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Full Length Research Paper

Lixiviation of manganiferrous aluminosilicate mineral in hydrochloric acid

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A study of the lixiviation of Manganiferrous Aluminosilicate Mineral in hydrochloric acid has been undertaken. Experiments on quantitative lixiviation of the mineral showed that its dissolution rate depends on hydrogen ion concentration, reaction temperature and particle size. The activation energy calculated from the experimental data was 34.19 kJ/mole and this suggests a diffusion controlled mechanism. A reaction order of 0.2 with respect to the acid concentration was also found. With 8.42 M HCl at 80°C, about 69.27% of the 10 g/L of the manganiferrous mineral was dissolved within 120 min using < 0.09 mm particle diameter.

Key words: Manganiferrous, lixiviation, dissolution, kinetics, hydrochloric acid.

INTRODUCTION

Manganese is a naturally occurring element that is found in rock, soil and water. It is ubiquitous in the environment and comprises about 0.1% of the earth crust. Crustal rock is a major source of manganese including manganese aluminosilicate mineral (MASM) found in the atmosphere. Ocean spray, forest fires, vegetation and volcanic activity are other major natural atmospheric sources of manganese. Important sources of dissolved manganese are anaerobic environment where particulate manganese oxides are reduced, the direct reduction of particulate manganese oxides in aerobic environments, the natural weathering of Mn(II)-containing minerals and acidic environments. The major anthropogenic sources of environmental manganese include municipal waste water discharges, sewage sludge, mining and mineral processing, emissions from alloy, steel and iron production, combustion of fossil fuels and to a much lesser extent, emissions from the combustion of fuel additives (Cidas, 2004; Mitra et al., 2003) .

In general, polymetallic manganese nodules including MASM are found just beneath the sea floor in parts of all the deep oceans of the world except the Arctic. They contain mainly two intimately mixed metal oxides, namely manganese dioxide and hydrated iron oxide. Besides, other valuable metals such as Cu, Ni, Co, Zn, Mo, etc., are also present in them in appreciable quantities (Devi et al., 2001). The presence of these metal values has prompted the researchers to project these nodules as future source of these metals and to concentrate on metallurgical extraction of the same metal (Furstenau and Han, 1983; Haynes et al., 1983; Nayak et al., 1995).

Many workers including Mitra et al. (2003) have developed many processing routes for the extraction of these metals, out of which about six routes have been identified for future potential application. One of these routes is processing of the nodule in the presence of hydrochloric acid (Devi et al., 2001; Kane and Cardwell, 1975), where the nodule is reduced at 500°C by HCl to form metal chlorides according to the following reactions:

$$MeO + 2HCl \rightleftharpoons MeCl2 + H_2O \text{ (Me = Ni and Cu)} \qquad (1.1)$$

$$Fe_2O_3 + 6HCl \rightleftharpoons FeCl_3 + 3H_2O \qquad (1.1a)$$

$$MnO_2 + 4HCl \rightleftharpoons MnCl_2 + 2H_2O + Cl_2 \qquad (1.2)$$

$$Co_2O_3 + 6HCl \rightleftharpoons 2CoCl_2 + 3H_2O + Cl_2 \qquad (1.2a)$$

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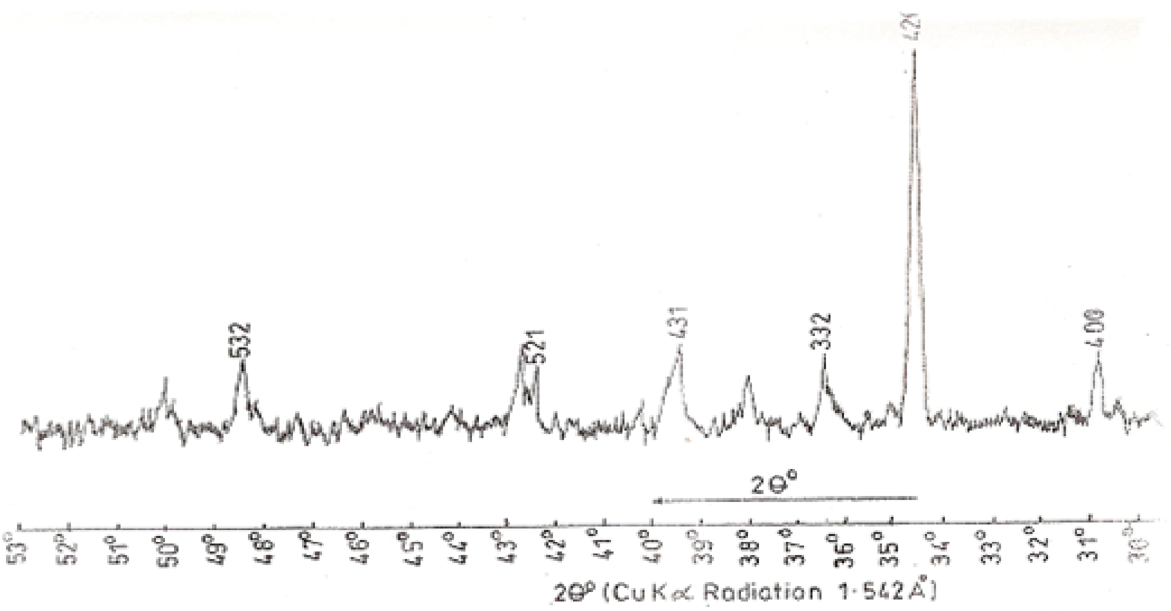

Figure 1. X-ray diffraction trace of MASM crystal.

Most of the iron chloride in this reaction (1.1a) is converted to oxide by pyro-hydrolysis. A portion of HCl is also oxidized to produce a Cl_2 gas (Equations 1.2 and 1.2a), which is reused in the downstream process route. In Hoboken-Overpelt (Van-Petegham, 1977), the nodule is leached in a 4 M HCl solution to dissolve almost all the metal values, consistent with reaction (1.1) through (1.2a), metal values are subsequently recovered from the solution using hydrometallurgical techniques (Devi et al., 2001). The processing of low grade Egyptian Manganese ore was studied (Amer, 1998). Here, almost complete extraction of manganese was achieved at temperature 220°C under oxygen pressure of 15 bars after 30 min of leaching and at MnO_2/FeS_2 molecular ratio 1.0. The residue is enriched in iron which could be used to produce feed stock for iron smelting. Recently, leaching efficiences of more than 97 and 97% manganese have been reported by Helal et al. (2006) and Tong et al. (2008) via reductive leaching of manganese from low grade ore in HCl and H_2SO_4 using H_2O_2 and cane molasses respectively.

The manganiferrous aluminosilicate rock has been found to be present in large deposit along the course of river Oyun, a major river passing through the University of Ilorin, in the North Central State of Kwara, Nigeria. This river which constitutes a major source of drinking water with four dams (Oyun, Elerinjare, UNILORIN and Kwara Poly), has been found to contain above normal concentration of manganese. The aim of this study is, therefore, to investigate the mechanism of dissolution of this mineral from the analysis of kinetic and thermodynamic data with the aid of some established shrinking core models (Levenspiel, 1984; Zuo-Mei et al., 1984).

MATERIALS AND METHODS

Materials

The Manganiferrous Aluminosilicate Mineral crystals were collected from garnet bearing pegmatite rock, the course of river Oyun, near Fufu, 20 km East of Ilorin town, Kwara State, Nigeria. The elemental analysis of the crystals was carried out by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and its phase characterization was done by powder X-ray diffraction analysis (XRD, PHILIPS Scientific using Cu target 40 kV, 55 mA).

The analysis of crystal MASM by ICP-MS revealed the following results: Fe (34.34%), Mn (26.75%), Pb (1.89%), S(1.47%), Cu (1.33%), Ag (0.76%), Zn (0.08%), P (90 ppm); Sn (55 ppm) and Ti (42 ppm). Other metals detected but with concentration less than 5 ppm include La, U, Y., V, K, Cd, Sb, Bi, Au, Th, Sc, Co and Nb. It is evident that the mineral is dominated by iron oxide (Fe_2O_3) and manganese oxide (MnO_2) at 49.06 and 42.33% respectively. The X-ray diffraction trace showed the garnet to be spessartite with characteristic diffraction peaks at 2.903 Å (400), 2.593 Å (423), 2.462 Å (332), 2.137 Å (521) and 1.888 Å (532) (Figure 1). Spessartite is typical of granites and pegmatites and alteration aureoles of contact and regional metamorphic rocks.

The reagents used for this research work are mainly BDH products of analytical grades. Doubly distilled water was used for the preparation of all HCl solutions.

Leaching procedure

Three different particles sizes (< 0.09 mm, 0.09 mm< ϕ < 0.112 mm and 0.112 mm< ϕ < 0.149 mm) were used for the investigation of lixiviation action of this principal earth material. The study was carried out at different HCl concentrations (0.5 M - 8.42 M) and at different temperatures (28 - 80°C) and time of contact (5 - 120 min) using a 500 ml Rasotherm glass reactor, equipped with a stirrer. When the desired temperature was attained, 10 g/L of the crystal was added to the HCl solution, stirring was started and the temperature of the reaction mixture was then maintained constant. The fraction of manganiferrous mineral dissolved was calculated by

Table 1. Effect of particle size.

Particle size (mm)	Fraction of MASM crystal dissolved
<0.09	0.641
0.09<ϕ<0.112	0.378
0.112<ϕ<0.149	0.193

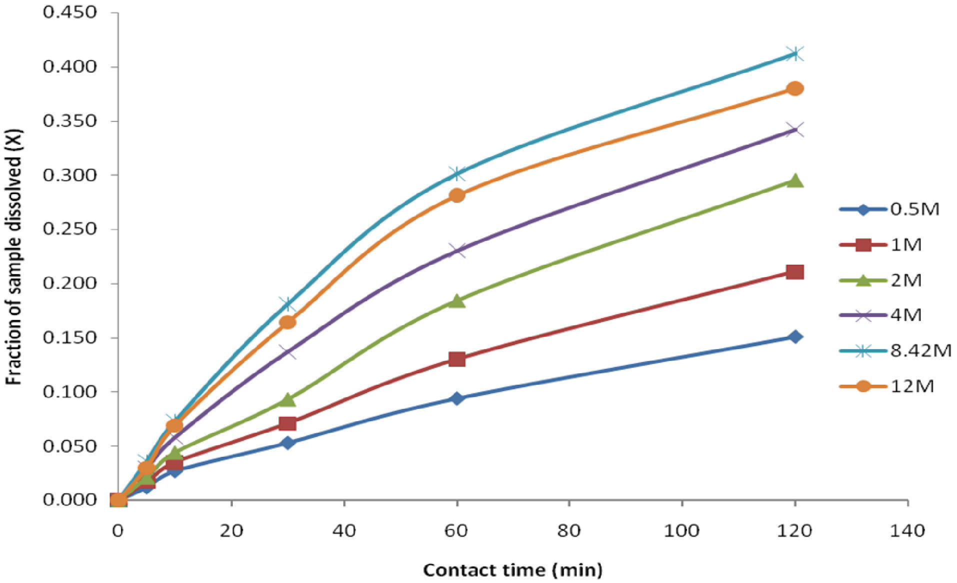

Figure 2. Fraction of Manganiferrous dissolved vs. contact time at different HCl concentration.

The concentration which gave the maximum dissolution (8.42 M) was subsequently used for the optimization of other leaching parameters. The activation energy, E_a and rate constants were evaluated from the Arrhenius plot.

RESULTS AND DISCUSSION

Understanding the mechanism of lixiviation of MASM is the main consideration. Lixiviation of solid particle may be described by a number of reaction models already proposed in the literature (Ucar, 2009).

Lixiviation studies

Today, solid-state chemical reactions are of great importance in various production operations involving the process of mineral raw materials. From the point of view of an extractive metallurgy engineer, processing raw materials means, firstly, converting natural mineral ore into a form suitable for extraction of the desired metal compound. Secondly, the required element or compound should be separated from associated material in the aqueous matrix by either extraction, ion exchange, crystallization, precipitation, selective leaching, etc.

Thirdly, the final product (e.g. metal) must be isolated by reduction, precipitation, etc. Therefore, the physico chemical basis of many of these processes depends on the branch of solid-state chemistry which deals with problems of reactivity of solids (Boldyrev, 1987).

Particle size effect

The effect of particle size on the dissolution of 10 g/L MASM crystal was investigated in 8.42 M HCl solution at 80°C for 120 min using three particle size fractions: < 0.09 mm, 0.09<ϕ<0.112 mm and 0.112 mm<ϕ<0.149 mm. The results of the investigation are presented in Table 1.

As expected, the results presented in Table 1 shows that the dissolution rates are inversely proportional to the average initial particle diameters.

Influence of HCl concentration

The influence of HCl concentration (0.5 - 12 M) on the dissolution of 10 g/L MASM crystal was investigated at 55°C using < 0.09 mm sized fraction. The fraction of mineral dissolved vs. contact time for the different HCl concentrations are illustrated in Figure 2.

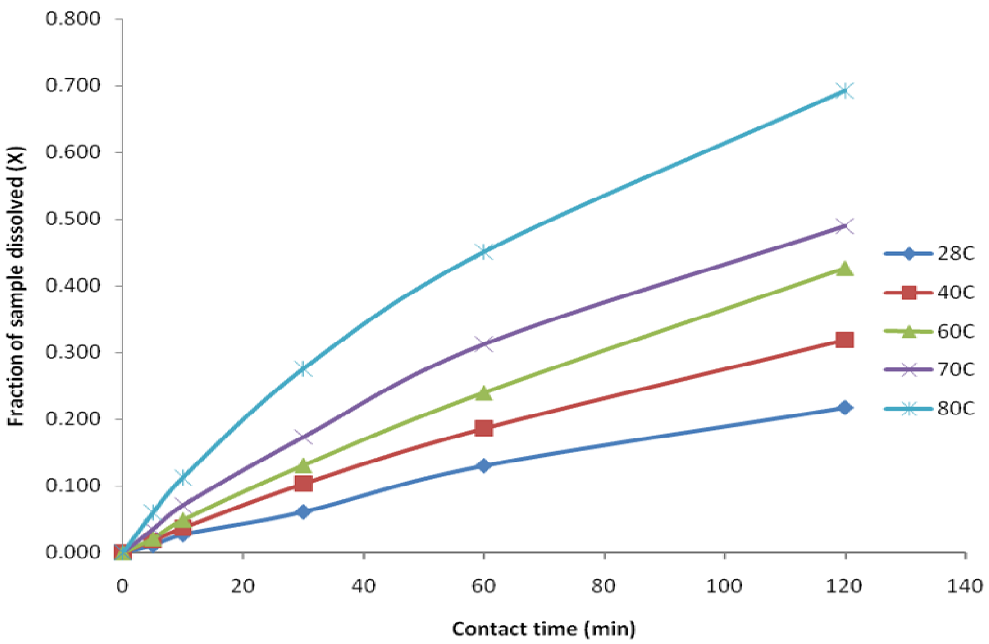

Figure 3. Fraction of manganiferrous dissolved vs. contact time at different temperatures.

From Figure 2, it shows that the fraction dissolved increases with time as well as with concentration of HCl. This is true up till concentration 8.42 M, after which there was a decline in the amount of MASM dissolved. Hence, the optimum concentration was put at 8.42 M and was used for subsequent verifications. The kinetic order of the reaction is calculated to be 0.2.

Effect of temperature

The effect of temperature on the release of manganese and iron from manganiferrous mineral was determined using < 0.09 mm particle size and the results are illustrated in Figure 3.

Other experimental conditions

HCl concentration = 8.42 M; Solid/liquid ratio = 10 g/L. The result from Figure 3 shows that the fraction dissolved increases with temperature. It is interesting to note that even at 28°C corresponding to the ambient temperature, the fraction dissolved appears to be significant. For instance, at 0.5 M HCl and at 28°C, about 10% of manganiferrous mineral was dissolved, while with 8.42 M HCl and at 80°C, about 69% of the manganiferrous mineral was dissolved within 120 min.

Kinetics of the dissolution

The dissolution rates of manganiferrous mineral were analyzed using two shrinking core models, under the assumption that the mineral is a homogeneous spherical solid phase (Aydogan et al., 2007; Levenspiel, 1984; Olanipekun, 1999), according to the following equations:

$$1-(1-\alpha)^{1/3} = k_1t \qquad (1.1)$$

$$1+2(1-\alpha)-3(1-\alpha)^{2/3} = k_2t \qquad (1.2)$$

Equation (1.1) is applicable to chemically controlled processes and equation (1.2) to diffusion controlled processes through the porous product layer (Antonijevic et al., 2004; Zuo-Mei et al., 1984).

The linearization of the curves in Figure 3 only fitted perfectly equation (1.2), where α is the fraction of mineral dissolved at various time, t, corresponding to each temperature and k_1, k_2 are apparent rate constants (Figure 4).

The rate constants, k_1, k_2 were calculated from equations (1.1) and (1.2) respectively and their correlation coefficient for each temperature are presented in Table 2.

The rate constant k_2 was found to be more acceptable as its correlation coefficient values are greater than 0.99 in all cases. The rate constants, k_2 obtained from Table 2 were therefore used to construct the Arrhenius plot (Figure 5), from which a value of 34.19 kJ/mole has been calculated for the activation energy and the dissolution rate can be said to follow a diffusion controlled process (Antonijevic et al., 2004; Aydogan et al., 2007; Baba, 2008; Olanipekun, 1999).

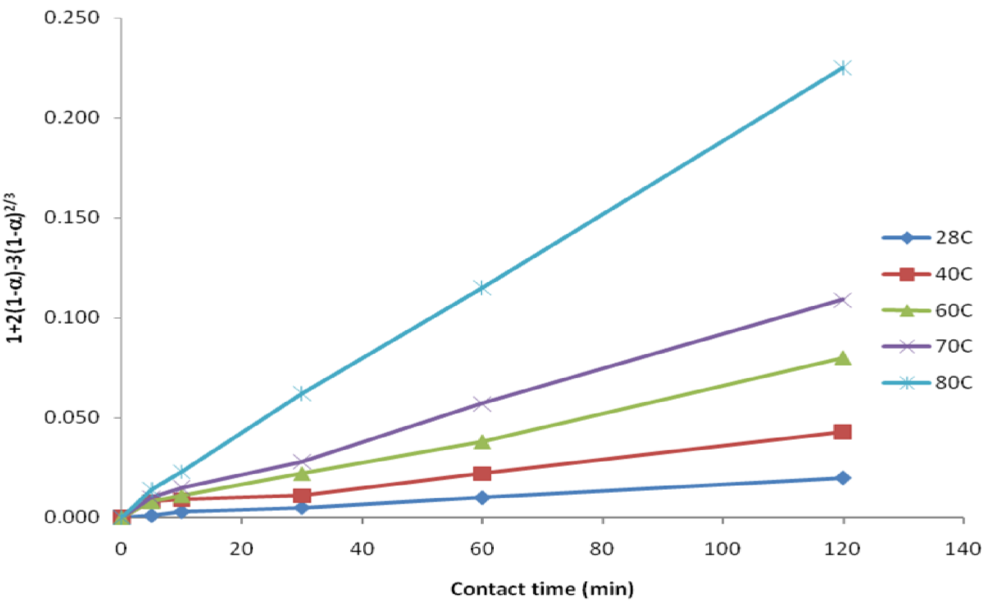

Figure 4. Plot of $1+2(1-\alpha)-3(1-\alpha)^{2/3}$ vs. time at different temperatures in 8.42M HCl.

Table 2. The k_1, k_2 and correlation coefficients values for different temperatures.

Temperature (^{0}C)	Apparent rate		Correlation coefficients (R^2)	
	k_1 (10^{-4} min^{-1})	k_2 (10^{-4} min^{-1})	k_1	k_2
28	5.59	1.66	0.894	0.985
40	7.46	3.06	0.897	0.987
60	10.25	6.67	0.906	0.987
70	13.04	9.08	0.934	0.978
80	16.73	12.90	0.877	0.991

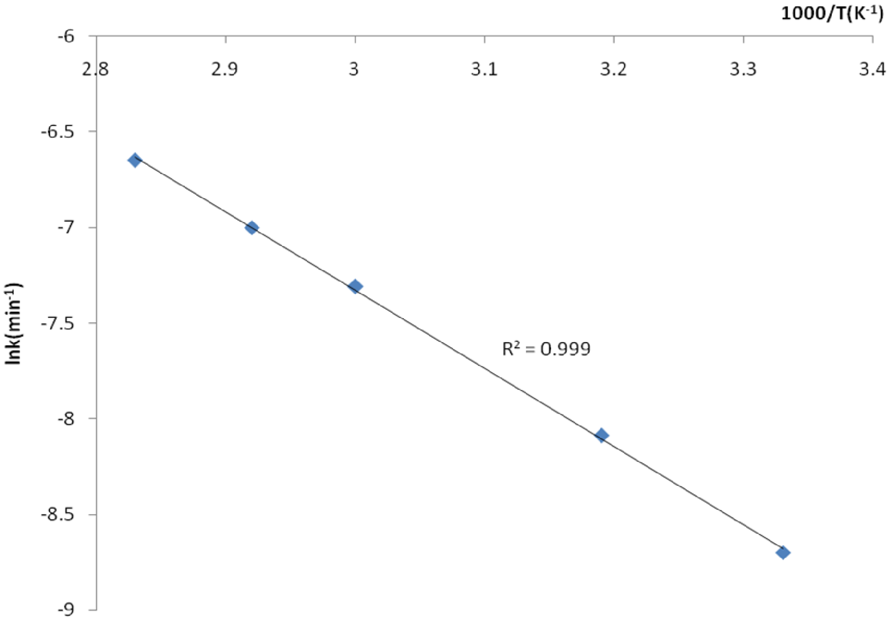

Figure 5. Plot of $\ln k_2$ vs. 1000/T (K^{-1}).

Conclusion

On the basis of the results of this study, the following conclusions can be drawn: A sample of manganiferrous rock was found to contain iron (34.36%) and manganese (26.75%) as major elements which are evidence that the mineral is dominated by iron oxide (Fe_2O_3) and manganese oxide (MnO_2) at 49.06 and 42.33% respectively. This mineral could therefore constitute a major geogenic or natural source of Mn and Fe in the river system.

The X-ray diffraction trace also supported the results from ICP-MS and showed the garnet to be spessartite, which is a type of Mn minerals.

The results of lixiviation study showed that the reaction rate increases with hydrogen ion [H^+] concentration, reaction temperature, but decreases with particle size.

A value of 34.19 kJ/mole was obtained as the activation energy for the dissolution process suggesting a diffusion controlled mechanism.

The results of the present work will be of great assistance to the policy makers in the pro-active management of river Oyun water system.

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