Reuse of Anode Slime Generated by the Zinc Industry to Obtain a Liquor for Manufacturing Electrolytic Manganese

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A hydrometallurgical process is proposed in this article to recover manganese from a zinc electrowinning residue. The article describes the digestion-leaching experiments, precipitation, and electrowinning assays to recover Mn from this residue. Anode slime is treated with sulfuric acidic in a furnace within a temperature range of 400–450°C, leached with water, and then filtered. The results show that the dissolution of manganese increases with increasing temperature in the digestion step. The recovery yield of manganese was higher than 90%. As manganese electrolysis requires an electrolyte free of Zn, Ni, Co, and Cu pollutants, the sulfuric acid liquor needs a purification step. Na_2S is used to remove pollutants. The results obtained in this study have shown that the proposed process for the recovery of manganese from this type of residue is technically viable.

INTRODUCTION

Solid residues from metallurgical industries can be considered secondary sources of metals. The different wastes include slag, dust, slimes, etc. Some of these wastes are effectively recovered, while a considerable amount of research is being carried out to be able to use others. The successful recovery of the metals they contain would also provide the secondary benefit of significantly reducing the volume of waste requiring disposal.

The production of metallic zinc from zinc sulfide concentrates, especially sphalerite, comprises various stages: roasting, leaching, and electrolysis. In the leaching stage with sulfuric acid, other metals present in the roasted calcine concentrate such as Fe, Cd, Co, Cu, etc. are also leached in addition to zinc. As metallic zinc electrolysis requires an electrolyte that is free from these pollutants, the sulfuric acid liquor needs a purification step to remove them. Iron is always present in raw materials employed as an impurity and has to be removed from the leach solution.

Manganese dioxide or potassium permanganate is usually added to the zinc sulfate electrolyte from the leaching process to oxidize iron impurities.[1]. The amount of manganese added varies widely with the amount of iron and other impurities in the solution.

In order to minimize the corrosion of the Pb-Ag anodes and lead pollution of the cathode zinc product, manganese has to be added to the zinc electrolyte, usually in the form of potassium permanganate $(KMnO_4)$.[2,3] For this reason, the zinc electrowinning production also generates anodic slime, which is of technological value.

The rapidly growing global demand for manganese has made it increasingly important to develop processes for the economic recovery of this metal from low-grade manganese ores and other secondary sources.

Manganese metal is essential to the metallurgical industry, with major applications in steel and aluminum production. Electrolytic manganese is a constituent of nonferrous metals, being added to aluminum products, for instance, to improve their strength, ductility, and hot-rolling properties. Other nonferrous applications of manganese include the production of dry-cell batteries, plant fertilizer components, animal feed, and as a colorant for bricks.

Hydrometallurgical processes have been used to reduce the environmental impact. Secondary sources containing a high concentration of metals have been reused by means of leaching techniques and recovered by cementation, precipitation, or other techniques. The most determining step in a

hydrometallurgical process is generally the first, which is the leaching of the valuable metals present in the raw material.

The aim of this study is to produce manganese sulfate solution from electrowinning zinc residue, which can be used to produce electrolytic manganese.

A process for recovering manganese from the slime would involve the following steps:

1. Dissolution of the manganese. Many hydrometallurgical processes in acid media have been studied to recover manganese from manganese minerals. Sulfuric acid was selected as the cheapest and the most effective leachant.[3–21]

The leach liquors contain manganese, zinc, copper, calcium, and potassium in addition to other impurities.

2. Purification of the leach solutions. The aqueous solution obtained in the acidic leaching step is sent to a purification step to separate the Zn, Cu, Ni, and Co. Several separation methods can be used, such as liquid–liquid extraction, precipitation, electrowinning, etc. The precipitation method was chosen in the current study.

The use of metal sulfide instead of hydroxide precipitation has gained prominence in hydrometallurgical processes in recent decades. The arguments for its preferential use are based on the high degree of metal removal at relatively low pH values.

The precipitation and separation of metal sulfides and separation are based on the different sulfide solubility of metals at a specific pH and temperature. Gaseous hydrogen sulfide (H_2S), sodium sulfide (Na_2S), or ammonium sulfide ($(NH_4)_2S$) is usually employed in the precipitation of metal sulfides.[22–26]

The zinc and other impurities in the solution were precipitated with Na_2S solution at pH 5–7, leaving manganese in solution for subsequent recovery:

$$Na_2S + Zn^{2+} \rightarrow ZnS(s) + 2Na^+ \qquad (1)$$
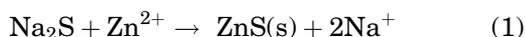
3. The resulting $MnSO_4$ solution for producing electrolytic manganese. The Mn^{2+} ion is not reduced easily in aqueous solution ($Mn^{2+}_{(aq)} + 2e^- = Mn_{(s)}$) because the H_2 gas overpotential on the Mn metal can only be close to -1.179 V under special conditions. This makes it very difficult to avoid simultaneous H_2 evolution at the cathode, thus losing current efficiency for Mn deposition and significantly lowering Faraday efficiency.

To prevent electrodeposited manganese from redissolving, a neutral or slightly alkaline pH must be maintained in the electrolyte surrounding the cathodes. For this reason, the proposed process has two kinds of compartments separated by a diaphragm. The diaphragm must be sufficiently impervious to prevent the acid formed in the anodic compartment from diffusing into the cathodic compartment, and yet it must be porous enough to allow the cell to be operated at low voltage (4.5–5.5 V).

The addition of ammonium sulfate to the manganese electrolyte can occur from precipitation of manganese hydroxides during electrodeposition, even when the pH value of manganese salt solutions is raised to around 9.0 in the absence of air, in addition to improving the conductivity of the solution.[27]

The $MnSO_4$ concentration was found to be a key parameter for achieving a high current efficiency. In electrolysis, both anode and cathode efficiencies improved with increased $MnSO_4$ concentration. Increasing the $(NH_4)_2SO_4$ concentration afforded a higher yield of cathodic manganese of improved quality, while increasing the H_2SO_4 concentration afforded a smaller yield of relatively pure MnO_2 at the anodes.[25]

Lead or lead alloy anodes are conventionally used in manganese electrowinning in sulfate medium.

During electrolysis of $MnSO_4$ solution, the predominant reactions at the electrodes are as follows:

Cathodic reactions:

$$Mn^{2+} + 2e^- \rightarrow Mn \qquad (2)$$

$$2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^- \qquad (3)$$

$$2\,H^+ + 2e^- \rightarrow H_2 \qquad (4)$$

Anodic reactions:

$$2\,H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (5)$$

$$2H^+ + SO_4^{-2} \rightarrow H_2SO_4 \qquad (6)$$

$$Mn^{+2} + 2e^- + O_2 \rightarrow MnO_2 \qquad (7)$$
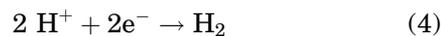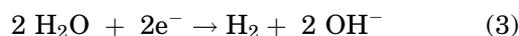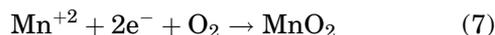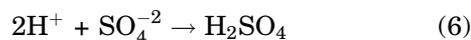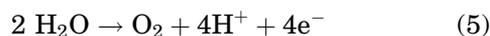
The use of electrowinning zinc residue to obtain electrolytic manganese is carried out in different stages. Figure 1 shows a simplified flowchart of the manufacturing process of manganese proposed in this article.

EXPERIMENTAL PROCEDURES

Characterization of the Manganese Residue

The anode slime was thoroughly homogenized and dried at 110°C. Representative samples were
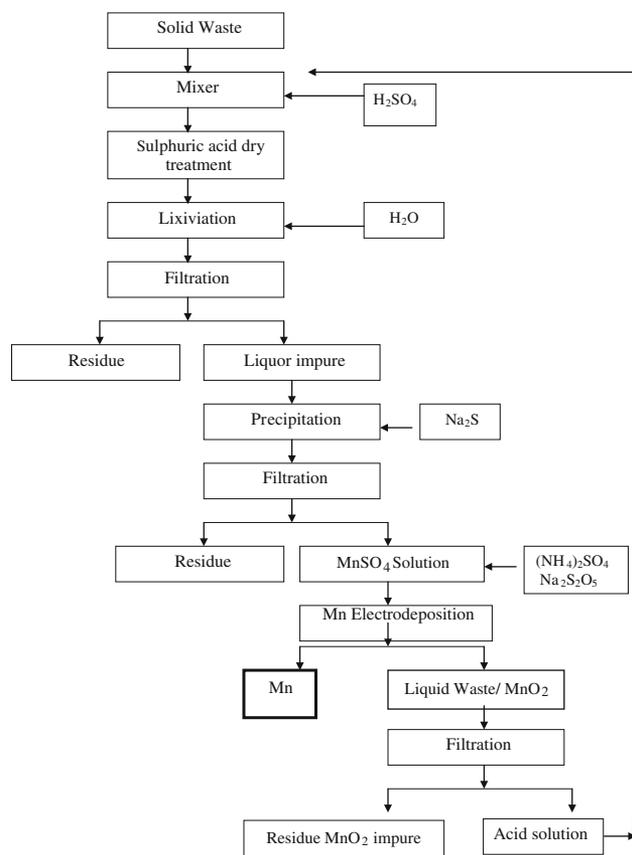
Fig. 1. Simplified process flowchart.
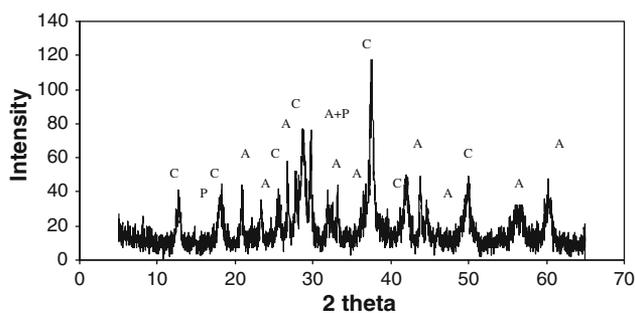
Fig. 2. X-ray diffractogram of electrowinning zinc residue (anode slime) [C]—criptomelane KMn_8O_{16}, [A]—anglesite $PbSO_4$, [P]—plaster-$2CaSO_4$-H_2O.

then taken for chemical characterization and the subsequent leaching test.

The chemical analysis of the zinc residue was determined by atomic absorption spectroscopy (Perkin Elmer A Analyst 200; Perkin Elmer, Waltham, MA) after acid digestion, and a gravimetric technique was used to analyze the sulfate content: 41.4% Mn, 1.55% Zn, 8.5% Pb, 3.71% CaO, 1.7% K_2O, 0.51% Na_2O, 0.38% MgO, 2.24% SrO, 0.11% Cd, 0.007% Co, 0.009% Ni, 0.7%Cu, 0.06% Fe, and 12.36% SO_4^{2-}.

The mineralogical composition was examined by XRD analysis (Phillips PW1430 system with CuK_α

radiation; Philips, Amsterdam, the Netherlands) (Fig. 2). Particle size distribution was determined by screening, the results of which are given in Table I.

Manganese Dissolution Experiments

The process involves sulfation in the presence of sulfuric acid to convert the zinc residue into soluble sulfates, followed by water leaching. Acid solutions for digestion were prepared by adding an appropriate amount of sulfuric acid to distilled water to achieve the required acid concentration.

The first leaching tests were performed within a temperature range of 110–140°C for 30–360 min, using a PARR Bomb, in which 2 g of manganese slime was mixed with 2 g of sulfuric acid. The samples were then leached with distilled water and the manganese was determined by atomic absorption spectroscopy (AAS). The results are given in Fig. 3.

Several experiments were carried out under more drastic conditions: An amount of H_2SO_4 solution was mixed with 10 g of the residue in a porcelain dish and placed in a Carbolite OWF 1100 furnace (Carbolite Ltd., Hope Valley, U.K.) at the required temperature (350–550°C) (Fig. 4).

The amount of H_2SO_4 used in the different tests varied from the stoichiometric amount to excesses of 300%. The assays were carried out varying the acid concentration (30–90% by mass) (Figs. 5 and 6).

The influence of reaction time at 400°C and 450°C was studied using a 33% excess of sulfuric acid with concentrations between 30% and 90% by mass. At the end of the predetermined heating period (30–120 min), the sample was removed from the furnace. The solid residue was then leached with distilled water and stirred to dissolve the sulfates. The slurry was washed several times and then filtered. The leach liquor was analyzed for Mn using AAS, subsequently calculating the percentage extraction (Figs. 7 and 8).

Several tests with 50 g of anode slime with the stoichiometric amount of sulfuric acid (70% by mass) were performed at 450°C or 400°C for 1 h. Then, they were leached with 500 mL water and filtered with the purpose of preparing several liters of solution to carry out electrolysis. Table II shows the chemical composition of the liquors thus obtained. The washwaters were not added in either case as a concentrated manganese dissolution was sought. The washwaters that have a low manganese concentration could be reused in this process during the leaching stage.

The solid residues were weighed, around 79% of the anode slime being found to have dissolved. The solid residue was characterized by x-ray diffraction (XRD) (Fig. 9) and atomic absorption spectroscopy: 7.2% Mn, 22% Pb, 7.5% Ca, 6.2% Sr, 0.09% Cd, 0.67% Cu, 0.1% Fe, 0.01% Mg, 0.12% K, 0.04% Na, 0.005% Ni, and 0.54% Zn.

Table I. Anode slime particle size distribution

Size (mm)	% Mass
> 10	4.70
10–5	3.39
5–4	2.32
4–1.7	9.09
1.7–1	9.91
1–0.5	16.69
0.5–0.29	16.66
< 0.29	37.24
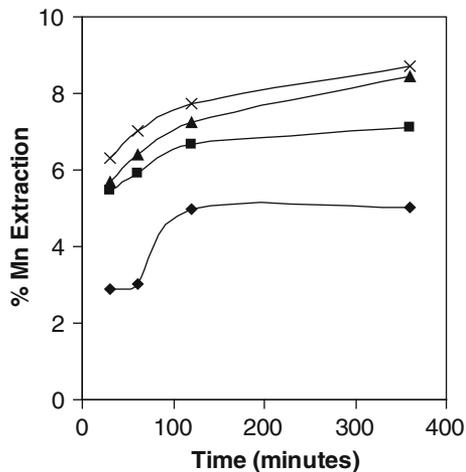
Fig. 3. Manganese dissolution in Parr bomb: ● 110°C; ■ 120°C; ▲ 130°C; × 140°C.
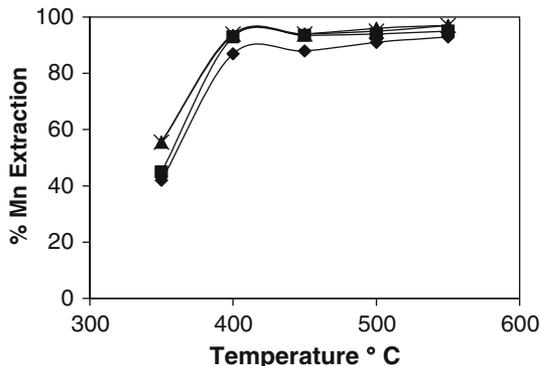
Fig. 4. Influence of temperature on Mn extraction (2 h—50% H₂SO₄) using different amounts of acid: ● Stoichiometric; ■ 33% Exc.; ▲ 167% Exc.; × 300% Exc.

Purification of the Leach Solution

In the purification step, sodium sulfide was added to remove impurities such as Zn, Co, Ni, and Cu. Precipitation assays were carried out at room temperature in a 250-mL covered glass reactor under constant stirring, monitoring the pH of the solution.

Different tests were carried out using Na_2S during 60 min; in some cases, the sulfide was in the
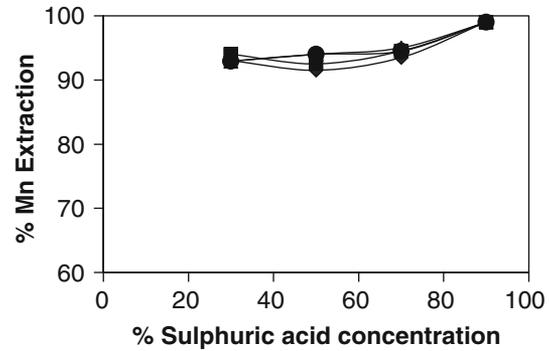
Fig. 5. Influence of sulfuric acid concentration on Mn extraction (2 h—450°C) using a different amount of acid: ● Stoichiometric; ■ 33% Exc.; ▲ 167% Exc.; × 300% Exc.
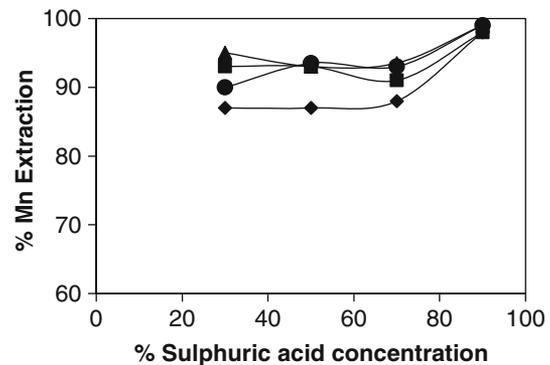
Fig. 6. Influence of sulfuric acid concentration on Mn extraction (2 h -400°C) using a different amount of acid: ● Stoichiometric; ■ 33% Exc.; ▲ 167% Exc.; × 300% Exc.

solid state, while in others it was in a concentrated solution. Some assays were performed with the stoichiometric amount and others with excess (6–30%). A small amount of ZnS was added as seeding to favor the formation of precipitate. After the reaction, the purified solution was filtered through a pressure filter. The final pH of the solution and the content of impurities were analyzed (Table III).

Finally, 10 L liquor purified using an excess of 14% Na_2S during 60 min were prepared. The metals content was determined by atomic absorption (Table IV). The resulting $MnSO_4$ solution can be used to produce electrolytic manganese.

Electrodeposition

The electrodeposition of manganese was performed using a laboratory installation. The electrolytic cell was made of methacrylate. The cell dimensions are 26 cm × 18 cm, with a depth of 20 cm. The cell contains 1 cathodic (13 × 17.5 cm) and 2 anodic (6 × 17.5 cm) compartments separated by cloth membranes or diaphragms. The insoluble anodes employed in this study for manganese electrowinning are alloys of lead and silver. A commercial stainless steel was chosen as the cathode for

the study. The typical conditions required for electrolysis were employed.[25]

Three different solutions were prepared:

1. Catholyte: 13 g/L Mn, 135 g/L $(NH_4)_2SO_4$, 1 g/L $(Na_2S_2O_5)$, pH = 8–7
2. Anolyte: 12 g/L Mn, 33 g/L NH_4, 1 g/L $(Na_2S_2O_5)$, 20 g/L H_2SO_4
3. Catholyte feed: 32 g/L Mn, 135 g/L $(NH_4)_2SO_4$, 1 g/L $(Na_2S_2O_5)$, pH = 6.5 or 7

The catholyte feed solution flowed by gravity from the feed tank to the electrolytic cells.

Electrolysis was carried out for 3 h with a current density of 350 A/m^2 within a temperature range of 30–40°C. H_2SO_4 was added when required to maintain the pH between 7 and 8.
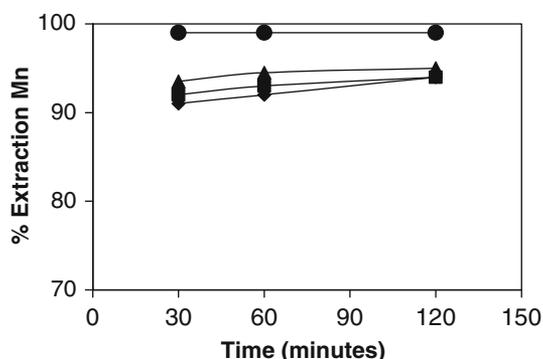
Fig. 7. Influence of reaction time on Mn extraction (at 450°C) with an excess of 33% sulfuric acid using a different concentration of acid: ● 30%; ■ 50%; ▲70%; × 90%.
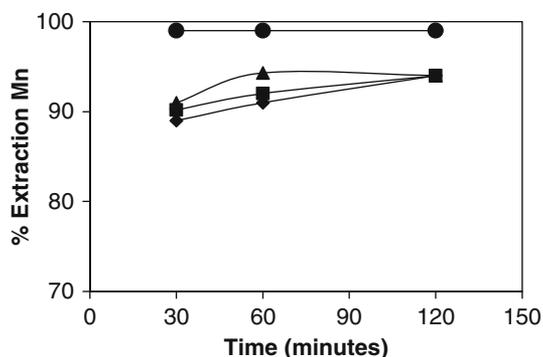
Fig. 8. Influence of reaction time on Mn extraction (at 400°C) with an excess of 33% sulfuric acid using a different concentration of acid: ● 30%; ■ 50%; ▲70%; × 90%.

Manganese is deposited on the surface of the cathode in the form of flakes, while small amounts of manganese dioxide accumulate on the anode.

The deposited plate was carefully scraped off the cathode surface. Table V shows the composition of the obtained electrolytic manganese. The manganese was characterized by x-ray diffraction (Fig. 10).

RESULTS AND DISCUSSION

Characterization of the Manganese Residue

Using XRD characterization, the crystalline phases present in the zinc residue were found to be cryptomelane, anglesite, and plaster (Fig. 2).

The electrolytic slime is a dark material with different sizes, sizes smaller than 1 mm predominating (Table I).

Dissolution of the Manganese

Effect of Temperature

Several leaching tests were conducted to determine the optimum conditions for manganese extraction. The first tests performed at low temperatures between 110°C and 140°C (Fig. 3) show the low dissolved manganese contents. After 360 min of reaction, only 8.7% had dissolved at 140°C. In all cases, an increase in time and temperature is seen to improve the extraction of the metal slightly.

As can be seen from Fig. 4, the amount of manganese extracted in assays at different temperatures (350–550°C) during 2 h using H_2SO_4 (50% mass) was found to be a function of the furnace temperature. Manganese recovery increased with increasing temperature. Mn extraction after 2 h
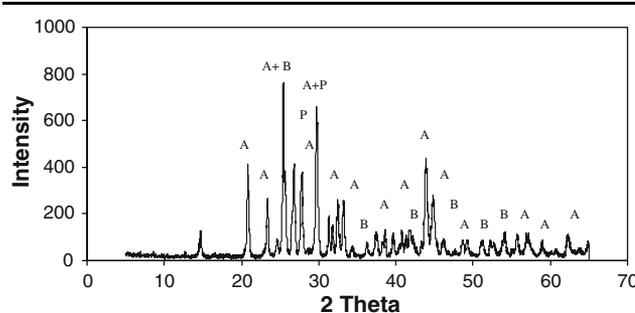
Fig. 9. X-ray diffractogram of the sulfate leaching residue. A—anglesite, P—plaster, B—anhydrite

Table II. Composition of leach solutions

T (°C)	Mn (g/L)	Zn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Pb (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Na (ppm)	Fe (ppm)
400	36.5	1550	1.1	2	330	4.7	375	190	1665	161	0
450	36.5	1555	1.1	2	332	4.4	283	198	1600	156	0

Table III. pH and concentration of the liquor after purification with different amounts of Na₂S

Na₂S Excess (%)	Reagent	Final pH	Zn(ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Mn (g/L)
20	Na₂S(s)	5.51	70	0.7	0.8	0	36.2
30	Na₂S(s)	5.65	27	0.6	0.7	0	36
0	Na₂S(l)	5.69	32	0.7	0.7	0	36.2
6	Na₂S(l)	5.67	9	0.6	0.4	0	36
14	Na₂S(l)	6.50	0.9	0.4	0.1	0	36
20	Na₂S(l)	7.38	0.6	0.2	0.1	0	35
26	Na₂S(l)	7.24	0.4	0.1	0.1	0	35.5
30	Na₂S(l)	7.40	0.3	0.1	0	0	34.7

Table IV. Composition of the liquor after purification with a 14% of Na₂S

T (°C)	Mn (g/L)	Zn (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Pb (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Na (ppm)	Fe (ppm)
400	36	0.9	0.4	0.1	0	4.7	370	190	1661	161	0
450	36	0.8	0.4	0.1	0	4.4	273	195	1607	158	0

Table V. Chemical composition of obtained electrolytic manganese

Element	% Mass
Mn	99.9
C	0.015
S	0.05
P	0.002
Ti	0.001
Mg	0.004
Fe	0.006
K	0.004
Si	0.002
Ca	0.003
Zn	0.004
Cu	0.001
Co	0.002
Ni	0.004
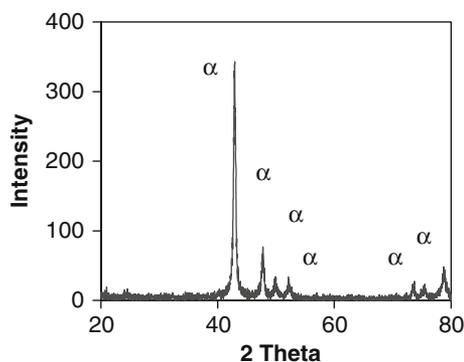
Fig. 10. X-ray diffractogram of obtained manganese electrolytic.

reached 42% and 93% for 350°C and 550°C, respectively, using the stoichiometric amount needed to leach the manganese.

Manganese extraction at 400°C and 450°C is higher than 92% using 33% excess acid. Figure 4 shows that higher temperatures are not needed to obtain the maximum amount of manganese in dissolution. Subsequent assays were performed at these temperatures to avoid high energy consumption.

Leaching extraction increases slightly with the amount of sulfuric acid. At 450°C, manganese extraction increased from 88% to 94% using the stoichiometric amount of acid and 300% excess acid, respectively. In all, 97% of the Mn dissolved at 500°C when using 300% excess acid.

The temperature effect was found to be more important than that corresponding to the amount of acid.

Effect of Sulfuric Acid Concentration and Pulp Density

The effect of acid concentration (30%, 50%, 70%, and 90% by mass) was determined at 450°C and 400°C with 2 h reaction time. Assays were carried out using the sulfuric acid needed to remove the manganese and with excesses of acid above the stoichiometric amount (33–300%).

A plot of the percentage of extracted manganese versus acid concentration is shown in Figs. 5 and 6. Overall, 93% of the manganese is dissolved in all the tests performed at 450°C using 30% acid. The results obtained at 400°C are slightly lower.

As can be seen in the figures, significant improvements are not seen in the dissolution of manganese when varying the concentration of sulfuric acid between 30% and 70%. However, when using 90% acid, about 99% of the manganese is removed, irrespective of the excess of acid used in the sulfation process.

The tests with 90% acid by mass provided a relatively thick slime that is difficult to handle. For

this reason, subsequent tests were also performed at lower acid concentrations.

Effect of Time

The influence of reaction time at 400°C and 450°C was studied using a 33% excess of sulfuric acid with concentrations between 30% and 90% by mass and residence times of between 30 min and 120 min (Figs. 7 and 8). Almost complete dissolution of the manganese is achieved after half an hour at 450°C using 90% acid by mass. A slight increase in metals extraction was achieved at lower acid concentrations by increasing the residence time in the furnace. Working with 30% acid by mass, between 91% and 94% Mn were extracted after 30 min or 120 min, respectively. Figures 7 and 8 show that a long digestion time (2 h) is not needed to obtain the maximum amount of manganese in dissolution.

The results obtained at 400°C are very similar, although the increase with reaction time is slightly higher.

Obtaining the Electrolyte

Table II shows the chemical composition of the liquors obtained when treating 50 g of sample with 70% acid for 1 h to obtain liquor with a suitable manganese concentration for electrolysis. It can be seen that manganese concentrations of 36.5 g/L were obtained, along with impurities such as zinc, calcium, magnesium, potassium, and sodium and smaller amounts of cobalt, nickel, and copper. Overall, 88% Mn was dissolved under these conditions, and 79% of the residue generated in the electrolysis of zinc was removed.

The leached residue obtained after sulfation-leaching treatment contains appreciable amounts of lead (Fig. 9). The x-ray diffractogram shows the intensities of the reflections corresponding to anglesite, plaster, and anhydrite.

Purification of the Leach Solution

The liquor from the sulfation-leaching process contains a significant amount of Zn and Cu, among other pollutants. Table III shows the results of different tests with sodium sulfide precipitation. The precipitation is most effective using Na_2S solution.

In the test carried out with a 20% excess of Na_2S solid reagent, 70 ppm Zn remain in solution. If the assay is carried out with Na_2S solution, however, then the remaining zinc content is only 0.6 ppm.

Increasing the excess of Na_2S is seen to improve the removal of zinc. Using the stoichiometric amount of sodium sulfide, 32 ppm Zn still remain in the liquor. With a 26% excess of Na_2S, the amount of Zn in the liquor is only 0.4 ppm. Copper was removed completely in all assays.

Another purification is observed in Co and Ni removal using excesses of reagent, passing from 0.7 ppm to 0.1 ppm in both cases. The pH of the solution increases with increasing amounts of sodium sulfide added and Mn can be lost by precipitation of the corresponding manganese sulfide.

The yield in the precipitation of sulfides is thus maximal with a 30% excess. However, bearing in mind the cost of the reagent (Na_2S) and the greater loss of manganese, an excess of 14% was chosen as the working condition.

Table IV shows the chemical composition of 10 L of purified electrolyte. The contents in Zn, Co, and Ni are within the permitted limits for the electrolysis of manganese.

Electrodeposition

The manganese obtained after 3 h of electrolysis was analyzed by XRD (Fig. 10). The intensities of the reflections correspond to alpha-Mn. The chemical composition of the cathode deposit is 99.99% Mn.

CONCLUSIONS

A comprehensive procedure has been developed for the separation and recovery of manganese from electrowinning zinc residue to achieve a solution that can be used for subsequent production of electrolytic manganese metal. The developed process can recover most of the manganese in the residue.

All the process conditions, including sulfuric acid leaching and purification, were optimized.

Anode slime is treated with sulfuric acid in a furnace within a temperature range of 400–450°C for 1 h, using 33% excess acid over the amount needed to dissolve all of the manganese. The most suitable acid concentration is 70% by mass, obtaining high extractions and a pulp that is easy to handle.

The subsequent leaching is performed at room temperature with water. More than 90% of the manganese present in the sample is dissolved.

The removal of Zn, Co, Cu, and Ni to values below 2 ppm takes place at room temperature using a concentrated solution of sodium sulfide with a 14% excess with respect to the stoichiometric amounts of sulfide required for the reaction. The purified liquor is suitable for electrolysis. Alpha-manganese is obtained with a purity of 99.99%. The solid residue remaining after leaching is rich in lead and could be recycled to recover this metal.

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