosite with sulfuric acid proceeds according to the equation:



Generally, ten percent excess acid (based on the amount required for the manganese portion only) is used instead of the theoretical amount required for the extraction of the manganese and the other soluble portions of the ore.

If the percentage of the acid soluble constituents of the ore is known, the proper amount of acid can then be calculated and excess acid is not needed.

The extraction of raw pyrolusite ore with sulfuric acid cannot be accomplished for reasons which are shown later in the thermodynamic calculations. Pyrolusite can be roasted to lower oxides of manganese which can be leached with this acid. Manganous oxide is the best oxide for leaching, and roasting to this form can be accomplished in a reducing atmosphere with the aid of hydrogen at 250°C or with coal at temperatures near 1000°C.

Filtration

Filtration has been found to be somewhat difficult although clear solutions have been obtained.

The general method used is as follows:

1. After the leach with sulfuric acid the solution was neutralized to a pH of 6.0 to 6.5 using hydrated lime, then air blown for 48 hours to precipitate ferric hydroxide.
2. Johns Manville celite filter cell was added to improve filtration.
3. Filtration was accomplished on a plate and frame press, and the cake was subsequently washed with tap water.

The solution of Butte rhodochrosite was filtered on a small hand plate and frame press. Initially a thin film of sludge on the vinyon filter cloths rendered them impermeable to the solution and filtration stopped. Pressure was increased until the cast-iron frame cracked. After it was replaced by one of steel, filtration was continued after one pound of filter aid was added to four liters of solution. This operation was done without neutralization

and additional impurities were introduced because of the effect of the acidic solution on the iron press. It was noted at this time that the solution cleared upon standing and that filtration problems can be greatly eased by allowing the sludge to settle.

The solution of Phillipsburg rhodochrosite was first neutralized with calcium oxide and calcium carbonate until the pH reached a value of six. It was then air-blown for 48 hours to precipitate ferric hydroxide and was filtered on a Sperry plate and frame press using three frames, each having a total filtering area of 200 square inches.

To leach 51 pounds of this ore, thirty-one pounds of sulfuric acid diluted to approximately 35 liters was employed. The excess acid was then neutralized and 5 pounds of filter aid (this amount occupied a loose volume of 3.5 U. S. gallons) were added before filtration was made on the press. During the filtration the pressure reached 60 pounds gage and would undoubtedly have gone higher had slippage not occurred in the centrifugal pump. When the cake was washed, the water pressure built up to 75 pounds. The time for the filtration of 35 liters was two hours. Further filtrations were performed using a 24-centimeter Buchner funnel with suction applied by water aspirator.

The amount of filter aid to be added for easy filtration will depend primarily upon the particle size to which the original ore has been ground. The finer the particle size the more difficult is the filtration. Other constituents of the sludge affecting the ease of filtration include the amounts of calcium precipitate and ferric hydroxide which is formed during the air oxidation.

Other methods of filtration are desirable. Two suggestions are centrifuge

and a precoated rotary vacuum filter. If an Oliver is first coated with a thick layer of filter aid and the knife blade so adjusted to scrape off the sludge as it cakes, this method should prove satisfactory. No industrial methods besides the plate and frame press have been attempted at this institution and those suggested are mere postulations.

Removal of Impurities

Of the inactive ingredients of the Montana ore, silica constitutes the major portion, and no other constituent is present in large amounts. None of these are attacked by sulfuric acid and all are removed in the initial filtration.

The active ingredients are characterized chiefly by calcium oxide and iron besides the manganese, but traces of zinc, lead, copper, silver, gold and aluminum can be found in these ores. Only calcium and iron are present in amounts which would affect the manganese dioxide. Since calcium is relatively insoluble as the sulfate, its presence causes no difficulty and is easily removed in the initial filtration.

The removal of iron was the most difficult task encountered during this development. Several methods have been tried but the most satisfactory one involves the use of a costly chemical.

The first reagent tried is known by its trade name Versene. It is a tetra sodium salt of ethylene diamine tetra acetic acid. This compound has the property of chelating (complexing with) iron such that it cannot be removed from solution. Versene F-3 Specific is a special reagent for iron and has been used successfully by the Bersworth Chemical Company (\$) to

prevent the deposition of that metal in copper electrolysis. A like procedure was tried for manganese and iron. An amount of Versene F-3 Specific to complex the iron, as determined from a graph in the Bersworth Bulletin, was added to a solution of manganous and ferrous sulfates. Upon electrolysis no manganese dioxide was deposited and it was assumed that the Versene prevented the deposition of the MnO_2 as well as the iron. As the Versene could also prevent the precipitation of iron in basic solution, sodium carbonate was added to precipitate manganese carbonate. Manganese was present in both the filtrate and residue and was apparently chelated along with the iron until the Versene was expended. Strong potassium hydroxide caused a precipitate of most of the manganese with little effect on the iron in solution. However the presence of the alkali metal in the electrolyte after the manganese is dissolved causes the inactive "alpha" phase instead of the "gamma" upon electrolysis.

The second reagent employed is the ammonium salt of nitrosophenyl hydroxyl amine, better known as cupferron. This reagent can quantitatively remove iron from a 20 percent sulfuric solution (2) without loss of manganese according to the equation:



The ferrous cupferrate precipitate can be filtered or it can be extracted with ether or chloroform in which case its recovery is then possible with the evaporation of the ether. The initial cost of the cupferron is too high to discard the cupferrate, and unless a suitable organic chemical as strong a base as potassium hydroxide is found to regenerate the cupferrate to a usable form, its use is not economically advisable. Potassium hydroxide

could be used, but again the alkali metal ion would be introduced.

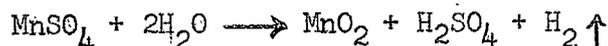
Ammonium hydroxide is not basic enough for the regeneration.

The final method used involves the differential solubility of manganese and iron in neutral and slightly acidic solution. Ferric hydroxide can be precipitated from a solution of pH equal to 5.0 but manganese hydroxide can be precipitated only in a solution above a pH of 8.0.

After leaching the ore with sulfuric acid, the solution was neutralized to a pH of 6.5 with calcium hydroxide or calcium carbonate and air blown to oxidize ferrous ion to ferric. Ferric hydroxide was thrown out of the solution with no appreciable loss of manganese. Calcium hydroxide was used because the calcium sulfate formed from the reaction with sulfuric acid was insoluble and could be removed along with the ore insolubles and ferric hydroxide in the initial filtration.

Electrolysis

After a pure manganous sulfate solution is obtained, it is electrolyzed and manganese dioxide is deposited according to the equation:



Electrolytic operation was performed in a plastic coated steel tank of approximately 25 gallons capacity. The power was supplied by a motor-generator set equipped with a variable rectifier circuit as shown on Figure 1 to adjust the voltage and current density at the proper values. The manganese dioxide deposited on an AGR graphite anode spaced one inch on either side from two chemical lead cathodes at which hydrogen was emitted. The anode size was $\frac{1}{2}$ " x 4" x 10" and the cathodes were $\frac{1}{16}$ " x 4" x 10". The sizes of the electrodes have no effect on the product formed and any sizes

or shapes can be used as long as the proper anode to cathode spacing is maintained. The best conditions as found by Magnuson(3) for electrolysis were as follows:

voltage	1.95 volts
amperage	6.7 amperes per sq. ft. of anode
temperature	93°C
H ₂ SO ₄ concentration	95 grams per liter
MnSO ₄ concentrations	150 grams per liter
Anode to Cathode spacing	1 inch

The effects of the above on current efficiency are shown on Figures 2, 3, 4 and 5 which were reported in previous work at this institution (3).

Anode Stripping

The deposit of manganese dioxide on graphite clings tenaciously to the surface and is difficult to remove. Methods suggested include scraping, boiling the spent manganous sulfate solution in which the anode is inserted and subsequent filtration to remove the product which had fallen off the electrode, and precoating the anode with oil before electrolysis, with subsequent removal of the product by scraping.

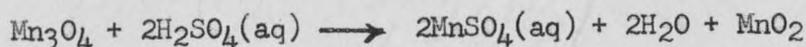
The best method found was to roast the anode in an electric oven at 115°C. As liquid evaporated the product contracted and cracked on the surface. When this condition was attained, the manganese dioxide could easily be removed by scraping.

If the electrolyte is not maintained above 90 degrees during electrolysis, the graphite anode softens and carbon is easily removed during the scraping operation. Soft anodes are thus the cause of excessive carbon content of the manganese dioxide.

THERMODYNAMIC CONSIDERATIONS

In order to consider the feasibility of some of the chemical processes which occurred during this investigation, the thermodynamic calculations were made and are so reported.

The thermodynamics for the extraction of raw pyrolusite ore with sulfuric acid indicate that the reaction is very unfavorable. With the approximate formula of the oxide as shown the reaction is as follows:



$$\Delta H_{f298}^{\circ} (-345) + 2(-211.84) \longrightarrow 2(-265) + 2(-68.32) + (-123)$$

$$\Delta H_{298} = -21.0 \text{ kcal/mole}$$

$$\Delta F_{298} (-319.58) + 2(-176.2) \longrightarrow 2(-224.7) + 2(-56.7) + (-102.9)$$

$$\Delta F_{298} = 10.88 \text{ kcal}$$

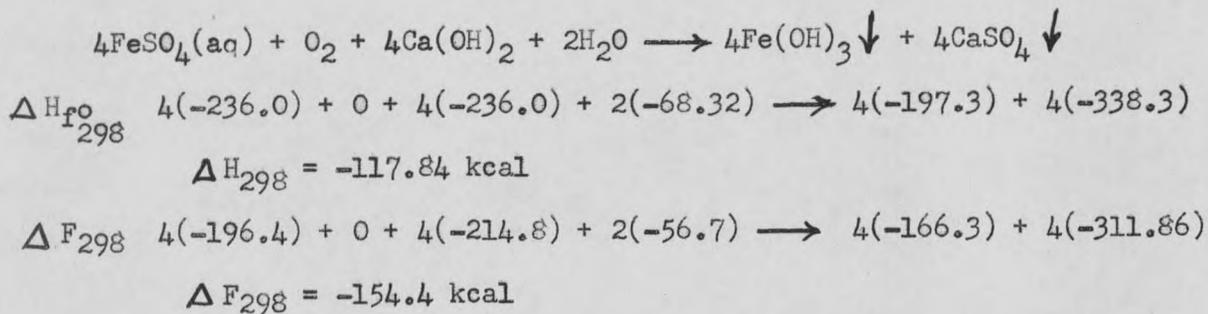
$$\Delta S \approx \frac{-21000 - 10880}{298} = -107 \text{ Entropy units}$$

Temperature of neutral energy

$$T = \frac{-21000}{-107} = 196^{\circ}\text{K}$$

The free energy of this reaction is 10,880 calories per mole and the temperature at which the value is zero is 196°K. For this reason pyrolusite should be roasted to lower oxides for leaching.

For the removal of ferric hydroxide from the manganeous and ferrous sulfate solution, the equation and thermodynamics are as follows:



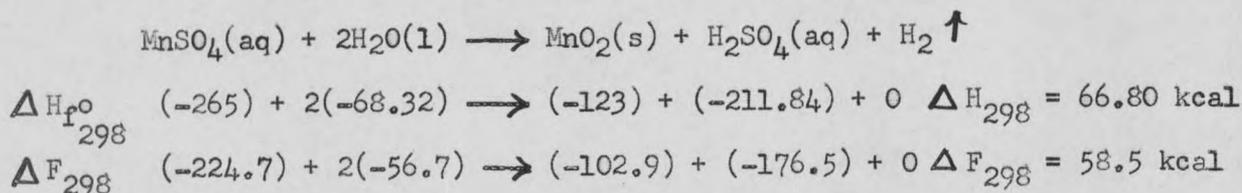
$$\Delta S = \frac{\Delta H - \Delta F}{T} = 122.8$$

From the above, the equilibrium constant can be calculated by

$$K_{\text{eq}} = e^{-\left(\frac{\Delta F}{RT}\right)} = 6.2 \times 10^5$$

The thermodynamics indicate that the reaction is very favorable as the value of the free energy is -154,400 calories per mole. This reaction should theoretically proceed as long as the proper pH is maintained.

The deposition of manganese dioxide proceeds according to the equation



At 93°C the value for the free energy is 56,600 calories per mole. When this value is converted to electrical units, the theoretical amount of power required is 0.344 kilowatt hours per pound of manganese dioxide. The value does not agree with the value of 0.54 kilowatt hours per pound calculated from Faraday's Law. Neither does it assume that the exact mechanism of the reaction proceeds from a manganese valence of two to four by the direct action of electric current. The thermodynamic calculations involve only the initial and final products, not the possible intermediates or the mechanism.

MATERIALS AND EQUIPMENT

The sources of manganese for all operations have been Montana ores obtained from Phillipsburg and Butte, Montana. Assays of these ores are given in Table I.

Originally an electrolytic tank of cedar was used for the electrolysis, but was replaced by the plastic coated steel because organic resins in the wood which were dissolved by the acidic solution caused a precipitate that contained manganese upon electrolysis.

A Karbate tank would also be suitable because an immersion heater made of that material showed no deterioration in the acid solution.

TESTING

Analyses of products and solutions as well as the fabrication of batteries were performed in this laboratory. Battery testing consisted of a low drain at $166 \frac{2}{3}$ ohms and a high drain at $16 \frac{2}{3}$ ohms with size "A" dry cells. End voltages for low and high drains specifications (7) were respectively 1.13 and 1.00 volts.

Acid concentrations were found with a standard pH meter, and manganous sulfate concentrations were determined by colorimetric means as described by Magnuson (3).

RESULTS

Filtration

Filtration has been accomplished with difficulty on a plate and frame press after filter aid was added to speed the operation. Other methods

suggested include centrifuge and a precoated rotary vacuum filter.

Removal of Impurities

A solution containing ten percent $\text{FeSO}_4 \cdot x(\text{H}_2\text{O})$ was reduced in a single trial with cupferron such that manganese dioxide with 1.72 percent iron was produced upon electrolysis. Results are inconclusive because of the unknown amount of water of crystallization in the ferrous sulfate used. They do show however that cupferron is a suitable reagent to remove iron even though its use has not been proven economically advisable.

The removal of iron by precipitation of ferric hydroxide in a solution of pH equal to 6.0 cannot be accomplished in one pass if the iron content is high. When Phillipsburg rhodochrosite was used as the source of manganese and the concentrations of manganous and iron sulfates were respectively 190 and 10 grams per liter, oxidation of the solution with air reduced the iron concentration to nine grams per liter although the pH was maintained above 5.0. After filtration and subsequent treatment as before, the iron content was reduced to eight grams per liter. To explain the above phenomenon the following hypothesis has been developed:

a. The precipitation mechanism proceeds according to the equation as follows and not by the one previously cited.



For each amount of ferrous sulfate converted to ferric hydroxide there is an equivalent amount of acid formed. It is readily seen that the hydrogen ion concentration cannot be maintained unless a substance such as calcium is present to react with the acid as it forms.

b. The precipitation of ferric hydroxide requires considerable water per mole. The affinity of ferrous and manganous sulfates to retain water for solution as the concentrations increase greatly retard the oxidation of the ferrous ion to the ferric state. Thus the precipitation of ferric hydroxide is retarded.

The difficulties which arise could, therefore, be overcome by using dilute solutions initially.

When the same Phillipsburg rhodochrosite solution containing four grams per liter of iron was diluted to twice its original volume, neutralization and air oxidation reduced the iron content to one gram per liter on the first trial. The second oxidation reduced the iron content to less than 0.001 grams per liter. The above hypothesis, therefore, appears to be correct and dilute solutions should be used to speed the removal of iron. In an industrial process it will then be necessary to use some method of evaporation to re-obtain the proper manganous sulfate concentration.

Electrolysis

Conditions employed for the deposition of manganese dioxide are shown in Table II. In all runs the current densities were maintained as close as possible to 6.7 amperes per square foot per cell and the voltages at 2.0 volts. The equipment however was not properly constructed to adjust both variables to the correct values. As long as the voltage did not become excessive, the current density was chosen as the more important variable.

Two cells connected in parallel were used in each run except for that run in which the solution from Butte rhodochrosite was electrolyzed. In this

case the operation was completed in a battery jar after resins from a cedar tank rendered that apparatus unsuitable. The actual line amperage is twice that as shown in Table II, and is assumed to be equally divided between the two cells.

All runs were continuous except that of the Butte ore electrolyte which was operated with different solutions as each became contaminated with precipitated resin.

It is readily noted that the current efficiency is low in all runs. These values are based on the weights of manganese dioxide which were stripped from the anodes, and upon the calculated value of 0.54 kilowatt hours per pound as determined by the Faraday Law. This law is used because it has been customary in the past to determine current efficiency according to this method. Of the two Phillipsburg ore runs, the current efficiency of the first is low because of the low temperature. It was noted in this case that the anodes were considerably softened at the temperature below 90°C. As a result carbon was easily removed from the electrode and the manganese content of the product was greatly reduced because of the excessive carbon. In the second run of electrolyte from Phillipsburg ore the acid concentration was kept below that of Magnuson's (3) and corresponded to that used by the Western Electrochemical Company (5). The efficiencies were better for the lower acid content and indicate that more suitable conditions should be developed for the larger scale operations.

Analyses of the products are shown in Table III. The effect of iron and carbon upon the battery life of the cells can be noted. The manganese dioxide from Butte rhodochrosite which had 59.7 percent manganese, 1.7 percent iron,

and low carbon content gave results as good as the product from the first run of Phillipsburg electrolyte which had 51 percent manganese, 0.886 percent iron, and relatively high carbon content. The low drain for the respective products were 110 hours and 106 hours; the high drain times were 3.95 hours for the Butte MnO_2 and 4.1 hours for the Phillipsburg.

From the above data it can be seen that the presence of iron or carbon causes a decrease in battery life of the cell. Iron and carbon contents should be kept as low as possible.

After the solution from the Phillipsburg rhodochrosite was treated for the second time to remove iron, it was electrolyzed and conditions of operation and product analysis are listed in Tables II and III as Run 2. This product gave specification low drain battery test of 138 hours and was short 15 minutes of the 5.5 hours required for high drain specifications. After 24 hours the batteries from the high drain test recovered to a line voltage on the $16 \frac{2}{3}$ ohm circuit of 1.35 volts. The manganese content of this product was 58.6 percent, the iron content 0.065 percent. The carbon content made up most of the difference between the maximum possible manganese percentage and the 58.6 percent actually present. If this carbon content were reduced it is believed that the product would also meet the high drain specifications. In an electrolytic operation, it will be necessary to maintain the proper temperature such that the anode deterioration is kept to a minimum. Then the carbon is not easily scraped from the electrode and the amount in the product is reduced.

SUMMARY

The following statements can be made from the results found at this institution:

1. Specification grade battery active manganese dioxide can be produced electrolytically from Butte and Phillipsburg rhodochrosite ores, providing the iron content of the product is kept low.
2. Iron can best be removed by making use of the selective solubility of ferric and manganous ions in solutions of pH between 5.0 and 6.5. If the solutions are kept dilute, ferric hydroxide will readily precipitate in this pH range upon air oxidation of the ferrous to the ferric ion. However, a series of oxidations may be necessary before the iron content is sufficiently reduced. The addition of calcium hydroxide is suggested to maintain the proper pH range.
3. Acid resisting plastic-coated tanks or those made of Karbate are suitable for electrolytic operation. Cedar vessels are not satisfactory.
4. Filtration can be accomplished on a plate and frame press if filtering aid is used. Other methods suggested include the use of a centrifuge or a precoated rotary vacuum filter.
5. Temperatures should be maintained above 90°C to prevent deterioration of graphite anodes and to improve current efficiencies.
6. It may be necessary to alter operating conditions on different apparatus in order that current efficiencies can be improved.

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