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Leaching kinetics of ionic rare-earth in ammonia-nitrogen wastewater system added with impurity inhibitors

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Abstract: Ammonia-nitrogen wastewater is produced during the dressing and smelting process of rare-earth ores. Such wastewater includes a very high concentration of NH_4^+, as well as other ions (e.g., NH_4^+, RE^{3+}, Al^{3+}, Fe^{3+}, Ca^{2+}, Cl^-, and SiO_3^{2-}) with a pH of 5.4–5.6. Its direct discharge will pollute, yet it can be recycled and used as a leaching reagent for ionic rare-earth ores. In this study, leaching kinetics studies of both rare earth ions and impurity ion Al^{3+} were conducted in the ammonia-nitrogen wastewater system with the aid of impurity inhibitors. Results showed that the leaching process of rare-earth followed the internal diffusion kinetic model. When the temperature was 298 K and the concentration of NH_4^+ was 0.3 mol/L, the leaching reaction rate constant of ionic rare-earth was 1.72 and the apparent activation energy was 9.619 kJ/mol. The leaching rate was higher than that of conventional leaching system with ammonium sulfate, which indicated that ammonia-nitrogen wastewater system and the addition of impurity inhibitors could promote ionic rare-earth leaching. The leaching kinetic process of impurity Al^{3+} did not follow either internal diffusion kinetic model or chemical reaction control, but the hybrid control model which was affected by a number of process factors. Thus, during the industrial production the leaching of impurity ions could be reduced by increasing the concentration of impurity inhibitors, reducing the leaching temperature to a proper range, accelerating the seepage velocity of leaching solution, or increasing the leaching rate of rare earths.

Keywords: ionic rare-earth; ammonia-nitrogen wastewater; impurity inhibitor; leaching; kinetics

The main component of ionic rare earth ore is clay minerals on which was adsorbed the rare earth stably mainly in the form of hydrated or hydroxy-hydrated cations. The content of rare earth is relatively low and the particle size is usually fine. Without any chemical reaction in the water, following the laws of ion exchange, therefore we can only use the method of electrolyte chemical leaching to extract rare earth[1–3]. The main leaching agent of rare earth is sodium chloride, ammonium sulfate, ammonium chloride, and ammonium sulfate is more commonly used at present[4,5]. The leaching process are commonly pool leaching, heap leaching and *in-situ* leaching[6,7]. In terms of the leaching kinetics of ion rare earth ore, rare earth researchers have carried out some research works. Tian et al.[8,9] studied the leaching kinetics process of an ionic rare earth ore leaching with ammonium sulfate in Longnan, Jiangxi. The results show that the leaching process of rare earth is the internal diffusion kinetic model while the leaching process of impurities Al^{3+} is controlled by chemical reaction. Li et al.[10,11] studied the leaching kinetics process of an ionic rare earth ore in Xinfeng, Jiangxi using mixed ammonium-salts (NH_4Cl:$(NH_4)_2SO_4$=7:3). When the concentration of leaching agent was below 2.5%, the leaching process model is hybrid control model; When concentrations is higher than 2.5%, the leaching process model is internal diffusion kinetic model.

Ouyang and Majeda et al.[12,13] studied an aluminum inhibiting agent named HZA. HZA could precipitate the aluminum ions that the aluminum leaching can be reduced by about 56% and hardly affect the leaching of rare earth. But this impurities inhibition was only used to suppress the Al^{3+}, it did not work for other impurity ions. In addition, metallurgical industry of rare earth will generate a lot of ammonia-nitrogen wastewater which will seriously pollute the environment and it is hard to be treated. To reduce emissions of ammonia-nitrogen wastewater and to reduce pollution, the author did the research of leaching kinetics of ionic rare earth using ammonia-nitrogen waste water added by impurities inhibitions[14]. After a series of experiments the best conditions were achieved. And the result was: the liquid-solid ratio of 0.8:1, leaching agent solution pH of 5.0, trickle leaching, ratio of top pressure water and raw ore of 0.1:1,

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ore loading of 200 g, loading naturally, the extraction column's height of 13.5 cm and flow rate of leaching agent of 2.0 mol/min. Under the best conditions the leaching rate of rare earth was 98%. The inhibition of Al^{3+}, Fe^{3+} and Ca^{2+} were respectively 90.56%, 94.21% and 58.48%. The precipitates created by inhibitor YZJ-01 reacted with impurity ion can make soil loose. And YZJ-01 is colorless, tasteless and non-toxic, so the precipitates, leaching residue and leaching liquid do no damage to the environment. However, the leaching kinetics of rare earth in the ammonia-nitrogen wastewater system in which were added by impurities inhibition is not related to reports, and the main factors affecting the leaching kinetics of this system is also not very clear. Leaching kinetics studies of both rare earth ions and suppression leaching of impurities were conducted in the ammonia-nitrogen wastewater added by new type impurities inhibition. The research achievements can provide the technical basis for *in-situ* leaching of ionic rare earth ore in the system of ammonia-nitrogen wastewater added by impurities inhibition.

1 Experimental

1.1 Samples and major reagents

1.1.1 Samples

Ionic rare earth ore samples were high-grade ionic rare earth ores taken from an ionic rare earth mine in Longnan, Jiangxi, the main components are as shown in Table 1.

Ammonia-nitrogen wastewater was taken from the mixture of wastewaters from two stages by a certain percentage. One is from the stage of mining and dressing of Aobeitang rare earth mine in Longnan. And another is from the rare earth hydrometallurgical stage of a rare earth smelter in Longnan. Each ammonia-nitrogen wastewater is the mixture of supernatant and raffinate in the ratio of their generations. Main ion components of the mixture ammonia-nitrogen wastewater are listed in Table 2.

1.1.2 Main chemical reagents

Ammonium sulfate, impurities inhibition YZJ-01, sodium hydroxide, xylenol orange, dimethyl yellow, disodium edetate, hexamethylenetetramine, acetyl acetone, methyl salicylate were used. All of these agents are of AR.

Table 1 Main components of the sample

Components	RE (ion phase)	SiO_2	Al_2O_3	TFe	CaO	MgO	K_2O	Na_2O
Content/%	0.115	67.32	15.21	0.74	0.28	0.22	4.21	1.32

Table 2 Main ion components of the mixture ammonia-nitrogen wastewater

Ion composition	pH	RE^{3+} (g/L)	NH_4^+ (g/L)	Al^{3+} (mg/L)	Fe^{3+} (mg/L)	Ca^{2+} (mg/L)	SiO_3^{2-} (mg/L)
Content	5.2	0.04	6.86	5.83	0.23	68.37	29.35

1.2 Major research methods

There are four leaching rate control models, including external diffusion control model, internal diffusion model, chemical reaction control model and hybrid control model. Through a series of leaching kinetics experiments of rare earth in the system of ammonia-nitrogen wastewater added by impurities inhibition, we tried to explore the leaching kinetics models of both rare earth ions and suppression leaching of impurities in the ammonia-nitrogen wastewater added by impurities inhibition.

The influencing factors of leaching rate for rare earth and impurities are: leaching agent concentration, rare earth ore particle size, stirring intensity of agitation leaching and temperature. A series of condition experiments had been conducted to determine the leaching kinetics equation of rare earth. Firstly, condition experiments of ore particle size were conducted to determine the right kinetics model by comparing the corresponding linear correlation of the experiment data to different kinetics equation models. Secondly, the rare earth apparent activation energy was obtained by condition experiments of effect of different temperatures on the leaching rate of rare earth. Similarly, reaction order was obtained by condition experiments of effect of leaching reagent concentration on the leaching rate of rare earth. After that the reaction specific rate constant in this leaching system was to be achieved by the parameters obtained before. And finally the leaching kinetics process of rare earth in the ammonia-nitrogen wastewater added by impurities inhibition could be concluded. To the kinetics of impurity ions, the effect of temperature on aluminum ion was studied to determine its kinetic control model.

The test method for kinetics is called "three-necked flask method"[15,16], and its experimental device consisting of three-neck flask, reflux condenser, thermometer, power electric mixer, thermostat water bath and stabilizer. Experimental apparatus is shown in Fig. 1.

1.3 Kinetic theoretical control models of rare earth leaching and impurities inhibited leaching

Research data[14,17] shows that the leaching process of ionic rare earth ore belongs to the liquid-solid phase reaction. The ionic rare earth adsorbed on the surface of clay minerals are exchanged down into the liquid phase by NH_4^+ while the exchanged rare earth in liquid phase can be adsorbed by clay minerals in a certain extent again in the leaching process. So the ionic rare earth leaching process is essentially a dynamic reversible reaction; The reaction of impurities inhibitions YZJ-01 with the other metal ions adsorbed on the clay minerals will generate water-insoluble precipitate. The chemical reactions[18,19] in the leaching system of ammonia-nitrogen wastewater added by impurities inhibitions YZJ-01 are