Preparation of polymeric aluminum ferric sulphate from waste residue of aluminum industry

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Abstract. Polymeric aluminum ferric sulphate(PAFS) was prepared from high-sulfur bauxite flotation tailings and red mud by roasting, acid leaching and polymerization. The effects of leaching temperature, leaching time, liquid-solid ratio on the leaching rate of Al^{3+} and Fe^{3+} were investigated. The optimal leaching conditions are as follows: leaching temperature 100°C, leaching time 90 min, sulfuric acid concentration 4.5mol/L and liquid-solid ratio 5 mg/L. Infrared spectroscopy and X-ray diffraction analysis was carried out on the PAFS prepared under the optimum process parameters. The characterization of PAFS shows that the synthesized PAFS had polymeric aluminum, iron and hydroxyl structures. Wastewater disposal test of synthetic PAFS shows that the removal rates of COD, turbidity and chromaticity are 45.61%, 75% and 94.18%, respectively.

1 Introduction

High-sulfur bauxite flotation tailings is a kind of solid waste discharged from the bauxite ore beneficiation process^[1]. Red mud, a highly alkaline residue, is a solid waste in production of alumina^[2]. With increasingly stringent environmental protection policies, how to dispose of red mud and bauxite tailings at low cost has become one of the problems that restrict the sustainable development of the aluminum industry. A lot of research has been conducted on red mud and bauxite tailings, which are mainly used for the production of construction materials^[3-5], filling materials^[6,7], refractory materials^[8], functional materials^[9-11], etc. However, there are still problems such as low value-added products or high process energy consumption or limited solid waste consumption, resulting that most of produced red mud and bauxite flotation tailings are stored in landfills^[12]. Based on the principle of complementary composition among multiple solid wastes, a study was conducted on the preparation of polymeric aluminium ferric sulfate flocculant (PAFS) from red mud and bauxite tailings, aiming to promote the reduction and resourceization of solid wastes in aluminum industry and to achieve the purpose of turning waste into treasure.

2 Experimental

2.1. Materials

High-sulfur bauxite flotation tailings and red mud were collected from an alumina plant of Chinalco, composed of particles less than 100 screen mesh. The chemical composition of raw material is shown in table1.

Mineralogical composition of raw material was established by X-ray diffraction. As shown in Fig.1, goethite, hematite, quartz, and boehmite were identified as main phases of red mud; diaspora, pyrite, illite, kaolinite, and anatase were identified as main phases of high-sulfur bauxite flotation tailings.

Table 1. Chemical composition of raw material

Composition	Fe ₂ O ₃	TiO ₂	Na ₂ O	K ₂ O	CaO
Red mud	67.01	3.92	1.725	0.078	0.35
Tailings	26.3	2.25	0.13	1.19	0.53
Composition	SiO ₂	Al ₂ O ₃	MgO	S	LOI
Red mud	5.01	7.90	0.09	0.095	13.24
Tailings	8.99	36.81	0.27	19.10	--

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Figure 1. XRD pattern of raw material

2.2. Apparatus

Chemical reagents: Concentrated sulfuric acid 98%; Analytical pure sodium bicarbonate; 35% hydrogen peroxide.

Equipment: Electronic Balance (AUW120D); Rex laboratory pH meter (PHS-3E); Electrothermal thermostatic water bath (DK-S22/S24). The water bath apparatus is shown in Fig.2, which is used to leach aluminum and iron from the waste slags.

1- Thermostatic water bath; 2- Beaker; 3- Stirrer;
4- Contact thermometer; 5- Control box

Figure 2 Schematic diagram of aluminum and iron leaching experimental device

2.3. Experimental method

With red mud and tailings as the main raw materials, the polymerized aluminum sulfate iron flocculant is synthesized by acid leaching, oxidation, alkalization, maturation and aging processes. The reaction mechanism of different process steps are shown in table 2.

Table 2. Flocculant preparation mechanism

Process steps	Mechanism of reaction
Microwave roasting of tailings	$\text{Fe}_2\text{S}=2\text{FeS}_{1+x}+(1-x)/2\text{S}_2$ $\text{S}_2+2\text{O}_2=2\text{SO}_2$ $4\text{FeS}_{1+x}+(4x+7)\text{O}_2=2\text{Fe}_2\text{O}_3+4(1+x)\text{SO}_2$
Acid leaching	$\text{Al}_2\text{O}_3+\text{H}_2\text{SO}_4=\text{Al}_2(\text{SO}_4)_3+3\text{H}_2\text{O}$

(red mud and sintered slag of tailings)	$\text{Fe}_2\text{O}_3+\text{H}_2\text{SO}_4=\text{Al}_2(\text{SO}_4)_3+3\text{H}_2\text{O}$
Alkalization (Aluminum and iron leaching solution)	$\text{Al}_2(\text{SO}_4)_3+n\text{H}_2\text{O}=\text{Al}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}+n/2\text{H}_2\text{SO}_4$ $\text{Fe}_2(\text{SO}_4)_3+n\text{H}_2\text{O}=\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}+n/2\text{H}_2\text{SO}_4$
Polymerization	$m\text{Al}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}=[\text{Al}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}]_m$ $k\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}=[\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}]_k$

The preparation process is shown in Fig.3.

Figure 3 Polymerized aluminum sulfate iron preparation process flow chart

The sulfur in the high sulfur bauxite flotation tailings was removed by roasting at 600°C for 20 min. The sulfur-containing flue gas from the roasting process are absorbed by red mud slurry; then the slag and red mud slurry are leached by a certain concentration of sulfuric acid to obtain a high concentration of aluminum and iron leachate; the leachate is finally made into polymerized aluminum sulfate and iron flocculant through alkalization, polymerization and maturation.

3 Results and discussion

3.1. Optimization of acid leaching process

The flue gas generated during the roasting of high sulfur bauxite flotation tailings is absorbed by the red mud slurry. A small amount of aluminum and iron ions are leached from the red mud slurry. In order to obtain a high and properly proportioned concentration of aluminum and iron ions, sintered slag is added to the slurry, which is half the weight of the red mud, and then further leached with sulfuric acid.

3.1.1 Effect of temperature on leaching rate of Al^{3+} and Fe^{3+}

The relationship between leaching rate of aluminum and iron and temperature is shown in Fig.4, which was obtained under the conditions of sulfuric acid concentration of 5.30 mol/L, liquid-to-solid ratio of 6 mL/g, and reaction time of 90 min.

It is clear from the illustrations that both Al^{3+} and Fe^{3+} leaching ratio increased with the increase of heating

temperature. The reasonable explanation is that the Brownian motion between molecules intensifies and more effective collisions are completed as the temperature increases. Although the increase in temperature is beneficial to improve the leaching rate, the increase in temperature will make the energy consumption increase. Considering comprehensively, 100°C was selected as the suitable acid leaching temperature.

Figure 4 Effect of temperature on leaching rate of Al³⁺ and Fe³⁺

3.1.2 Effect of time on leaching rate of Al³⁺ and Fe³⁺

The relationship between leaching rate of aluminum and iron and time is shown in Fig.5, which was obtained under the conditions of sulfuric acid concentration of 5.30 mol/L, liquid-to-solid ratio of 6 mL/g, and reaction temperature of 100°C.

Figure 5 Effect of time on leaching rate of Al³⁺ and Fe³⁺

As seen in Fig.5, the leaching rate of aluminum and iron increased with the increase of leaching time. For the first 90 min, the aluminum and iron leaching rates increased significantly, and then the increase was not obvious. Considering that the leaching process was carried out at high temperature, the suitable acid leaching time was determined to be 90 min from the viewpoint of energy consumption and efficiency.

3.1.3 Effect of sulfuric acid concentration on leaching rate of Al³⁺ and Fe³⁺

The relationship between leaching rate of aluminum and iron and sulfuric acid concentration is shown in Fig.6, which was obtained under the conditions of reaction temperature of 100°C, liquid-to-solid ratio of 6 mL/g, and reaction time of 90 min.

Figure 6 Effect of sulfuric acid concentration on leaching rate of Al³⁺ and Fe³⁺

As shown in Figure 6, the leaching rates of Al³⁺ and Fe³⁺ first increased and then decreased with the increase of sulfuric acid concentration. Specifically, when the sulfuric acid concentration is less than 4.5 mol/L, the higher the acid concentration, the more molecules can be activated per unit volume, which is more conducive to the leaching reaction. However, when the sulfuric acid concentration is higher than 4.5 mol/L, sulfuric acid reacts with aluminum and iron oxides to produce sulfate, which is enriched on the oxide surface and deteriorates the leaching conditions. Therefore, the high concentration of sulfuric acid does not promote the leaching of metal oxides. It is more appropriate to choose 4.5 mol/L sulfuric acid for leaching.

3.1.4 Effect of liquid-to-solid ratio on leaching rate of Al³⁺ and Fe³⁺

The relationship between leaching rate of Al³⁺ and Fe³⁺ and liquid-to-solid ratio is shown in Fig.8, which was obtained under the conditions of reaction temperature of 100°C, sulfuric acid concentration of 4.5 mol/L, and reaction time of 90 min.

It can be seen from Fig.7 that the leaching rate of Al³⁺ and Fe³⁺ increases with the increase of liquid-solid ratio. Especially when the liquid-solid ratio is less than 5 mg/L, it has a significant effect on the leaching rate. Considering comprehensively, the liquid-solid ratio of 5 mg/L is more reasonable.

Figure 7 Effect of liquid-solid ratio on leaching rate of Al³⁺ and Fe³⁺

3.2. Leachate polymerization and product characterization

Al³⁺ and Fe³⁺ are polymerized by adding alkali to the leaches, which are obtained under optimal leaching conditions. The polymerization process involves the following chemical reactions^[13].

According to the literature^[14,15], 1 mol/L sodium bicarbonate solution was used as the alkali, and the polymerization temperature was controlled at 85°C. The alkali was slowly added and stirred until the pH of the solution reached 2.95. After the alkalization, the solution was matured for 4h at 60°C with a stirring rate of 300 r/min. Finally, the liquid PAFS was obtained by static cool down for 24h.

PAFS (liquid) was dried under vacuum and low temperature environment. XRD and IR patterns of the prepared PAFS samples are shown in Fig.8.

Figure 8 XRD and Infrared spectroscopy of the prepared PAFS

It can be seen from Fig.8 (a) that only the diffraction peak of sodium sulfate exists, but there are no diffraction peaks such as aluminum sulfate, ferric sulfate and sodium bicarbonate. It can be inferred that Al³⁺、Fe³⁺ and SO₄²⁻ in the solution polymerize into amorphous material.

As seen in Fig.8(b), the absorption peak formed between 3400 and 3550cm⁻¹ is generated by the stretching vibration of the OH-group, and the area occupied by this peak is wide, so it is presumed that the hydroxyl content in PAFS is high. The absorption peak near 1635 cm⁻¹ is due to the bending vibration of adsorbed water, coordination water and crystalline water; the SO₄²⁻ absorption peak at 1000~1200cm⁻¹ is generated by the stretching vibration of SO₄²⁻. In the low wave number interval from 553 to 732cm⁻¹, there are also Al-OH-Al (732cm⁻¹) and Fe-OH-Fe (671cm⁻¹) in-plane bending vibration peaks^[16], but the intensity of both is greatly diminished. Rather, the bending vibration peaks interact to form a peak between 610 and 640, which is consistent with the results of the literature^[17].

3.3. Industrial wastewater disposal test

The industrial wastewater was obtained from a chemical plant in Xinxiang, Henan Province, with original pH=6.52, COD=198.6 mg/L, turbidity=260 NUT, and chromaticity=8(times). Experimental synthetic PAFS and commercial PAFS (purchased from Zhengzhou Yisheng Chemical Co., Ltd.) were used for flocculation tests, respectively. The initial pH of the wastewater was adjusted to 7.0 and then the mass of the PAFS injection was controlled to be 0.18% of the wastewater. The treatment effect is shown in Table 3, which shows that the COD removal performance of the experimental synthetic PAFS is slightly lower than that of commercial product, while the turbidity and chromaticity removal rates are comparable.

Table 3. Flocculation test results of industrial wastewater

Flocculant	COD/%	Chromaticity/%	Turbidity/%
Synthetic PAFS	45.61	75.0	94.18
Commercial PAFS	50.65	75.0	93.23

4 Conclusions

In this paper, solid wastes (red mud and bauxite tailings) from the aluminum industry were used as raw materials to synthesize PAFS by roasting, acid leaching and polymerization, and the following conclusions can be obtained.

(1) It is feasible to synthesize PAFS by roasting, acid leaching and polymerization with red mud and bauxite tailings as raw materials. This technology is expected to promote the reduction of solid waste in aluminum industry and turn waste into treasure.

(2) The optimal leaching conditions of Al^{3+} and Fe^{3+} are as follows: leaching temperature 100°C , leaching time 90 min, sulfuric acid concentration 4.5mol/L and liquid-solid ratio 5 mg/L .

(3) Wastewater disposal test shows that the COD removal performance of the experimental synthetic PAFS is slightly lower than that of commercial product, while the turbidity and chromaticity removal rates are comparable.

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