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Manganese Reduction Leaching of Sinai Low Grade Ore Material

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Summary: Manganese leaching from Sinai low-grade ore material (8.52% Mn) was investigated by using hydrochloric acid in the presence and absence of hydrogen peroxide as a reducing agent. Sample characterization by XRD denoted the presence of a variety of Mn minerals including mainly cryptomelane, chalcophanite, pyrolusite and crednerite together with the iron minerals goethite, hematite and minor pyrite beside gibbsite and dolomite. Although pyrite can act as a reductant for the tetravalent Mn minerals, however, it was necessary to involve H_2O_2 as an additional reductant to realize over 97% Mn leaching. Both Zn and Cu, which are present in the Mn minerals chalcophanite and crednerite respectively, are simultaneously leached.

The relevant leaching factors were optimized as 2M HCl and 0.4M H_2O_2 in a solid -liquid ratio of 1/12 at 95ºC for 1h leaching time. At these conditions, the obtained leaching efficiencies amounted to more than 97% for Mn, 98% for Zn beside about 81% for Al and complete leaching of Cu. Under these condition Fe dissolution did not exceed 14%.

Introduction

Manganese is a strategic element, which has several industrial applications such as steel production carbon-zinc batteries production, fertilizers, as well as colorants for bricks, dyes and medicines. The world annual consumption of manganese is above 1,300,000 annual tons and it is destined to increase. Low grade ores are gaining increasing attention due to development in exploitation technologies.

Various hydrometallurgical methods have actually been suggested in the literature for 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 kinds of reducing agents. To realize the latter, several procedures have been suggested; namely mixed methanol-sulphuric solution(2), sulphuric and oxalic acid mixture(3), iron Π sulphate(4), aqueous sulphur dioxide(5-8), sulphuric acid and hydrogen peroxide(9), hydrochloric acid and nickel matte(10), hydrochloric acid and pyrite.(11-14) Recently the dissolution of MnO_2 has reported in an aqueous alcoholic-

HCl acid mixture.[15] These authors have pointed out that the chloride ion was responsible for the reduction of higher valence state oxides. On the other hand leaching processes in basic media involve the use of ammonium sulphite[16], in addition to several patented leaching processes.[17-19]

The high grade Paleozoic manganese deposit of south west Sinai has essentially been exploited, however, extensive tonnages of low grade ore material still exist and require developed technologies for their economic processing. A proper technological sample of the latter has been collected from Abu Zeneima locality (11.00% MnO) and was subjected to processing via reduction leaching using hydrochloric acid and hydrogen peroxide. The redox chemistry of the latter in aqueous solution shows that it is indeed a strong oxidizing agent in either acid or basic solution.[20]

However, H_2O_2 behaves as a reducing agent only towards very strong oxidizing agents as MnO_4. The relevant leaching factors affecting Mn leaching were studied. These factors involved the concentration of both acid and H_2O_2 besides leaching temperature and time as well as the pulp density and the grain size of the ore material.

Experimental

To define the mineralogical composition of the working ore material, bulk and sieved samples were subjected to Philips X-ray diffractometer, model PW 223/20 where the copper tube was operated at 40 Kv and 20 mA. The obtained diffractograms were properly interpreted using standard diffraction mineral patterns. The obtained results revealed the presence of several Mn minerals as cryptomelane, chalcophanite, pyrolusite and crednerite associated with some iron minerals as well as the Al mineral gibbsite and the carbonate mineral dolomite. Major elements were analyzed using a standard analytical method for rock analysis.[21-22] Trace elements analyses were performed using unicam 969 atomic absorption spectrometry. Manganese was aspirated through nebulizer in presence of La^{+3} as a releasing agent at wave length 403.10nm.[23] Cu, Zn and Al were measured at the following wave lengths. 222.60nm, 307.60nm, 309.30nm respectively.[24] Repeated for both analysis in-house and international standards gave a good reproducibility of standard deviation that equal

0.57. The leaching experiments were carried out using 10 gm sample fractions to which the proper acid and H_2O_2 contents were added. The obtained ore slurry was then agitated at the required temperature using a hot magnetic plate. Except otherwise cited, 2h leaching time was allowed while a solid/ liquid ratio of 1:12 was used. At the end of each leaching experiment, the slurry was filtered, and the filtrate (leach liquor) was analyzed for the leached Mn and associated metal values. The leaching efficiency is calculated by referring the leached metal amount in the leach liquor to its original input value.

Results and Discussion

Ore analysis: The obtained chemical analysis of the working Abu Zeneima working ore material is shown in table (1). From the obtained analytical and mineralogical results, the following potential mineralogical composition of the working Abu Zeneima low grade Mn ore material is suggested Table (2).

Table 1. Chemical composition of Abu Zeneima working ore material

Component	Wt%	Component	Wt%
MnO	11.00	Na_2O	0.67
MgO	5.94	K_2O	0.34
CaO	8.32	P_2O_5	0.55
SiO_2	16.00	LOI*	26.80
TiO_2	0.33	ZnO	2.00
Al_2O_3	8.80	CuO	0.25
Fe_2O_3	20.08	Total	101.08

*LOI includes 13.07% CO_2 present in dolomite and 13.73% water present in gibbsite (4.66%) and in the iron mineral goethite (9.07%).

Table 2. Potential mineralogical composition of Abu Zeneima working ore material

Mineral/Oxide	Wt%
Quartz	16.00
Dolomite	27.00
Gibbsite	13.46
Iron oxide minerals *	29.15
Manganese minerals (equiv.MnO)	11.00
Zn O**	2.00
Total	98.94

* Calculated as goethite
** Involved in the Mn mineral chalcophanite

Effect of HCl concentration: A series of leaching experiments was carried out at different HCl concentration (1.25 to 3.25 M). From the obtained leaching efficiencies as shown in Fig (1), it is clear that as the HCl concentration increases, the dissolution efficiencies of all the studied metal values increase. Thus, at 2M acid concentration, the economic metal values of Mn, Cu and Zn are almost completely dissolved while the leaching efficiency of Al attains 84.80%. At this acidity level, the dissolved iron content amounts to 16%. Increasing the HCl concentration to only 2.25M has slightly improved the leaching efficiency of Al to 86.32%, how ever; iron dissolution amounted to about 40%.

It can thus be concluded that the unleached Al (<10%) might correspond to some clay minerals in the ore material and therefore an acidity of 2M would be sufficient for almost complete recovery of the studied four economic metal values and keeping iron dissolution to minimum.

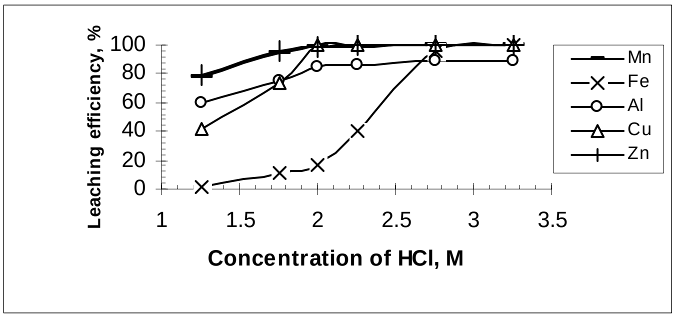

Fig 1. Effect of HCl concentration upon the leaching efficiencies of Abu Zeneima studied metal values (0.4M H_2O_2, 95°C, 1/12 pulp density, 2h, -74µm)

Effect of H_2O_2 concentration: In order to evaluate the effect of H_2O_2, a second series of leaching experiments was carried out using 2M HCl. These experiments were performed in the absence and presence of different concentrations of H_2O_2 varying from 0.2 to 1.0 M.From the obtained data as shown in Fig (2), it is evident that while about 67% of input Mn has been dissolved in the absence of H_2O_2 about 80% of Al and down to 65% and about 76% of Cu and Zn respectively have been leached. Apart from Al, these results are indeed lower than the corresponding yield in presence of 0.4M H_2O_2.

It can thus be concluded that reduction of Mn in its minerals to the bivalent state is necessary before its dissolution. On the other hand, increasing the H_2O_2 molarity beyond 0.4 M has an adverse effect upon iron dissolution that increased from about 29 to 35% at 0.6 and 1.0 M H_2O_2 respectively.

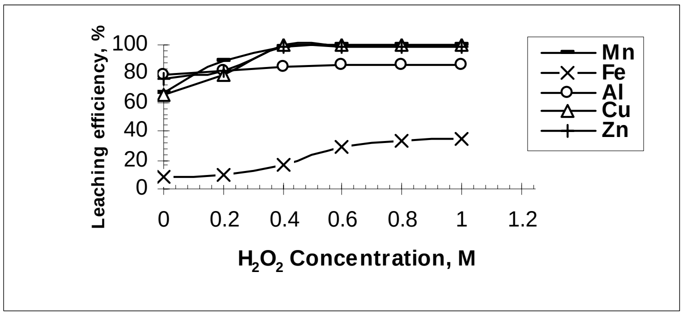

Fig 2. Effect of H_2O_2 concentration upon the leaching efficiencies of Abu Zeneima studied metal values (2M HCl, 95°C, 1/12 pulp density, 2h, -74µm)

Effect of time: In a trial to improve the leaching conditions, another experimental leaching series was performed using < 2h leaching time. The obtained results show that at only half an hour leaching time, the leaching efficiencies of Mn, Cu and Zn have not been impaived to any great extent. However, the leaching efficiency of Al was decreased to 71.00 % and that of Fe down to 14%. Therefore, it can be concluded that 1h leaching time would be adequate and could be considered as optimum as the decrease in the leaching efficiency of Al is not serious beside it decreased iron contamination from about 16% in 2h to 14% only.

Effect of temperature: In order to reduce the heat energy and in turn the leaching costs, three leaching experiments were carried out at room, 60ºC and 85ºC under the same leaching conditions previously used at 95ºC. The resultant leaching efficiencies shown in Fig (3), indicate that temperature plays an important role specially in case of Al and Cu. Accordingly, the obtained leaching yield for Al was decreased down to only 16.90% while that of Cu was decreased to about 55% as compared to about 84% and 91% for Mn and Zn respectively. The leaching efficiency has steadily increased to almost complete leaching of Mn, Cu and Zn together with about 85% for Al.

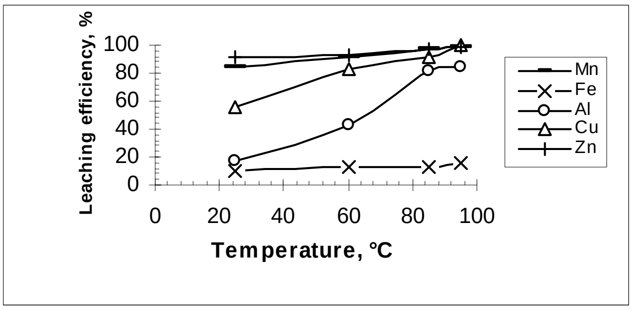

Fig 3. Effect of temperature upon the leaching efficiencies of Abu Zeneima studied metal values (2M HCl, 0.4M H_2O_2, 2h, 1/12 pulp density, -74µm)

Effect of pulp density: Working with the fixed concentration of 2M HCl and 0.4M H_2O_2 solution, another 3 leaching experiments were preformed at pulp densities 1:8, 1:10 and 1:14 under the same leaching conditions used for the pulp density 1:12. In other words, the acid quantities varied in the meantime of varying the input wt./vol. ratio. It was found that 1:8 and 1:10 pulp ratios, the leaching efficiencies of all the studied metal values were decreased. By increasing the acid amount and applying a pulp ratio of 1:14, did not however affect the leaching efficiencies of Mn, Al, Cu and Zn but that of iron was increased to about 22.5%. This result supports the conclusion of presence of some clay minerals equivalent to about 13% of Al in the working ore material.

Conclusion

A reductive leaching process for Sinai low grade Mn ore material has been successfully applied using a proper molarity of hydrochloric acid and hydrogen peroxide. In the proposed process, the other associated metal values have also been leached; namely Al present in gibbsite as well as the Cu and Zn values replacing some Mn in its minerals. The studied leaching factors were optimized as 2M HCl and 0.4M H_2O_2 at 95ºC for only 1h leaching time and using an ore ground to 200 mesh size. Almost complete leaching efficiencies were realized under these conditions for Mn, Cu and Zn while that of Al attained about 81% and iron contamination is equivalent to 14% dissolution.

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