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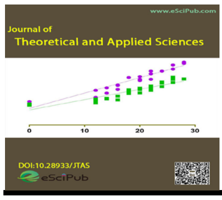

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Study on factors affecting rare earth leaching rate in acid leaching process of fly ash

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ABSTRACT

There is a large amount of enrichment of rare earth elements in Zhungeer coal and coal ash, making it possible to use fly ash as a source for industrial production of rare earth elements. In order to optimize the leaching process of rare earth elements in fly ash and increase the leaching rate, the circulating fluidized bed fly ash of Zhungeer Power Plant was used as the material, and the single factor test and orthogonal test were used to influence the leaching rate of rare earth elements in the acid leaching process of fly ash The factors were discussed, and the results showed that when fly ash and 3mol/L hydrochloric acid were leached at a ratio of 1:10 for 2h at 130 ^{0}C, the element leaching effect was the best, and the leaching rate could reach 97%.

Keywords: Fly ash, Hydrochloric acid, Rare earth, Leaching rate

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Rare earth elements include 17 lanthanide elements, scandium and yttrium in the periodic table. Rare earth elements are widely used in more than 40 industries such as national economy and national defense industry due to their unique magnetic, optical and electrical properties [1]. Rare earth elements, as "industrial vitamins", have extremely high strategic value, and China's reserves and production of rare earth resources are the first in the world [2]. However, due to a series of problems such as over-exploitation and resource waste of rare earth resources in recent ten years, Rare earth resources in China have become scarce [3]. Therefore, It is clearly pointed out in China's 11th Five-Year Plan that "scarce resources should be rationally utilized, strategic reserve resources and precious resources should be protected, and wastes with potential for resource utilization should be comprehensively recycled [4].

In recent years, studies on the extraction of high-value elements from fly ash have gradually increased [5]-[6], and breakthroughs have been made in the extraction of aluminum, lithium, gallium and other elements [7]-[8]. Many scholars have also carried out a lot of studies on the extraction of rare earth from coal and fly ash. Sun Yuzhuang [9] et al discussed the recovery and utilization of rare earth elements in coal and fly ash and proposed that the recovery and utilization index of rare earth elements in raw coal is 300mg/Kg. Liu Huidong et al. [10] achieved the joint extraction of gallium-niobium and rare earth from fly ash by alkali sintering and step-by-step leaching. Wang Hongbin et al. [11] separated scandium from alumina extraction by one-step acid solution. Ji Wanshun et al. successfully extracted yttrium from fly ash leaching solution by using the method of mixed extraction of two extraction agents [12]. Coal ash has vitreous structure with quartz and mullite as the main crystalline phase. During the formation of microbeads by high temperature cooling, short-range mullite crystalline phase is formed in microscopically, and its expression is 3SiO2·2Al2O3. And its long process distribution is very disordered glass state [13]-[14]. Due to the particularity of fly ash structure, in order to improve the leaching rate of rare earth in fly ash, it is necessary to destroy the glass phase in fly ash as much as possible to release the rare earth. Through acid leaching process, the glass phase in fly ash can be destroyed to transfer the rare earth into solution, and finally extracted in the form of precipitation. In this paper, the effects of leaching temperature, leaching time, solid-liquid ratio and hydrochloric acid concentration on the leaching rate of rare earth were studied, and the optimal technological parameters were obtained through experiments.

1. Test

1.1 Test materials

The fly ash used in the test comes from the fly ash of the circulating sulfide bed in Zhungeer Power Plant. The main components are shown in Table 1

Table 1 Composition of fly ash

Composition	SiO_2	Al_2O_3	CaO	Fe_2O_3	TiO_2	MgO	P_2O_5	K_2O	other
Content / %	44.64	44.0	3.73	3.35	1.70	0.54	0.49	0.53	1.02

It can be seen from Table 1 that SiO_2, Al_2O_3 and Fe_2O_3 account for more than 90%, among which

Al_2O_3 content is 44% and al/SI ratio is 1.12, which belongs to typical high aluminum powder coal ash. CaO, TiO_2, MgO, P_2O_5, K_2O accounted for about 8%, including 1.02% unburned coal.

1.2 Test instruments and equipment

Test reagents: Chemical reagents mainly include analytical pure hydrochloric acid, hydrofluoric acid, electronic pure nitric acid, perchloric acid, high-grade pure sodium hydroxide. Test water is deionized water.

Test instruments: electronic balance, vacuum blast drying oven, controllable temperature magnetic stirrer, inductively coupled plasma mass spectrometer (ICP-MS).

1.3 Test method and process

Will fly ash samples fully grinding 45 mesh sieve, with electronic balance in a flat bottom flasks, 20 g ash add ptfe magneton, adding HCl solution, leaching time, different under different temperature conditions to be controlled temperature magnetic stirrer to set parameters, working status in a flat bottom flask, at a constant rate rotating stirring, to stir, Filtration separation, volume determination and storage are carried out according to leaching time.

After constant volume, 1ml was put into the POLYtetrafluoroethylene digestion tank, and HCl was drained out on the electric heating plate. 10ml 3% HNO_3 solution was added into the digestion tank, and transferred to a 50mL colorimetric tube. The solution was watered with 3% HNO3 solution for several times, and the volume was constant to 50mL.

2. Test process, results and discussion

2.1 Influence of leaching temperature on leaching rate

Under the conditions of solid liquid volume mass ratio of 1:10, hydrochloric acid concentration of 1mol/L and leaching time of 1h, the equalization method was adopted to increase the leaching rate every 10℃, and the influence of leaching temperature on the leaching rate within the range of 90℃ to 130℃ was studied. The test results are shown in Figure 1.

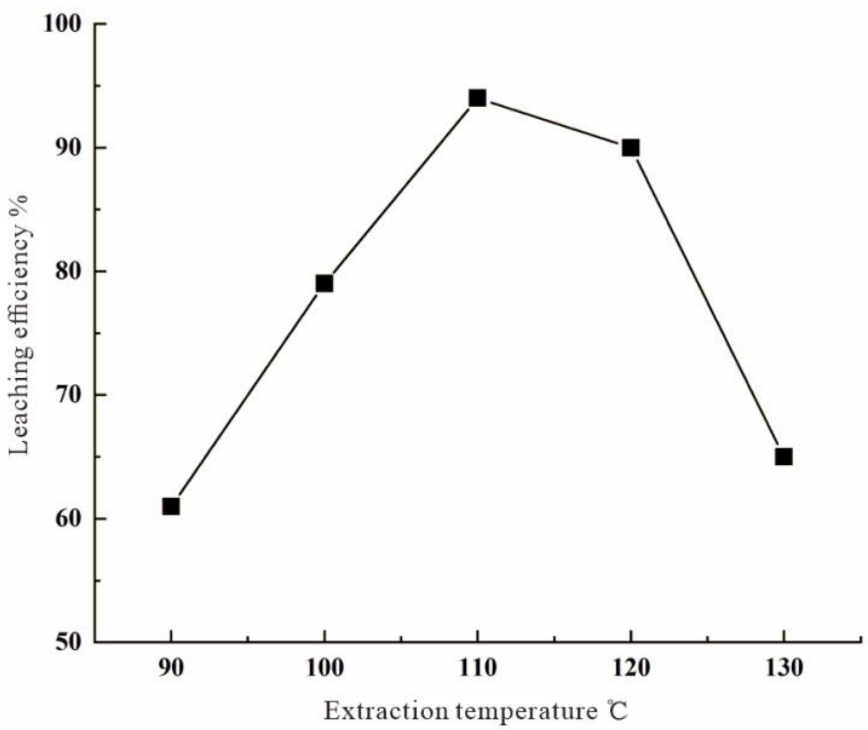

Figure.1 The influence of temperature on leaching rate

It can be seen from Figure 1 that temperature has a great influence on the leaching rate of rare earth. Between 90℃ and 130℃, the leaching rate of rare earth generally increases first and then decreases. When the temperature reaches 110℃, the leaching rate of rare earth reaches the peak of 94%. When the temperature exceeds 110℃, the leaching rate begins to decrease. With the increase of temperature, the intermolecular activity is intense, and the leaching rate of rare earth increases gradually. When the temperature reaches 110℃, the hydrogen chloride hydrate in the leaching solution reaches the euboiling point, and the hydrogen chloride in the leaching solution begins to volatilize, leading to the reduction of the leaching rate of rare earth. Therefore, the appropriate leaching temperature is 110℃.

2.2 Influence of hydrochloric acid concentration on leaching rate

Under the conditions of leaching temperature 110℃, solid-liquid ratio 1:10 and leaching time 1h, the influence of hydrochloric acid concentration 1mol/L, 2mol/L, 3mol/L and 4mol/L on the leaching rate of rare earth was studied. The test results are shown in Figure 3.

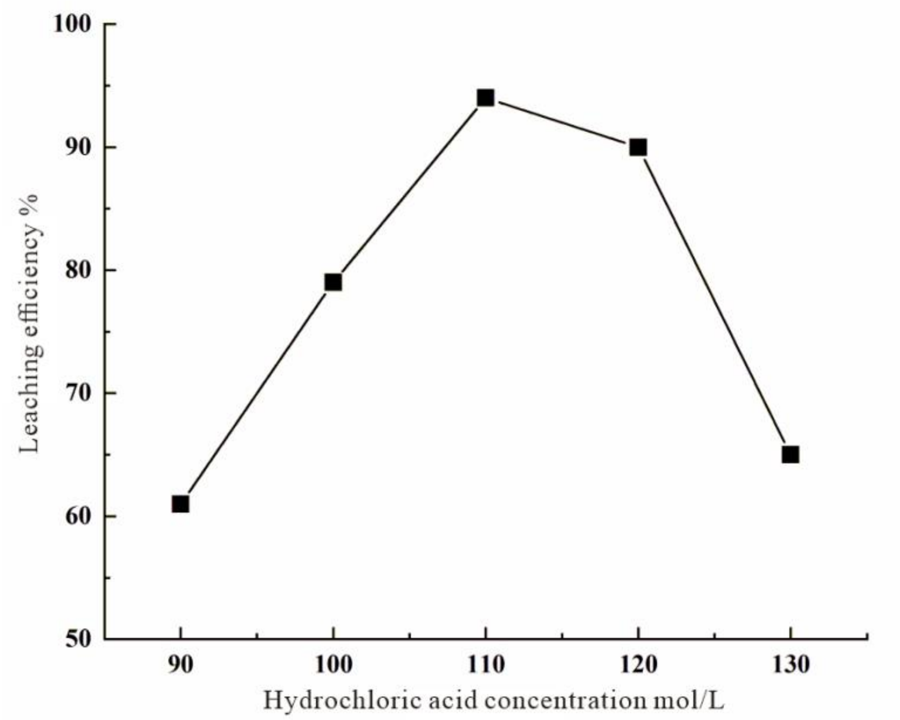

Figure.2 Effect of hydrochloric acid concentration on leaching rate

As can be seen from Figure 2, when hydrochloric acid concentration is 1mol/L, the leaching rate is only 48.5%; when hydrochloric acid concentration is 3mol/L, the leaching rate is 86.2%. It can be seen that hydrochloric acid concentration has a great influence on the leaching rate of rare earth, and the leaching rate increases significantly when hydrochloric acid concentration increases to 4mol/L. With the increase of hydrochloric acid concentration, leaching liquid of H + damage increase structure of fly ash, glass phase of rare earth was released, the process of rare earth leaching rate increased significantly, with the continue increase of acid concentration, dissolved other impurities also increased, forming a small amount of colloidal particles in the surface of solid particles, hindered the hydrochloric acid in the contact between solid particles and H +,Thus, the leaching rate is reduced. Therefore, the appropriate concentration of hydrochloric acid is 3mol/L.

2.3 Influence of leaching time on leaching

rate

Under the conditions of leaching temperature 110℃, solid-liquid volume mass ratio 1:10 and hydrochloric acid concentration 3mol/L, leaching time was set at 0.5h, 1h, 2h and 3h to investigate the influence of different leaching time on rare earth leaching rate. The test results are shown in Figure 2, as shown below: Leaching time on rare earth leaching rate is less affected, as the extension of leaching time, rare earth leaching rate is increased, the leaching time of 2 h, the leaching rate was 91.7%, and extend the leaching time, leaching rate change is not obvious, that when the leaching time at 2 h, fly ash can be basic completely leaching, leaching of rare earth, therefore, appropriate leaching time is 2 h.

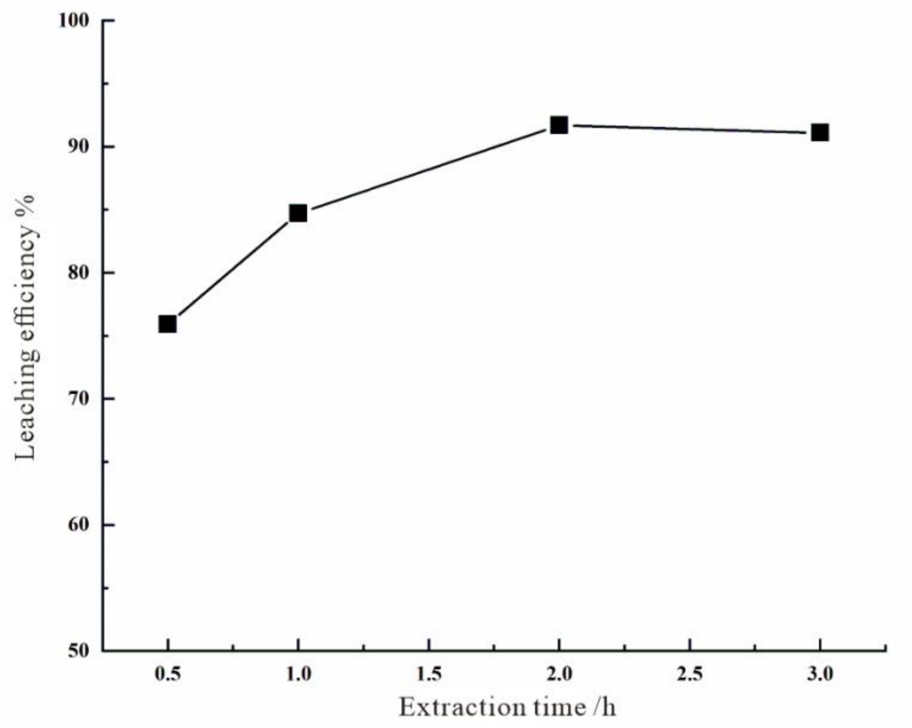

Figure.3 The effect of time on leaching rate

2.4 Influence of solid-liquid ratio on leaching rate

Under the conditions of 110℃ leaching temperature, 2h leaching time and 3mol/L hydrochloric acid concentration, four experiments were set with solid liquid volume mass ratio of 1:2, 1:5, 1:10 and 1:20 to comprehensively consider the influence of different solid liquid ratio on rare earth leaching rate. The test results are shown in Figure 4. When the solid-liquid ratio is 1:2, the leaching rate is only 28.1%; when the solid-liquid ratio is 1:10, the leaching rate is 94.1%. With the increase of the solid-liquid ratio, the leaching rate of rare earth is significantly improved. Generally speaking, the larger the volume of leaching agent is more conducive to the leaching of elements. The leaching rate decreased slightly, mainly because, with the increase of hydrochloric acid in the leaching solution, the silicic acid produced gradually increased, the silicic acid in the solution when washing fly ash will produce adsorption effect, adsorption of leached rare earth, reduce the leaching rate of rare earth. Therefore, solid-liquid ratio of 1:10 is determined as the best condition. The above results show that under single factor test conditions, the leaching rate of rare earth can reach 94.1% when the optimal technological parameters are solid-liquid ratio 1:10, leaching time 2h, leaching temperature 110 ℃ and hydrochloric acid concentration 3mol/L.

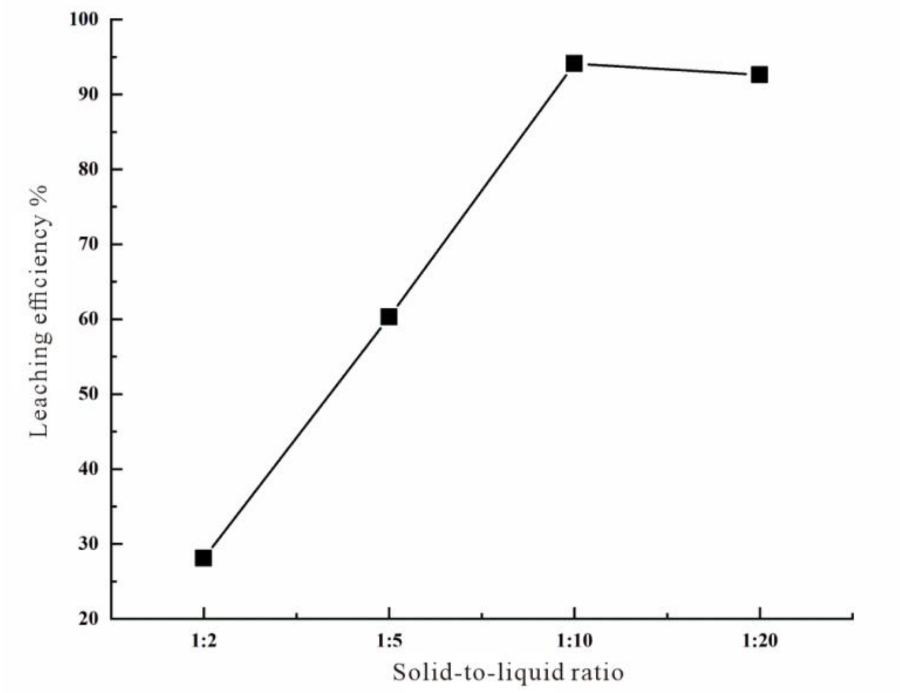

Figure.4 The effect of solid-liquid ratio on leaching rate

2.5 Orthogonal test

In order to ensure the accuracy of the test results, a four-factor and three-level orthogonal test was designed on the basis of the above tests, as shown in Table 2, to explore the optimal parameters of leaching rare earth from fly ash by acid leaching process.

Table 2 results of Orthogonal test

Test number	Element				Rareearth element leaching rate / %
	A/ Leaching temperature（℃）	B/ Leaching time（h）	C/Solid-liquid ratio	D/HCl concentration（mol/L）	
1	90	1	1:5	1	43.2
2	90	2	1:10	2	70.8
3	90	3	1:20	3	58.9
4	110	1	1:10	3	50.1
5	110	2	1:20	1	90.0
6	110	3	1:5	2	61.0
7	130	1	1:5	2	62.4
8	130	2	1:20	1	44.4
9	130	3	1:10	3	97.0
K_1	0.5763	0.5190	0.5533	0.5920	
K_2	0.6703	0.6840	0.7263	0.6473	
K_3	0.6793	0.6997	0.6443	0.6867	
R	0.1030	0.1507	0.1730	0.0947	

Influence of leaching temperature on the leaching rate of rare earth elements in fly ash: In the acid leaching process, the selection of temperature is crucial. It can be seen from Table 6 that the leaching effect is best when the temperature is 130℃, so the leaching temperature is 130℃.

The effect of leaching time on the leaching rate of rare earth elements in fly ash: the leaching effect of rare earth elements is the best when the leaching time is 3h. In industrial production, the production efficiency is the first, and the optimal leaching time is 3h.

The influence of solid-liquid ratio on the leaching rate of rare earth elements in fly ash is as follows: when solid-liquid ratio is 1:5, the leaching effect is very low; when solid-liquid ratio is increased to 1:10, the leaching effect is the best, so the optimal solid-liquid ratio condition is 1:10

The influence of hydrochloric acid concentration on the leaching rate of rare earth elements in fly ash: The concentration of hydrochloric acid is crucial to the leaching efficiency of acid leaching process. With the increase of hydrochloric acid concentration, the leaching rate of rare earth elements gradually reaches the peak. When the concentration of hydrochloric acid reaches 3mol/L, the leaching rate of rare earth elements is the highest.

Process conditions: According to the orthogonal test results of leaching rare earth elements from fly ash, the optimal horizontal combination is obtained as follows: leaching temperature 130℃, leaching time 3h, solid-liquid ratio 1:10, hydrochloric acid concentration 3mol/L.

2.6 Verification test

The optimal combination was obtained by orthogonal test: leaching temperature 130 ℃ , leaching time 3h, solid-liquid ratio 1:10, hydrochloric acid concentration 3mol/L. By observing the orthogonal test results in Table 5, it is found that the optimal combination exists in the orthogonal test table. Under these conditions, the leaching rate of rare earth can reach 97%. Therefore, the best leaching conditions of rare earth elements in acid leaching process of pulverized coal are as follows: extraction temperature 130℃, leaching time 3h, solid-liquid ratio 1:10, hydrochloric acid concentration 3mol/L.

3. Conclusion

Through single factor test and orthogonal test, the factors affecting the leaching rate of rare earth in acid leaching process of fly ash were studied. The results showed that the best leaching conditions of rare earth in acid leaching process of fly ash were as follows: leaching temperature 130℃, leaching time 3h, solid-liquid ratio 1:10, hydrochloric acid concentration 3mol/L, under which the leaching rate of rare earth could reach 97%.

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