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KINETICS OF WEATHERED-CRUST ELUTION-DEPOSITED RARE-EARTH ORE IN A LEACHING PROCESS

KINETIKA POSTOPKA LUŽENJA ELUCIJSKO NANESENE PREPERELE SKORJE RUDE REDKIH ZEMELJ

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The leaching reaction kinetics of weathered-crust, elution-deposited rare earth with mixed ammonium salts was studied. The influence of the concentration of the reagents and the particle size of the ore on the leaching rate was investigated. The results showed that the diffusion process and the leaching rate could be improved by increasing the reagent concentration and decreasing the leaching flowing rate and particle size. The leaching process could be explained using the shrinking-core model, which could be controlled with the diffusion rate of the reacting reagents in a porous solid layer. The leaching rate followed the equation $1–2/3\eta – (1 – \eta)^{2/3} = 7.126 \times 10^{–4}C^{0.3038}R^{0.1942}t$.

Keywords: leaching reaction, leaching rate, rare-earth ore, leaching process

Proučevana je kinetika reakcije luženja preperele skorje elucijsko nanesene rude redkih zemelj. Preiskovan je bil učinek koncentracije reagentov in velikosti zrn rude na hitrost luženja. Rezultati so pokazali, da je mogoče proces difuzije in hitrost luženja povečati s povečanjem koncentracije reagentov ter z zmanjšanjem hitrosti luženja in zmanjšanjem velikosti delcev. Postopek luženja se lahko razloži z modelom krčenja jedra, ki ga je mogoče kontrolirati s kontroliranjem hitrosti difuzije reagentov, ki reagirajo v poroznem trdnem sloju. Hitrost luženja je skladna z enačbo
$1 – 2/3\eta – (1 – \eta)^{2/3} = 7{,}126 \times 10^{–4} C^{0{,}3038}R^{0{,}1942}t$.

Ključne besede: reakcija luženja, hitrost luženja, ruda redke zemlje, postopek luženja

1 INTRODUCTION

Weathered-crust, elution-deposited, rare-earth ore is China's unique rare-earth mineral resource.[1–3] There are many advantages of the ore: a widespread distribution of rich reserves, a low radioactivity, it is rich in the middle and heavy rare earths, it is an easily extracted rare earth, it is simple to process by leaching giving high-quality products, etc. The development and utilization of the ore in the world have a significant influence. In China, special attention has been paid to rare-earth mineral resources in recent years. Therefore, high efficiency and the comprehensive exploitation of the weathered-crust, elution-deposited, rare-earth ore was intensively investigated over the past decade.

The leaching of the rare-earth ore is a liquid-solid multiphase reaction process, where the most common reaction is carried out in two ways: by using the integral-scaled model and the shrinking-core model. In the latter, a mixed ammonium salt solution is used as a leaching agent, causing the particle size of the ore to change only a little during the leaching reaction. For this reason, the leaching process of the rare-earth ore is usually based on the shrinking-core model. The leaching rate is connected with the concentration, the temperature, the surface area of the solid phase, etc. The leaching process can be controlled by the outer diffusion, the inner diffusion, or the chemical reaction.[4,5] The influences of the concentration of the reagents and the particle size of the ore on the leaching rate were investigated to achieve a high rare-earth concentration, a low consumption of the leaching reagent and a high leaching rate.

2 EXPERIMENTAL WORK

2.1 Analysis of the ore samples

Ore samples are mostly random and taken from non-cemented sands; they are of a pale flesh-red color, containing clay minerals, quartz sand, rock-forming feldspar etc., obtained from Dingnan County of Jiangxi Province. They contain about 40–70 % of clay minerals, such as halloysite, illite, kaolinite and a small quantity of montmorillonite. Some 90 % of rare-earth ions adsorp-

Table1: The main components of the ore
Tabela 1: Glavne sestavine rude

main components	REO	SiO_2	Al_2O_3	Fe_2O_3	CaO	others
content (%)	0.1146	61.80	14.28	3.190	0.470	20.15

tion is in a state of kaolinite and mica. The chemical composition of the ore is presented in **Table 1**.

2.2 Process and Method

Prior to the leaching experiments, the ore sample was sieved through a +20 mesh, 20–60 mesh, 60–100 mesh, 100–140 mesh, +140 mesh to obtain five natural grain grades. Then the synthetic ore samples, according to the proportion of the natural grain grades, were weighed into a glass flask. The leaching agent with a certain liquid-solid ratio and a flow velocity puts the rare-earth ore into consideration. Then there is continuous leaching and the collected leaching solution. The RE^{3+} concentration was determined using the EDTA titration method,[6] measuring the volume of the leaching reagent. The leaching process was evaluated by the RE leaching rate, which was calculated according to the following formula:

$$\eta = \varepsilon/\varepsilon_0 \tag{1}$$

where ε and ε_0 are the amount of leaching-out RE^{3+} and the total RE^{3+} content of the sample ore.

2.3 Leaching mechanism for rare earth

The leaching process of the weathered-crust, elution-deposited, rare-earth ore is a kind of ion-exchangeable process between the positive ions in the solution and the clay minerals.[7,8] The chemical reaction equation is as follows:

$$[Al_4(Si_4O_{10})(OH)_8]m\cdot RE^{3+}_{(S)} + 3nNH_4^+(aq) \rightarrow$$
$$\rightarrow [Al_4(Si_4O_{10})(OH)_8]m\cdot(NH_4^+)_{3n(S)} + nRE^{3+}_{(aq)} \tag{2}$$

The weathered-crust, elution-deposited, rare-earth ore is composed of ore particles, while the leaching process of the ore is a typical liquid-solid heterogeneous reaction. The leaching process can be described by the shrinking-core model and subdivided into five steps, as follows:[9]

- Diffusion of the leaching reagent (NH_4^+) through the film surrounding the particle to the surface of the clay minerals (Outer diffusion);
- Penetration and diffusion of NH_4^+ to the surface of the un-reacted core (Inner diffusion);
- Reaction of RE^{3+} with NH_4^+ (Chemical reaction);
- Diffusion of the RE^{3+} exchanged though the remainder back to the exterior surface of the clay minerals (Inner diffusion);
- Diffusion of the RE^{3+} exchanged though the exterior surface back into the solution of the fluid (Outer diffusion).

The kinetic control model of the RE leaching process can be divided into four models.[10,11]

1. Chemical reaction control:
   $1 - (1 - \eta)^{1/3} = k_1 t$
2. Diffusion through the liquid film control:
   $1 - (1 - \eta)^{1/3} = k_1 t$
3. Diffusion through the porous ore matrix control:
   $1 - \frac{2}{3}a - (1 - a)^{2/3} = k_3 t$
4. Mixed control:
   $1 - (1 - a)^{1/3} = \frac{k_1 k_2}{k_1 + k_2} \frac{C_0 M}{r_0 p}$

where, k_1, k_2, k_3 are the constants for the different control steps, respectively. a, t, C_0, r_0, p and M represent the rare-earth leaching rate, the leaching time, the initial concentration of the leaching reagent, the initial radius of the ore particle, the mole density of the ore particle and the mass of the ore particle, respectively.

3 RESULTS AND DISCUSSION

According to the optimum process of mixed ammonium salts, the leaching rare-earth ore experiment showed that the leaching rate of the rare-earth ore can reach up to 94.05 % when 2.0 % NH_4NO_3 and $(NH_4)_2SO_4$ with a quality ratio of 7 : 3, solid-liquid ratio of 0.5 : 1, and flow rate of 0.5 mL/min. The rare-earth leaching dynamics was researched on the basis of this process to determine the influence of the factors of the leaching rate and the control steps.

3.1 Effect of the leaching-reagent concentration

The initial average particle size of 0.2414 mm for the rare-earth ore was leached by different concentrations of mixed ammonium salts under the conditions of NH_4NO_3 and $(NH_4)_2SO_4$ with a quality ratio of 7 : 3 , a solid-liquid ratio of 0.5 : 1, and a flow rate of 0.5 mL/min. The influence of the different concentrations of reagents on the leaching rate was investigated. According to the reaction system, the reaction rate is proportional to the concentration of the product, increasing the leaching-

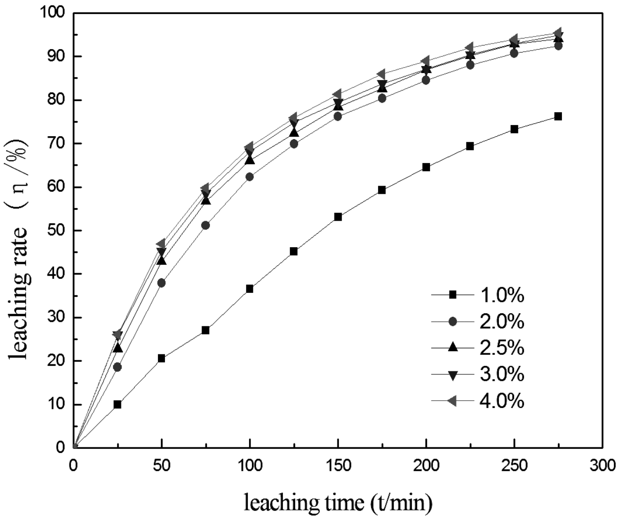

Figure 1: Effect of the concentration of reagents on rare-earth leaching rate
Slika 1: Vpliv koncentracije reagentov na hitrost luženja redke zemlje

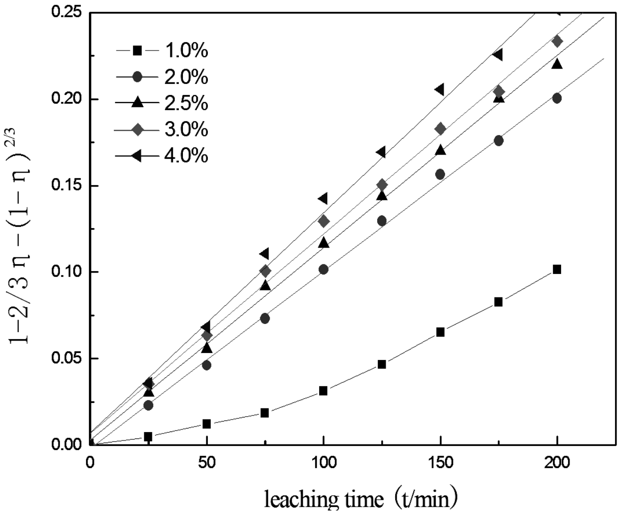

Figure 2: Leaching kinetic data for different concentrations of rare earth
Slika 2: Podatki za kinetiko luženja pri različnih koncentracijah redke zemlje

agent concentration is conducive to an improvement of the leaching reaction rate, thereby increasing the rare-earth leaching rate. **Figure 1** shows how the leaching rate of the rare earth increases as the initial concentration of ammonium salt increases, when the leaching agent concentration of 2.0 % in 275 min for the rare-earth leaching rate is 92.79 %, with the mass fraction of leaching agent increases, the unit volume of ammonium nitrate leaching agent rate increases, leading to the main leaching agent in a large number of Al^{3+} impurities, some of which will cover the surface of the rare-earth ore and hinder RE^{3+} leaching.

The date of the rare-earth leaching rate was substituted into the shrinking-core model in **Figure 2**. When the mass fraction of the leaching agent is greater than or equal to 2 %, it satisfies the equation $1 - 2/3\eta - (1 - \eta)^{2/3} = kt$. Indicating that the leaching process step of the rare-earth ore is inner-diffusion controlled, and it can be used in the model equation:

$$1 - 2/3\eta - (1 - \eta)^{2/3} = k'C^aR^bt \quad (3)$$

where η is the rare-earth leaching rate (%); C is the concentration of the leaching reagent (g/L); R is the initial radius of the ore particle (mm) and t is the leaching time (min). This equation reflects the influence of leaching concentration and the particle size of the rare earth on the leaching rate.

Figure 2 can be drawn for different concentrations of the NH_4NO_3 and $(NH_4)_2SO_4$ compounds of the rare-earth leaching agent and the apparent rate constant k value, assuming that the apparent rate constant is proportional to the power function of the concentration of the leaching agent, for which $\ln k = B + a \ln C$, and a least squares linear fit with the slope requirements.

Figure 3 shows a linear relationship between $\ln k$ and $\ln C$, and the apparent reaction order is 0.3038, so that $a = 0.3038$.

3.2 Effect of the particle size of the ore

A rare-earth ore with a different particle size was leached by mixed ammonium salts under the condition of 2 % NH_4NO_3 and $(NH_4)_2SO_4$ with a quality ratio of 7 : 3, a solid-liquid ratio of 0.5 : 1, and a flow rate of 0.5 mL/min. The influence of the different particle size on the leaching rate was investigated.

Figure 4 presents the effect of particle size on the rare-earth leaching. It shows that the rare-earth leaching rate of ore particles with a smaller size is greater. It is known that the smaller the particle size, the more pores, and at the same time this shortens the length of the pore, thereby reducing the resistance of the inner diffusion and shortens the spread time with the effect of speeding up the rare-earth leaching. The leaching process could be

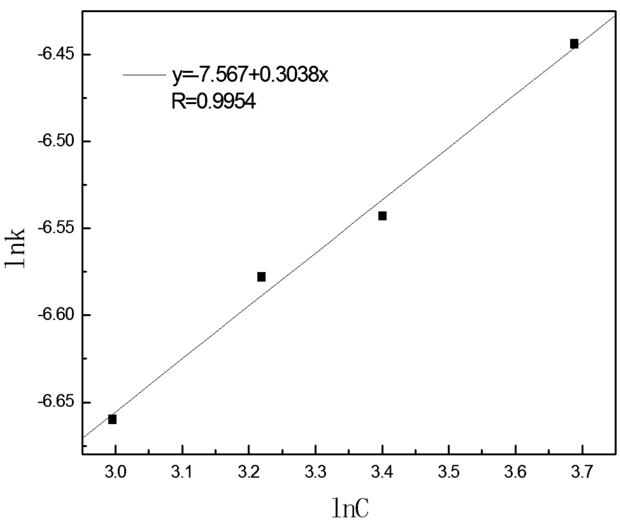

Figure 3: Relation between $\ln C$ and $\ln k$
Slika 3: Odvisnost med $\ln C$ in $\ln k$

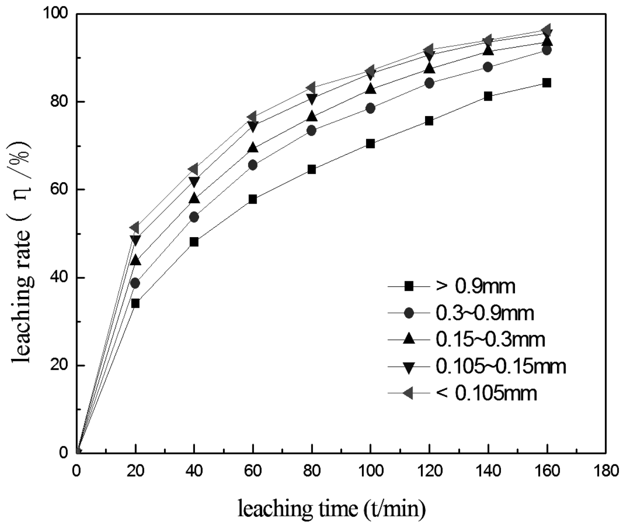

Figure 4: Effect of particle size on rare-earth leaching rate
Slika 4: Učinek velikosti zrn na hitrost luženja redke zemlje

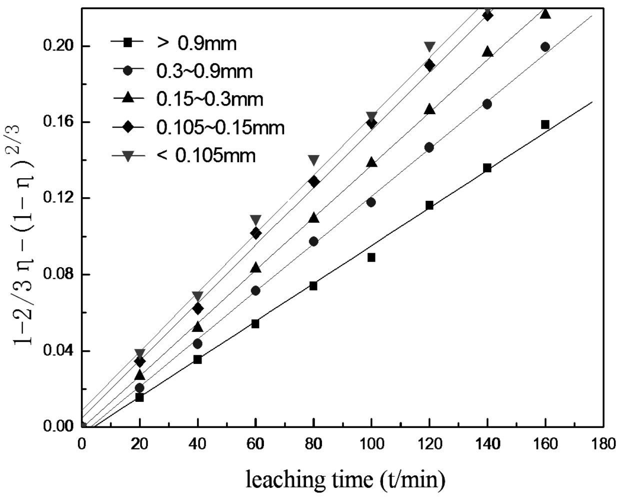

Figure 5: Leaching kinetic data for rare earths of different particle size
Slika 5: Podatki o kinetiki luženja redke zemlje pri različnih velikostih zrn

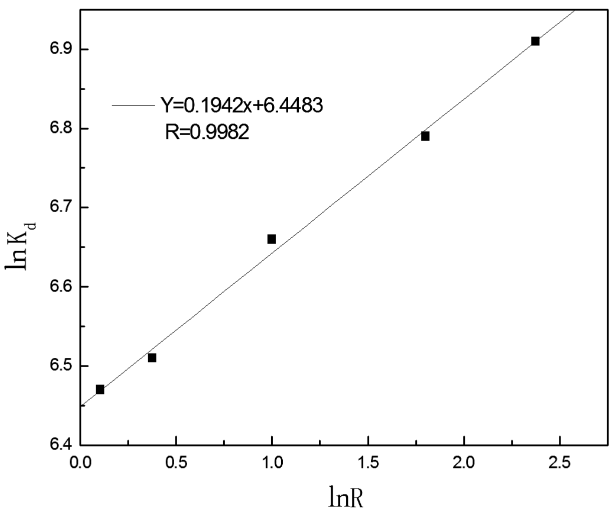

Figure 6: Relation between ln k_d and ln R
Slika 6: Odvisnost med ln k_d in ln R

explained with the shrinking-core model according to the ore particle-size experiment in **Figure 5**.

As shown in **Figure 6**, a good linearity exists between ln k_d and ln R, and the leaching process could be controlled by the diffusion rate of the reacting reagents in a porous solid layer. Furthermore, ln k_d = 6.4483 + 0.1942 ln R, so that b = 0.1942.

a and b were presented in the equation $1 - 2/3\eta - (1 - \eta)^{2/3} = k'C^aR^bt$, changing one factor, fixing others at the same time, so that k' is 7.126×10^{-4}. As a result, the equation of the mixed ammonium salts leaching the rare-earth ore is:

$$1 - 2/3\eta - (1 - \eta)^{2/3} = 7.126 \times 10^{-4}\, C^{0.3038}R^{0.1942}t \qquad (4)$$

4 CONCLUSIONS

The leaching kinetics of weathered-crust, elution-deposited, rare earth with mixed ammonium salts was investigated. The shrinking-core model with inner diffusion control was used to describe the leaching process of the rare earth. It was summarized as follows: the leaching rate increases with the increasing leaching reagent concentration and a decreasing of the particle size. The kinetics of the weathered-crust, elution-deposited, rare-earth leaching equation can be expressed as:

$$1 - 2/3\eta - (1 - \eta)^{2/3} = 7.126 \times 10^{-4}\, C^{0.3038}R^{0.1942}t.$$

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