

Leaching of manganese ore with aqueous sulphur dioxide solutions

PRAFULLA R RAISONI and SHARAD G DIXIT

Department of Chemical Technology, University of Bombay, Matunga, Bombay 400 019, India

Abstract. Manganese can be easily leached from chemically inert manganese ore by aqueous solutions of SO_2 . Total manganese dissolution occurs at 650 rpm, 0.2% solid, 426 μm , pH=1 and 310 K in only 6-8 min. The rate data for manganese fits the equation: $1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = kt$. Diffusion through the siliceous layer appears to be rate-controlling.

Keywords. Manganese leaching; manganese dissolution.

1. Introduction

During the past few years, study of dilute solutions of sulphur dioxide as a leaching agent has attracted the attention of several researchers. This is especially true in the case of sea-bed nodules. The reaction between metal oxide and sulphur dioxide has been studied in detail by Miller and Wan (1983), Khalafalla and Pohlman (1981), and Raisoni and Dixit (1987). It has been observed that (i) the sulphurous acid leaching method is rapid, effective and sensitive (the entire dissolution reaction completed in only 8-10 min). (ii) Dissolution takes place at ambient temperature and pressure. (iii) Sulphur dioxide is a waste gas. It is believed that about 10^9 million tonnes of SO_2 per year are added to the global environment. Thus, by utilizing SO_2 as a leaching agent, air pollution can be minimized. (iv) The aqueous SO_2 solution (lixiviant) offers highly reducing and highly oxidizing conditions with oxygen (Dixit and Raisoni 1987). Therefore, these leachants may be used to leach out valuable metals from minerals, ores and concentrates as primary sources while anodic slimes, flue dust, electronic scraps, alloys, filaments of the electric bulbs etc are other polymetallic secondary sources.

In this paper we report the results of the leaching of Mn from Mn-ore which has been reported to be highly non-reactive towards H_2SO_4 leaching. This is a typical case where the capability of aqueous solutions of SO_2 as a leaching agent is demonstrated. In particular, the effect of process conditions and kinetic factors affecting the rate have been investigated.

2. Materials and methods

2.1 Materials

Goa Mn-ore (M/s Electrolytic Manganese Limited, Thane, India), a highly inert ore to H_2SO_4 leaching was used. It contained 51.91% Mn as estimated by the EDTA method. SO_2 gas (M/s Star Freez, Bombay, India) was used as such. The total SO_2 concentration was determined by the iodometric method.

2.2 Leaching experiment

Leaching experiments were carried out in a one-litre cylindrical glass reactor, immersed in a thermostatically controlled water bath. The upper lid had three openings through which a stirrer, a fritted solution sampler and a gas sparger were introduced into the glass reactor. Experiments were generally carried out at 0.2% solid of size 426 μm , 650 rpm, pH = 1 and 310 K (unless reported otherwise). SO_2 gas was bubbled through a solvent (H_2O , 500 ml) to attain pH = 2 and the total SO_2 concentration was determined iodometrically. pH was adjusted using AR grade H_2SO_4 . The dissolution reaction was initiated by adding the required amount of solid (0.2%) to the reactor. The sample was withdrawn at regular intervals for analysis. The total Mn content was estimated by the EDTA method.

3. Experimental results and discussion

Leaching of Mn from Mn-ore (which was difficult to dissolve) by aqueous solutions of SO_2 was carried out to study the effect of different parameters such as stirring speed, particle size, concentration of SO_2 and temperature.

3.1 Effect of stirring speed

The ratio of solid to liquid was deliberately kept low to ensure a constant bulk solution concentration. The speed of rotation was varied from 250–850 rpm. The results in figure 1 reveal that the fraction of Mn extracted (in 5 min) increases up to 650 rpm. However, a further increase in rpm did not show any effect on the extraction. Therefore, a speed of 650 rpm was fixed for the rest of the experiments.

3.2 Effect of particle size

The effect of particle size was studied by taking the following size fractions: 1900, 855,

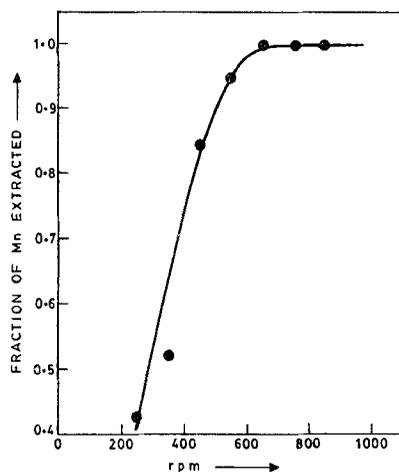


Figure 1. Effect of stirring speed on Mn extraction.

605, 426, 301 and 152 μm . The fraction of Mn extracted against time (figure 2) shows that, as the particle size decreases, the rate of Mn dissolution increases. However, beyond 426 μm , the particle size had no effect on MnO_2 dissolution, which was completed in only 8 min. Thus, fine grinding of sample is not necessary and this helps in keeping down the costs.

3.3 Effect of SO_2 concentration

The effect of SO_2 concentration on the MnO_2 dissolution was studied at 0.2% solid, 426 μm , 650 rpm and 310 K. The concentration was varied from 0.2 to 0.68 M. The results shown in figure 3 indicate that as concentration increases, the initial rate (in 2 min) of Mn dissolution also increases but the overall reaction was complete in only 8 min. Thus, the total manganese leached depended on the total amount of SO_2 in water, and not on SO_2 concentration.

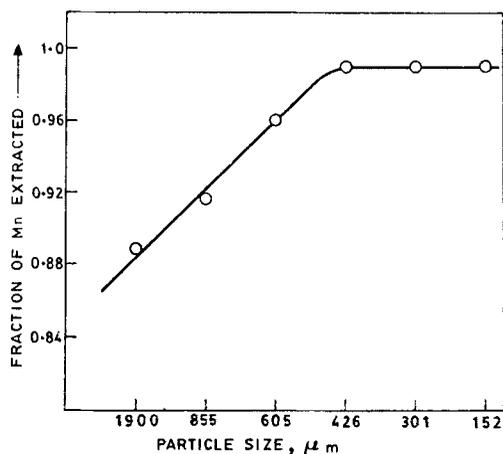


Figure 2. Effect of particle size on Mn extraction.

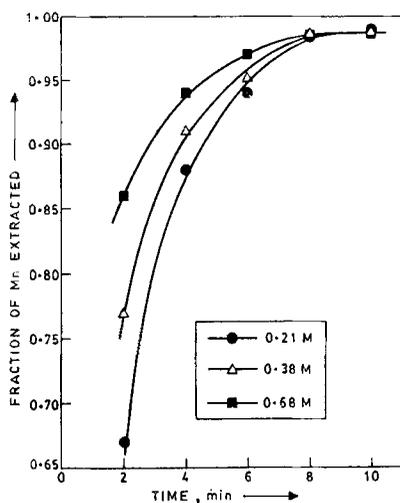


Figure 3. Effect of SO_2 concentration on Mn extraction.

3.4 Effect of temperature

Leaching of Mn from Mn-ore was studied by varying the temperature from 270.5–310 K at 0.2% solid, 650 rpm, pH = 1, 426 μm . The results (figure 4) show that as the temperature increases (270.5–310 K), the dissolution rate of Mn also increases. However, a further rise in temperature (320 K) resulted in slight decrease in the dissolution of Mn (not shown in figure 4). This is due to the decrease in SO_2 concentration in water. Thus, manganese can be easily leached out from chemically inert Mn-ore at 0.2% solid, pH = 1, 426 μm and 310 K. The entire dissolution is completed within 8–10 min.

3.5 Kinetics of dissolution

Miller and Wan (1983) demonstrated conclusively that the overall kinetics of dissolution of electrolytic manganese dioxide (EMD) in aqueous solutions of SO_2 is controlled by the electrochemical reaction at the interface. Thus, the following equation is expected to hold

$$1 - (1 - \alpha)^{1/3} = kt, \quad (1)$$

where α is the fraction of Mn extracted, k the constant and t is time in minutes.

However, when the experimental data were plotted according to the above equation, straight lines were not obtained. Alternatively, the following diffusion equation applies:

$$dn(\text{Mn})/dt = (-4\pi r^2/\sigma)D(dC/dr), \quad (2)$$

where r is the radius of the unreacted particle, n is the number of the solution, C the bulk solution concentration, D the effective diffusion coefficient and σ the stoichiometry factor.

The above equation may be integrated, assuming the constancy of C . Ginstling and Brounshetein (1950) have given a solution of the above equation assuming the constancy of C as follows,

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = 2VDC/\sigma r_0^2, \quad (3)$$

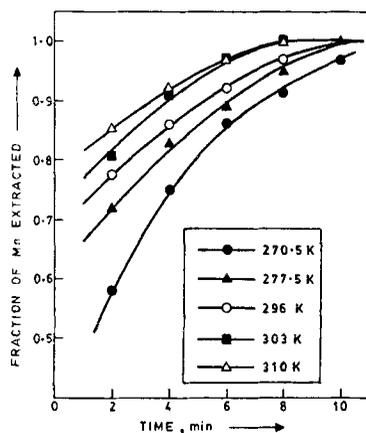


Figure 4. Effect of temperature on Mn extraction.

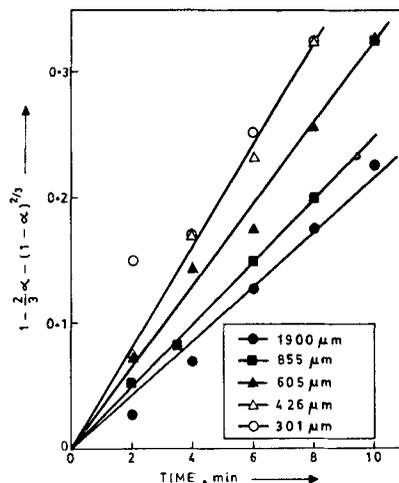


Figure 5. Plot of $1 - (2/3)\alpha - (1 - \alpha)^{2/3}$ against time for various particle sizes.

where V is the volume of the solution. In the present case the constancy of C is assured because the solid concentration has been taken as very low (0.2%).

The experimental data have been plotted in figure 5 to test the validity of equation (3). Excellent straight lines passing through the origin have been obtained. Thus the rate of Mn dissolution is controlled by diffusion. In the present case, diffusion through the unreacted siliceous layer is possible and the validity of (3) indicates that it is rate-controlling.

The above results also clear the fact that the kinetic factors for the pure material (in this case the electrolytic manganese dioxide) and the ore could be entirely different.

4. Conclusions

H₂SO₃ leaching is a rapid, effective and sensitive method compared to H₂SO₄ leaching. Reactions can be carried out at an ambient temperature and pressure within 8–10 min, while several days are required for mineral acid leaching. Total Mn dissolution from Mn-ore is possible in only 8 min and diffusion through silica layer controls the reaction rate.

Acknowledgement

This work was funded by CSIR, New Delhi.

References

- Crank J 1957 *Trans. Faraday Soc.* **53** 1083
- Dixit S G and Raisoni P R 1987 *Ind. J. Tech.* **25** 517
- Ginstling A M and Brounshetein B I 1950 *J. Appl. Chem. USSR* (English transl.) **23** 1327
- Khalafalia S E and Pohlman J E 1981 *US B.M.R.I* §518
- Miller J D and Wan R Y 1983 *Hydrometallurgy* **10** 219
- Raisoni P R and Dixit S G 1987 *Minerals engineering* (in Press)