

Dissolution of Manganese from Polymetallic Material Using Sulfuric-Oxalic Acid Medium

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Received 19 March 2016; accepted 16 May 2016; published 19 May 2016

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Abstract

Sedimentary rocks have been found to host several Mn minerals in addition to some economic metal values. Besides recoverable Al occurring as gibbsite mineral, the latter include Cu, Zn, Co, Ni, U as well as rare earth elements. In this work, the ore material was subjected to sulfuric acid leaching in the presence of oxalic acid as a reductant to maximize the extraction of Mn. The optimum leaching conditions to achieve almost complete leaching efficiency of Mn with Fe dissolution not exceeding 13% involved 0.5 M sulfuric acid and 0.25 M oxalic acid in a solid/liquid ratio of 1/15 at 85°C for 105 min using an ore size of -150 µm. The leaching behavior of the associated interesting metal values (Al, Cu and Zn) has also been investigated.

Keywords

Polymetallic Mn Material, Oxalic-Sulfuric Acid, Agitation Dissolution

1. Introduction

Various hydrometallurgical methods have been suggested in the literature for the treatment of low grade manganese ores. Such ores can be treated either by reduction roasting followed by acid leaching [1] or directly by reductive acid leaching using different reducing agents. To realize the latter, several procedures have been suggested; namely mixed methanol-sulfuric solution [2], coke [3], non aqueous dimethyl sulfoxide [4], iron(II) sulphate [5], aqueous sulfur dioxide [6]-[8], sulfuric acid and hydrogen peroxide [9] [10], hydrochloric acid and nickel matte [11], hydrochloric acid and pyrite [12] [13]. The latter authors have pointed out that the chloride ion at high concentrations was responsible for the reduction of higher valence state oxides. On the other hand,

leaching processes in basic media involve the use of ammonium sulfite as reductant [14], in addition to several patented leaching processes [15]-[17]. Recently, Sahoo *et al.* (2001) have been able to leach Mn-Iron low grade ore assaying 24.7% Mn and 28.4% Fe using sulfuric acid in the presence of oxalic acid as a reductant.

In Egypt, sediments composed of shale, siltstone, clay, ferruginous sandstone, calcareous sandstone and feldspathic sandstone [18]-[20]. This polymetallic ore is associated with varying amounts of U, Mn, Zn, Cu, Co, Ni, REE, V, etc.

Several local leaching studies have actually been performed upon the Mn ores with different constituents and grades of the economic metal values. These studies include those of Amer [21] [22], El Hazek *et al.* [23] and Lasheen *et al.* [24]. Thus, Amer [21] [22] investigated the leaching characteristics of U, Cu and Mn from a similar ore material by pug leaching using H_2SO_4 acid—as well as using $\text{Fe}_2(\text{SO}_4)_3$ or FeCl_3 as lixivants. El Hazek *et al.* [23] investigated manganese leaching from a low-grade ore (about 11% MnO) from Sinai using hydrochloric acid in the presence of hydrogen peroxide as a reducing agent. On the other hand, Lasheen *et al.* [24] have also studied the recovery of manganese and some associated metal values from a more rich ore material (48.4% MnO) using nitric acid medium in presence of molasses as reductant.

The present work has also been oriented towards studying the acid leaching characteristics of Mn and some of the associated metal values by using oxalic acid as a reductant. The leaching characteristics of this ore material have previously been studied using sulfuric acid only in a manner not to allow Mn leaching. Besides Mn, the studied metal values included Al, Cu and Zn. In the performed leaching experiments, the relevant parameters were so chosen in order to keep iron dissolution—which highly contaminates Mn products—to the least possible amount.

2. Experimental

2.1. Analytical Procedures

The major oxides of the working sample were determined using the rapid silicate analysis method of Shapiro and Brannock [25]. For the analysis of Cu, Zn, Co and Ni the atomic absorption technique was adopted using a Unicam Atomic Absorption Spectrometer model 969 at the following wavelengths 222.60, 307.60, 243.70 and 305.10 nm respectively [26]. Al and Mn were detected by AAS at the wavelengths 309.30 and 403.10 nm respectively [26]. On the other hand, an oxidimetric titration method against ammonium metavanadate was used for U analysis in the presence of diphenylamine sulfonate indicator. Prior to titration, proper reduction of U was performed using ammonium ferrous sulfate [27].

To define the mineralogical composition of the working ore material, the collected study sample was subjected to X-ray diffraction analysis. For this purpose, a Philips X-ray diffractometer, model PW 223/20 was used where the copper tube was operated at 40 kV and 20 mA.

2.2. Leaching Procedure

Different leaching conditions were studied to attain the maximum possible leaching efficiency of the studied metal values. These conditions include the reagent concentration, time, temperature, ore sample to reagent ratio and the ore grain size. Leaching was carried out in a well-stirred 3 necked round flask fitted with a thermometer and condenser. The leaching efficiency of each metal value was calculated from the analysis of the pregnant leach solution after filtering and washing the slurry.

3. Results and Discussion

3.1. Solid Characterization

From the obtained analyses, it was found that the ore material assays about 27% Al_2O_3 together with other metal contents of 8.4% MnO mainly as pyrolusite (MnO_2), 3.4% ZnO in addition to 1900 ppm Cu, 1000 ppm Co, 730 ppm Ni, and 400 ppm U besides a total rare earth elements (REE) content of 6200 ppm (Table 1).

On the other hand, the obtained diffractogram was properly interpreted using standard diffraction mineral patterns [28] and revealed the presence of several minerals such as gibbsite, dolomite together with a variety of manganese minerals as cryptomelane $\text{KMn}_8\text{O}_{16}$, chalcophanite $\text{ZnMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$, pyrolusite MnO_2 and crednerite CuMnO_2O_4 . In the light of this mineral composition, it was possible by proper calculation of the obtained

chemical analysis, together with some dissolution tests, to infer the mineralogical composition (mode) shown in **Table 2**. It is notable that gibbsite $[Al(OH)_3]$, representing an important mineral of Al, amounted to 33% while dolomite—which would consume acid—assays about 21%.

3.2. Study of Leaching Parameters

3.2.1. Effect of Sulfuric Acid Concentration

To study the effect of sulfuric acid concentration on the leaching efficiency of Mn and other associated metal values, a number of preliminary leaching experiments were performed using different acid concentrations ranging from 0.2 to 1 M. In these experiments, the other leaching conditions were fixed at 0.24 M oxalic acid, 2 h agitation time at 90°C with a solid/liquid ratio (pulp density) of 1/15 using $-150\ \mu\text{m}$ ore grain size. From the results shown in **Table 3**, it is clear that the amount of input acid, which depends in turn upon its concentration

Table 1. Chemical composition of Abu Zeneima gibbsite ore material.

Major constituent	Wt., %	Trace constituent	Conc., ppm
SiO ₂	13.50	ΣREE	6200
Al ₂ O ₃ *	27.00	Cu	1900
Fe ₂ O ₃	12.30	Co	1000
CaO	6.53	Ni	730
MgO	4.66	U	400
Na ₂ O	1.04		
K ₂ O	1.55		
MnO	8.40		
ZnO	3.40		
H ₂ O ^(humidity)	1.81		
LOI**	21.30		
Total	101.49		

*Total alumina corresponding to gibbsite and clay minerals; **LOI includes H₂O^(crystalline) and CO₂.

Table 2. Estimated mineralogical composition (mode) of Abu Zeneima gibbsite ore material.

Mineral/Oxide	Wt., %
Gibbsite	33.00
Dolomite	21.45
Fe ₂ O ₃ *	12.30
MnO**	8.40
ZnO***	3.40
Qz, Silicates	21.49
Total	100.04

*Equivalent for both goethite and hematite; **Equivalent for the detected Mn minerals; ***Present in chalcophanite.

Table 3. Effect of sulfuric acid concentration upon leaching efficiency of Mn and associated metal values (0.24 M oxalic acid, 2 h, S/L ratio 1/15, 90°C, $-150\ \mu\text{m}$ grain size).

Sulfuric acid conc., M	Leaching Efficiency, %				
	Al*	Mn	Zn	Cu	Fe
0.2	14.3	74.3	73.2	76.4	11.9
0.5	36.7	98.2	94.1	92.1	14.7
0.8	54.0	98.7	91.2	88.5	16.9
1.0	72.6	98.7	92.0	87.3	20.3

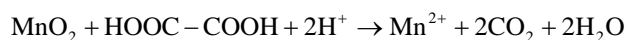
Al* calculated as gibbsite.

and the solid/liquid ratio, has a direct influence upon the dissolution of the interesting metal values specially Al and Fe. However, at only 0.5 M acid concentration, the leaching efficiencies of the 3 working metal values *i.e.* Mn, Zn and Cu attained about 98%, 94% and 92% respectively. As a matter of fact, the leaching efficiencies of Zn and Cu are always comparable to that of Mn due to their existence in its two mineral species detected by XRD; namely Zn and Mn in chalcophanite and Cu and Mn in crednerite. However, in case of Cu, it is noticed that its leaching efficiency slightly decreased as acid concentration increased from 0.5 to 1 M; a matter which might be due to hydrolysis or else to partial reduction by oxalic acid to its monovalent state (Cu^+).

On using sulfuric acid without oxalic acid, the Mn leaching efficiency at the three acidities of 1, 2 and 4 M was only 1.5%, 1.9% and 2.5% respectively, a matter which indicates the necessity of using a reducing agent.

It is interesting to mention that a leaching experiment using concentrated HCl with a solid/liquid ratio of 1/3 at 100°C for 4 h resulted in almost complete leaching of Mn (99.7%) together with 96.5% Cu, complete leaching of Al in the gibbsite mineral as well as over 85% of Zn. In this regard, it is also significant to mention that 2 M HCl at 90°C for 2 h with a solid/liquid ratio of 1/12 gives 67% Mn leaching. This is because the chloride ions at such high concentrations are responsible for the reduction of higher valence state oxides.

Finally, it is interesting to indicate herein that Mn leaching is due to the reduction of its dioxide by the added oxalic acid. According to Ehrlich (1980), MnO_2 reduction by oxalic acid in acid medium may be represented by the following reaction:



Regarding the acid amount required for reacting with all the basic constituents of the working ore material, an acid consumption test was performed using 250 g ore in 4 M H_2SO_4 with a S/L ratio of 1/3 at 80°C for 4 h. Analysis of the remaining acid after proper complexing the hydrolyzed cations revealed that the acid consumption attains about 750 Kg/t ore. Calculation of the input acid concentration of 0.5 M in a S/L ratio of 1/15 would indicate that the input acid amount is just the necessary amount for reacting with the basic ore components under the mentioned conditions.

3.2.2. Effect of Oxalic Acid Concentration

To study the amount of oxalic acid that would be responsible for the reduction of Mn in the working ore material, a set of leaching experiments was performed using different oxalic acid concentrations ranging from 0 to 0.40 M. The other leaching conditions were fixed at 2 h agitation time at 90°C with a solid/liquid ratio (pulp density) of 1/15 and using $-150 \mu\text{m}$ ore grain size. From the results shown in **Table 4**, it is clear that addition of oxalic acid is necessary to improve the leaching efficiencies of Mn and the other associated metal values. Thus, at 0.24 M oxalic acid concentration, almost complete Mn leaching was achieved besides about 94% of Zn and 92% of Cu. However increasing the oxalic concentration to 0.40 M has not led to any perceptible improvement in the leaching efficiencies of Zn and Cu.

3.2.3. Effect of Leaching Time

For studying the effect of the leaching time, another series of experiments was made using 0.5 M sulfuric acid and 0.24 M oxalic acid at 90°C with a solid/liquid ratio (pulp density) of 1/15 using $-150 \mu\text{m}$ ore grain size. From the results shown in **Table 5**, it is clear that at leaching time of 105 min, sufficiently high leaching efficiencies of Mn, Zn and Cu of about 98%, 95% and 92% have been realized. However, extension of leaching time to 120 min has increased the undesirable Fe leaching efficiency to 14.7% compared to 12.7% at 105 min.

3.2.4. Effect of Leaching Temperature

The influence of temperature upon the leaching efficiency of Mn and other associated metal values was studied through a series of experiments at temperatures ranging from 25°C to 100°C. The other leaching conditions were fixed at 0.5 M sulfuric acid and 0.24 M oxalic acid for 2 h agitation time in a solid/liquid ratio (pulp density) of 1/15 and using $-150 \mu\text{m}$ ore grain size. From the results shown in **Table 6**, it is clear that almost complete Mn leaching was achieved at 90°C (98.2%). Also both Zn and Cu have attained high leaching efficiencies of 94.1% and 92.1% respectively and raising the leaching temperature to more than 90°C didn't improve their leach ability. On the other hand, the leaching temperature has great influence on dissolution of the undesirable Fe where its leaching efficiency has increased from 14.7% to 18.0% when the leaching temperature was raised from 90°C to 100°C.

Table 4. Effect of oxalic acid concentration upon leaching efficiency of Mn and associated metal values (0.5 M sulfuric acid, 2 h, 90°C, S/L ratio 1/15, -150 µm grain size).

Oxalic acid conc., M	Leaching Efficiency, %				
	Al*	Mn	Zn	Cu	Fe
0.00	12.5	1.5	51.0	64.2	9.8
0.08	21.8	68.5	67.0	72.1	10.5
0.16	28.2	74.4	83.0	81.1	11.2
0.24	36.7	98.2	94.1	92.1	14.7
0.32	35.9	99.5	94.2	92.8	14.6
0.40	36.5	98.5	93.6	93.2	15.1

Al* calculated as gibbsite.

Table 5. Effect of time upon leaching efficiency of Mn and associated metal values (0.5 M sulfuric acid and 0.24 M oxalic acid, 90°C, S/L ratio 1/15, -150 µm grain size).

Time, min	Leaching Efficiency, %				
	Al*	Mn	Zn	Cu	Fe
30	12.7	61.5	60.5	61.2	9.5
60	20.4	78.2	71.0	73.7	11.2
90	29.8	91.4	88.0	87.2	12.1
105	36.0	98.2	94.5	92.2	12.7
120	36.7	98.2	94.1	92.1	14.7

Al* calculated as gibbsite.

Table 6. Effect of temperature upon leaching efficiency of Mn and associated metal values (0.5 M sulfuric acid and 0.24 M oxalic acid, 2 h, S/L ratio 1/15, -150 µm grain size).

Temp., °C	Leaching Efficiency, %				
	Al*	Mn	Zn	Cu	Fe
25	8.5	64.0	47.2	41.9	3.6
50	11.2	77.4	71.2	72.8	8.2
75	23.5	89.7	86.5	90.1	10.9
90	36.7	98.2	94.1	92.1	14.7
100	52.8	98.5	92.5	93.2	18.0

Al* calculated as gibbsite.

3.2.5. Effect of Solid/Liquid Ratio

Working at the same acid concentrations but varying the solid/liquid ratio could provide for improved metal leaching through the increased amount of the input acid. The effect of solid/liquid ratio was then studied using 0.5 M sulfuric acid and 0.24 M oxalic acid for 2 h at 90°C and using -150 µm ore grain size. The obtained data are tabulated in **Table 7** and demonstrate that decreasing the pulp density to 1/15 was beneficial for the extraction of the studied metal values. Thus as the S/L ratio is decreased from 1/5 to 1/15, the Mn leaching efficiency increased from 80.2% to 98.2% whereas the leaching efficiencies of Zn and Cu increased from 77.6% to 94.1% and from 79.4% to 92.1% respectively.

3.2.6. Effect of Ore Grain Size

Finally, the effect of the grain size of the study ore material was studied in the range of -250 down to -88 µm while fixing the other leaching conditions at 0.5 M sulfuric acid and 0.24 M oxalic acid for 2 h at 90°C in the S/L ratio of 1/15. The obtained results shown in **Table 8**, indicate only a slight improvement in the leaching efficiencies of all the metal values with finer grain sizes. As a matter of fact, increased ore grinding generally represents excessive energy consumption and having high leaching efficiencies in this work at relatively coarse size would realize important cost reduction.

Table 7. Effect of solid/liquid ratio upon leaching efficiency of Mn and associated metal values (0.5 M sulfuric acid and 0.24 M oxalic acid, 2 h, 90°C, -150 µm grain size).

Solid/Liquid Ratio	Leaching Efficiency, %				
	Al*	Mn	Zn	Cu	Fe
1/5	21.5	80.2	77.6	79.4	8.2
1/10	31.2	83.4	85.2	86.2	11.4
1/15	36.7	98.2	94.1	92.1	14.7
1/20	56.8	98.8	95.5	94.2	16.8

Al* calculated as gibbsite.

Table 8. Effect of grain size upon leaching efficiency of Mn and associated metal values (0.5 M sulfuric acid and 0.24 M oxalic acid, 2 h, 90°C, S/L ratio 1/15).

Grain Size, mesh µm	Leaching Efficiency, %				
	Al*	Mn	Zn	Cu	Fe
-60 - 250	34.8	97.1	92.5	90.0	14.2
-80 - 188	36.0	97.5	94.0	91.2	15.2
-120 - 125	38.7	98.2	94.4	91.7	15.7
-170 - 88	37.2	98.6	93.9	92.2	15.8

Al* calculated as gibbsite.

3.2.7. Effect of Prior Reductive Roasting

Another route for leaching Mn can be achieved by prior reductive roasting. Accordingly, two samples were roasted at 650°C and 850°C with and without 20% w/w oxalic followed by sulfuric acid leaching. Surprisingly, prior roasting improved the leaching efficiency of Mn even in the absence of reductant. Thus, 82% of input Mn was leached after prior roasting at 850°C in absence of the reductant and 96.3% in presence of the reductant. Accordingly, it can be noted that normal roasting would be advantageous for extracting Mn as it changes its mineral phase to more acid soluble forms. However, prior roasting has resulted in adverse effect upon the leaching efficiencies of Al, Cu, and Zn; a matter which is most probably due to partial formation of relatively refractory oxides or ferrites of these metals.

3.3. Potentiality of Selective Metals' Recovery

Applying the optimum leaching conditions upon the polymetallic ore material, a suitable volume of the leach liquor was prepared to study the potentiality of recovering the leached metal values. Due to important differences in the pH values at which the hydroxides of the latter would precipitate, the prepared leach liquor was subjected to a selective precipitation test. However, since the difference between the pH values at which the hydroxides of Cu²⁺ and Fe²⁺ precipitate *i.e.* 5.3 and 5.5 respectively [29], it would be greatly advantageous to selectively precipitate Cu by cementation using metallic Zn. The latter should be performed prior to the hydroxides of Al and Fe at pH values of 4.1 and 5.5 respectively. Raising the pH of the filtrate to 7 would result in precipitation of Zn(OH)₂ and finally increasing the pH to 8.5 - 9 would lead to Mn precipitation as its hydroxide.

However, due to the lack of material in the present work, the obtained leach liquor was subjected to only two precipitation steps; namely at pH 7 and at pH 8.5 - 9. At the former pH, all the Al, Cu, Fe and Zn would collectively precipitate leaving only Mn in solution which was then precipitated at pH value ranging from 8.5 to 9. After filtration of the obtained Mn(OH)₂, it was washed, dried and calcined at 1000°C for 1 h. Analysis of the calcined product through XRD has indicated that the obtained diffractogram (**Figure 1**) matches with that of the trioxide Mn₂O₃ (ASTM card no.10 - 69). Accordingly, it has been possible to propose the flowsheet schematically shown in **Figure 2** for the processing of Abu Zeneima polymetallic ore material.

4. Conclusions

Sulfuric acid leaching of polymetallic ore material (Al, Mn, Zn and Cu) in presence of oxalic acid as a reductant

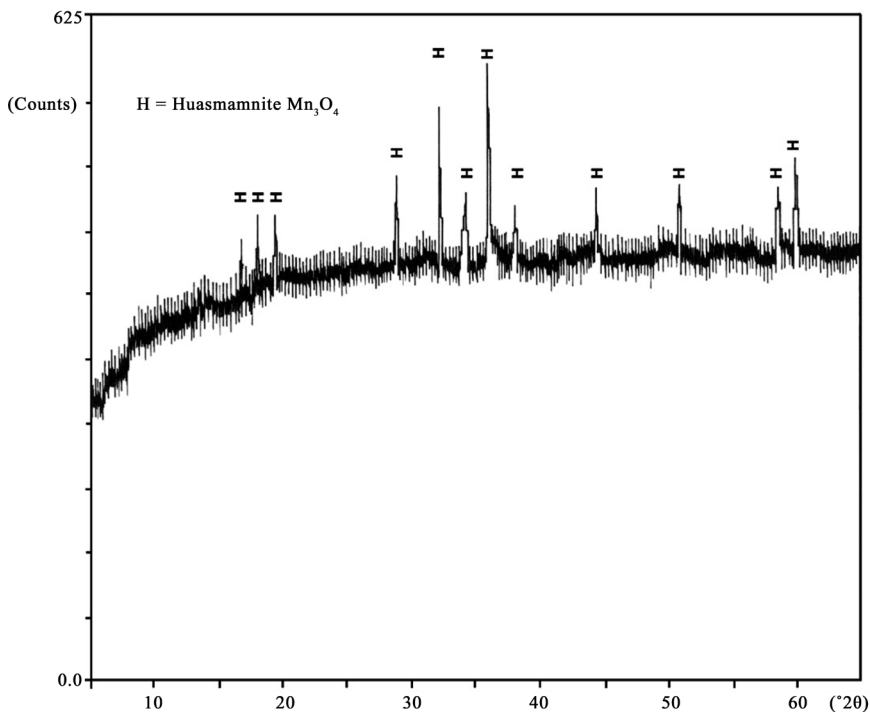


Figure 1. XRD analysis of manganese product H = Hausmannite Mn₂O₃.

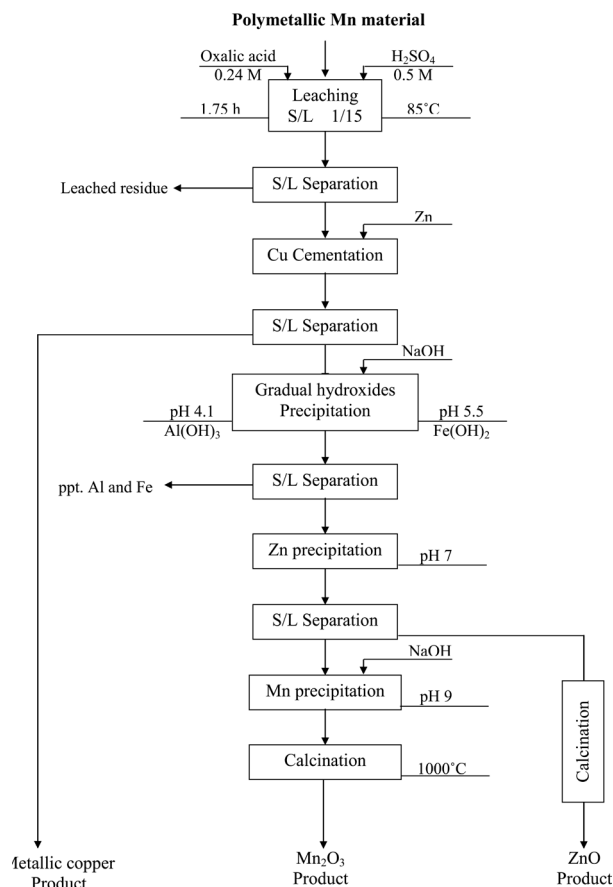


Figure 2. Proposed flowsheet for the processing of polymetallic Mn material.

proved quite successful. The studied optimum conditions for leaching about 98% of Mn, 94% of Zn and 92% of Cu involved using 0.5 M sulfuric acid in presence of 0.24 M of oxalic acid for 105 min at 85°C in an S/L ratio of 1/15 and using an ore ground to less than 80 - 100 mesh size.

Selective recovery of the leached metal values can actually be achieved by alkali precipitation at different pH values except Cu. The latter could be recovered by cementation using metallic Zn powder prior to the alkali precipitation steps.

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