



Kinetics of dissolution of iron oxide in clay in hydrochloric acid solutions

U.K.Sultana, A.S.W.Kurny*

Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka, (BANGLADESH)

E-mail : aswkurny@mme.buet.ac.bd

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ABSTRACT

Samples of clay containing 8.15% iron oxide and 27.49% alumina were leached in hydrochloric acid. The effects of concentration of acid, time and temperature on the rate of dissolution of iron contained in the clay sample was investigated. Temperatures studied in this investigation were in the range 40°C to 80°C, concentrations of hydrochloric acid were in the range 0.2M to 2M. The diffusion controlled reaction model i.e., $t/\tau = 1 - (2/3)X - (1-X)^{2/3}$ seemed to be the most appropriate one to fit the kinetic data of leaching of clay in hydrochloric acid. The Arrhenius activation energy for Hydrochloric acid leaching was found to be 50.82 kJ/mole.

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KEYWORDS

Clay washing;
Iron oxide leaching;
Kinetic model,
Activation energy.

INTRODUCTION

The presence of impurities, particularly iron bearing materials, impairs the characteristics of clay and affects its utility for various applications^[1]. Traditionally iron is removed by physical mineral processing techniques^[2, 3]. But recent studies have shown that even traces of iron can be removed by acid washing^[4].

Both inorganic and organic acids have been used for acid washing. Results of investigations on leaching of iron oxides in clays in oxalic acid solutions dominate the published literature. Chiaraizia and Horowitz studied dissolution of goethite in several organic acids in the presence of reducing agents^[5]. Pnias et al examined the mechanisms of dissolution of iron oxides in aqueous oxalic acid solution^[6]. Ambikadevi and Lalithambika

tested several organic acids and concluded that oxalic acid is most efficient for the dissolution of iron oxide from ceramic minerals^[7].

Results of investigations on leaching of iron oxides in clays in inorganic acids solutions, on the other hand, are rather limited. Sidhu et al investigated the dissolution of iron oxides and oxyhydroxides in hydrochloric and perchloric acids^[8]. Reports on the determination of the rate of reactions, rate controlling steps and reaction mechanisms for the leaching of iron containing ores in hydrochloric acids have also been published^[9, 10].

The progressive conversion model and the shrinking core models are the two simple models generally considered for the non-catalytic reaction of particles with the surrounding fluids. In the progressive conversion model reaction is assumed to occur throughout the

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particles at different rates at different locations, which is unrealistic in maximum leaching reactions. Hence shrinking core model is preferred for solid spherical particle reaction kinetics. Liquid film diffusion controlled process, diffusion controlled process and chemical reaction controlled process are the three models generally considered for the preliminary selection of the kinetic model. In this assumption the model can also be of mixed process^[11]. Generally a kinetic model is matched with the results of leaching experiments and data from the selected model is used to determine activation energy^[12].

The primary aim of this investigation was to determine the rate of reaction for the removal of iron during leaching in hydrochloric acid from a clay sample collected from Narsingdi in Bangladesh. The mechanism of reaction was identified and the activation energy was determined.

EXPERIMENTAL PROCEDURE

Material composition

The sample of clay under investigation was collected from Narsingdi (near Dhaka). The sample, as determined by x-ray fluorescence spectroscopy, contained 27.5% of Alumina, 59.5% of silica and 8.15% of iron oxide.

Leaching procedure

Leaching was carried out in a three necked round bottom flask fitted with a reflux condenser and a mechanical stirrer. The flask was placed on a thermostatically controlled heating mantle. Temperature of the solution was controlled to specified values and was continuously monitored by a thermometer. Samples of clay weighing 6 gm were taken in 400 ml of leaching solution. The optimum concentration of hydrochloric acid was determined by leaching in 0.2M, 0.4M, 0.6M, 0.8M, 1.0M, 1.2M, 1.4M, 1.6M and 2M hydrochloric acid solutions. The leaching was performed in the

optimised acid concentration at temperatures of 40, 60 and 80°C and for 1, 2, 4, 5, 10, 20, 30, 45, 60, 90 minutes at each temperature. A constant stirring speed of 800 rpm was maintained during all leaching experiments. At the end of leaching for a specified period of time at a specified temperature 5 ml of leaching solution was taken out of the round bottom flask by a pipette. The collected sample of leach liquor was cooled, filtered and used for iron estimation.

Iron estimation procedure

Iron in the leach liquor was estimated by a Shimadzu UV-vis Spectrophotometer, Tartaric acid, Thyoglycolic acid, Nitric acid and Ammonia solution were used as complexing agents^[13].

The details of the procedure is shown in Figure 1.

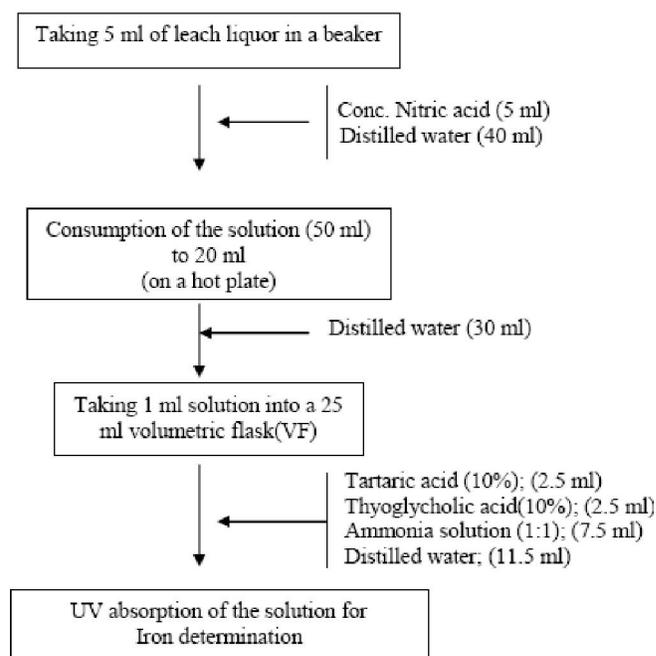


Figure 1 : Flow sheet for determination of iron.

The chemical reactions involved can be described as follows:

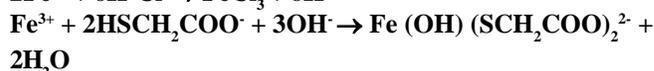
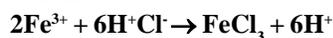


TABLE 1 : Composition of the clay.

Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	CaO	K ₂ O	MgO	Na ₂ O	TiO ₂	MnO	Cr ₂ O ₃	SO ₃	Cl
27.49	8.14	59.45	0.21	2.59	0.52	0.22	0.85	0.08	0.03	0.11	0.02
P ₂ O ₅	Co ₂ O ₃	CuO	ZnO	Ga ₂ O ₃	SrO	Y ₂ O ₃	ZrO ₂	BaO	PbO	Rb ₂ O	NiO
0.08	0.005	0.007	0.005	0.004	0.003	0.01	0.032	0.07	0.008	0.013	0.01

RESULTS AND DISCUSSION

Elemental analysis of the clay

The composition of the clay, as determined by x-ray fluorescence spectroscopy, is shown in TABLE - 1.

Effect of Acid Concentration

The extent of iron dissolution of iron as a function of concentration of HCl is shown in Figure 2.

It is evident that the rate of iron dissolution is affected directly by the hydrogen ion [H⁺] concentration in the leach liquor. The higher the concentration of HCl, the higher is the extent of the dissolution of iron oxide. The increase in the extent of removal of iron is negligible at concentrations of HCl higher than 1.6 M.

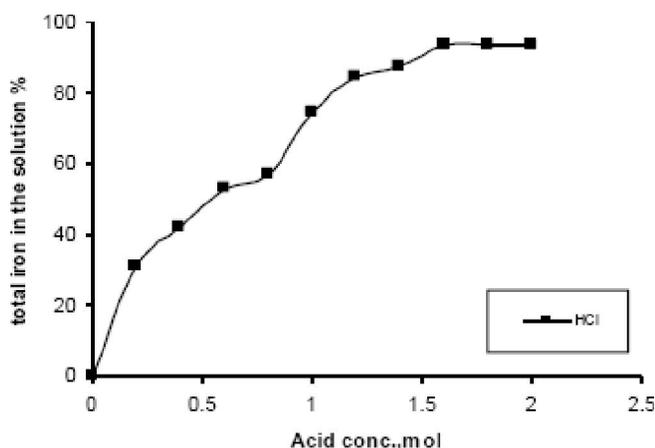


Figure 2 : Effect of acid concentration on dissolution of iron.

Effect of time and temperature

Figure 3 shows the effect of time and temperature on the extent of leaching of iron oxide in the clay sample in 1.6 M hydrochloric acid. It can be seen that during the initial period of leaching at all temperatures under investigation, the rate of dissolution of iron oxide was rather fast. However, the curves become almost flat within a short period (20 min to 25 min) of time, after which the increase in the extent of removal of iron is negligible. It can be also seen that the rate of leaching is faster at higher temperatures. This is to be expected.

Identification of reaction mechanism

The particles were assumed to be perfectly homogeneous spherical solid phases and the shrinking core model was selected to analyze the rate of iron dissolution. Such plots are quite extensively used in kinetic

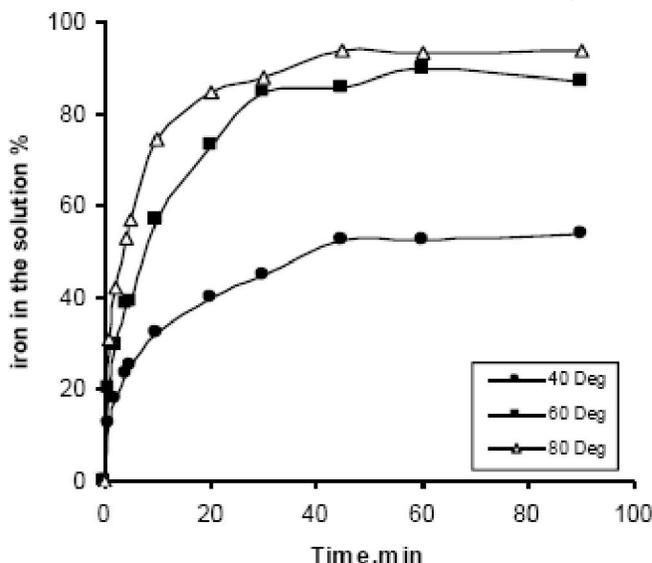


Figure 3 : Effect of time and temperature on the extent of dissolution of iron during leaching.

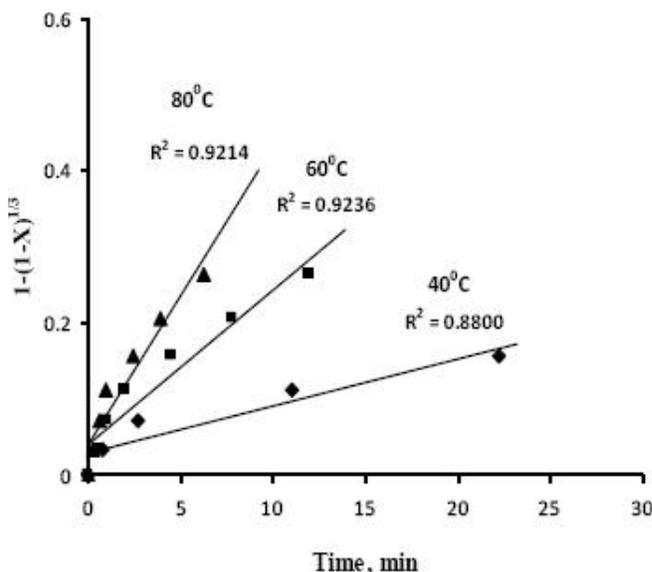


Figure 4 : plot of $1-(1-X)^{1/3}$ versus time at various temperatures for Iron dissolution.

studies^[11]. The kinetic relationships are expressed in terms of the fraction of reacted particle, X, with time. Three established models i.e. chemical reaction controlled process, liquid film diffusion controlled process and diffusion controlled process were considered for initial selection of the reaction mechanism. The equations for these models are as follows:

1. Chemical reaction controlled process:

$$t/\tau = 1 - (1-X)^{1/3} \quad (1)$$

2. Liquid film diffusion controlled process:

$$t/\tau = 1 - (1-X)^{2/3} \quad (2)$$

3. Diffusion controlled process:

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$$t/\tau = 1 - (2/3)X - (1-X)^{2/3} \quad (3)$$

Where,

t = time for complete disappearance of particles

X = fraction of reacted particles

From Figure 3 time for different fractions of reacted particle of iron were calculated at 40°C, 60°C and 80°C. Data was then plotted according to equation 1 in Figure 4. Correlation of coefficient values of the plotted lines is also shown in the Figure. It can be seen that the correlation is not high enough for all temperatures to suggest that the dissolution of iron oxide in clays is a chemical reaction controlled process.

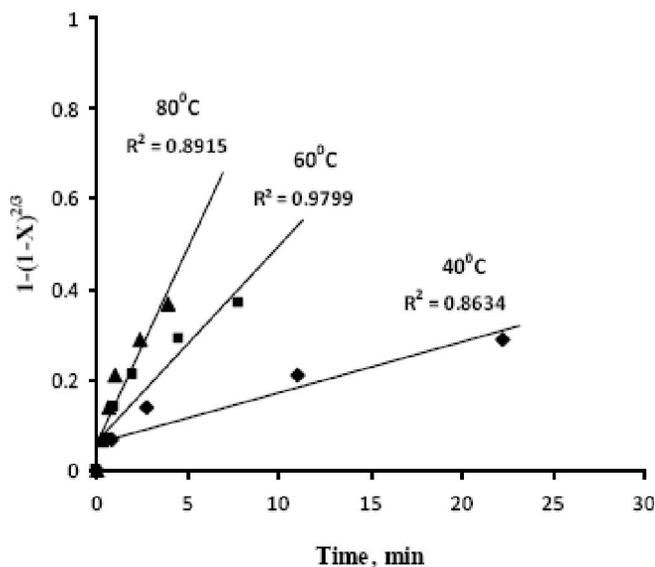


Figure 5 : plot of $1-(1-X)^{2/3}$ versus time at different temperatures for iron dissolution.

The plot of $1-(1-X)^{2/3}$ versus time at different temperatures is shown in Figure 5. This equation is considered for liquid film diffusion controlled process. It can be seen that the correlation factor is low and the lines do not pass through the zero point. Therefore, liquid film diffusion controlled process could not be the mechanism of dissolution of iron in the present system.

In order to test the possibility of diffusion through a solid reaction product, the right hand side of Equation 3 was plotted against time for different temperatures (Figure 6). This plot yielded a very high correlation at all temperatures under investigation. Moreover, the plotted lines passed through the zero point. Therefore, the data could be correlated to a diffusion controlled process.

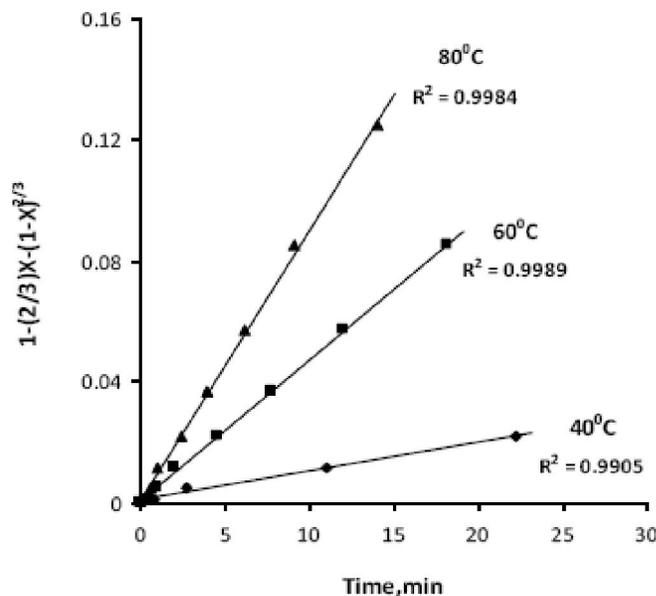


Figure 6 : plot of $1-(2/3)X-(1-X)^{2/3}$ versus time at different temperatures for iron dissolution.

Evaluation of activation energy

Both the conventional integral approach and differential approach were used to evaluate the activation energy of the leaching reaction.

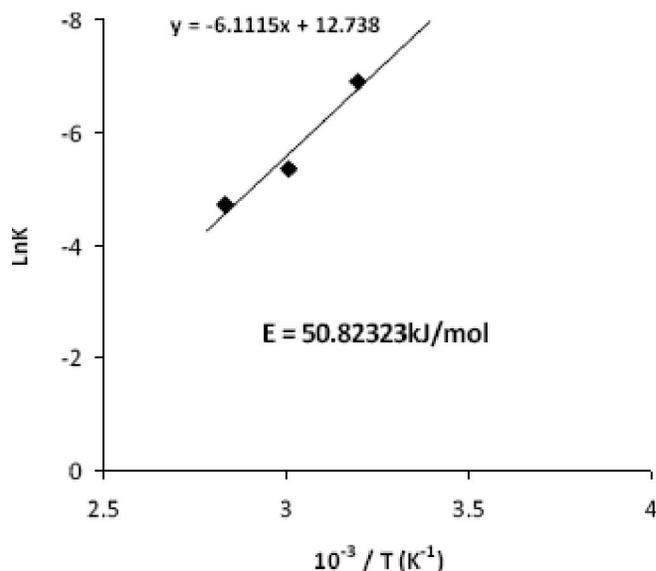


Figure 7 : Arrhenius type plot of Figure 6.

Integral approach

In the integral form, t/τ versus time (t) was plotted. The reaction rate constants, k, at various temperatures for leaching in hydrochloric acid were obtained from linearised plots (Figure 6). The rate constant was then plotted against temperature according to the Arrhenius type equation in Figure 7. The plot of $\ln k$ vs. $1/T$ was a

straight line and the slope of this straight line is equal to $-E/R$. The apparent value of activation energy for the dissolution of iron in hydrochloric acid was estimated to be 50.82 kJ/mole.

Differential approach

In the differential approach, the time required for a given value of X was calculated first and then plots of $\ln(t)$ versus temperature were obtained from Figure 8. As before the slope of these curves are equal to $-E/R$ and the activation energies were estimated in the range of 48.70 kJ/mole to 57.94 kJ/mol for X values of 0.3 to 0.5.

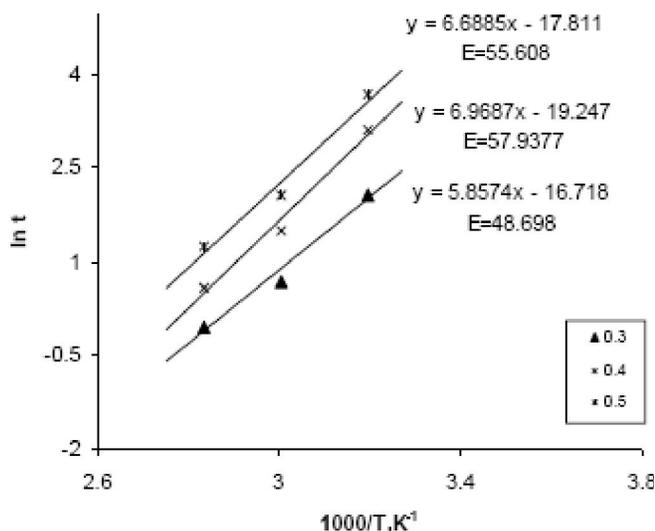


Figure 8 : Plots for calculation of apparent activation energy of leaching using differential approach.

Thus the activation energy values obtained by the two approaches are nearly identical. This suggests that the identification of the mechanism is correct.

CONCLUSION

Clay sample was leached with Hydrochloric acid for the observation of dissolution behavior of iron and a suitable kinetic model was fitted for this and also the activation energy was calculated. The following conclusions can be drawn from the study:

Increasing the acid concentration and temperature enhances the dissolution of iron and for the present study the optimum acid conc. and temperature were estimated 1.6M and 80°C respectively.

The kinetic data of iron dissolution by 1.6 M Hydrochloric acid fits the Diffusion controlled process.

$$t/\tau = 1 - (2/3)X - (1-X)^{2/3}$$

The apparent activation energy evaluated from the

experimental data is 50.82 kJ/mole.

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