[Article ID] 1003 - 6326(2000)04 - 0531 - 04

Leaching kinetics of rare earth from black weathering mud with hydrochloric acid①

CHI Ru-an(池汝安)[1], ZHU Guo-cai(朱国才)[1], TIAN Jun(田 君)[2]
(1. Institute of Nuclear Energy Technology, Tsinghua University, Beijing 102201, P.R.China;
2. Institute of Applied Chemistry, Jiangxi Academy of Sciences, Nanchang 330029, P.R.China)

[Abstract] The affecting factors of leaching rate such as reacting temperature, mud particle size and concentration of reagents were determined by studying the leaching kinetics of rare earth from black weathering mud. The apparent activation energy is 9.08 kJ/mol from calculating the experimental data. The results show that the leaching process can be described by the shrinking core model and the leaching rate is controlled by diffusion of reacting reagents and reaction product in the porous solid layer. The leaching kinetics is established as: $K = 7.50 \times 10^{-5} \times \exp(-9080/RT)/r_0^2$.

[Key words] kinetics; black weathering mud; leaching rare earth

[CLC number] TF111.31; TF111.13 **[Document code]** A

1 INTRODUCTION

Pansi rare earth deposit in western Sichuang is the secondary largest rare earth deposit in China[1]. It was discovered and appraised in 1986 and exploited rapidly in recent year[2]. For its serious weathered, it derives about 20% black rare earth mud. The black rare earth mud is a secondary enriched body of rare earth, which contains about 3% ~ 7% REO. Its middle (Eu_2O_3) and heavy rare earth(Y_2O_3) partitioning is higher than bastnasite[3]. Therefore it is a new rare earth resources with enriching middle and heavy RE, and worth to recover[4].

Rare earth exists in the amorphous Mn-Fe oxide of the black weathering mud with colloid sediment phase[5,6]. It can be leached by hydrochloride acid[7]. In order to make clear the mechanism of the RE leaching and determine the suitable technical path of RE recovering, it is necessary to study the leaching kinetics of rare earth for the black weathering mud.

2 EXPERIMENTAL

2.1 Properties of black weathering mud

The main chemical compositions of black weathering mud are listed in Table 1.

The existing states of rare earth in the black weathering mud are listed in Table 2.

The black weathering mud contains 3.73% RE from Table 1, which is higher than weathering crust of Southern China[8]. The rare earth exists mainly with colloid sediment phase, which account for 71.0% from Table 2.

2.2 Experimental principle

Table 1 Compositions of black weathering mud (%)

Composition	Content	Composition	Content
RE	3.73	SiO_2	32.37
MnO_2	13.60	PbO	2.24
Fe_2O_3	12.68	BaO	1.41
Al_2O_3	6.80	H_2O	6.43

Table 2 Existing states of RE in black weathering mud

Phase state	Phase distribution/ %
Water dissolving phase	5.60×10^{-2}
Ion phase	1.26×10^{-3}
Colloid sediment phase	71.00
Mineral phase	29.10

The leaching reactions of black weathering mud with hydrochloride acid are as follows:

$$RE_2O_3 + 6H^+ = 2RE^{3+} + 3H_2O \quad (1)$$

$$RE(OH)_3 + 3H^+ = RE^{3+} + 3H_2O \quad (2)$$

$$Fe_2O_3 + 6H^+ = 2Fe^{3+} + 3H_2O \quad (3)$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \quad (4)$$

$$PbO + 2H^+ = Pb^{2+} + H_2O \quad (5)$$

$$BaO + 2H^+ = Ba^{2+} + H_2O \quad (6)$$

$$MnO_2 + 4H^+ = Mn^{2+} + 2H_2O \quad (7)$$

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O \quad (8)$$

Above reactions show that the leaching process is a solid-liquid multiphase reaction. Assuming that the mud particles are globular shape particles, the leaching process can be described by Shrinking Core Model[9].

The kinetics type can be determined by treating experimental data. For the kinetics type of inner diffusion controlling, the plot of $1 - 2/3\alpha - (1-\alpha)^{2/3}$

① **[Foundation item]** Projects (59674021) and (59804004) supported by the National Natural Science Foundation of China and project (59725408) supported by the National Outstanding Youth Foundation of China **[Received date]** 1999 - 05 - 09; **[Accepted date]** 1999 - 06 - 22

vs time is a straight line which passes 0 point(here, α is the RE leaching ratio).

2.3 Experimental methods

The leaching kinetics experiments were carried out in a tri-mouth flask[10]. The sample was collected by a measuring pipe, and rapidly turned to a measuring flask to dilute 100 times with distilled water and analyzed the RE and Mn concentration by spectrophotometric and titration methods.

3 RESULTS AND DISCUSSION

3.1 Effect of leaching temperature on RE leaching

The results of RE leaching from black mud with hydrochloric acid at different temperatures and times are shown in Fig.1.

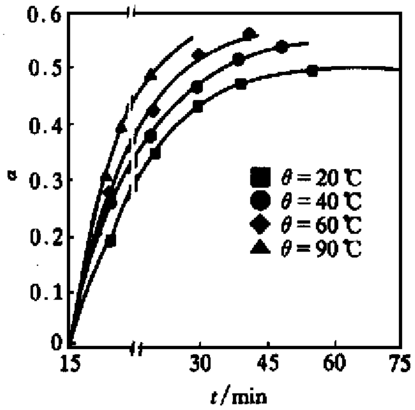

Fig.1 RE leaching ratio (α) at different temperatures and times

The results indicate that RE leaching recovery increase with increasing leaching temperature and time.

3.2 Leaching kinetics equation

The kinetics equation is obtained by trial or error method[9,10] from the experimental data shown in Fig.1. A set of line can be plotted with plotting $1 - 2/3\alpha - (1-\alpha)^{2/3}$ vs t from the experimental data shown as Fig.2. Therefore the kinetics equation can be expressed as

$$1 - 2/3\alpha - (1-\alpha)^{2/3} = Kt \qquad (9)$$

where K is a rate constant.

3.3 Leaching apparent activation energy

From the K values of leaching process at different temperatures, the Arrhenius diagram can be built as Fig.3. According to Arrhenius equation: $\ln K = \ln A - E/RT$, the apparent activation energy of the leaching process can be calculated from the slope of line in Fig.3, which is 9.08 kJ/mol. It proves that leaching process is controlled by inner diffusion for its activation energy from 4 kJ/mol to 12 kJ/mol.

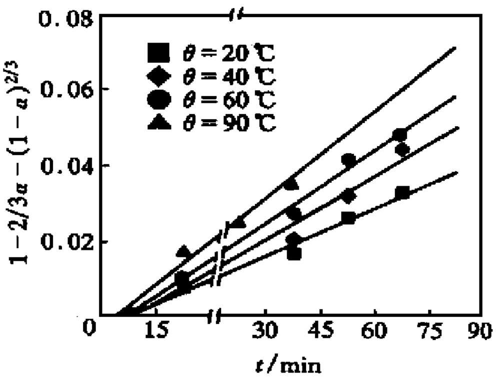

Fig.2 Plot of $1 - 2/3\alpha - (1-\alpha)^{2/3}$ vs t

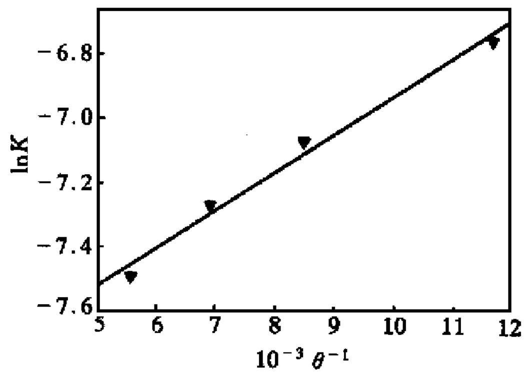

Fig.3 Arrhenius diagram of leaching system

3.4 Effect of particle size of mud on RE leaching

The effect of particle size of mud on RE leaching is shown in Fig.4.

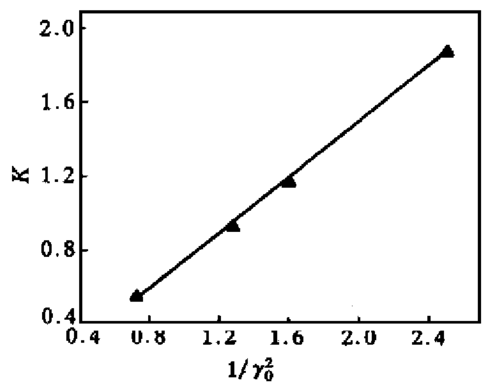

Fig.4 Effect of particle size of mud on RE leaching (r_0 —Particle size)

From the line relationship between K and $1/r_0^2$ in Fig.4, a kinetics equilibrium equation can be obtained as[11]

$$K = 7.50 \times 10^{-5} \times (1/r_0^2) \cdot \exp[-9080/(RT)] \qquad (10)$$

The results indicate that the leaching rate increases with decreasing particle size of the mud, which further proves that the leaching process is controlled by inner diffusion.

3.5 Effect of hydrochloric acid concentration on RE leaching

The effect of hydrochloric acid concentration on RE leaching is shown in Fig.5.

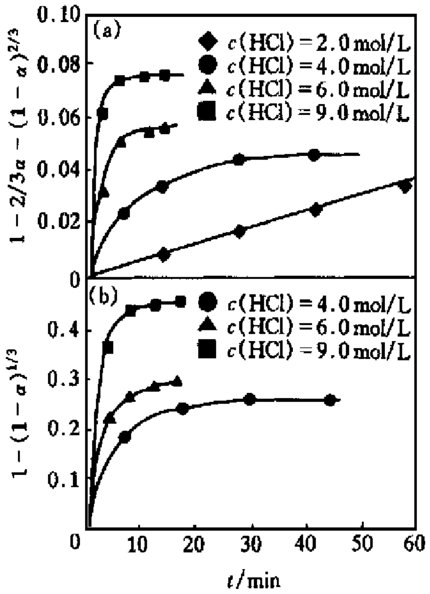

Fig.5 Effects of HCl concentration on RE leaching

Fig.5 shows that the plot of $1 - \alpha - (1 - \alpha)^{2/3}$ vs t is not straight line and so does $1 - \alpha - (1 - \alpha)^{2/3}$ vs t at HCl concentration above 2.0 mol/L. Therefore the leaching process is controlled by mixture rate model.

The results can be explained as follows with the increase of HCl concentration, the reaction of Mn-Fe oxide leached in the mud would be speed up, and the Mn-Fe amorphous structure of mud would be destroyed; the mud becomes loose or porous, the leaching agent and product become more easily diffusing, the RE leaching is speed up. Therefore the leaching process can be represented by a mixture rate controlling model.

4 CONCLUSIONS

The leaching kinetics of rare earth in black weathering mud is studied, the factors of temperature, particle size of the mud and HCl concentration are considered. The results show that the leaching process can be described by Shrinking Core Model. The leaching rate is controlled by diffusion of porous solid layer.

The apparent activation energy is 9.08 kJ/mol, and an empirical equation of the leaching kinetics is established as

$$K = 7.50 \times 10^{-5} \times (1/r_0^2) \cdot \exp(-9080/RT)$$

With the increase of HCl concentration, the leaching agents and products would be easily diffused. The leaching rate increases obviously for destroy of Mn-Fe oxide in mud. The leaching rate controlling step changes from inner diffusion to mixture rate controlling model.

[REFERENCES]

[1] CHI Ru-an and WANG Dian-zuo. Beneficiation of Rare Earth Ore and Extraction Technology [M]. Beijing: Science Press, (in Chinese), 1996. 196 - 327.

[2] SHI Ze-min. Existing state and partitioning characteristics of rare earth elements in Changbei rare earth deposits of Sichuan Province [J]. Chinese Rare Earths, (in Chinese), 1992, 13(3): 1 - 9.

[3] CHI Ru-an, ZHU Guo-cai, SHI Zi-min, et al. Rare earth partitioning and existing state of southwest MN rare earth ores [J]. Nonferrous Metals, (in Chinese), 1998, 50(4): 85 - 89.

[4] ZHU Guo-cai and CHI Ru-an. Extraction of rare earth from black weathering mud [J]. Rare Metals, 1999, 18 (1): 69 - 74.

[5] CHI Ru-an, ZHU Guo-cai, ZHANG Ping, et al. Chemical behavior of cerium element in rock weathering system [J]. Trans Nonferrous Met Soc China, 1999, 9(1): 158 - 164.

[6] DENG Ru-xin and CHI Ru-an. Physicochemical properties and partitioning of black weathered rare earth mud [J]. Chinese Rare Earths, (in Chinese), 1996, 17(2): 35 - 39.

[7] CHI Ru-an and WANG Dian-zuo. Rare earth partitioning characteristics in the ionic type rare earth ores and its application [J]. Chinese Journal of Rare Metals, (in Chinese), 1993, 17(2): 94 - 99.

[8] CHI Ru-an, ZHU Guo-cai and ZHANG Ping. Rare earth partitioning of granitoid weathering crust in Southern China [J]. Trans Nonferrous Met Soc China, 1998, 8 (4): 693 - 699.

[9] LI Hong-gui. Lecture notes of leaching kinetics [J]. Rare metal and Cemented Carbide, (in Chinese), 1992 (3): 28 - 32.

[10] CHEN Jia-yong, YANG Shou-zhi, KE Jia-jun, et al. Research and Development of Hydrometallurgy [M]. Beijing: Metallurgical Industry Press, 1998. 174 - 181.

[11] Sohn H Y and Wadsworthj M E. Rate Process of Extraction Metallurgy [M]. New York: Plenum Press, 1974. 10 - 12, 141 - 143.

(Edited by HUANG Jin-song)