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Removal of ferric ions from aluminum solutions by solvent extraction, part I: Iron removal

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ABSTRACT

This study investigated removal of ferric ions from aluminum solutions to explore the basic data for the recovery of aluminum resources from coal spoil. A novel synergic extractant, consisting of di-(2-ethylhexyl) phosphoric acid (P204) and tertiary amine (N235) with sulfonated kerosene (SK) as diluent, was adopted in this research. The influences of reaction time, pH, temperature, and phase ratio, on the extraction processes were systematically investigated. Result showed the Fe removal was greater than 97% in only one contact under optimal conditions. The corresponding stripping processes were also performed focusing on the effects of phase ratio, H_2SO_4 concentration, and reaction time. Almost 99% Fe was easily stripped using 1 mol/L H_2SO_4. These findings indicated that compared with single extractants, the new synergic extractant shows significant advantages.

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1. Introduction

Coal spoil (CS) is a byproduct generated during mining, washing, and processing of coal. Numerous CS stacks have accumulated without proper treatment, which not only cover large areas of land but also cause many environmental problems. It is therefore imperative to develop new technologies [1–4] to promote the utilization of CS, especially in coal-based, energy-consuming countries such as China.

In fact, CS is a valuable mineral resource. Its main components are SiO_2 and Al_2O_3, and generally, the content of the latter ranges from 15% to 40%. With increasing demands for aluminum oxide and declining in bauxite reserves, CS has drawn increasing attention as a potential alternative non-bauxite aluminum resource. Although many methods have been proposed for the extraction of aluminum from CS, the previous research of the current authors found that a sulfuric acid leaching route presents more promising prospects. A proposed process is as follows: activation of coal spoils using compound activation followed by leaching in sulfuric acid, crystallization of aluminum sulfate and removal of ferric sulfate by solvent extraction, enabling the production of Al_2O_3 or other aluminum compounds.

Removal of ferric sulfate (Fe^{3+}) from aluminum sulfate by solvent extraction is a key step in the process due to the relatively high iron content with an Al/Fe weight ratio of 30.27 in crystallized $Al_2(SO_4)_3 \cdot 18H_2O$, which leads to poor Al_2O_3 quality. A variety of extractants such as P204 [5–9], OPAP [5,6], HEHEHP [10], Aliquat 336 [11], Cyanex 921 [14] and LIX860 [12] have been used for solvent extraction of Fe^{3+}. Among them, di-(2-ethylhexyl) phosphoric acid (P204) is the most widely used extractant in hydrometallurgical process for the separation and purification of metals such as aluminum and iron. It has been proved that mechanism [13] of Fe^{3+} extraction with P204 is ion-exchange at low acidity and solvent effect at high acidity and P204 is a very effective extractant for Fe^{3+} removal. However, the extracting of Fe^{3+} with P204 requires a long contacting time and the stripping of Fe^{3+} from the loaded P204 is very difficult, which hinders the use of P204 to remove Fe^{3+} from acid solution. In view of the above, in order to achieve a higher Fe removal within a shorter time and to make the stripping process easier, this research proposed a synergistic solvent extraction (SSX) system, and the effects of a number of experimental parameters, on the Fe^{3+} removal were systematically investigated.

2. Experimental

2.1. Reagents and equipment

Di-(2-ethylhexyl) phosphoric acid (P204, Shanghai Aoke Industrial Co., Ltd., China), Tertiary amine (N235, Shanghai Rare-Earth Chemical Co., Ltd., China), sulfonated kerosene (SK, Shanghai Rare-Earth Chemical Co., Ltd., China), n-pentyl alcohol (Sinopharm

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Chemical Reagent Co., Ltd., China), isoamyl alcohol (Sinopharm Chemical Reagent Co., Ltd., China) and cyclohexane (Sinopharm Chemical Reagent Co., Ltd., China) were used without purification.

$Al_2(SO_4)_3 \cdot 18H_2O$, $Fe_2(SO_4)_3$ and H_2SO_4 (Analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. $Al_2(SO_4)_3 \cdot 18H_2O$ was dissolved in deionized water. The solution was filtered through a G4 sand-core funnel to eliminate residual solids, and then recrystallized to obtain a highly pure starting material. The concentrations of Al^{3+} and Fe^{3+} (denoted by Al_2O_3 and Fe_2O_3 in the standard) were determined by chemical titration and spectrophotometric method respectively according to the national standard GB/T 1574-1995. The content of Al^{3+} was titrated with zinc acetate standard solution utilizing ethylenediamine tetra-acetic acid (EDTA) as a masking agent; By using a 4802 UV–VIS double beam spectrophotometer (Unico (Shanghai) Instrument Co., Ltd., China), the concentration of Fe^{3+} was determined colorimetrically at 570 nm after adding tiron reagent. The starting solution was prepared with a mass ratio of Al^{3+}/Fe^{3+} of 30.27, which was consistent with previous research results, by dissolving $Al_2(SO_4)_3 \cdot 18H_2O$ and $Fe_2(SO_4)_3$ in deionized water, giving an initial pH of 1.5–2 and Fe^{3+} concentration of around 1.26 g/L. The pH of the aqueous phase was determined using a SevenMulti pH and Ion Meter (S40, Mettler Toledo) and thermal control was provided by a Huber Refrigeration bath circulator (CC-415, Huber Kältemaschinenbau GmbH).

2.2. Procedures

Initial experiments using different proportions of extractants and the effects of experimental parameters on the extents of Fe^{3+} removal and stripping were studied in 100 mL globe-shaped funnels by mixing 20 mL each of the aqueous and organic phases for predetermined periods of time at 600 rpm. The emulsion was then allowed to stand for 10 min, after which samples of the aqueous phase were withdrawn for analysis. Fe removals were calculated using the amount of Fe^{3+} in aqueous phase divided by the amount of total Fe^{3+}, while the distribution ratios (D) were calculated as the ratio of the concentration of Fe^{3+} in the organic phase and that in the aqueous phase at equilibrium.

3. Results and discussion

3.1. Effect of organic compositions

Solvent extraction of ferric ions from sulfate solutions was carried out with the synthetic solution containing 1.26 g/L Fe^{3+} and the organic systems consisting of 30% P204 and 30% N235 in diluent SK separately, and the SSX organic system consisting of 15% P204 and 15% N235 in SK at 25 °C and an A/O ratio of 1:1. The extent of Fe removal and the distribution ratios (D) are presented in Table 1. With the organic systems consisting of 30% P204 in SK, the iron removal was 66.5% and the distribution ratio D 2.0, nevertheless, with the organic system consisting of 15% P204 and 15% N235 in SK, the iron removal increased to 88.2%, and the distribution ratio to 7.5. This is the evidence of synergistic effect with the addition of N235 to the P204 system, leading to a significant improvement of iron removal. It should be pointed out that using
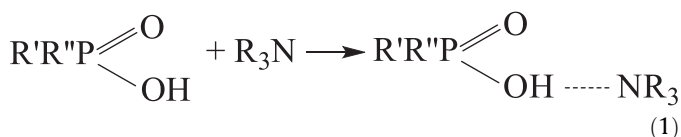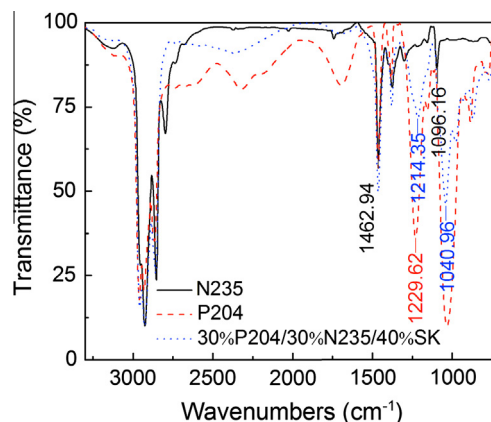
SK as the diluent could be attributed to the subsequent reasons. First, a diluent should be of low toxicity, so that it could be used in large-scale industrial processes. The median lethal dose (LD_{50}), the dose required to kill half the members of a tested population after a specified test duration, is frequently used as a general indicator of a substance's acute toxicity. A lower LD_{50} is indicative of increased toxicity. Universally used diluents in liquid–liquid extraction are SK, n-pentyl alcohol, isoamyl alcohol, and cyclohexane, with their LD_{50} of 36,000, 2200, 1300 and 12,705 mg/kg respectively, which implies that SK enjoys the lowest toxicity. Furthermore, Fe removals using the SSX system in SK, n-pentyl alcohol, isoamyl alcohol, and cyclohexane diluents were 88.19%, 81.38%, 78.27% and 86.62% respectively under the same experimental conditions. As a result, SK was chosen to be the diluent, owing to its low toxicity and high Fe removal ability.

Infrared spectra (Magna-IR 550, 4000–400 cm^{-1}) of P204, N235 and the SSX system is presented in Fig.1. Peaks from 2800 to 3000 and 1300 to 1500 cm^{-1} represent the —C—H symmetric and asymmetric deformation vibrations and stretching vibrations [11]. The characteristic peak at 1229.62 cm^{-1} due to the stretching vibration of the P=O bond in P204 [14] has shifted to 1214.35 cm^{-1} in the SSX system, while the peak at 1096.16 cm^{-1} in N235 which is assigned to C—N stretching vibration has shifted to 1040.96 cm^{-1} in the SSX system. This phenomenon suggests that both P204 and N235 played roles in the extraction reaction in the mixed P204 and N235 system and it is this reaction that has promoted Fe extraction [15]. Thermodynamically speaking, it seems rather difficult to explain synergistic mechanism from the viewpoint of saturation of coordination due to complexity of the system, nevertheless, it can be explained probably by a number of chemical equilibria in the solvent system. When P204

$$\left(R'R''P{\Large\diagup}\begin{matrix}O\\\\OH\end{matrix} \right)$$

and N235 (R_3N) are present in the organic phase, they can form a molecular association, particularly in a low-acidity solution as shown below:

$$R'R''P{\Large\diagup}\begin{matrix}O\\\\OH\end{matrix} + R_3N \longrightarrow R'R''P{\Large\diagup}\begin{matrix}O\\\\OH\end{matrix} \text{-----} NR_3 \tag{1}$$

The formation of a molecular association compound will increase the dissociation of P204 to hydrogen ions, which will result in an increase in the extraction of Fe^{3+} by cation exchange. The addition of N235 to P204 also shows synergism from the viewpoint of kinetics. The kinetics of Fe extraction using P204-N235

Fig. 1. IR spectra of P204, N235 and the SSX system.

Table 1
Fe removal using P204, N235, and their mixture.

Extractant	SK	Fe removal (%)	D
30% P204	70%	66.51	1.99
30% N235	70%	68.47	2.17
15% P204/15% N235	70%	88.19	7.47