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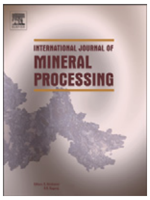

# Effect of polyaluminum chloride on the flotation separation of coal from kaolinite

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ABSTRACT

The effect of the polyaluminum chloride (PAC) on reducing the kaolinite entrainment in coal flotation is studied in this paper. The settling experiments show that the settling velocity of kaolinite was the highest when pH was around 5.5. With the addition of PAC, the settling velocity of kaolinite increased at low PAC concentration whereas it reduced at high PAC concentration. The flotation results show that PAC significantly reduced the concentrate ash content. The particle size measurements and the aggregate images show that kaolinite was aggregated by low concentration PAC and was dispersed by high concentration PAC while coal was not aggregated by PAC. The zeta potential measurements indicate that PAC neutralized the negative charge of kaolinite at low concentration and then increased the positive charge of kaolinite at high concentration. The electrostatic double layer repulsion induced the dispersion of kaolinite when the PAC concentration was high.

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## 1. Introduction

The contamination of flotation concentrate by gangue minerals has arisen for a long time in the separation of minerals (Kirjavainen, 1996; Miettinen et al., 2010; Ndlovu et al., 2013; Wang et al., 2015). The submicron sized gangue minerals contaminate the flotation concentrate mainly by entrainment, slime coating, and mechanical entrapment (Arnold and Aplan, 1986; Holuszko et al., 2008; Peng and Zhao, 2011). Among the three mechanisms, entrainment is the most ubiquitous one. It was found that the entrainment is proportional to the water recovery (Warren, 1985; Savassi et al., 1998; Yianatos and Contreras, 2010). As the water recovery is higher for finer particles, the entrainment would increase with the decrease of the particle size and vice versa.

Researchers have tried various methods to reduce the gangue contamination. Ultrasonic treatment (Qi and Aldrich, 2002; Ozkan, 2012) was used to reduce the slime coating of the gangue minerals on the valuable minerals. Parameter adjustments such as increasing the froth height (Tao et al., 2000), increasing the bias water (Tao et al., 2000; Stevenson et al., 2007), and joining a declined settling zone on flotation column (Ni et al., 2015) were also proved to be effective in intensifying the water drainage in the froth zone so as to reduce the entrainment and the mechanical entrapment. Besides, the aggregation of the gangue minerals by flocculants or depressants was also developed (Cao and Liu, 2006; Liu et al., 2006; Gong et al., 2010; Huang et al., 2012; Liu and Peng, 2014). It is proposed that some depressants have dual functions, namely increasing the hydrophilicity and enlarging the particle size of gangue minerals, in reducing the gangue contamination (Cao and Liu, 2006; Liu et al., 2006).

However, the research in reducing the gangue contamination by selective aggregation is mainly focused on the flotation of sulphide or oxidized minerals. Scarce research can be found in the selective aggregation of the gangue minerals in coal flotation. One reason may be that coal is more likely to be aggregated than the gangue minerals such as quartz, kaolinite, and montmorillonite because coal can be easily flocculated through hydrophobic interaction (Song et al., 2004; Song, 2008; Yang and Song, 2014) due to its high hydrophobicity. In this research, the polyaluminum chloride (PAC, here after), an inorganic coagulant, was tried to achieve the selective aggregation of kaolinite in coal flotation.

PAC is the hydrolysis and polymerization product of aluminium salts. It is widely used in the water purifying process (Chuang et al., 2007; Wang et al., 2007; Sun et al., 2013). The chemical formula of PAC can be described as $[Al_2(OH)_nCl_{(6-n)}]_m$, where m represents the polymerization degree. The chemical composition of PAC is very complex and it is highly dependent on the reaction process. Normally, there are three categories of Al(III) in the PAC solution, namely the monomer hydrolysis product $Al_a$, the polymeric hydrolysis product $Al_b$, and the amorphous colloid $Al_c$ (Duan and Gregory, 2003; Wang et al., 2004). The composition of Al(III) in the PAC solution varies greatly in different conditions. $Al^{3+}$, $Al(OH)_2^+$, $Al(OH)^{2+}$, and $Al(OH)_4^-$ are the four monomer species of $Al_a$, and they would transform mutually by

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the change of pH, electrolyte, aging time, etc. (Duan and Gregory, 2003). The structure of $Al_b$ is still not very clear. There are some hypothetical models such as the core-links model (Jardine and Zelazny, 1986) and the Keggin model (Bottero et al., 1982). It is proposed that the aggregation mechanisms of the ultra-fine particles by PAC are mainly the charge neutralization by the positive charged $Al_a$ and $Al_b$, and the enmeshment by the precipitate of $Al_c$, i. e., the aluminum hydroxide (Wang et al., 2002; Duan and Gregory, 2003; Xiao et al., 2008).

In this research, it is found that PAC with low concentration selectively aggregated the kaolinite particles so the kaolinite entrainment in coal flotation was reduced. The charge neutralization was the main aggregation mechanism. With higher concentration, the kaolinite particles were dispersed due to the electrostatic double layer repulsion.

## 2. Materials and methods

### 2.1. Materials

The bituminous coal sample was provided by a coal preparation plant in Zaozhuang, China. The proximate and ultimate analysis of the sample is shown in Table 1. The coal sample was sieved using a screen with mesh of 74 μm and the undersize product was used to conduct the flotation experiments, the particle size measurements, the aggregate image observation, and the zeta potential measurements. The pure kaolinite was provided by the Wanquan Co. Ltd., China. The X-ray diffraction measurements (D8 Advance, Bruker, Germany) was conducted to analyze the mineral composition of the $+2.0\ g\cdot cm^{-3}$ density fraction of the coal sample and the kaolinite sample.

The results of the X-ray diffraction measurements are shown in Fig. 1. Kaolinite, quartz, and calcite were the main gangue minerals in the coal sample. The relative proportions of the three minerals were 49.7%, 33.4%, and 16.9%, respectively. The proportion of the $+2.0\ g\cdot cm^{-3}$ density fraction in the coal sample was 21.3%. Therefore, the main gangue mineral in the coal sample was kaolinite and its proportion was approximately 10%. Mica was the only impurity in the pure kaolinite sample and its proportion was <5%.

The PAC with the basicity of 0.5–0.7 was purchased from Sinopharm Chemical Reagent Co. Ltd., China. The $Al_2O_3$ content was 22% and the effective pH range was 3.5–7.0. The PAC was dissolved in deionized water with the concentration of 1 g/L at the pH of 5.0–5.5. Analytically pure hydrochloric acid and sodium hydroxide (Sinopharm, China) were used to modify the pH. Sodium chloride (Sinopharm, China) with analytical purity was used as the electrolyte in zeta potential measurements. Kerosene and 2-octanol were used as the collector and the frother in the flotation experiments. The deionized water with conductivity of 20 μS/cm was used in all experiments at 20 °C.

### 2.2. Kaolinite settling experiments

The settling experiments of the kaolinite were conducted in a 100 mL cylinder. The kaolinite suspension with solid concentration of 5.7 wt% with different pre-set pHs was agitated in a beaker using a magnetic agitator at 500 rpm for 2 min at 20 °C, then the PAC solution was added and the agitating speed was decreased to 100 rpm. After 2 min, the suspension was gently poured into the cylinder to reach the scale of 100 mL. The cylinder was inverted for 3 times and then was left to settle on the table. During the settling, the position of the mud-line was recorded. All settling experiments were performed twice and the averages were reported.

**Table 1**
Proximate and ultimate analysis of the bituminous coal sample.

| Proximate analysis (ad) | | | | Ultimate analysis (daf) | | | | |
|---|---|---|---|---|---|---|---|---|
| Moisture (%) | Ash (%) | Volatile matter (%) | Fixed carbon (%) | C(%) | H(%) | N(%) | O(%) | S(%) |
| 2.11 | 28.86 | 33.05 | 35.98 | 79.73 | 4.88 | 1.70 | 12.49 | 1.20 |

### 2.3. Flotation experiments

The flotation experiments were conducted in a 0.5 L mechanical flotation cell. The mixture of 20 g of the coal and 10 g of the kaolinite was used as the flotation feed. The kaolinite was mixed in the feed to magnify its contamination of the flotation concentrate. The impeller speed and the aeration rate were fixed to 1800 rpm and 0.69 cm/s, respectively. In each experiment, the feed was agitated with water at pH around 5.5 in the flotation cell for 2 min. Then, the PAC solution was added in the pulp. The volume of the pulp after the addition of PAC solution was kept the same in all experiments so as to keep the froth depth unchanged. After 2 min, the collector was added and another 2 min of conditioning was kept. The frother was added and 10 s later the aeration valve was turned on. The flotation concentrates were scrapped out into trays. The flotation was kept for 2 min. The tailings and the concentrates were filtered and were dried in an oven for 5 h at 60 °C.

### 2.4. Particle size measurements

Particle size measurements of coal and kaolinite with the addition of PAC were conducted using the laser diffraction particle size analyzer (S3500, Microtrac, the US). The coal or kaolinite suspension of 100 mL with pH 5.5 and the solid concentration of 5.7 wt% was agitated using the magnetic agitator at 500 rpm at 20 °C for 2 min. The PAC solution was then added into the suspension. The agitation speed was reduced to 100 rpm and was continued for 2 min. Subsequently, the suspension of 2 mL was taken out and transferred to the sample cell by pipette. The laser obscuration around 15% was obtained. To protect the aggregates from fracture, the stirring speed of the impeller and the pump in the sample cell was respectively adjusted to 500 and 600 rpm, which was in a relative low level. Ultrasonic treatment was not applied.

### 2.5. Aggregate image observation

The coal or kaolinite suspension of 100 mL with solid concentration of 5.7 wt% at pH around 5.5 was agitated using a magnetic agitator at 500 rpm for 2 min. Then, the PAC solution was added into the suspension. The suspension was then agitated at 100 rpm for 2 min. The suspension was taken out at different positions by a dropper and was dropped on a glass slide. After putting the cover glass on, the glass slide was put on the object stage of the microscope (XSP-13CC, Batuo, China). Five pictures at different positions of the suspension on the glass slide were taken by the built-in CCD camera.

### 2.6. Zeta potential measurements

The coal or kaolinite particles of 6 g were dissolved in 100 mL of 0.1 mM NaCl solution with different pre-set pHs. The suspension was kept agitating at 500 rpm using a magnetic agitator. After 2 min, the PAC solution was added in the suspension and the agitation continued for another 2 min. 20 mL of the suspension was taken out and transferred into tube by pipette. The suspension in tube was kept settling for 24 h. The supernatant of 1 mL was taken out by pipette to conduct the zeta potential measurement (ZetaPALS, Brookhaven, the US). For each suspension, ten runs of measurements were performed and the averages were reported.

## 3. Results and discussion

### 3.1. Effects of pH and PAC concentration on kaolinite settling velocity

Fig. 2 shows the kaolinite settling results with the pH ranges from 2.5 to 11.5. The settling velocity was calculated by the distance between the

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