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Kinetics of Rare Earth Leaching from a Mangnese-Removed Weathered Rare-Earth Mud in Hydrochloric Acid Solutions

R. Chi[a]; J. Tian[ab]; G. Zhu[c]; Y. Wu[a]; S. Li[a]; C. Wang[a]; Z. A. Zhou[d]
[a] Wuhan Institute of Technology, and Hubei Key Laboratory of Novel Reactor & Green Chemical Technology, Wuhan, P. R. China [b] Institute of Applied Chemistry Jianxi Academy of Sciences, Nanchang, P. R. China [c] Institute of Nuclear Energy Technology, Tsinghua University, Beijing, P. R. China [d] Mineable Oil Sands Unit, Alberta Research Council, Edmonton, Canada

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Kinetics of Rare Earth Leaching from a Mangnese-Removed Weathered Rare-Earth Mud in Hydrochloric Acid Solutions

R. Chi
Wuhan Institute of Technology, and Hubei Key Laboratory of
Novel Reactor & Green Chemical Technology, Wuhan, P. R. China

J. Tian
Wuhan Institute of Technology, and Hubei Key Laboratory of
Novel Reactor & Green Chemical Technology, Wuhan, P. R. China
and Institute of Applied Chemistry Jianxi Academy of Sciences,
Nanchang, P. R. China

G. Zhu
Institute of Nuclear Energy Technology, Tsinghua University,
Beijing, P. R. China

Y. Wu, S. Li, and C. Wang
Wuhan Institute of Technology, and Hubei Key Laboratory of
Novel Reactor & Green Chemical Technology, Wuhan, P. R. China

Z. A. Zhou
Mineable Oil Sands Unit, Alberta Research Council,
Edmonton, Canada

Abstract: The kinetics of leaching rare earth from a manganese-removed weathered rare earth mud (MRW-RE mud) in hydrochloric acid solutions was investigated in this study as a function of temperature, particle size, and HCl concentration. It was found that the leaching process can be described by a shrinking-core model, with the apparent activation energy about 10.17 kJ/M. When the concentration of hydrochloric

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Address correspondence to R. Chi, Wuhan Institute of Technology, Wuhan 430073, P. R. China. Tel: 86 27 87194500; E-mail: rac@mail.wit.edu.cn

acid was below 4M, the RE leaching rate was controlled by the diffusion of reactants and leaching products through a porous ore. However, when HCl concentration was higher than 4 M, the leaching process was limited by both chemical reaction and reagent diffusion. Based on the experimental results, an empirical equation relating the rate constant of rare earth leaching to the particle size and leaching temperature was established for the purpose of process deign.

Keywords: Kinetics, leaching, hydrochloric acid, rare earth, rare earth mud

INTRODUCTION

China has the largest rare earth (RE) deposit in the world. How to utilize and recover this valuable resource effectively and efficiently has been a focus in the current research and development activities. Conventional methods for recovering RE from the ores involve physical separation, high temperature roasting, and/or chemical leaching techniques (1–4). Depending on the ore characteristics and geological properties of RE deposits, it is important to select suitable RE recovery methods in a cost effective and environmentally friendly manner. For example, the recently discovered Panxi rare-earth deposit, the second-largest in China (3), mainly contains RE minerals of bastnasite [Ce(La, Nd, ...)FCO_3] (4). However, the deposit is severely weathered, with about 20% RE deposit being characterized as weathered RE mud. In the weathered RE mud, about 3 to 10% RE oxides are in the enriched form, coexisting as colloidal oxides highly disseminated in an amorphous matrix of Mn-Fe oxides and Si-Al oxides (5). Although the content of RE elements at this level in the weathered RE mud is of sufficient economic value, it is generally ineffective to recover RE minerals from the ores of colloidal sizes using conventional physical processing methods such as flotation, gravity, magnetic and electrostatic separation (6–8). An alternative is to use acid leaching to recover RE from the weathered RE mud in an aqueous medium (9–11).

One of the challenges in recovering RE from the weathered RE mud using the acid leaching method is that the weathered RE mud from the Panxi RE deposit contains up to 14% manganese, mainly as MnO_2, MnO(OH) and Mn_2O_3, existing in the form of amorphous Mn-Fe oxides. They are the carriers of rare earth elements. The presence of manganese in the ore interferes with both leaching and the subsequent recovery of RE elements from the resultant leachates (9, 12), due to the high solubility of manganese in the acid medium and its co-existence with RE in the leachates. To improve the RE recovery and the quality of obtained products, and reduce the consumption of leaching chemicals, it is necessary to selectively remove manganese prior to RE leaching. Our recent study (9, 12) demonstrated that reduction leaching using sodium sulfite at pH 3–7 could dissolve almost all of the manganese while keeping RE and Fe in the form of insoluble solids. In addition, after reduction leaching, the bonding among manganese and iron oxides in the weathered RE mud are broken down. Consequently, the RE loaded on manganese and iron oxide matrix can be easily recovered using acid leaching followed by oxalic precipitation (13). In order to understand the mechanisms of RE leaching and select suitable technologies for recovering RE from the manganese-removed weathered rare earth mud (MRW-RE mud), a systematic study was initiated in our group. This communication reports our work on the leaching kinetics of rare earth from the MRW-RE mud in hydrochloric acid solution.

EXPERIMENTAL

Ore Properties and Sample Preparation

The original ores (weathered RE mud) came from Panxi Rare-Earth Mine in China. After subjecting to reduction leaching using sodium sulfite (12), the main chemical composition of the manganese-removed weathered RE mud (MRW-RE mud) is shown in Table 1. It was observed that the MRW-RE mud contained 6.94% RE oxide, more concentrated than the RE oxide content in the original weathered RE mud (4.83%). This was mainly attributed to the removal of substantial amount of Mn oxide, which was reduced to less than 1% from the original 14%. The results demonstrated that reduction leaching using sodium sulfite was very effective in removing Mn without causing significant loss of RE. Such pre-treated ores were therefore ready for further extraction of RE from the mud.

To select suitable methods for RE recovery, the partitioning state of rare earth in the MRW-RE mud was determined by the phase analyses using the techniques described in Table 2. The results shown in Table 3 suggest that the rare earth existed mainly as colloidal oxides, accounting for 71.0%. Less than 30% of the MRW-RE mud was in the minerals (in the form of bastnasite). The amount of RE soluble in water and in ionic-exchangeable form was negligible. The analysis in Table 3 also indicated that it would be very difficult to efficiently recover RE from the MRW-RE mud using conventional physical separation methods, due to the colloidal size of RE oxides. Using the acid leaching method was therefore a more promising technique to recover the RE effectively.

The partitioning of RE in the MRW-RE mud was determined by Jiangxi Analytical and Testing Center, Nanchang, China using ICP-MS technique

Table 1. Main chemical composition of the MRW-RE mud

Composition	REO	MnO_2	Fe_2O_3	Al_2O_3	SiO_2	CaO	BaO	F
Content (%)	6.94	0.95	6.68	11.61	35.46	1.69	12.97	1.11

Table 2. Methods of rare earth extraction from the MRW-RE mud

Partitioning state	Extraction reagent	Procedures
Water soluble	De-ionized water	500 g ore sample was leached with 2.5 L water for 1 hour. Leachate was filtrated and analyzed.
Ion-exchangeable	2%$(NH_4)_2SO_4$ solution	500 g ore sample was leached with 2.5 L solution for 1 hour. Leachate was filtrated and analyzed.
Colloidal oxide	0.5 M $NH_2OH \cdot HCl$ + 2 M HCl solution	500 g ore sample was leached with 2.5L solution for 1 hour under stirring, leachate was filtrated and analysed.
Minerals	Sodium peroxide and sodium hydroxide	Sample extracted previously was roasted with sodium peroxide and sodium hydroxide at 900°C, followed by leaching with HCl. The purified rare earth was precipitated by oxalic acid.
Bulk	Sodium peroxide and sodium hydroxide	The raw ores were roasted with sodium peroxide and sodium hydroxide at 900°C, followed by leaching with HCl. The purified rare earth was precipitated by oxalic acid.

(Inductively Coupled Plasma Mass Spectrometry, SCIEX ELAN 250). The results in Table 4 showed that the MRW-RE mud contained mainly light rare earth elements (i.e., from La to Nd). The cerium element accounted for up to 42.71%, beneficial for the downstream Ce concentration. The amount of heavy rare earth elements (i.e., from Td to Y) was negligible. The analysis suggested that the MRW-RE mud contained relatively concentrated light rare earth elements.

Apparatus, Reagents and Experimental Procedures

The leaching kinetic experiments were carried out in a three-necked glass flask partially immersed in a heated water bath, with the temperature controlled within ±1°C. The three-necked glass flask was fitted with a thermometer, mechanical stirrer and a reflux condenser (9, 16). The mixture inside the flask was kept stirring at 450 rpm driven by a variable speed motor. The

Table 3. Partitioning state of RE in the MRW-RE mud

Partitioning state	Water soluble	Ion-exchangeable	Colloidal oxide	Minerals
Distribution (%)	5.6×10^{-2}	1.26×10^{-3}	71.0	29.10

Table 4. Partitioning of RE in the MRW-RE mud

Element	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7
Content (%)	32.41	42.71	3.43	12.20	1.87	0.61	1.22	0.15
Element	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3	
Content (%)	0.69	0.15	0.34	0.04	0.27	0.06	1.85	

reason to choose this stirring speed was to eliminate the effect of external diffusion caused by stirring on the leaching process, as demonstrated from our earlier work (9). The leaching temperature varied from room temperature to 95°C.

For each test, 50 g of the ore sample with a given size distribution was placed in the reactor. A 250 mL hydrochloric acid solution with a given concentration was then added in the reactor. The ore was well mixed with the acid solution for various leaching times at the desired temperature. To examine the leaching efficiency for a given period of time, 1 mL of the slurry was removed using a micropipette at a given time, and transferred quickly to a 100 mL volumetric flask, diluting to 100 mL with distilled water. The diluted sample was then filtered. The collected filtrate was sent for analysis to determine the RE concentration. The rare earth ion contents were determined by titration with EDTA using xylenol orange as an end point indicator and hexamethylene tetramine as a buffer solution. All the chemicals used in this study were reagent grades purchased from Beijing Chemical Reagent Company. From the chemical analysis, the amount or the fraction of RE leached out from the ore were obtained from mass balance calculation.

PRINCIPLES OF LEACHING KINETICS

After removing Mn by reduction leaching, the Mn-Fe amorphous matrix in the weathered RE mud can be considered as a porous structure. When mixing the MRW-RE mud with hydrochloric acid solution, the following leaching reactions occur:

$$RE_2O_3 + 6HCl \Longleftrightarrow 2RECl_3 + 3H_2O \qquad (1)$$

$$RE(OH)_3 + 3HCl \Longleftrightarrow RECl_3 + 3H_2O \qquad (2)$$

$$MnO + 2HCl \Longleftrightarrow MnCl_2 + H_2O \qquad (3)$$

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

$$2MnO(OH) + 6HCl \Longleftrightarrow 2MnCl_2 + Cl_2 + 4H_2O \qquad (5)$$

In addition, Fe_2O_3, CaO, MgO, and BaO present in the ore will also react with HCl. It is obvious from the above reactions that the leaching process is a solid-liquid two phase reaction involving different species. It also suggested that a substantial amount of the HCl added would be consumed to dissolve other unwanted metal species. Because of this reason, the concentration of HCl might have to be relatively high to achieve an acceptable RE leaching rate.

Leaching process involves fluid-solid reactions. For the noncatalytic reactions of solid particles with the surrounding fluid, two simple idealized models, i.e., the continuous-reaction model and the unreacted-core model, are most commonly used to describe the industrial operation (14, 15). The continuous-reaction model deals with the process where the reactant liquid enters and reacts throughout the solid particle at all times, most likely at different rates at different locations within the particle. In this case, the limit step controlling the leaching reaction is the diffusion of reactants from the liquid to the solid particle. The unreacted-core model involves the reactant to penetrate and react with the unreacted shrinking core moving inward toward the center of the particle. Either the penetration or inner diffusion of reactant, or the chemical reaction could limit the leaching process. Therefore, for porous solids, the leaching kinetics can be generally controlled by either outer or inner diffusion, chemical reaction, or their combination. When there is more than one rate limiting step in the leaching kinetics, the process is considered as a mixed control, with the overall leaching kinetics being controlled by the slowest step (15). To simplify the analysis, we assume that the MRW-RE mud particles are spherical. The leaching process in our case can then be approximately described by an unreacted shrinking core model (14–17). Which step controls the leaching process can then be conveniently identified by plotting the experimental data as a function of leaching time. If the leaching reaction is inner diffusion controlled, the plot of $1-(2/3)\alpha-(1-\alpha)^{2/3}$ vs. time should be a straight line passing through the origin (α is the portion of RE leached out). For chemical reaction controlled leaching process, the plot of $1-(1-\alpha)^{1/3}$ vs. time is a straight line passing through the origin. When the reaction is controlled by mixed steps, the plot of $1-(2/3)\alpha-(1-\alpha)^{2/3}$ vs. time will not be a straight line, neither will the plot of $1\text{-}(1\text{-}\alpha)^{1/3}$ vs. time.

RESULTS AND DISCUSSION

Effect of Leaching Temperature

To identify the suitable leaching model and mechanisms of recovering RE from MRW-RE mud with hydrochloric acid solutions, the leaching kinetic experiments were conducted at different temperatures with 2M hydrochloric acid solution for different leaching time periods. The average particle size d_{50} (i.e., 50% solids passing through a screen of a given size) of the ore used was 0.02 mm in radius. The results in Fig. 1 showed that RE leaching recovery increased with increasing leaching temperature and time, as expected.

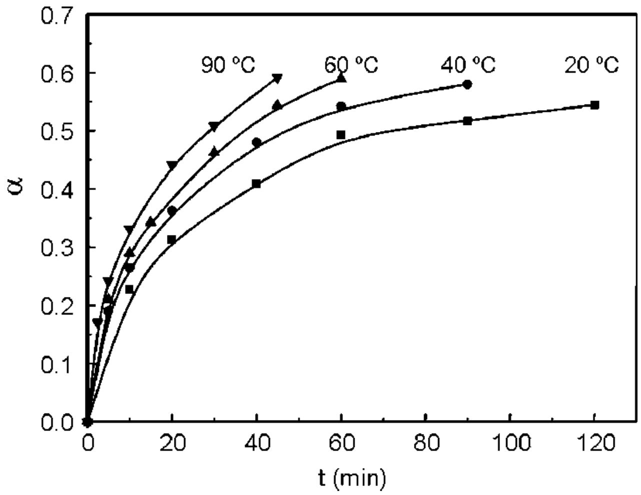

Figure 1. Effect of temperature on RE leaching ratio (α) (solid : liquid = 1 : 5; [HCl] = 2 M; $r_0 = 0.020$ mm).

Leaching reaction is generally endothermic. Increasing the leaching temperature would therefore enhance the leaching reactions. In addition, at higher temperatures, leaching chemical species could have higher diffusion rates, due to the increased thermal or activation energies. Both scenarios are expected to enhance the leaching process. To identify which step limited the leaching process, the results were analyzed using different kinetic models by trial-and-error method (16, 17). The results in Fig. 2 showed that

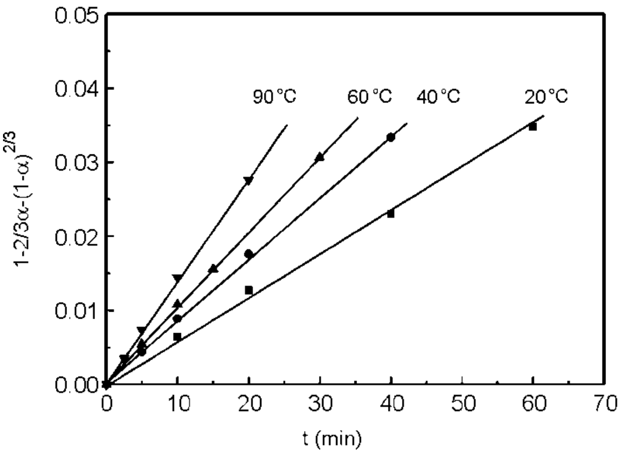

Figure 2. RE leaching kinetics under different temperatures (solid : liquid = 1 : 5; [HCl] = 2 M; $r_0 = 0.020$ mm).

a set of straight lines can be obtained by plotting $1-(2/3)\alpha-(1-\alpha)^{2/3}$ vs. time. Based on this observation, the kinetic equation can therefore be expressed as:

$$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}=kt \tag{6}$$

where k is the leaching rate constant (min^{-1}).

The results in Fig. 2 suggest that the leaching process is well described by the shrinking core model, and the rate limiting step was the inner diffusion of chemical reagent. It can be conceived that with the completion of the reaction of dissolving RE at the solid surfaces, the reaction interface moves towards the center, and the shell thickness increases. Although increasing the temperature could increase the diffusion of hydrochloric acid into the solid matrix, the results in Fig. 2 suggest that the chemical reaction accelerated at a much faster pace than the reagent diffusion. Therefore, a faster RE leaching at a higher temperature was mainly attributed to the enhanced leaching chemical reaction.

To further justify that the leaching process was limited by the diffusion and penetration of HCl into the solid sphere, the values of leaching rate content k at different temperatures were estimated as follows.

According to Arrhenius equation, the rate constant k (min^{-1}) can be represented by:

$$k=Ae^{-E/RT} \tag{7}$$

or

$$\ln k=\ln A-\frac{E}{RT} \tag{8}$$

where A is a coefficient, R is the gas constant, T is leaching reaction temperature (Kelvin, K), and E is activation energy (kJ/M).

From the plot of lnk vs. 1/T shown in Fig. 3, the apparent activation energy E of the leaching process calculated from the slope of the straight line is 10.17 kJ/M. This value falls within the activation energy conventionally found for inner diffusion-controlled leaching processes [between 4 kJ/M and 12 kJ/M (17)]. The results here suggested again that the leaching process in this study was indeed controlled by the diffusion of leaching chemical species into the solid particles. To enhance the leaching process, it is therefore desirable to create a suitable environment to accelerate the inner diffusion rate of leaching chemicals.

Effect of Particle Size

To search for possible methods for improving the leaching process, the MRW-RE mud was classified into four different size fractions. The ore samples at each size fraction were then leached at 20°C with 2 M hydrochloric acid. It was observed from Fig. 4 that the leaching rate increased with decreasing

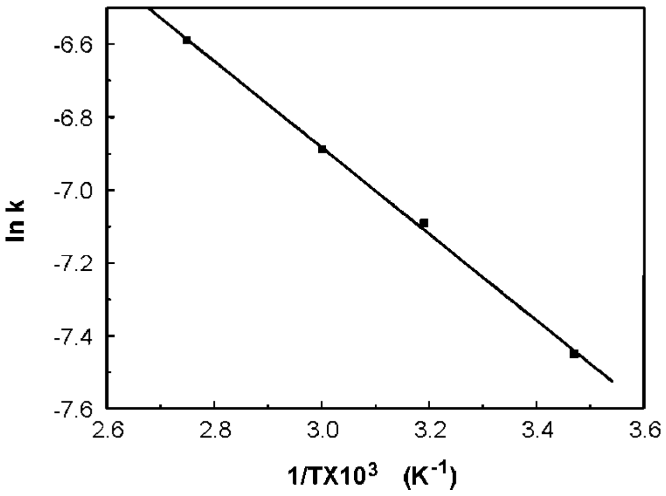

Figure 3. Determination of RE leaching activation energy (solid : liquid = 1 : 5; [HCl] = 2 M; r_0 = 0.020 mm).

the particle size. One of the obvious consequences with decreasing particle size is an increased solid-liquid interfacial area, thereby possibly contributing to the enhanced external diffusion of chemicals and reactions at solid surfaces.

To examine whether this increased RE leachability with decreasing particle size is due to the chemical reaction or reagent diffusion, the data were plotted as $1-(2/3)\alpha-(1-\alpha)^{2/3}$ vs. t (Fig. 5). All the data points for a

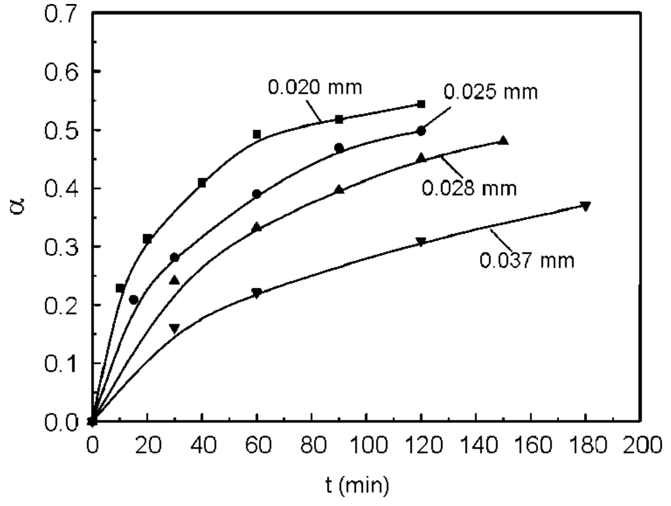

Figure 4. Effect of particle size on RE leaching ratio (α) (solid : liquid = 1 : 5; [HCl] = 2 M; T = 20°C).

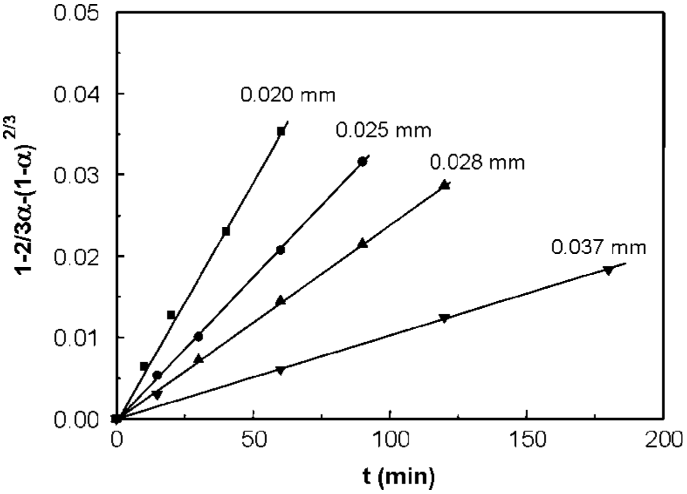

Figure 5. Effect of particle size on RE leaching kinetics (solid : liquid = 1 : 5; [HCl] = 2 M; T = 20°C).

given particle size fell on straight lines, suggesting that for the particle size ranges tested in this study the RE leaching process was controlled by the inner diffusion of chemicals into the particles. The results here would suggest that increasing the solid-liquid interfacial area, by either decreasing the particle size or increasing the porosity of the solids, would contribute to the enhanced RE leaching process. However, reducing the particle size by grinding could be limited by the substantially increased energy consumption. Increasing the porosity of the solids might therefore be a more economical approach to accelerating RE recovery. This finding justifies and supports the importance of manganese reduction leaching before RE leaching to generate porous structures of the ores.

For process design purposes, a rate constant is normally needed. To facilitate the process evaluation and design, the leaching rate constants for different particle sizes of MRW-RE mud in 2 M HCl solution were calculated from the slopes of straight lines give in Fig. 5. It is interesting to note from the results in Fig. 6 that a straight line can be obtained when plotting k vs. $1/r_0^2$. By combining all the testing results, and the linear relationship between lnk and 1/T in Fig. 3, and between k and $1/r_0^2$ in Fig. 6, the kinetic Equation at 2M HCl concentration can be obtained as (9, 16):

$$k = \frac{5.08 \times 10^{-4}}{r_0^2} e^{-10.17/RT} + 7.23 \times 10^{-5} \qquad (9)$$

The rate constant equation (Eq. 9) established above would provide a valuable guideline for the process design, in terms of the effect of particle size and temperature on the leaching kinetics.

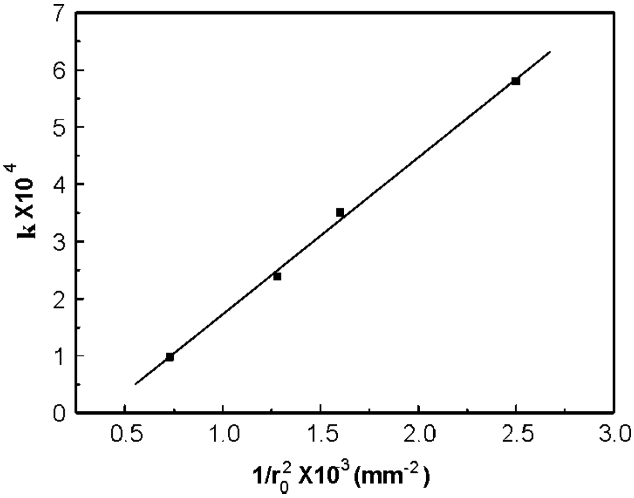

Figure 6. Effect of particle size on RE leaching rate constant (solid : liquid = 1 : 5; [HCl] = 2 M; T = 20°C).

Effect of Hydrochloric Acid Concentration

The leaching process involves the use of substantial amount of leaching chemicals. It is therefore necessary to find out suitable conditions to maximize the leaching process with an optimum economical efficiency. Leaching tests were then carried out at different hydrochloric acid concentrations. The average particle size of ore samples used was 0.02 mm in radius, and the leaching temperature remained at 20°C. The results are shown in Fig. 7. As expected, much faster leaching rate was achieved using a high concentration of HCl. However, using a highly concentrated acid not only poses corrosion problems to equipment, but also increases the operating cost. In terms of leaching kinetics and operational considerations, an optimum HCl concentration should be the concentration at which the reagent diffusion rate is the same as the reaction rate. In this way, leaching reagents can diffuse into the inner phase of the ore particles fast enough without delaying the leaching reactions.

Based on this reasoning, the results were analyzed using different kinetic models to determine the reaction mechanisms at different HCl concentrations. As shown in Fig. 8, a set of straight lines were obtained when plotting $1-(2/3)\alpha-(1-\alpha)^{2/3}$ against leaching time t at HCl concentration below 4M. The results suggested that the leaching kinetics was controlled by the inner diffusion of HCl at this HCl concentration range. However, when the HCl concentration was above 4M, no straight lines could be obtained. This finding would indicate that at high HCl concentrations (>4M), the diffusion of leaching chemicals may not be the only limiting step to control the leaching process.

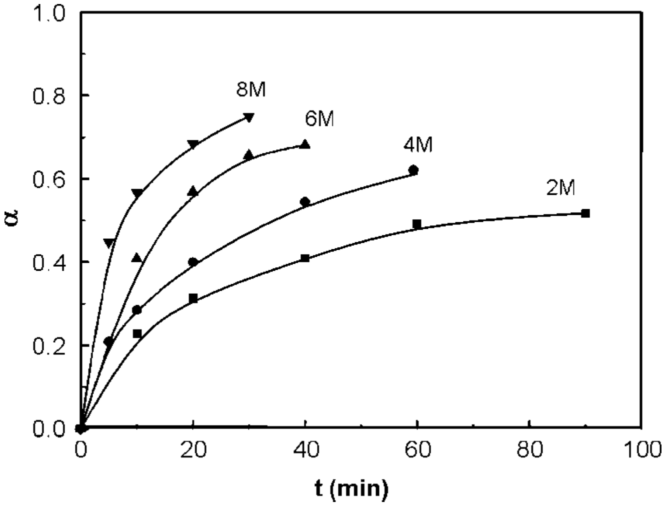

Figure 7. Effect of HCl concentration on RE leaching ratio (α) (solid : liquid = 1 : 5; $r_0 = 0.020$ mm; T = 20°C).

To find out which step controls the leaching process at higher HCl concentrations, the results were plotted as $1-(1-\alpha)^{1/3}$ vs. time in Fig. 9. Again, no straight lines could be obtained at HCl concentrations above 4 M, indicating that the leaching process was not entirely chemical reaction controlled either. Combining both results in Figs. 8 and 9 would suggest that the leaching process at higher HCl concentrations (>4 M) was not controlled by chemical reaction or reagent diffusion alone, but a mixed process limited by both chemical reaction and reagent diffusion.

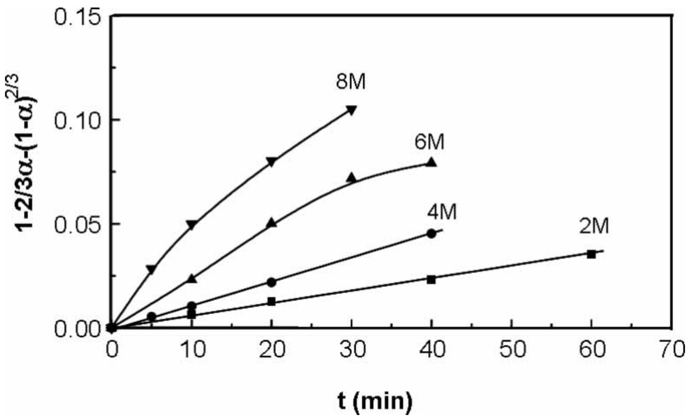

Figure 8. Effect of HCl concentration on RE leaching kinetics (inner-diffusion controlled) (solid : liquid = 1 : 5; $r_0 = 0.020$ mm; T = 20°C).

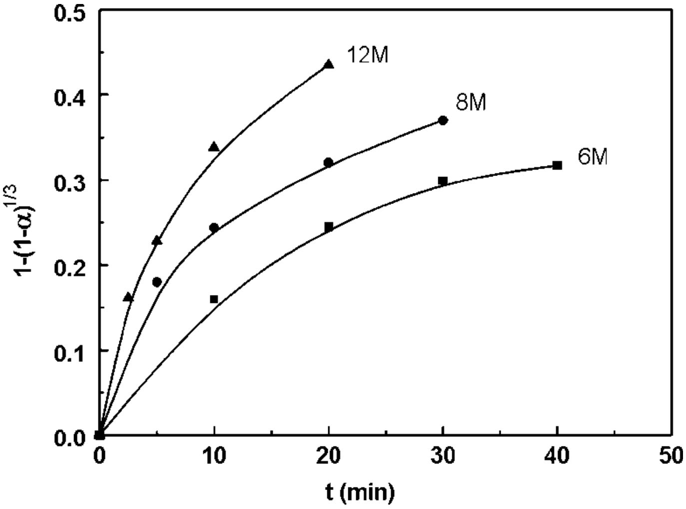

Figure 9. Effect of HCl concentration on RE leaching kinetics (chemical reaction controlled) (solid : liquid = 1 : 5; $r_0 = 0.020$ mm; T = 20°C).

This finding would suggest that with increasing HCl concentration, the leaching reaction of porous solid layer oxide speeds up, accompanied by the faster destruction of the amorphous structure of RE carrier. The MRW-RE mud ores then became very loose or porous, thereby accelerating the diffusion of leaching agent and products. The diffusion of leaching chemicals could increase significantly to match or even exceed the chemical reaction rate. Therefore at some spots in the ores where there are excessive leaching chemicals available, the leaching process could be limited by the chemical reaction. At other spots where there are not sufficient leaching chemicals, the diffusion of chemicals could limit the leaching process. Because of these scenarios, the overall leaching process can be represented by a mixed controlling rate model. For this reason, different techniques may have to be explored to enhance RE leaching process with different HCl concentrations, which will be the focus of our future research program.

CONCLUSIONS

Based on the present investigations the following conclusions can be drawn:

1. The kinetics of leaching rare earth from a manganese-removed weathered rare earth mud (MRW-RE mud) in hydrochloric acid solutions was affected by temperature, particle size, and HCl concentration, as expected.
2. At HCl concentration below 4 M, the leaching rate was controlled by the diffusion of reactants and leaching products through a porous ore.

However, when HCl concentration was higher than 4 M, the leaching process was limited by both chemical reaction and reagent diffusion.

3. The apparent activation energy for the leaching process at 2M HCl was found to be about 10.17 kJ/M, and an empirical kinetic equation relating the rate constant of rare earth leaching to the particle size and leaching temperature was established as:

$$k = \frac{5.08 \times 10^{-4}}{r_0^2} e^{-10.17/RT} + 7.23 \times 10^{-5}$$

NOMENCLATURE

A	coefficient in Arrhenius equation
E	activation energy (kJ/M)
k	rate constant (min^{-1})
K	Kelvin temperature
r_0	particle radius (mm)
R	gas constant
t	leaching time (min)
T	leaching reaction temperature (Kelvin, K)
α	the fraction of RE leached out
MRW-RE mud	manganese-removed weathered rare earth mud

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