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DISSOLUTION KINETICS OF MAGNESITE ORE WITH SULFURIC ACID SOLUTIONS

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ABSTRACT

Dissolution kinetics of magnesite ore (mainly $MgCO_3$)in sulfuric acid solutions have been studied to ascertain the effect of different variables on the rate of dissolution. The chosen parameters were particle size, concentration of sulfuric acid, temperature and solid-liquid ratio. The dissolution rate increased with decrease in particle size and solid-liquid ratio and with increase in the sulfuric acid concentration and temperature.The reaction rate has been discussed in terms of the shrinking core model for spheres. The activation energy was found to be 55 kJ mol^{-1} It is shown that the reaction is chemically controlled and that dependence of the dissolution rate on sulfuric acid activity is first order.

MANYEZİT CEVHERİNİN SÜLFÜRİK ASİT ÇÖZELTİLERİYLE ÇÖZÜNME KİNETİĞİ

ÖZET

Manyezit cevherinin sülfürik asit çözeltileri içerisindeki çözünme kinetiği, çeşitli değişkenlerin etkisi dikkate alınarak, incelenmiştir. Değişken parametre olarak, katı parçacık boyutu, sülfürik asit konsantrasyonu, katı-sıvı oranı ve sıcaklık seçilmiştir. Parçacık boyutu ve katı-sıvı oranındaki azalma ile çözünme hızının arttığı gözlenmiştir. Buna karşın, sülfürik asit konsantrasyonu ve sıcaklıktaki artma ile çözünme hızında artış olmuştur. Reaksiyon hızı, küresel parçacıklar için "shrinking core" modeli esas alınarak tartışılmıştır. Bu reaksiyona ait aktivasyon enerjisi 55 kJ mol^{-1} olarak hesaplanmıştır. Reaksiyon hızını kontrol eden basamağın, yüzeyde meydana gelen kimyasal reaksiyon olduğu ve sülfürik asit aktivitesine göre birinci dereceden olduğu tesbit edilmiştir.

1. INTRODUCTION

Basic data on leaching of magnesite with sulfuric acid are of interest from the point of view of the industrial process of obtaining pure $MgCO_3$ for high grade magnesia production. Large quantity of magnesia is consumed by the refractory industries in the manufacture of basic refractory bricks and linings for open hearths in the steel industry(1).

In addition, data on leaching of magnesite with sulfuric acid is also important to produce magnesium sulfate. Magnesium sulfate is probably incompletely dissociated in aqueous solution. The anhydrous sulfate cannot be obtained from solution, but only by dehydration of one of the hydrates. Hydrolytic decomposition may take place at relatively low temperatures (250°C), but if the heating is carried out in the precense of a small amount of concentrated sulfuric acid, a relatively stable anhydrous product is obtained which can be heated without further decomposition to about 800°C(1). In industry, there are several usages of anhydrous magnesium sulfate which supporting Pt and V_2O_5 catalysts used in production of sulfuric acid(1,2).

Magnesite can be selectively leached with ammonium chloride or carbon dioxide. But, these leaching agents are mild and not sufficiently effective. Thus, it is required to decompose magnesite into MgO for using the leaching agents such as NH_4Cl or CO_2.

Shcherbakova et al. (3) manufactured $MgSO_4 . 7H_2O$ by treating magnesite with sulfuric acid in the precense of a magnesium sulfate mother liquor in which was decreased the corrosiveness of the medium and increased productivity of the process.

Cross et al.(4) treated magnesite with sulfuric acid and added MgO to The resultant liqour to neutralize excess acid. Then, magnesium sulfate was crystallized and decomposed to recover pure MgO.

Ranjitham and Khangaonkar(5) examined the leaching behaviour of calcined magnesite with ammonium chloride solutions and found that the reaction is chemically controlled.

Raschman(6) studied the leaching kinetics of magnesium oxide clinker with hydrochloric acid. He determined the dependence of the leaching rate on temperature and HCL concentration and found that the reaction order is -0.24 (with respect to H^+) and activation energy is 61.3 kJ mol^{-1}.

Grohmann and Grill (7) produced pure MgO treating magnesite with HCl.

Sulfuric acid solution has been chosen here as leaching agent for magnesite ore. In this study, the kinetics of dissolution of magnesite in sulfuric acit solutions were investigated, and the effects of particle size, temperature, acid concentration and solid-liquid ratio have been determined.

2. EXPERIMENTAL

2.1. Materials

The magnesite sample used in the study was supplied from Pasinler-Erzurum, Turkey. The chemical composition of the ore is given in Table 1. The avarege density of magnesite in the ore used hasbeen determined as 2947 kg m^{-3}. The sample was sieved to give 825-425,425-250 and 250-180 µm-size fractions by using ASTM standart sieves. All the chemicals used in this investigation were of reagent grade.

2.2. Method

Dissolution experiments were carried out in a 100 mL glass flask equipped with a magnetic stirrer, a thermostated bath, a thermometer and a condenser. The sulfuric acid solution(100 mL) in the reaction vessel was placed in the water bath to attain the required temperature.1 g of magnesite ore was then introduced into the reaction vessel. The amount of the solid was only changed in the experiments in which the effect of solid-liquid ratio was studied. At the end of the each run, the content of the vessel was filtered. The amount of Mg^{+2} in the filtrates were determined by titration(8). Stirring speed was held constant at 350 min^{-1} in all experiments.

3.RESULTS

3.1.The effect of particle size

The effect of particle size on dissolution rate was studied by using 825-425, 425-250 and 250-180 µm fractions at a fixed temperature of 60°C. The sulfuric acid concentration was 3.00 M (in excess of stoichiometric amount). As seen in Fig.1, the reaction rate increases as the particle size decreases, because of an increase in surface area by weight unit.

3.2. The effect of sulfuric acid concentration

This effect was studied with experiments carried out at the acid concentrations 1.09,1.80,3.00 and 4.50 M and 60°C. The 425-250 µm size fraction was used. As shown in Fig. 2, The rate of dissolution increases with increasing acid concentration.

3.3. The effect of the solid-liquid ratio

This effect was investigated by using the ratios in the ranges from 0.5:100 to 4.0:100 (w/w). In the experiments the sulfuric acid concentration was 3.00 M,the temperature was 60°C and the size fraction used was 425-250 µm. The results are seen in Fig.3. As the solid-liquid ratio increases, the rate of dissolution decreases.

3.4. The effect of temperature

To study the effect of temperature, the 425-250 µm- size fraction was used. Experiments were carried out at 40, 50, 60, 70 and 80°C. The sulfuric acid concentration was 3.00 M.From Fig.4 it is seen that dissolution rate is extremely sensitive to reaction temperature. For example at 80°C and a retention time of 30 min., 99% dissolution was achieved, while at 40°C and a retention time of 60 min. only 36.8 % dissolution was possible.

4. DISCUSSION

The dissolution reaction of magnesite in sulfuric acid solutions can be described by the following equation:

$$MgCO_{3(s)} + H_2SO_{4(aq)} \rightarrow MgSO_{4(aq)} + CO_{2(g)} + H_2O_{(1)} \quad (1)$$

Equation 1 shows the particles dissolve and become progressively smaller in size, and there is no solid product layer formed during the leaching reaction. Hence the possibility of ash layer diffusion is not present. On the other hand, if rate very sensitive to the temperature variations, chemical reaction may be considered to be the rate -controlling factor(9).

Assuming that the process is controlled by a chemical reaction on the solid surface, the rate expression for a heterogeneous reaction such as:

$$A(\text{fluid}) + bB(\text{solid}) \rightarrow \text{Products} \tag{2}$$

can be written as follows:

$$(-1/S) \quad dN_B/dt = k_o \quad \exp(-E/(RT)) \quad a_A^n \tag{3}$$

For spherical particles, in terms of chemical control in the shrinking care model, the following relationship between fraction reacted(x) and time is well established(10):

$$1-(1-x)^{1/3} = k_a t \tag{4}$$

The apparent rate constant $k_a(\text{min}^{-1})$, which involves many factors, can be written as(11):

$$k_a = (bk_s C_A)/(R_o \rho_B) \tag{5}$$

If a straight line is obtained when $1-(1-x)^{1/3}$ is plotted versus t it can be concluded that the reaction is chemically controlled(12).

Plots of $1-(1-x)^{1/3}$ versus t are shown in Fig.5 for different sizes, in Fig.6 for different temperatures and in Fig .7 for different sulfuric acid concentrations.

These results indicate that the dissolution rate of magnesite in sulfuric acid solutions is chemically controlled. The slope of all straight lines in these figures were calculated and then the times for complete conversion given by

$$1/k_a = t^* \tag{6}$$

was obtained.

In addition, the apparent rate constant (k_a) should be inversely proportional to the inital particle radius. Data presented in Fig.8 are consistent with a surface reaction rate control in these conditions. It was assumed in these calculations that the solid phase consisted of spherical particles with an arithmetic average radius between the radii corresponding to the upper and lower size fractions.

Figure 9 shows the plot k_a versus sulfuric acid activity, which is linear. If this pilot yields a straight line passing by the origin, there is a first order relation between the sulfuric acid activity and the reaction rate (13). The sulfuric acid activity was calculated by Meissner 's method (14). This method corrects the variation of activity with temperature.

The $k_a$values for different temperatures have been used to construct an Arrhenius plot, giving the activation energy as 55 kJ mol^{-1} for the dissolution (Fig.10). The value of activation energy is consistent with the chemical reaction control hypothesis (15). In-addition, Fig. 8 further supports the concept that in the leaching of magnesite by sulfuric acid, the rate controlling step is a chemical reaction occurring at the surface of the magnesite particles (16,17).

On the basis of the preceding results, Eq. (4) can now be written as follows:

$$1-(1-x)^{1/3} = (1886/R_o\ \rho_B)a_A \exp(-55{,}000/RT) \quad t \tag{7}$$

5.CONSLUSIONS

Magnesite can be completely dissolved by sulfuric acid solution. Reducing the particle size and the solid- liquid ratio, increasing the temperature and the sulfuric acid concentration increases the dissolution rate. It was observed that the dissolution of magnesite in sulfuric acid solutions is very sensitive to temperature.The kinetic data indicated that a surface chemical reaction is dominant, with activation energy 55 kJ mol^{-1}

List of Symbols

a_A	mean ionic activity of H_2SO_4
b	stoichiometric coefficient of B(solid) reacting with each mole of A (fluid)
C_A	concentration of fluid (mol m^{-3})
E	activation energy (J mol^{-1})
k_s	rate constant for surface reaction (m s^{-1})
k_o	frequency factor (ms^{-1})
k_a	apparent rate constant (s^{-1})
N_B	mole of solid (mol)
n	apparent order
R_o	initial particle radius (m)
R	universel gas constant (J mol^{-1} K^{-1})
S	geometric surface area (m^2)
t	time (s)
t^*	the time at which $x=1$ (s)
T	absolute temperature (K)
x	fraction reacted

ρ_B molar density of solid (mol m^{-3})

Table 1

Chemical analysis of the magnesite

Compenent	%
MgO	46.36
CaO	1.06
Fe_2O_3	0.41
SIO_2	0.71
Loss at red heat	51.46 (at 800°c)
Total	100.00

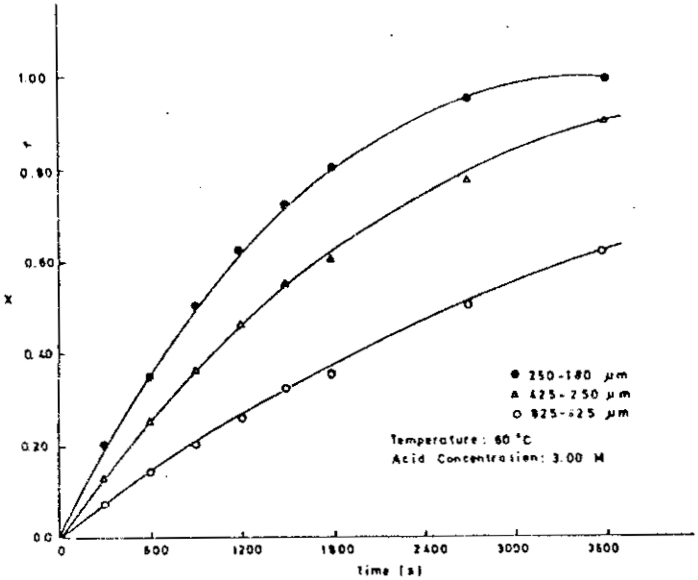

Figure 1. The effect of particle size on the dissolution rate.

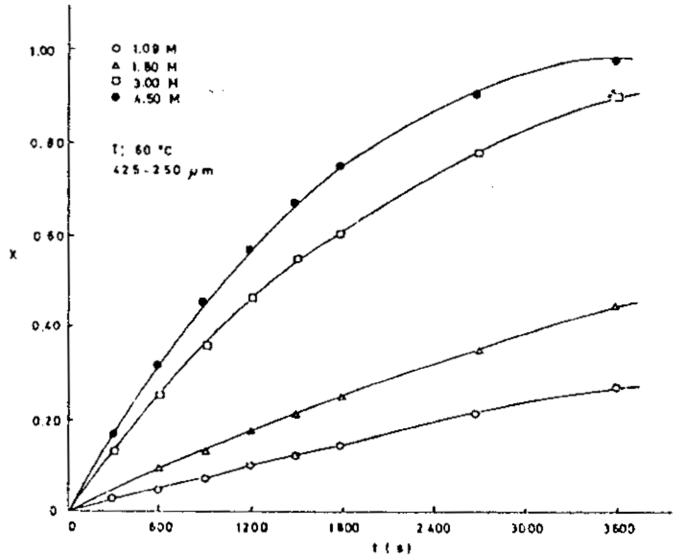

Figure 2. The effect of sulfuric acit concentration on the dissolution rate.

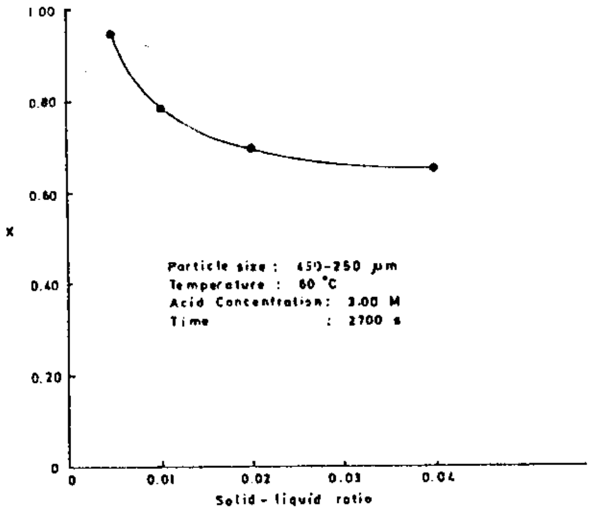

Figure 3. The effect of the solid-liquid ration on the dissolution rate.

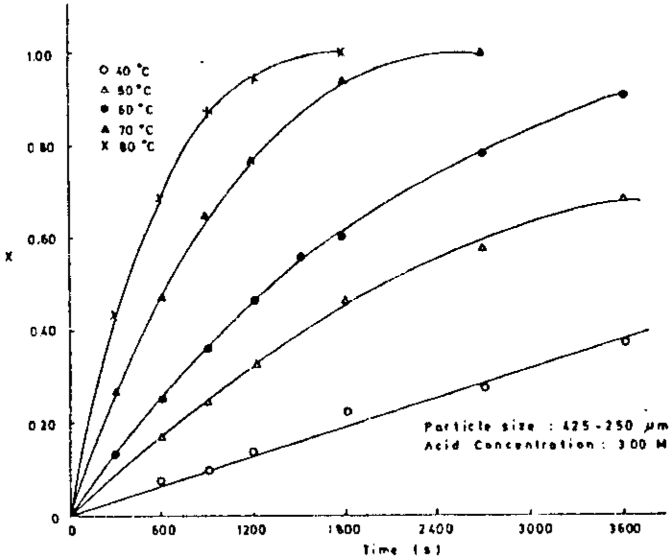

Figure 4. The effect of temperature on the dissolution rate.

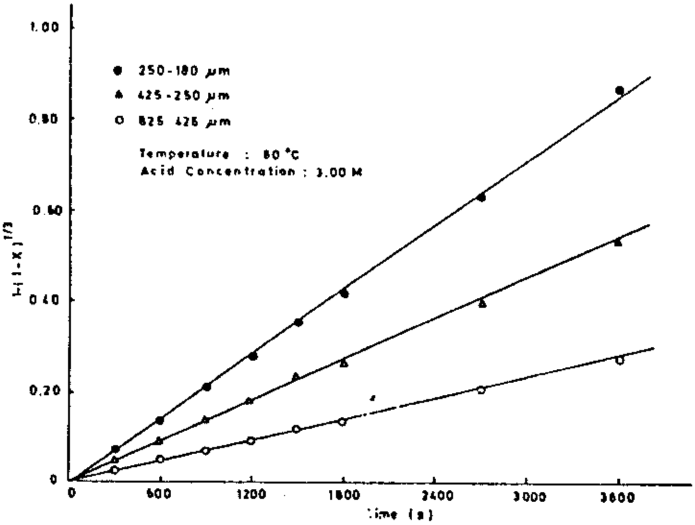

Figure 5. $1-(1-x)^{1/3}$ versus t plots for different particle sizes of the magnesite.

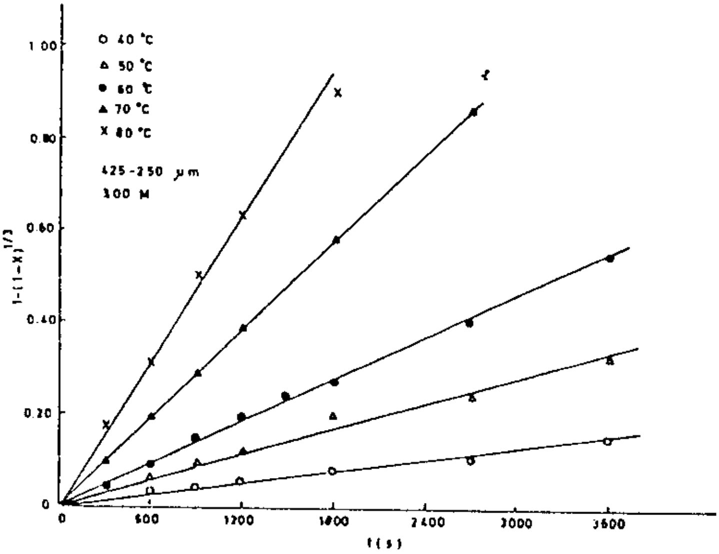

Figure 6. $1-(1-x)^{1/3}$ versus t plots for different temperatures.

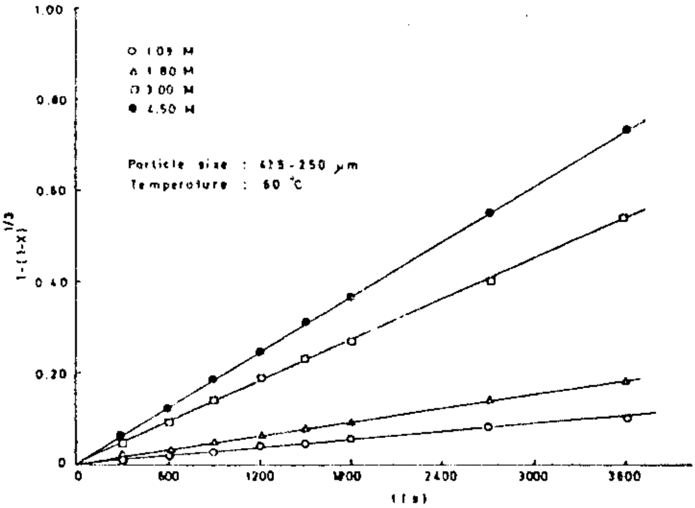

Figure 7. $1-(1-x)^{1/3}$ versute t plots for different sulfuric acid concentrations.

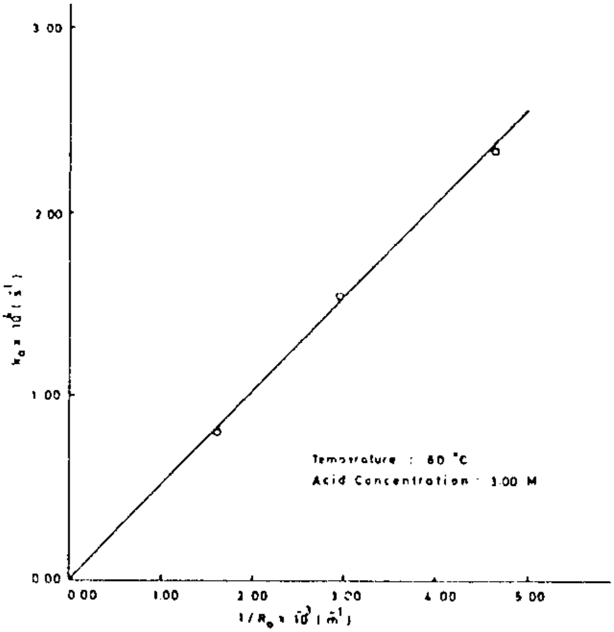

Figure 8. Relationship between k_a and inverse initial particle size of magnesite.

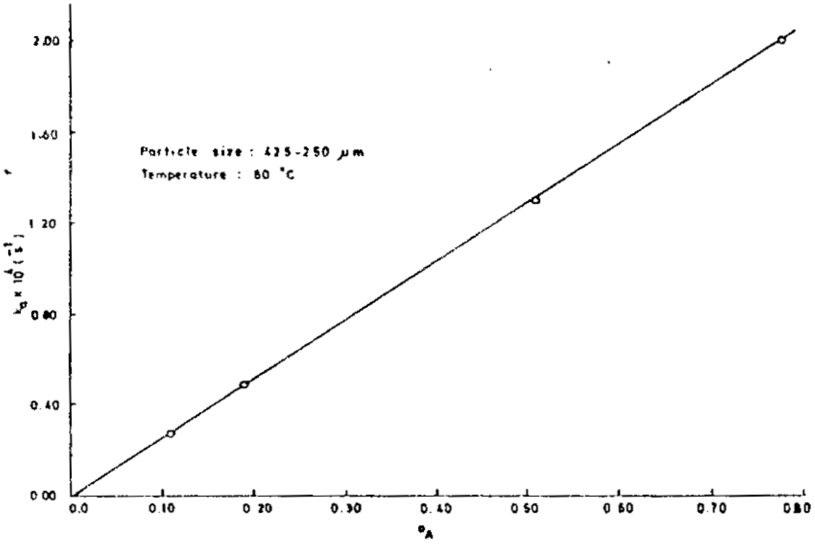

Figure 9. Relationship between k_a and sulfuric acid activity.

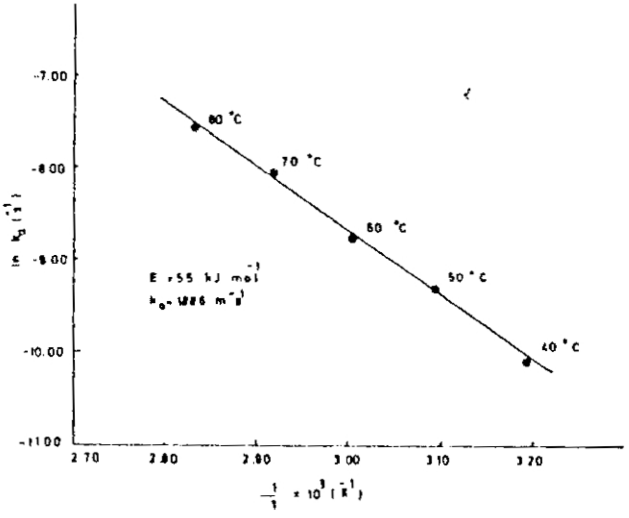

Figure 10. Arrhenius plot obtained with particle size of 425-250 mm and a molarity of H_2SO_4 of 3.00M.

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