Research Article

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A novel separation method of the valuable components for activated clay production wastewater

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Abstract: The acidic wastewater produced by the wet production of activated clay contains valuable components such as iron and aluminum. The precipitation method was successfully introduced to separate iron and aluminum from the activated clay production wastewater step by step, which can not only recover the valuable components, but also avoid environmental pollution. In the separation process, gypsum, iron aluminum phosphate, alumina, and sodium sulfate were prepared, and the phase compositions of separation products were analyzed by XRD and IR. The main influencing factors in the separation of iron and aluminum components were studied by single factor experiment. The results show that at the optimized conditions, phosphorus/iron molar ratio 6.0, the system pH 3.0, the reaction temperature 343 K, and the reaction time 90 min, the iron(III) ion in the system can form a sodium-containing aluminum iron phosphate double salt, and the filtrate after separating Fe3+ and part of Al3+ can meet the requirements for forming high-purity Al2O3. During the phosphate precipitation process, the hypothesis should be correct that Al3+ reacts with PO43- to form an AlPO4 skeleton, Fe3+ isomorphically replaces Al3+ in the [AlO4] tetrahedral, and adsorption occurs simultaneously, with Na+ occupying the terminal acid sites, P(Al)–OH.

Keywords: wastewater, precipitation, mechanism, activated clay

1 Introduction

Bentonite is a clay rock composed mainly of montmorillonite. Montmorillonite is a 2:1 layered silicate mineral composed of [SiO4] tetrahedral sheet and [AlO6] octahedral sheet [1], its structural formula can be expressed as (Na, Ca)0.3–0.6[(Al, Mg)2Si4O10(OH)2]·nH2O [2,3]. Montmorillonite has many advantages, such as large specific surface area, good adsorption and cation exchange. The activated clay prepared with acid activation can be widely used in the decolorization of edible oil refining [4], sewage treatment [5], petrochemical refining and waste oil regeneration [6] and other fields. However, the wastewater generated during the acid activation process has not been reasonably separated and utilized.

Sulfuric acid [7], nitric acid [8], hydrochloric acid [9], etc. are usually used to activate bentonite for activated clay preparation. The acid activate process is divided into wet method, dry method and semi-dry method [10]. Sulfuric acid wet activation is the most important process for activated clay production. When bentonite is infiltrated in the sulfuric acid solution system, the free H+...
quickly produces metal-proton exchange reaction with the interlayer cations Na\(^+\), Ca\(^{2+}\) of montmorillonite [11]. The octahedral cations, Al\(^{3+}\), Mg\(^{2+}\), Fe\(^{3+}\), etc., in the montmorillonite structure were partially dissolved out [12], which increased the negative charge of the montmorillonite structure layer and improved the adsorption decolorization performance [13]. Therefore, the acidic wastewater produced by wet process activated clay contains a certain amount of valuable components such as aluminum, iron, and magnesium. The wastewater composition is slightly different due to the raw materials and process.

In industry, the wastewater discharged in activated clay production is mainly neutralized by lime, carbide slag, etc. [14]. Although the neutralization process is simple and has good effects, there are valuable components such as aluminum and iron in the wastewater that cannot be effectively separated and utilized, and the neutralization slag is difficult to handle or use. Although the wastewater produced by the activated clay process has been used to separate valuable components to produce polyaluminum ferric sulfate, aluminum sulfate, alum, cryolite, etc., there are still harsh reaction conditions and low product purity, and it is difficult to remove iron impurities. Compared with other chemical precipitation methods, the advantage of phosphate precipitation method is that the product is more stable under acidic conditions, and phosphoric acid, phosphate, phosphorus-containing organic matter, etc. are usually as a precipitant. The report pointed out that under strong acid conditions, Fe\(^{3+}\) was first used to replace Pb\(^{2+}\) in Pb-EDTA solution, and then disodium hydrogen phosphate was used to efficiently recover Pb\(^{2+}\) bearing precipitates [17]. Tang et al. [18] also combined phosphate precipitation with biological adsorption to separate the lead in the solution well. In Amran and Bouhidel study [19], the valuable components in the acid leaching solution of sludge can be precipitated in steps effectively using different dosage of phosphoric acid.

In this article, the precipitation principle and precipitation-dissolution equilibrium of insoluble electrolyte in supersaturated state were applied. Based on the characteristics of valuable components of acid wastewater generated in the activated clay production process and the needs of production and environmental protection, the separation of iron and aluminum in the wastewater after pre-neutralization treatment was accomplished using phosphate precipitation and alkali precipitation respectively. By means of chemical composition analysis, IR and XRD analysis, the properties of separated product was studied. This paper focuses on achieving the efficient separation of valuable components such as iron and aluminum and solving the worries about the difficulty of acid wastewater handling in the activated clay production process.

## 2 Experimental

### 2.1 Materials and equipment

Trisodium phosphate dodecahydrate (AR) and sodium hydroxide (AR) are purchased from Chengdu Kelong Chemical Reagent CO., LTD., China.

The activated clay acidic raw liquid (HWW) is the wastewater generated during the sulfuric acid production process of an enterprise in Jiangxi, China. The main components and pH value of the waste liquid HWW and the solution (HWWS) after neutralization and filtering with calcium hydroxide are shown in Table 1.

The equipment used in experiment mainly includes beaker (100, 250, 1,000, 2,500 mL), collector type constant temperature magnetic stirrer (Zhengzhou Yingyu Lingke Instrument Equipment Co., Ltd., China, DF-101S), circulating water type vacuum pump (Lingke Instrument Equipment Co., Ltd., China, DF-101), circulating water type vacuum pump (Gongyi Yuhua Instrument Co., Ltd., China, SHZ-D(III)), electric heating constant temperature oven (Shanghai Pudong Rongfeng Scientific Instrument Co., Ltd., China, 202-1), box-type resistance furnace (Mianyang Golden Crown Co., Ltd., China, KSD-6-1300), magnetic stirrer (Shanghai Pudong Rongfeng Scientific Instrument Co., Ltd., China, JT2003), Youpu series ultrapure water machine (Chengdu Ultrapure Technology Co., Ltd., China, UPT-11-10T), digital pH meter (Shanghai Yidian Scientific Instrument Co., Ltd., China, PHS-3C).

### 2.2 Experimental principle

The activated clay production wastewater mainly contains Fe\(^{3+}\), Al\(^{3+}\), SO\(_4^{2-}\), H\(^+\). After neutralization for HWW, the iron and aluminum components in wastewater are separated step by step, and the separation theory is based on the metathesis reaction. During the neutralization process, calcium hydroxide interacts with the free acid in

<table>
<thead>
<tr>
<th>Table 1: Main components and pH value of HWW and HWWS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>HWW</td>
</tr>
<tr>
<td>HWWS</td>
</tr>
</tbody>
</table>
the system to produce calcium sulfate and water; when separating iron and aluminum components, it is accomplished by controlling the pH of the system, because the pH of the complete precipitation of iron phosphate is lower than that of aluminum phosphate. The iron and aluminum components can be separated in the form of double salts; Sodium hydroxide is used to produce aluminum hydroxide, which is then calcined to obtain alumina; the sodium sulfate filtrate is evaporated to crystallize.

In the separation process of valuable components for HWW, the extraction of iron and aluminum components is the key. The phosphorus/iron molar ratio \( n_{Pi}/n_{Fe} = 5.0, 5.5, 6.0, 6.5, 7.0 \), reaction temperature \( T = 313, 323, 333, 343, 353 \) K, reaction time \( t = 30, 60, 90, 120, 150 \) min, system pH \((pH=1.5, 2.0, 2.5, 3.0, 3.5)\), etc. during the separation of iron and aluminum components were studied by single-factor experiment factors.

During the stepwise separation of valuable components in HWW, the main reactions took place as follow.

\[
\begin{align*}
\text{Ca(OH)}_2 + 2\text{H}^+ + \text{SO}_4^{2-} &= \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \quad (1) \\
2\text{CaSO}_4 \cdot 2\text{H}_2\text{O} &= 2\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} + 3\text{H}_2\text{O} \quad (2) \\
\text{Fe}^{3+} + \text{Al}^{3+} + 2\text{PO}_4^{3-} &= \text{FeAl(PO}_4)_2 \quad (3) \\
\text{Na}^+ + \text{Fe}^{3+} + \text{Al}^{3+} + \text{PO}_4^{3-} &= \text{Na}^–\text{Fe}–\text{Al}–\text{PO}_4 \quad (4) \\
\text{Al}^{3+} + \text{PO}_4^{3-} &= \text{AlPO}_4 \quad (5) \\
\text{PO}_4^{3-} + \text{H}_2\text{O} &= \text{HPO}_4^{2-} + \text{OH}^- \quad (6) \\
\text{HPO}_4^{2-} + \text{H}_2\text{O} &= 2\text{H}_2\text{PO}_4^- + \text{OH}^- \quad (7) \\
2\text{Al}^{3+}(\text{Fe}^{3+}) + 3\text{HPO}_4^{2-} &= (\text{Al}^{3+}, \text{Fe}^{3+})_2(\text{HPO}_4)_3 \quad (8) \\
\text{Al}^{3+}(\text{Fe}^{3+}) + 3\text{H}_2\text{PO}_4 &= (\text{Al}^{3+}, \text{Fe}^{3+})(\text{H}_2\text{PO}_4)_3 \quad (9) \\
(\text{Al}^{3+}, \text{Fe}^{3+})(\text{H}_2\text{PO}_4)_3 + 6\text{H}_2\text{O} &= 2(\text{Al}^{3+}, \text{Fe}^{3+})(\text{OH})_3 + 3\text{H}_2\text{PO}_4 + 3\text{H}^+ \quad (10) \\
(\text{Al}^{3+}, \text{Fe}^{3+})(\text{H}_2\text{PO}_4)_3 = (\text{Al}^{3+}, \text{Fe}^{3+})(\text{PO}_4)_3 + 3\text{H}_2\text{O} \quad (11) \\
\text{Al}^{3+} + 3\text{OH}^- &= \text{Al(OH)}_3 \quad (12) \\
2\text{Al(OH)}_3 \triangleleft \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (13) \\
\text{Na}^+ + \text{SO}_4^{2-} \triangleleft \text{Na}_2\text{SO}_4 \cdot x\text{H}_2\text{O} \quad (x = 7, 10) \quad (14) \\
\text{Na}_2\text{SO}_4 \cdot x\text{H}_2\text{O} \quad (x = 7, 10) \triangleleft \text{Na}_2\text{SO}_4 + x\text{H}_2\text{O} \quad (x = 7, 10) \quad (15)
\end{align*}
\]

2.3 Procedures

The separation process of valuable components for the activated clay production wastewater mainly includes: neutralization, separation of iron and aluminum components, aluminum extraction, and evaporative crystallization.

In the neutralization stage, two groups of 600 mL HWW were added in a 1,000 mL beaker respectively, meanwhile added an appropriate amount of calcium hydroxide \((\text{Ca(OH)}_2)\) suspension at room temperature to adjust the system pH at the final reaction to about 1.0 under stirring for 2 h. After the reaction was completed, the obtained filtrate and the solution produced for washing precipitate were mixed to obtain the acidic waste liquid (HWWS) used in the experiment. The components of HWWS was showed in Table 1 and its pH was 1.08. The filter cake obtained by neutralization was washed and dried at 373 K for 12 h to obtain a gypsum product (HWWS-PG).

The separation process of iron and aluminum components is based on the metathesis reaction. In a 100 mL beaker placed in a water bath with a set reaction temperature, 50 mL HWWS and a certain amount of trisodium phosphate dodecahydrate \((\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O})\) were added into at the same time, to reaction under stirring for a period of time. During reaction, the sodium hydroxide (NaOH) solution of 100 g L\(^{-1}\) was applied to adjust the system pH. When the reaction was accomplished, the reaction solution cooled was filtered, washed, and dried to obtain a solid product and a no ferric solution.

The no ferric solution was took as raw material in aluminum extraction process, which was diverted in a 250 mL beaker. The 100 g L\(^{-1}\) NaOH was applied to adjust the system pH to above 5.5. After reaction 60 min under stirring, the reaction solution was aged for 60 min, then filtered. The no ferric and aluminum filtrate was stored for future use, the filter cake was washed with ultrapure water to neutral and dried in 378 K for 2 h. The dried filter cake \((\text{Al(OH)}_3)_n\) (HWWS-AH) was transferred to a ceramic crucible and calcined at 1,273 K for 120 min to obtain an alumina product \((\text{Al}_2\text{O}_3)_n\) (HWWS-AO).

The no ferric and aluminum solution mainly contains sodium sulfate, which is evaporated and crystallized to obtain sodium sulfate containing crystal water. Crystalline hydrate was transferred to a 308 K oven and dried for 2 h to obtain sodium sulfate product \((\text{Na}_2\text{SO}_4)_n\) (HWWS-SS).
2.4 Characterization

The content of iron [20] and aluminum [21] in the sample was analyzed by EDTA titration method, and the sulfate content was determined by barium sulfate gravimetric method [22]. The content of iron [23] and phosphorus [24] in the filtrate was analyzed by ultraviolet-visible spectrophotometry at 510 and 700 nm respectively. The instrument (EvolutionTM 300) was produced by Thermo Corporation of the United States. Ultrapure water was used as the reference solution.

The sample was tested by the infrared spectroscopy ( Nicolet-5700) produced by Nicholi Instruments from United States, and the KBr was used for sample preparation. The scanning range is 400 to 4,000 cm\(^{-1}\).

The X’pert Pro X-ray diffractometer manufactured by PANalytical Company from Netherlands was used for XRD analysis. The test conditions as follows, Cu target, tube voltage 40 kV, tube current 40 mA, emission slit (DS) (1/2)°, Anti-scattering slit (SS) 0.04 rad, receiving slit (AAS) 5.5 mm, scanning step 0.03°, scanning range 3–80°, time per step 10 s, continuous scanning.

The solid state \(^{31}\)P NMR experiments were performed on a Bruker AVANCE NEO 400 WB spectrometer operating at 162.02 MHz for \(^{31}\)P. A 3.2 mm double resonance MAS probe was used for the experiments. The spinning rate was set to 10 kHz. The \(^{31}\)P chemical shift was calibrated using \(\text{H}_2\text{NO}_4\text{P} = 0.81\) ppm for \(^{31}\)P.

X-ray fluorescence spectrometry (XRF) was tested on a X-ray fluorescence spectrometer (Axios) with ceramic light tube, whose maximum power is 2.4 kW.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Composition of alkali-acid reaction precipitation slag

A total of 41.7 g residue (calculated as \(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\)) was obtained by neutralizing from 1,200 mL HWW, it is slightly lower than the theoretical value of 4.21 g (100 mL HWW). Figure 1 is the XRD diffraction pattern of the filter residue sample (HWWS-PG) obtained after neutralization treatment for activated clay production wastewater. It can be seen that the filter residue samples are mainly calcium sulfate dihydrate (\(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\), PDF # 33-0311) and a small amount of calcium sulfate hemihydrate (\(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}\), PDF # 41-0294).

Adding an appropriate amount of calcium hydroxide (\(\text{Ca(OH)}_2\)) in HWW, the reaction (1) mainly reacted. The obtained residue quality is lower than the theoretical value mainly due to calcium sulfate dissolution, transfer loss, and the part residue contains only half of the crystal water. The main reason for the calcium sulfate hemihydrate formation is that in strong acidity systems, the calcium sulfate hemihydrate crystals are more stable, so structural adjustment reaction (2) occurred; on the other hand, during the drying process, part of the calcium sulfate dihydrate will lose crystals water to convert calcium sulfate hemihydrate [25].

3.2 Separation influencing factors of iron and aluminum components by salt-salt reaction

3.2.1 Phosphorus/iron molar ratio (\(n_p/n_{fe}\))

Figure 2 shows the iron and phosphorus content changes in the filtrate after the separation of iron and aluminum components under different phosphorus/iron molar ratios. It can be seen from the Figure 2 that as the \(n_p/n_{fe}\) value increases, the iron ions concentration in the solution decreases linearly and the total phosphorus concentration decreases; when the \(n_p/n_{fe}\) is 6.0, the iron content in the filtrate is less than 3 mg L\(^{-1}\), while the total phosphorus content is still at a higher concentration level. In a
strong acid system, \(\text{PO}_4^{3-}\) can quickly interact with \(\text{Fe}^{3+}\). Due to the presence of \(\text{Al}^{3+}\) and \(\text{Na}^+\), insoluble phosphate double salts containing iron, aluminum, and sodium are generated (reactions (3)–(5)). When \(\text{PO}_4^{3-}\) is excessive, these reactions are promoted forward, which will be beneficial to \(\text{Fe}^{3+}\) precipitate. Therefore, by adding an appropriate excess of phosphate, the purpose of \(\text{Fe}^{3+}\) precipitation separation in the strong acid system can be achieved.

### 3.2.2 Reaction time (\(t\))

Figure 3 presents the content changes of iron and phosphorus in the filtrate for the iron and aluminum components separation at different reaction time conditions. With the reaction time extension, the iron and total phosphorus contents in the solution both showed a trend of decreasing first and then increasing. After reaction for 90 min, the content of iron and total phosphorus in the system decreased to a relatively low level, which are respectively 4.75 and 88.3 mg L\(^{-1}\). Due to the low solubility of phosphates containing iron and aluminum, precipitates can be quickly formed during reaction, and there is also a reverse dissolution process, which gradually forms a precipitate-dissolution equilibrium; the excess \(\text{PO}_4^{3-}\) and \(\text{Al}^{3+}\) in the system reduced \(\text{AlPO}_4\), which has a larger solubility, its partial dissolution and desorption of the partial adsorbed \(\text{PO}_4^{3-}\) lead to an increase for total phosphorus content in the system. The main reason for the increase of iron content in the later period is that some iron fails to enter the aluminum phosphate structure and forms iron hydroxide. Due to the poor stability of iron hydroxide in strong acid system, it is converted into iron ions in solution.

![Figure 3: Content of iron and phosphorus in the filtrate at different reaction time. \(n_p/n_{Fe} = 6.0, T = 333 K, \text{pH} = 2.0\).](image)

### 3.2.3 Reaction temperature (\(T\))

Figure 4 is a graph showing the reaction temperature effect on the iron and aluminum components separation. As the reaction temperature continues to increase, the residual iron and phosphorus contents in the resulting filtrate rapidly decrease at 313 to 343 K, and tend to be stable when it exceeds 343 K. The iron concentration in filtrate can be less than 1 mg L\(^{-1}\). By increasing the reaction temperature, the iron separation effect can be significantly improved, indicating that the formation of phosphates containing iron and aluminum is easy to proceed under higher temperature conditions. The temperature increase effectively accelerates the molecular motion, which increases the effective collisions number and reaction speed. Therefore, increasing temperature has a significant positive effect on the iron and aluminum components separation.

### 3.2.4 System pH

The effect of system pH on the iron and aluminum components separation is depicted in Figure 5. It can be seen from Figure 5 that under low pH conditions, the separation effect of iron components is poor, and as the pH value increases, the separation effect is improved significantly. When the system pH is 3.0, the iron and total phosphorus concentration in the filtrate can reach to after separation 0.56 and 5.86 mg L\(^{-1}\) respectively. Therefore, the system pH 3.0 is the better operating condition for the follow-up operations. Under low pH conditions, the free \(\text{H}^+\) in the system can react with \(\text{OH}^-\) to generate \(\text{H}_2\text{O}\), which promotes the formation of soluble mono (di)
hydrogen phosphate (reactions (6)–(9)), in turn making Fe$^{3+}$ unable to be separated as precipitation. By adjusting the system pH with sodium hydroxide, it can effectively inhibit the progress of the reactions (6) and (7), and promote the precipitation separation of Fe$^{3+}$ and PO$_4^{3-}$ as forming insoluble salts.

### 3.2.5 Separation of iron and phosphorus under the optimal conditions

Based on the single-factor experiments, the iron and aluminum separation results are showed in Table 2 using optimized process conditions, phosphorus/iron molar ratio 6.0, system pH 3.0, reaction temperature 343 K, reaction time 90 min. It can be seen from Table 2 that under optimized operating conditions, the separation effect is outstanding and relatively stable. The average content of iron and total phosphorus in the filtrate are 0.07 and 0.85 mg L$^{-1}$ respectively, and the average iron recovery rate ($\eta_{Fe}$) is 98.26%. During the iron component separation, the iron concentration in the filtrate after separation has a positive correlation with the total phosphorus content. The more stable the iron-containing phosphate produced in the system, the better the iron separation effect. The optimization experiment results show that it is feasible to separate iron and aluminum components in HWWS by phosphate precipitation method. The iron and total phosphorus content in the filtrate after iron removal are very low, which can meet the needs of subsequent separation to obtain high-purity products.

Figure 6 is the infrared spectrum and solid state $^{31}$P NMR spectra of iron aluminum-containing phosphate after calcination, respectively. The filter cake obtained under optimized conditions was washed using ultra-pure water and dried at 378 K for 2 h to obtain iron aluminum-containing phosphate products (HWWS-FP), and then the intermediate products were calcined in a 923 K resistance furnace for 120 min to obtain products (HWWS-FPC).

It can be seen from Figure 6a that 1,153 cm$^{-1}$ could be ascribed to the P–O bond, 1,096, 1,009, 875 cm$^{-1}$ could be assigned to the characteristic absorption peaks of P–O–H (Al), 661 and 600 cm$^{-1}$ belong to the deformation vibration of O–P–O, which is slightly smaller than the reported value [26,27], the stretching vibration of O–P–OH in O–P(OH)$_2$, at 1,621 cm$^{-1}$, peaks at 463 cm$^{-1}$ belongs to the bending vibration of P–O–Al, the value is less

![Figure 4: Content of iron and phosphorus in the filtrate at different reaction temperature. $n_{Fe}/n_{Fe} = 6.0, t = 60$ min, pH = 2.0.](image)

![Figure 5: Content of iron and phosphorus in the filtrate at different system pH. $n_{Fe}/n_{Fe} = 6.0, T = 333$ K, $t = 60$ min.](image)

### Table 2: Analysis results of filtrate after iron and aluminum separation under optimized conditions

<table>
<thead>
<tr>
<th>Serial number</th>
<th>Fe$_{initial}$ (mg L$^{-1}$)</th>
<th>Fe$_{final}$ (mg L$^{-1}$)</th>
<th>P$_{final}$ (mg L$^{-1}$)</th>
<th>$\eta_{Fe}$ (%)</th>
<th>Relative standard deviation (RSD) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTFY-YH-1</td>
<td>3.83</td>
<td>0.12</td>
<td>2.26</td>
<td>96.87</td>
<td></td>
</tr>
<tr>
<td>BTFY-YH-2</td>
<td>3.83</td>
<td>0.03</td>
<td>0.09</td>
<td>99.22</td>
<td>1.25</td>
</tr>
<tr>
<td>BTFY-YH-3</td>
<td>3.83</td>
<td>0.05</td>
<td>0.19</td>
<td>98.69</td>
<td></td>
</tr>
</tbody>
</table>

$a \eta_{Fe} = (Fe_{initial} - Fe_{final})/Fe_{initial} \times 100\%.$
than 486 cm\(^{-1}\) reported in the literature. The incorporation of iron will cause the characteristic absorption peak of aluminum phosphate to move to a low wave number, because the mass and radius of Fe\(^{3+}\) are larger than Al\(^{3+}\), and the Fe–O bond is longer than Al–O bond [28]. Peaks at 3,556 and 3,611 cm\(^{-1}\) could be assigned to Al(\(\text{OH}\))\(_3\) [29], peaks at 1,437 and 3,455 cm\(^{-1}\) could be ascribed to carbonate and adsorbed water, respectively [30].

In Figure 6b, the peak at \(-14.12\) ppm was corresponded to AlPO\(_4\) according Xu’s work [31]. Because it contains active hydrogen bonds, such as –OH, its characteristic peak is really wide.

In Figure 7, XRD diffraction pattern of iron aluminum-containing phosphate before and after calcination were shown. The result was displayed that the uncalcined iron aluminum-containing phosphates are amorphous, and the crystallization can be ordered through calcination. Due to the presence of sodium in the separation system, the product contains a certain amount of sodium. The sample analysis result of calcinated product is consistent with the standard card of the K–Fe–Al–PO\(_4\) phase, but the characteristic diffraction peak moves to a high diffraction angle, owing to Na\(^+\) radius is less than that of K\(^+\), and the sodium isomorphically replaces potassium which causes the spacing between crystal planes to become smaller. When Al\(^{3+}\) reacts with PO\(_4^{3-}\) to produce AlPO\(_4\), Fe\(^{3+}\) can participate in the reaction at the same time, so that part of Al\(^{3+}\) is replaced by Fe\(^{3+}\), and the radius of Fe\(^{3+}\) is larger than Al\(^{3+}\), resulting in an increase of interplanar spacing, so the characteristic absorption peak of AlPO\(_4\) moves to the direction of low diffraction angle [32]. The detection and analysis also found that there is a small amount of metaphosphate. The main reason for its formation is that orthophosphate will hydrolyze in the solution system to form mono (di) hydrogen phosphate, which will lose water to generate metaphosphate at high temperature (reactions (6)–(11)). In order to determine the compound of calcined separation product, the XRF analytical method was adopted. The result (Table 3) showed that in addition to containing phosphorus, iron, aluminum, the product also contains sulfur, sodium, potassium, calcium and silicon. However, in the XRD analysis results, no crystalline iron phosphate or sulfate

![Figure 6: Infrared spectrum (a) and solid state \(^{31}\text{P} \text{NMR} \) spectra (b) of the intermediate product (HWWS-IP) for iron and aluminum components separation under optimized conditions.](image1)

![Figure 7: XRD patterns of iron aluminum-containing phosphates generated during the iron and aluminum separation under optimized conditions. (a) Uncalcined sample (HWWS-FP); (b) calcined sample (HWWS-FPC).](image2)
was detected, so it can be speculated that iron, sodium, and potassium entered the aluminum phosphate skeleton, and the product contained sulfur due to adsorption.

### 3.3 Aluminum components separation using alkali-salt reaction

The filtrate after iron and aluminum components separation under optimized conditions was used for aluminum extraction experiment. A total of about 200 mL of filtrate was collected, in which the aluminum content was 2.43 g L\(^{-1}\). According to the aluminum extraction step shown in section 4.3, the total mass of aluminum oxide prepared is 1.17 g, which was lower than the theoretical value of 1.84 g owing to transfer loss.

Figure 8 is the XRD patterns of aluminum-containing samples during aluminum extraction. (a) Aluminum hydroxide (HWWS-AH), (b) alumina (HWWS-AO), (c) alumina (after washing, HWWS-AOW).

The XRD pattern of sodium sulfate obtained by evaporation and crystallization for the solution after aluminum extraction was depicted in Figure 9. The filtrate is concentrated by evaporation and cooled to crystallize for producing sodium sulfate containing crystal water (reaction (14)). Through drying, the crystal water will lost (reaction (15)). The characteristic diffraction peaks of anhydrous products completely match with the standard card (PDF # 37-1465). In figure, no other substances diffraction peaks are found, which means the product purity is high.

### 3.4 Sodium sulfate recovery by evaporation and crystallization

The solution after aluminum extraction is about 250 mL. Due to the incorporation of the solution for washing aluminum hydroxide and the loss in the operation process, the SO\(_4^{2-}\) concentration in the system has dropped significantly to 67 g L\(^{-1}\). The total mass of sodium sulfate product obtained by evaporation, crystallization and drying is 23.65 g.

[Table 3: Composion of the iron aluminum-containing phosphates generated (wt%)]

<table>
<thead>
<tr>
<th>P(_2)O(_5)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>SO(_3)</th>
<th>Na(_2)O</th>
<th>SiO(_2)</th>
<th>K(_2)O</th>
<th>CaO</th>
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</thead>
<tbody>
<tr>
<td>41.93</td>
<td>38.71</td>
<td>11.84</td>
<td>6.34</td>
<td>0.83</td>
<td>0.18</td>
<td>0.08</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Note: The chemical elements in the iron aluminum-containing phosphates generated are in the form of oxide.
3.5 Mechanism of iron aluminum phosphate double salt formation

Owing to the solubility product of iron phosphate and aluminum phosphate are very small, about $K_{sp, iron \text{ phosphate}} = 1.3 \times 10^{-22}$ and $K_{sp, aluminum \text{ phosphate}} = 5.8 \times 10^{-19}$ respectively at 298 K, so the PO$_4^{3-}$ in the solution system rapidly reacts with Fe$^{3+}$ and Al$^{3+}$ to produce a pale yellow or white precipitate, which is sodium-containing iron aluminum phosphate. The product can be judged to be Na–Fe–Al–PO$_4$ phase by XRD analysis, that is consistent with XRF analysis results. The solid state $^{31}$P NMR results showed that it mainly contains AlPO$_4$, and contains P=O, P–O–H, O–P–O, O==P(OH)$_2$, P–O–Al and other chemical bonds by IR analysis, but the absorption peaks of aluminum-containing chemical bonds move to a low wave number due to iron intervention. During the iron aluminum phosphate formation, aluminum phosphate is first generated. According to the Lowenstein rule [34], [PO$_4$] and [AlO$_4$] tetrahedrons in the aluminum phosphate skeleton are alternately connected by sharing vertex, so there is only Al–O–P bonding without Al–O–Al and P–O–P bonds, and there is only even-numbered rings in the skeleton structure. For the macro ring, its generation needs a template agent to construct [35]. In the aluminum phosphate framework, a part of Fe$^{3+}$ isomorphous replaces Al$^{3+}$ in the [AlO$_4$] tetrahedron, some are adsorbed in the pores, and there are acid sites at the end positions, like P–OH and Al–OH, which partly occupied by Na$^+$. Therefore, in the strongly acidic system, iron aluminum phosphate double salt mainly forms small ring compounds, as shown in Figure 10. At the same time, due to the hydrolysis of PO$_4^{3-}$, a certain amount of HPO$_4^{2-}$ and H$_2$PO$_4$ can be produced in the system. For (Al$^{3+}$, Fe$^{3+}$)$_2$(HPO$_4$)$_3$, it is easier to hydrolyze to produce (Al, Fe)(OH)$_3$ and H$_2$PO$_4$. During precipitation calcination at high temperature, (Al$^{3+}$, Fe$^{3+}$)(H$_2$PO$_4$)$_3$ entrained will lose water and convert to (Al$^{3+}$, Fe$^{3+}$)(PO$_4$)$_3$ [36].

4 Conclusion

In this paper, based on the characteristics of strongly acidity, complex components, and difficulty in separation and comprehensive utilization for the activated clay production wastewater, and results of chemical composition analysis, the valuable components in the wastewater are separated successfully by stepwise precipitation. The influencing factors of the iron and aluminum components separation process were studied by single factor experimental method. The separation conditions were selected based on the iron and phosphorus content of target filtrate, and the phase composite of solid products in the separation process were analyzed. The main conclusions are as follows.

1. The phosphate precipitate produced during the iron and aluminum components separation changes from disorder to order under high temperature conditions; according to the analysis results of IR and XRD, it is conjectured that in a strongly acid sulfate system, when Al$^{3+}$ reacting with PO$_4^{3-}$ to form AlPO$_4$ skeleton, Fe$^{3+}$ can isomorphously replaces Al$^{3+}$ in [AlO$_4$] tetrahedron, and partly replaces Al$^{3+}$ in the pores, meanwhile, Na$^+$ occupies the acid site at the terminal position. The molecular structure of sodium-containing iron aluminum phosphate double salt is speculated.

2. The precipitation method was used to successfully separate valuable components such as iron and aluminum from the acid wastewater produced by...
activated clay. Gypsum, sodium-containing iron aluminum phosphate, aluminum oxide, and sodium sulfate were prepared. The comprehensive utilization of wastewater and no waste production in separation process are achieved.

(3) The operating conditions of the separation process for iron and aluminum components were investigated using the single factor experimental method. The optimized operating parameters were: phosphorus/iron molar ratio 6.0, system pH 3.0, reaction temperature 343 K, and reaction time 90 min. Under optimized conditions, the phosphate precipitation method can be used to effectively separate iron and produce sodium-containing iron aluminum phosphate double salts. The filtrate after iron separation can meet the requirements for the subsequent generation of high purity products.

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