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Leaching hydrodynamics of weathered elution-deposited rare earth ore with ammonium salts solution

HE Zhengyan (何正艳)[1], ZHANG Zhenyue (张臻悦)[2], CHI Ru′an (池汝安)[2], XU Zhigao (徐志高)[1,*], YU Junxia (余军霞)[2], WU Ming (吴 明)[1], BAI Ruyu (白如钰)[1]

(1. Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, Hubei Province, South-Central University for Nationalities, Wuhan 430074, China; 2. Key Laboratory for Green Chemical Process of Ministry of Education, Wuhan Institute of Technology, Wuhan 430073, China)

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Abstract: In order to reveal the permeability rule of leaching agent solution and the effects of anions in the leaching process of weathered crust elution-deposited rare earth (RE) ores, the effects of ammonium concentration, temperature, particle size and porosity on the permeability were discussed in detail with $(NH_4)_2SO_4$, NH_4Cl and NH_4NO_3 as the leaching agent. It was found that the permeation velocity of ammonium salts increased linearly with the increase of hydraulic gradient. The seepage of ammonium salts solution in the RE ores followed Darcy's law and displayed a laminar flow. The properties of the leaching agent solution and RE ores were the main factors that affect the permeability of RE ores. With the decrease of ammonium concentration and increase of temperature, the viscosity of solution decreased and the permeability coefficients of RE ores increased. And the effects of temperature on the viscosity and permeability were larger than ammonium concentration. The permeability of RE ores became worse with the decrease of particle size and porosity, and the particle size played a more important role compared with porosity. The permeability coefficient of RE ores increased and the viscosity of ammonium salts solution decreased in the order of $(NH_4)_2SO_4$, NH_4Cl and NH_4NO_3, implying that the penetrating power of anions increased in the order of SO_4^{2-}, Cl^- and NO_3^-. The results may play a vital role in improving the permeability of weathered crust elution-deposited RE ores.

Keywords: hydrodynamics; weathered elution-deposited rare earth ore; ammonium salts; permeation velocity; rare earths

The weathered crust elution-deposited rare earth (RE) ores are rich in middle and heavy rare earth which accounts for more than 80% of middle and heavy rare earth reserves in the world[1]. It is a very valuable mineral resource due to making up the low content of middle and heavy rare earth in mineral type RE ores[2]. The RE of weathered crust elution-deposited RE ores are mainly adsorbed on the clay minerals as hydrated ions or hydroxyl hydrated ions, which can be exchanged into solution with electrolyte solution by ion-exchange method[3]. The RE in the leachate can be recovered by chemical precipitation with oxalic acid or ammonium bicarbonate[4].

The leaching technologies of weathered crust elution-deposited RE ores was barrel leaching and bath leaching with sodium chloride as leaching agent in the early 1970s, and then developed to heap leaching and in-situ leaching with ammonium salt as leaching agents[5]. In heap leaching and *in-situ* leaching technologies, the leaching agent solution slowly infiltrates into the RE ores by the effects of gravitational potential, capillary potential, macro pressure potential and so on[6]. During the penetration process, the RE ions adsorbed on the clay minerals are exchanged by the cation in the leaching agent, and transferred into solution[7]. The leaching efficiency of RE mainly depends on the exchangeability of the cations and RE ions and the permeability of leaching agent solution in the ores[8–11]. Usually, the exchange reaction can be conducted fast, so the permeability of leaching agent solution in the ores is the most important factor that determines the leaching efficiency of RE[12]. Furthermore, the permeability of ores also plays a vital role in the stability of ores slope and the formulation of injection and collection system in the leaching technology[13].

The permeability of weathered crust elution-deposited RE ores that contained large amount of clay minerals are often bad due to the small particle size, large specific area, small porosity and so on[14–16]. That is adverse to the high efficiency of RE leaching and the comprehensive utilization of resource. Thus, it is of great significance to investigate the hydrodynamics of weathered crust elution-deposited RE ores to improve the permeability.

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* **Corresponding author:** XU Zhigao (**E-mail:** 18345960@qq.com; **Tel.:** +86-27-67843918)

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Previous researches showed that the leaching efficiency of RE and impurities using ammonium chloride (NH_4Cl) or ammonium nitrate (NH_4NO_3) as leaching agent both surpass ammonium sulfate ($(NH_4)_2SO_4$)[17,18]. However, in the actual exploitation of weathered crust elution-deposited RE ores, the common leaching agents are $(NH_4)_2SO_4$ due to a relatively low leaching efficiency of impurities[19]. With the development of the leaching technology and the impurities removal technology, ammonium chloride and ammonium nitrate begin to be applied in part of RE ores[20]. The study on the permeability of $(NH_4)_2SO_4$, NH_4Cl and NH_4NO_3 in the weathered crust elution-deposited RE ores will be beneficial to comparing roundly the advantages and disadvantages of the three leaching agents, and further guide the application of leaching agents.

In this study, the effects of ammonium concentration, temperature, particle size and porosity on the permeability of weathered crust elution-deposited RE ores using $(NH_4)_2SO_4$, NH_4Cl and NH_4NO_3 as the leaching agent solution were discussed in detail to reveal permeability rule and the effects of anions and provide theoretical basis for the improvement of ores permeability.

1 Experimental

1.1 Materials and characterization

The experimental RE ores sample was original RE ores collected from Dingnan (DN) County in Jiangxi Province of southern China. The main chemical composition of the RE ore was analyzed by X-ray fluorescence (Axios advanced, Panalytical B.V.) and the result is listed in Table 1. The RE ores contain 58.09 wt.% SiO_2 and 19.53 wt.% Al_2O_3. It demonstrates that the weathered crust elution-deposited RE ores mainly compose of quartz and clay minerals of aluminosilicate.

The particle size distribution of weathered crust elution-deposited RE ores mainly depends on the weathered degree of protolith. The more completely the protolith is weathered, the more the content of clay minerals with fine particles is and the less the content of unweathered residual mineral (e.g. feldspar, quartz, etc.) with large particles is[5]. The accumulative distribution curve of particle size of RE ores is shown in Fig. 1. The particle size of RE ores below 0.83 mm accounted for 79.15%. It indicates that the protolith is weathered completely and the permeability of the studied RE ores is poor due to the fine particles and high content of clay mineral.

Table 1 Main chemical compositions of the RE ores (wt.%)

Component	REO	Al_2O_3	MnO_2	ZnO	CaO	MgO	K_2O	SiO_2	P_2O_5
Content	0.10	19.53	0.01	0.01	0.02	0.52	3.54	58.09	0.20
Component	SO_3	TiO_2	Fe_2O_3	Rb_2O	SrO	ZrO_2	BaO	Loss	
Content	0.04	1.40	8.07	0.02	0.01	0.02	0.04	8.36	

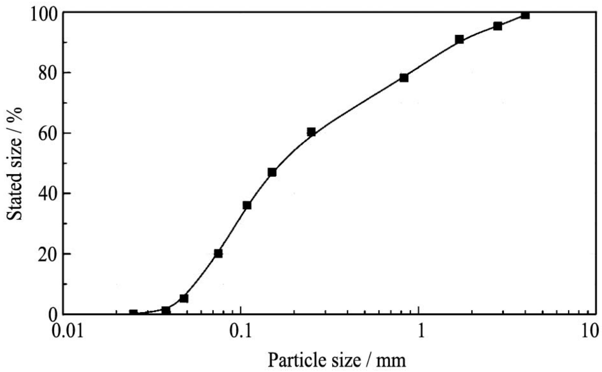

Fig. 1 Accumulative distribution curve of particle size

All chemicals in this study were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) with analytical grade. The used deionized water was produced by an ultra-pure water system (Super series, Nison Instrument (Shanghai) Co., Ltd.).

1.2 methods

The RE ore sample was mixed thoroughly and dried in an oven at 70 ºC for 8 h. A certain mass of dried RE ore sample was packed uniformly in a jacketed glass column with 45 mm inner diameter and the packed ore height was controlled at a desired height by vibration. Then some gravel was put on the top of RE ore as a buffer layer, which could prevent the RE ore from stirring up by solution. The outlet at the top and the inlet at the bottom of the glass column were connected to a thermostatic water tank using silicone tubes in order to regulate the experimental temperature. The leaching agent solution was rapidly added into the glass column by a peristaltic pump till a specified liquid column height, and then added at a variational flow rate to keep the liquid column height constant. The schematic diagram of experimental apparatus is shown in Fig. 2. Leachate was collected from the bottom of the glass column at the same time interval, and the volume of leachate was measured. The experiment was finished until the volume of collected leachate was kept stable.

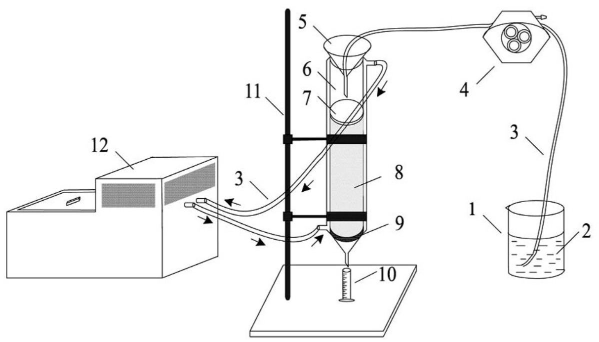

Fig. 2 Schematic diagram of experimental apparatus
1–Beaker; 2–Leaching agent; 3–Silicone tube; 4–Peristaltic pump; 5–Funnel; 6–Jacketed glass column; 7–Gravel; 8–RE ore sample; 9–Sand core filter plate; 10–Precision measuring cylinder; 11–Iron support; 12–Thermostatic water tank