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Leaching of Pyroxmangite Ore With Calcium Fluoride and Sulfuric Acid

By S. R. Droes, K. P. V. Lei, and T. G. Carnahan

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CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere	min	minute
$A \cdot h$	ampere hour	mL	milliliter
cm	centimeter	mL/min	milliliter per minute
cm^2	square centimeter	mol/L	mole per liter
°C	degree Celsius	mm	millimeter
g	gram	μm	micrometer
g/L	gram per liter	mt	metric ton
h	hour	pct	percent
kg	kilogram	rpm	revolution per minute
$kW \cdot h/kg$	kilowatt hour per kilogram	V	volt
mA/cm^2	milliampere per square centimeter		

LEACHING OF PYROXMANGITE ORE WITH CALCIUM FLUORIDE AND SULFURIC ACID

By S. R. Droes,[1] K. P. V. Lei,[2] and T. G. Carnahan[3]

ABSTRACT

The U.S. Bureau of Mines investigated calcium fluoride (CaF_2) assisted sulfuric acid (H_2SO_4) leaching as an alternative to the melting-quenching procedure to obtain Mn from domestic manganese silicate resources. Pyroxmangite [(Mn, Fe) SiO_3] ore containing, in percent, 34.4 Mn, 22.8 Si, 2.6 Ca, and 1.3 Fe was leached in a 500-mL resin kettle. Ninety-six percent of the Mn was extracted under conditions of 330 g/L ore, 245 g/L H_2SO_4, 35 g/L CaF_2, 90° C, and 2 h.

To incorporate electrowinning in recovering Mn, the ore was leached with a simulated spent anolyte solution containing, in grams per liter, 12 Mn, 140 H_2SO_4, 130 $(NH_4)_2SO_4$ (ammonium sulfate), and 5 CaF_2. Manganese extraction of 92 pct was achieved from 130 g/L ore leached at 90° C in 3 h. The Fe, silica (SiO_2), and other impurities were precipitated from the pregnant solution by neutralization with ammonia (NH_3). Manganese of greater than 99-pct purity was deposited at a cathode current density of 50 mA/cm^2 at 30° C, with a current efficiency of 65 pct in a two-compartment cell. A flowsheet was proposed for the leaching and electrowinning procedure.

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INTRODUCTION

The United States is almost 100 pct dependent on foreign sources for manganese (*1*).[4] Domestic manganese silicate resources containing approximately 17 million mt of manganese have been identified, which could decrease this dependence if efficient or improved technology were developed to extract the metal values. The pyroxmangite ores of the Sunnyside district of San Juan County, CO have been estimated to contain a resource of 2.4 million mt of manganese. However, manganese extraction from pyroxmangite was described as infeasible because of the refractory nature of silicate minerals (*2*).

Previous U.S. Bureau of Mines investigations of pyroxmangite showed that melting at temperatures as high as 1,500° C followed by rapid quenching converted 92 pct of the Mn into an acid-leachable form. The Mn was then recovered from the pregnant solution by electrolysis (*3*). It is uncertain that the high energy demand due to melting can be justified in treating a low-value ore from a small deposit.

Fluoride ion enhances the solubility of monosilicic acid [$Si(OH)_4$], because of the formation of fluorosilicate complexes (*4*). The addition of fluoride to acid solutions has been reported to facilitate the decomposition of the metal-silicate matrix during leaching and thereby improve the dissolution of metal values from silicate minerals. Adams and Van Dalen showed that the time required for 85-pct dissolution of alumina from kaolin was decreased from 3 h to 75 min with the addition of 0.16 mol/L F^- to the leach liquor (*5*). Bremner, Eisele, and Bauer found that the dissolution of Al increased from 50 pct to more than 90 pct with the addition of fluoride to the hydrochloric acid (HCl) leaching of Wyoming anorthosite (*6*). Recently, Bailey and Chapman have shown that the addition of 0.68 mol/L F^- increased the dissolution of Al in kaolinite from 10 to over 90 pct in HCl (*7*).

The objectives of this investigation were to determine if Mn can be extracted directly from pyroxmangite ore by leaching in the presence of CaF_2 without the melting-quenching step, and if the Mn can be prepared by electrolysis. This hydrometallurgical technique can provide an opportunity for developing several large low grade manganese silicate resource in the United States and decrease the dependence on foreign sources for manganese.

MATERIALS AND EQUIPMENT

The ore used was obtained from Sunnyside Gold Corp., Silverton, CO, and came from the Washington Vein, 2700 Stope, and the No Name Vein, 2769 Drift. Approximately 14 kg of the ore was pulverized to 100 pct passing 70-mesh Tyler screens. X-ray diffraction patterns showed that the ore was primarily pyroxmangite, with quartz and rhodochrosite ($MnCO_3$) as minor components. The size fractions and analysis of 100 g of the pulverized ore are presented in table 1. The analysis indicates that Mn is not concentrated in any particular size fraction of the ore. The composite pulverized ore contained, in percent, 34.4 Mn, 22.8 Si, 2.6 Ca, and 1.3 Fe.

Table 1.–Size fractions and analysis of pyroxmangite ore

Size, µm	Fraction, pct	Element, pct			
		Mn	Si	Ca	Fe
212 to 149	15.2	32.4	29.0	1.7	0.5
149 to 105	13.2	31.5	29.3	1.6	.8
105 to 74	11.7	30.1	29.7	1.6	1.3
74 to 44	12.8	29.7	29.3	1.5	2.4
<44	47.1	31.8	27.5	1.6	1.6

Reagent-grade H_2SO_4, Mn metal, CaF_2, and $(NH_4)_2SO_4$ were used in the experiments. Leaching tests were conducted in a 500-mL resin reaction kettle equipped with ports for an iron-constantan thermocouple, laboratory stirrer, thermometer, and water-cooled condenser. Heat required for leaching was provided by a temperature-controlled heating mantle capable of maintaining the leaching temperature within ±3° C in a range from 0° to 300° C. The pregnant leach solution was purified in the resin kettle by sparging in 99.99 pct NH_3 through a gas dispersion tube.

The acrylic electrolysis cell was 5.5 cm wide, 6.5 cm long, and 8.0 cm deep. The anode and cathode chambers were separated by a porous polypropylene membrane placed in the middle of the cell. A membrane was required to prevent the acid formed at the anode from diffusing into the catholyte and redissolving electrodeposited manganese. Solution was continuously pumped with a peristaltic pump through the cell from the cathode to the anode chamber at 0.5 mL/min. Current for electrolysis was supplied by a 0- to 60-V, 0- to 50-A rectifier. Current density was determined with a volt-ohm-milliammeter connected in series with the electrolysis circuit.

The anode was a 0.5-cm-thick Pb-Ca (1 pct Ca) alloy that had been immersed in a 0.01 mol/L solution of silver nitrate ($AgNO_3$) for 10 min to retard formation of sludge during electrolysis. The area of the submerged portion of the anode was 6.5 cm long by 4 cm wide, or 26.0 cm^2. The cathode, 0.13-cm-thick AISI type 316 stainless steel sheet, was positioned 3 cm from the anode. To limit plating to

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[4] Italic numbers in parentheses refer to items in the list of references at the end of this report.

the surface facing the anode, the back side of the cathode was insulated with masking tape, and the edges were insulated with 0.158-cm-ID rubber tubing split lengthwise. The plating area for the cathode was 4.5 cm long by 3.5 cm wide, or 15.75 cm^2. To allow continuous operation, at least three cathodes were prepared to replace the one in the cell whenever necessary.

PROCEDURES

The leaching tests consisted of bringing the H_2SO_4 or spent anolyte solution to the required temperature and then adding the CaF_2 through the thermometer port. The mixture was stirred at 600 rpm for 10 min to ensure uniform mixing of the CaF_2 before the ore was charged through the thermometer port. The contents were stirred at 600 rpm for the duration of the leach and then filtered immediately. The residue was dried for 24 h at 90° C. The residue and filtrate were analyzed for Mn, Si, Fe, Ca, and F. Whenever periodic samplings were required to monitor the leaching progress, approximately 2 to 3 mL of slurry were withdrawn from the reactor and filtered through a 47-mm-diameter membrane filter with a pore size of 1.0 μm. The filtrate was analyzed for Mn, Si, Fe, Ca, and F.

Metallic impurities such as Fe and Si were precipitated from the pregnant leach solution by sparging with NH_3 gas until the pH was raised to 6.5. The precipitate was filtered and analyzed.

The cathodes were cleaned with emery cloth and rinsed with acetone prior to electrolysis. The cell was filled with an initial electrolyte solution containing, in grams per liter, 11 to 13 Mn, 125 to 130 $(NH_4)_2SO_4$, 33 H_2SO_4, and 0.1 to 1.0 SO_2 (sulfur dioxide). The pH of this solution was increased to 7 by sparging with NH_3. Electrolysis of Mn was conducted at a cathode current density of 45 to 50 mA/cm^2 and at a rectifier voltage of 5 V. Purified feed solution containing 32 to 40 g/L Mn was pumped at a flow rate of 0.3 to 0.5 mL/min to maintain Mn concentration at 11 to 13 g/L in the catholyte during electrolysis. The cathode required replacement about every 3 h because of formation of Mn dendrites.

RESULTS AND DISCUSSION

PRELIMINARY LEACHING TESTS WITH SULFURIC ACID

Leachings were conducted for 6 h using a 5-pct slurry of 98 g/L H_2SO_4 and pyroxmangite ore with and without the addition of CaF_2 at 30°, 50°, and 90° C. The dissolution of Mn at various times is shown in figure 1. Even at 90° C, the dissolution of Mn after 6 h was less than 20 pct without the addition of CaF_2. However, when CaF_2 was added at a molar ratio of F-Mn of 0.4:1 (5 g/L CaF_2), the dissolution increased to 87 pct after only 1 h, with an ultimate dissolution of 95 pct after 3 h.

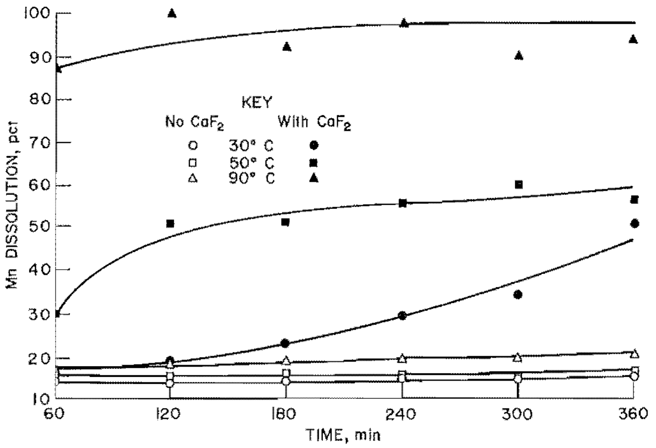

Figure 1.–Effect of time, temperature, and CaF_2 addition on Mn dissolution.

When CaF_2 was added, the time for reaching a steady state of dissolution of Mn decreased with increasing temperature. At 30° C, steady state was not established even after 6 h, and the dissolution of Mn was 47 pct. The time to reach a steady state at 50° C was 5 h, with a Mn dissolution of 58 pct. Steady state was reached after 2 h at 90° C, and the extraction of Mn was 93 pct. These results show that addition of fluoride to H_2SO_4 solutions has a major effect on the dissolution of Mn. Furthermore, the dissolution achieved when using fluoride with H_2SO_4 is comparable to leaching melted and quenched pyroxmangite. For instance, when melted and quenched pyroxmangite was leached at 40° C with 2.5*M* H_2SO_4 and 25 pct solids, a reported 90-pct dissolution of Mn was achieved within 1 h (*3*). Similar tests were conducted with untreated pyroxmangite ore in the presence of fluoride. Table 2 shows the results of leaching 25-pct-solids slurries of pyroxmangite ore with a F-Mn ratio of 0.4:1 (35 g/L CaF_2) at 40° C and 90° C, for comparison with the melting-quenching results. Although it was reported that temperature has little effect on dissolution of Mn from melted and quenched pyroxmangite, temperature had a significant effect when untreated ore was leached in H_2SO_4 with CaF_2. Table 2 shows there was a marked difference between the extractions achieved at 40° C (37 to 39 pct) and those achieved at 90° C (81 to 96 pct). These results indicate that leaching of pyroxmangite for 2 h at 90° C in the presence of CaF_2 resulted in 96-pct dissolution of Mn, comparable to 91-pct dissolution achieved in 1 h when the ore was melt-quenched prior to acid leaching. Furthermore, leaching with CaF_2 and H_2SO_4 removes the high energy consumption step of melting and quenching.

Table 2.–Manganese dissolution at 40° C and 90° C, percent

Method and time	40° C	90° C
Melt-quench process:		
1 h	90	91
2 h	NA	NA
CaF_2-H_2SO_4 leaching:		
1 h	37	81
2 h	39	96

NA Not available.

Although the addition of CaF_2 to H_2SO_4 leaching solutions resulted in extractions comparable to those of the melting-quenching procedure, the effect of fluoride on the recovery of an electrolytic Mn product was not known. Therefore, the possibility of incorporating a fluoride-assisted leaching step into electrolytic production of Mn was investigated.

LEACHING WITH SPENT ANOLYTE

In electrolysis of Mn from sulfate solutions, a feed solution containing, in grams per liter, 30 to 40 Mn, 120 to 140 $(NH_4)_2SO_4$, and 0.1 to 1.0 SO_2 was fed to a diaphragm cell, with Mn metal plated at the cathode and spent anolyte containing H_2SO_4 recycled to the leaching step (*8*). The spent anolyte contained, in grams per liter, 10 to 20 Mn, 125 to 150 $(NH_4)_2SO_4$, and 25 to 40 H_2SO_4.

Leaching tests were conducted using a simulated spent anolyte containing, in grams per liter, 14 Mn, 135 $(NH_4)_2SO_4$, and 38 H_2SO_4 to determine conditions required to produce a suitable cell feed for electrolysis using fluoride-assisted leaching. Since the high concentration of $(NH_4)_2SO_4$ in the spent anolyte may influence the requirements for maximum dissolution of Mn, the effects of time, acid concentration, and fluoride concentration on the dissolution of Mn in simulated spent anolyte at 90° C were determined.

Effect of Time

A 10-pct slurry of pyroxmangite ore and simulated spent anolyte with 11 g/L CaF_2 at 90° C was continuously stirred at 600 rpm for 3 h. The 10-pct slurry was chosen so that, even at extractions as low as 50 pct, a cell feed solution of at least 34 g/L Mn could be produced. Results of leaching tests conducted using 38 and 76 g/L H_2SO_4 with and without fluoride are shown in figure 2. At a H_2SO_4 concentration of 38 g/L, there was only 10 pct dissolution of Mn in the first hour when no fluoride was added, compared with greater than 15 pct achieved when fluoride was added to simulated spent anolyte. With or without the addition of fluoride, no further dissolution of Mn occurred after 1 h. When the concentration of H_2SO_4 was increased, however, the dissolution in the first hour increased to 30 pct when no fluoride was added, compared with greater than 80 pct when fluoride was added to the simulated spent anolyte. At the higher acid concentration, the time required for the maximum dissolution increased from 1 h without fluoride to 2 h with the addition of fluoride.

Effect of Acid Concentration

Tests were made with different concentrations of H_2SO_4 in the simulated spent anolyte. Each test was performed with a 10-pct slurry at 90° C and 11 g/L CaF_2, and for 3 h. The percent dissolution of Mn at various H_2SO_4-Mn mole ratios is shown in figure 3. The data show that a ratio of at least 2:1 is required to achieve a dissolution of 90 pct and that ratios up to 12:1 increased the dissolution by less than 5 pct.

Effect of Fluoride Concentration

A 10-pct slurry of pyroxmangite and simulated spent anolyte with 140 g/L of H_2SO_4 and varying ratios of F-Mn was allowed to react at 90° C for 3.0 h. The ratios were 0, 0.05:1, 0.1:1, 0.2:1, 0.4:1, and 0.8:1, and corresponded to concentrations of CaF_2, in grams per liter, of 0, 1.25, 2.5, 5, 10, and 20, respectively. Test results are summarized in figure 4. Although dissolution of Mn increased from 15 pct with no CaF_2 added to 50 pct with a F-Mn ratio of only 0.05:1, a ratio of at least 0.2:1 was required for 90-pct dissolution of Mn in simulated spent anolytes.

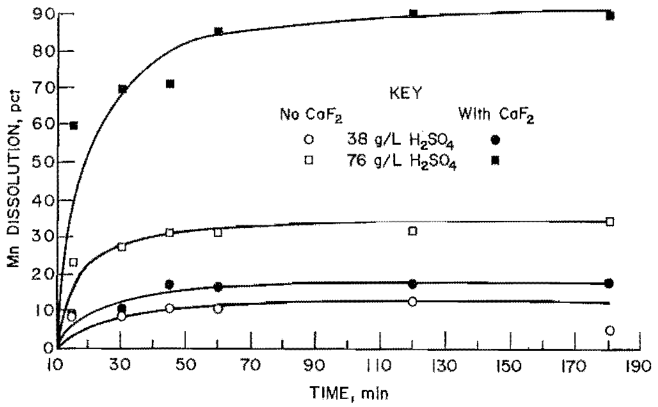

Figure 2.–Effect of time, acid concentration, and CaF_2 addition on Mn dissolution in synthetic anolyte.

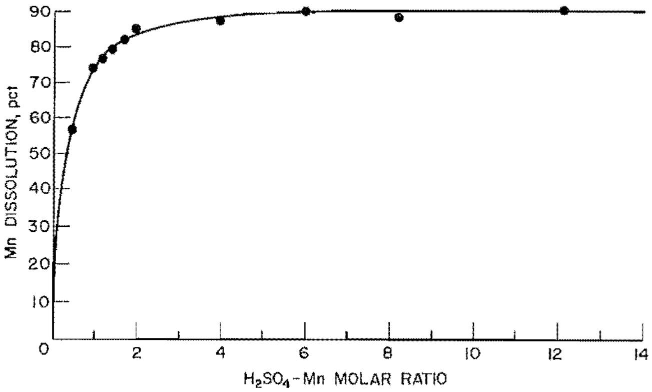

Figure 3.–Effect of H_2SO_4-Mn molar ratio on Mn dissolution in synthetic anolyte.

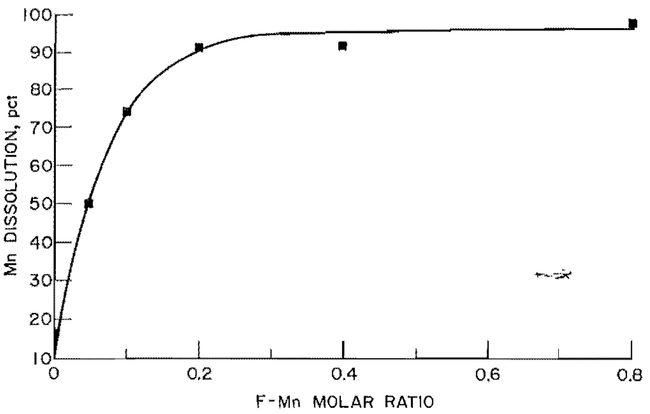

Figure 4.–Effect of F-Mn molar ratio on Mn dissolution in synthetic anolyte.

Based on the above results, pyroxmangite was leached with a simulated spent anolyte containing, in grams per liter, 142 H_2SO_4, 130 $(NH_4)_2SO_4$, and 11 Mn, at 90° C, 2:1 H_2SO_4-Mn ratio, 0.2:1 F-Mn ratio, and 3 h. Ninety-two percent of the Mn was extracted, and a filtrate containing 40 g/L Mn was produced.

PURIFICATION OF FILTRATE

The filtrate was purified to provide a suitable cell feed for electrolysis; namely, the more electropositive elements were removed from solution. In commercial practice, the filtrate is neutralized to pH 6.5 to precipitate Fe and Al. Sulfide precipitation is then used to remove Cu, Zn, Ni, and Co. Finally, ferrous sulfate ($FeSO_4$) is added and oxidized to precipitate ferric hydroxide [$Fe(OH)_3$] and other metallic impurities (*8*). This procedure was initially used with filtrate from fluoride-assisted leaching of pyroxmangite, and was found unnecessary since neutralization of the leach liquor to pH 6.5 with NH_3 gas was sufficient to purify the solutions for electrolysis.

ELECTRODEPOSITION TESTS

The objective of these tests was to determine the technical feasibility of depositing metallic Mn from pyroxmangite feed solution. Results obtained by electrodepositing Mn from a purified synthetic feed solution and from purified pyroxmangite leach solutions were compared in terms of quality of deposit and current efficiency.

Manganese was electrodeposited continuously for 10 h from both synthetic feed solution and from solution prepared by leaching pyroxmangite. All Mn deposits were light gray and reasonably fine grained. In each of the runs dendrite formation on the edge of the deposit was a problem, resulting in frequent replacement of the cathodes. On a commercial scale, the cathode would have a greater plating area in proportion to the length of its edges, and tree formation could be less of a problem. Table 3 shows the electrodeposition results. A cathode was plated for 3.2 A·h from synthetic feed solution with 64 pct current efficiency. This is comparable to the same electrolysis conducted with the pyroxmangite feed solution and a current efficiency of 69 pct. Current efficiency from this study was comparable to values of previous researchers (*8*) and the reported industrial value of 60 pct (*9*). Solution made from fluoride-assisted leaching of pyroxmangite was easily purified and was as responsive to electrolysis for the production of metallic Mn as solutions from other sources.

Table 3.–Results of manganese electrodeposition tests made with synthetic and pyroxmangite feed solutions

Feed solution	Cathode	Electrolysis, A·h	Mn deposited, g	Current efficiency, pct
Synthetic	1	3.2	2.1	64
	2	2.4	1.6	66
	3	2.4	1.3	56
Pyroxmangite ..	1	3.2	2.2	69
	2	2.3	1.5	66
	3	2.4	1.7	72

Initial electrolysis tests were conducted with an untreated Pb-Ca anode. After a few minutes of electrolysis, a sludge developed in the anode compartment that resulted in low current efficiencies, and electrolysis had to be stopped after only 1 h (0.8 A·h). It was found that immersion of the lead anode in 0.1 mol/L $AgNO_3$ reduced the amount of sludge generated and allowed for longer electrolysis. Approximately 40 pct of $(NH_4)_2SO_4$ in the catholyte was lost during electrolysis. This loss was attributed to the generation of free NH_3 and to the precipitation of $(NH_4)_2SO_4$ in the sludge.

ENVIRONMENTAL PROTECTION AGENCY-EXTRACTION PROCEDURE TOXICITY TEST

The Environmental Protection Agency (EPA)–Extraction Procedure (EP) Toxicity Test procedure was conducted to determine the stability of the leaching residue with regard to waste disposal (*10*). Results of the test and limits for the metals of concern are shown in table 4. The concentrations of metal contaminants were below the EPA limits. While Mn and F are not listed as hazardous constituents under the EPA test, the Mn and F levels in the filtrate of the leaching residue were 1.0 and 0.14 g/L, respectively.

Table 4.–Analysis of EP Toxicity Test filtrate for metals of concern, milligrams per liter

Element	Filtrate	EPA limit	Element	Filtrate	EPA limit
Al	4.8	NAp	F	.14	NAp
As	1.7	5.0	Fe	18.0	NAp
Ba	.03	100.0	Mn ...	[1]1.0	NAp
Cd	<.1	1.0	Pb ...	2.3	5.0

NAp Not applicable.

[1]gram per liter.

SUMMARY OF PROCESS SEQUENCE

Based on the test results, a flowsheet for recovering Mn from pyroxmangite ore is proposed and shown in figure 5. Included is a material balance for processing 1,000 kg of the manganese ore.

The acidity of the spent anolyte from the Mn electrolysis is first adjusted to 140 g/L H_2SO_4, then minus 70-mesh pyroxmangite ore and CaF_2 are added to provide a 10-pct slurry. The leaching is conducted at 90° C for 3 h. Ninety-two percent of the Mn in the ore is extracted, and a filtrate containing 40 g/L Mn is produced. Two percent of the SiO_2 and 84 pct of the Fe report to the filtrate. The Fe, SiO_2, and other impurities are precipitated and removed after increasing the pH to 6.5 with NH_3 gas. The NH_3 sparge increases the $(NH_4)_2SO_4$ concentration to 130 g/L, which is the proper level for electrolysis. The filtrate is used as the catholyte feed solution for the Mn electrolysis.

Catholyte is fed to a diaphragm-type electrowinning cell filled with an initial solution of 11 to 13 g/L Mn, 130 g/L $(NH_4)_2SO_4$, and 33 g/L H_2SO_4 at a pH of 6.5. The flow of catholyte is adjusted periodically to maintain the concentration of Mn at 11 to 13 g/L in the catholyte.

Electrolysis is conducted using Pb-Ca (1 pct Ca) anodes treated with 0.1 mol/L $AgNO_3$ solution and AISI type 316 stainless steel cathodes. A rectifier voltage of 5.0 V and a current density of 45 to 55 mA/cm^2 based on cathode area are maintained throughout electrolysis. Under these conditions, a current efficiency of 66 to 72 pct is achieved. The spent anolyte, containing 11 to 13 g/L Mn and 38 g/L H_2SO_4, is recycled for leaching after makeup acid is added. Reagent consumption for CaF_2-H_2SO_4 leaching of 1 mt pyroxmangite is 834 kg H_2SO_4, 136 kg NH_3, and 21 kg CaF_2. Electrolysis power requirement is 8 kW·h/kg of Mn.

Although H_2SO_4 is generated during electrolysis, the 38-g/L concentration is lower than the required concentration for leaching of pyroxmangite ore. Further research on staged leaching of pyroxmangite ore to decrease the acid consumption is needed. The use of staged leaching to reduce the amount of acid required would also reduce the consumption of fluoride. Thirty-five percent of the fluoride reports to the leach residue and 15 pct reports to the Fe residue.

CONCLUSIONS

The addition of CaF_2 to H_2SO_4 leaching solutions results in extractions of Mn comparable to those reported when pyroxmangite is melted, quenched, and leached. Because manganese metal can be recovered by electrolysis of these leach solutions, the addition of CaF_2 to leaching solutions is a practical alternative to melting and quenching treatment.

In addition, spent anolyte from electrolysis of fluoride-assisted leach solutions can be used in a cyclic process to leach pyroxmangite. Solid residues of the process pass the EPA-EP Toxicity Test for metals of concern.

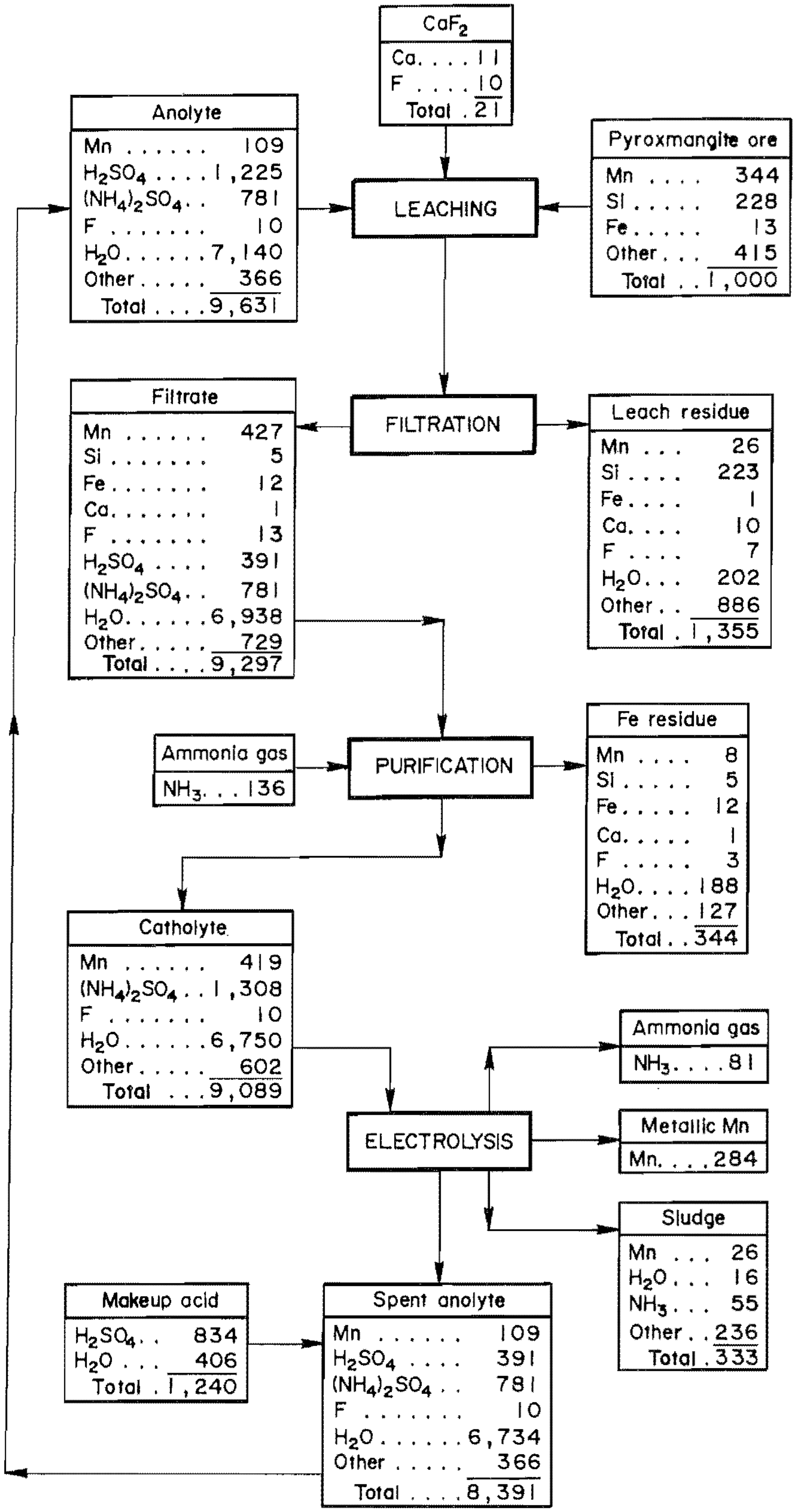

Figure 5.–Proposed flowsheet for production of Mn from pyroxmangite ore.

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