

Reduction leaching of rare earth from ion-adsorption type rare earths ore with ferrous sulfate

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Abstract: The practice of *in-situ* leaching of the ion-adsorption type rare earths ore with ammonium sulfate could only leach most of rare earth in ion-exchangeable phase, but not the colloidal sediment phase. Therefore, the reduction leaching of rare earth from the ion-adsorption type rare earths ore with ferrous sulfate was innovatively put forward. The soak leaching process and the column leaching process were investigated in the present study. It was determined that ion-exchangeable phase could be released, and part of colloidal sediment phase rare earth could be reduction leached by the cations with reduction properties. The mechanism of reduction leaching was discussed with the Eh-pH diagram of cerium. Moreover, the stronger reduction of reductive ions, the greater acidity of leaching agent solution, and the higher reductive ion concentration, could result in the higher rare earth efficiency and the bigger cerium partition in the leaching liquor. In the ferrous sulfate column leaching process, the rare earth leaching rate and the rare earth efficiency were a little higher than with $(\text{NH}_4)_2\text{SO}_4$ agent, and the rare earth efficiency and the partitioning of cerium in leaching liquor could be about 102% and 5.31%, respectively. However, the ferrous sulfate leaching process revealed some problems, so compound leaching with magnesium sulfate and a small amount of ferrous sulfate was proposed to an excellent alternative leaching agent for further studies, which may realize efficiency extraction and be environment-friendly.

Keywords: rare earth; reduction leaching; ferrous sulfate; the ion-adsorption type rare earths ore

Rare earth elements (REEs), which contain 15 lanthanides, scandium and yttrium, are extensively used in areas such as new energy, new materials, energy conservation and environmental protection and electronic information, especially for the mid and heavy rare earths^[1]. The ion-adsorption type rare earths ore is a new kind of exogenous rare earth minerals and mainly located in Jiangxi, Guangdong, Guangxi and other provinces in South China^[2]. There are many advantages of the ores, such as complete in rare earth partition, low radioactivity, and rich in the middle and heavy rare earth elements. These ores are the main resource of mid and heavy rare earth in the world^[3]. Rare earth in the ores exists in four phases^[4]: (a) Water soluble phase: Water soluble phase rare earth refers to the rare earth dissolved in water, which accounts for less than one in ten thousand of total rare earth and would be negligible. (b) Ion-exchangeable phase: Ion-exchangeable phase rare earth refers to the rare earth adsorbed on clay minerals by electrostatic interaction, which accounts for more than 80% of total rare

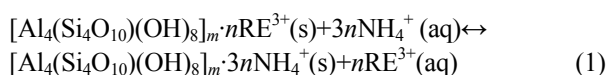
earth. It can be easily released into leaching liquor when encountering the cations (NH_4^+ , Mg^{2+} , Fe^{2+} and Fe^{3+}). (c) Colloidal sediment phase: One part of colloidal sediment phase rare earth refers to the rare earth adsorbed on iron manganese colloid by coordination. Another part refers to the rare earth oxide or hydroxide bonded with or deposited on the mineral, mainly $\text{CeO}_2/\text{Ce}(\text{OH})_4$. (d) Minerals phase: minerals phase rare earth refers to rare earth mineral crystals with ionic compounds as well as diffusion of rare earth ions to displace mineral crystals in the ores, such as bastnaesite, apatite and so on.

Nowadays, rare earth is recovered by *in-situ* leaching process with $(\text{NH}_4)_2\text{SO}_4$ solution in the industry, the leaching reaction is shown as Eq. (1). The leaching process of the ore is a kind of ion-exchangeable process between the positive ions in the solution and the clay minerals. Although average grade for the ion-adsorption type rare earths ore is 0.03%–0.3% in REO, the simple leaching process and high HREE composition make it very attractive^[4].

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where: s and aq represent solid phase and aqueous phase, respectively. The practice of *in-situ* leaching with $(\text{NH}_4)_2\text{SO}_4$ solution had revealed serious environmental problems, such as ammonia-nitrogen pollution in water body^[5]. Meanwhile, ammonium sulfate could only leach most of the rare earth in ion-exchangeable phase, but not the colloidal sediment phase. On the one hand, new studies in laboratory investigation recently were focused on the decrease or even elimination of ammonia-nitrogen emissions caused by ammonium sulfate leaching process^[6-8]. It is particularly worth mentioning that the magnesium salt compound leaching technology^[9] has been proposed and the technology may realize the ecological friendly leaching of the ion-adsorption type rare earths ore. On the other hand, the rare earth adsorbed on iron manganese colloid, which is one part of colloidal sediment phase rare earth, could only be released by ions with stronger adsorption ability or strong acidic conditions^[10]. Research works are carried out to recover colloidal sediment phase rare earth from particular rare earth mud with strongly acidic solution or ammonium chloride roasting method^[11,12]. These methods have some problems such as large acid consumption, small processing capacity. It is not suitable for recovering colloidal sediment phase rare earth from the ion-adsorption type rare earths ore. And it could not recover another part of colloidal sediment phase rare earth, namely $\text{CeO}_2/\text{Ce}(\text{OH})_4$.

In this paper, the reduction leaching of rare earth from ion-adsorption type rare earths ore with ferrous sulfate was innovatively put forward, with which partial colloidal phase and most ion-exchangeable phase rare earth could be leached together. The leaching characteristic of colloidal phase rare earth and effects of different factors on rare earth leached were investigated and discussed. It would be useful to provide a scientific approach and a theoretic basis for leaching colloidal phase rare earth. It would also be significant in better application of ion-adsorption type rare earths ore and the improvement of resource utilization.

1 Experimental

Table 2 Partitioning of rare earth in different phases for LT ore sample (%)

Phases	All	Ion-exchangeable	Colloidal sediment	Minerals	Phases	All	Ion-exchangeable	Colloidal sediment	Minerals
La_2O_3	20.30	21.87	9.37	23.17	Dy_2O_3	3.99	4.43	1.69	2.04
CeO_2	10.46	2.99	55.84	20.26	Ho_2O_3	0.79	0.88	0.22	0.80
Pr_6O_{11}	5.29	5.32	5.07	5.37	Er_2O_3	2.21	2.36	1.52	1.19
Nd_2O_3	17.49	18.68	9.93	16.97	Tm_2O_3	0.33	0.29	0.22	1.51
Sm_2O_3	3.66	3.98	2.24	1.35	Yb_2O_3	1.40	1.51	0.74	1.31
Eu_2O_3	0.70	0.68	0.26	2.56	Lu_2O_3	0.20	0.20	0.16	0.21
Gd_2O_3	4.09	4.57	1.72	1.61	Y_2O_3	28.39	31.46	10.76	20.97
Tb_4O_7	0.71	0.78	0.25	0.68					

1.1 Characterization and composition of experimental rare earths ore

The ion-adsorption type rare earths ore was collected from Liutang (LT) Rare Earth Mine area located in the Chongzuo City, Guangxi Province, China. The existing state of rare earth in the LT rare earths ore was determined with the sequential fractionating extraction methods by column leaching^[13]; the results are shown in Table 1. The rare earth existed mainly in ion-exchangeable phase and its content was 1.50 wt.%, accounting for 83.33 wt.% of total rare earth. There was 7.78 wt.% colloid sediment phase and 8.89 wt.% mineral phase, and hardly any aqueous soluble phase.

The partitioning of the different phase from the LT rare earths ore had been determined with ICP-AES (PerkinElmer, Co., Ltd., Optima 8300). As shown in Table 2, it is evident that the LT ore was a kind of rare earths ore with middle Y and rich Eu. And in the colloidal sediment phase, the partitioning of cerium could be 55.84%, more than half of total rare earth.

1.2 Apparatus and experimental procedure

All chemicals used in the experiments were of analytical grade, such as ferrous sulfate, manganese sulfate, ammonium sulfate, sulfuric acid and so on.

In the soak leaching process, 200 g dried rare earths ore in an average particle size of 1.0 mm was obtained by the method of quadrature, and was put into in a 400 mL beaker. 200 mL leaching agent solution with a certain concentration and pH was put in the beaker to take a soak leaching experiment. Leaching temperature was 25 °C and leaching time was 12 h. The beaker was covered by plastic film to prevent moisture loss. There was a stir once every 2 h in the leaching process. After leaching process, the leaching liquor was achieved with vacuum suction filter for solid-liquid separation. The leach-

Table 1 Rare earth content in different phases for LT ore sample (wt.%)

Phases	All	Water soluble	Ion-exchangeable	Colloidal sediment	Minerals
Content	1.80	negligible	1.50	0.14	0.16

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