Characterization of a hybrid polyacrylamide and its flocculation properties in cyanide tailing suspensions
Ya Liu, Cuicui Lv, Jian Ding, Peng Qian, Yang Yu, Shufeng Ye and Yunfa Chen

ABSTRACT
An inorganic-organic hybrid flocculant Al(OH)₃-polyacrylamide (Al-PAM) with narrow molecular weight distribution was synthesized using inverse microemulsion polymerization. The hybrid polymer Al-PAM was characterized by Infrared spectroscopy, thermogravimetric analysis, transmission electron microscopy and scanning electron microscopy, and it was found that it had a 'star-like' structure in which Al(OH)₃ colloidal particles acted as cores linking PAM chains. The properties of Al-PAM were investigated in flocculating 10 wt% cyanide tailing suspensions. It was found that as the amount of Al-PAM with high molecular weight and aluminum content increased, the initial settling rate of particles accelerated, achieving the maximum 6.6 m/h, 17.3 times the rate of the control without flocculants. The turbidity of the supernatant decreased to 35 ± 2 NTU accordingly, compared to 353 ± 2 NTU of that in the control, which meant that 90.0% of turbidity was removed from the cyanide tailing suspensions. The flocculation mechanism was further explored by flocule size and ζ potential measurements. The superior performance of cationic Al-PAM in flocculating negatively charged particles compared to commercial non-ionic GG indicated that electrostatic repulsion between tailing particles was a crucial factor in deciding the flocculation performance of the polymer. The study demonstrated that both charge neutralization and bridge adsorption were conductive to the particle flocculation.

Key words | acrylamide, cyanide tailing suspensions, flocculation, inorganic-organic hybrid polymer, inverse microemulsion

INTRODUCTION
The amount of cyanide slags released from gold plants increases by more than 10 million tons per year with the fast progress of the gold extraction industry. Cyanide tailing suspensions are the universal and final remains of gold-bearing minerals after cyanidation to extract gold and a series of flotation to recover valuable elements such as sulfur, iron, cooper, lead etc. in the gold extraction industry (Zhang et al. 2012). Therefore, cyanide ions and various flotation reagents like butyl xanthate and terpenic oil as well as metal ions remain in cyanide tailing suspensions, which makes it a much more complex system compared with single tailing suspensions such as silica suspensions and kaolin suspensions (Yang et al. 2004; Wang et al. 2014a). According to the National discharge standard, wastewater containing higher than 0.5 mg/L cyanide ions and 20 mg/L total organic carbon (TOC) is prohibited from discharging into the environment. In recent years, the cyanide slag consumes water by twice or more times its mass in the flotation process and produces cyanide tailing suspensions which contain 10 wt% to 20 wt% tailing solids, hazardous flotation reagents, cyanide ions etc. Accordingly, water management plays a key role in the sustained development of resources recovery in cyanide slags, and it is highly desirable to effectively accelerate the settlement of tailing particles in suspensions to reuse water and reduce the pollution of wastewater emissions to the environment. Therefore, rapid dewatering of the cyanide tailing suspensions to be selected as the treated effluent is of great interest in the gold extraction industry. For cyanide tailing suspensions, the principal ingredient of the suspended particles is gangue, with a low specific gravity and a fine particle
size ranging from 0.04 μm to 70 μm, which leads to the slow settlement of particles from suspensions. In addition, the surface of tailing particles is negatively charged through hydrolysis and adsorption of residual ions and flotation reagents in suspensions, which causes electrostatic repulsion between particles. Thus, it is quite difficult for the particles to aggregate and settle out from the suspension by gravity.

Polymer flocculation has been widely investigated and carried out by the gold extraction industries thanks to its excellent performance in dewatering mineral tailings (Wang et al. 2014a; Chen et al. 2016). In recent years, the inorganic-organic hybrid polymer has been developed as an attractive flocculant for achieving high efficiency or high function owing to the synergistic effects of nanoparticles and polymers in various industrial and environmental processes (Wang et al. 2014c; Miranda et al. 2015). Polymer adsorption is critical to govern the stability of colloidal suspension systems, relying upon the nature of the polymer used and the characteristic of its adsorption (Zhang et al. 2010; Alagha et al. 2011). The inorganic-organic hybrid Al(OH)3-polyacrylamide polymer (Al-PAM) was first introduced as a flocculant by Yang et al. (2004) synthesized using solution polymerization, and the ion bonds between aluminum hydroxide particles and PAM chains in Al-PAM were displayed. The flocculation effect of cationic Al-PAM was confirmed to be superior to that of a commercial PAM or AlCl3/PAM blend for kaolin suspensions. Alagha et al. (2011) synthesized Al-PAM with the same method to investigate the adsorption kinetics on silica and alumina using dissipative quartz crystal balance. The cationic Al-PAM showed stronger affinity on silica surfaces with negative charge than alumina surfaces with positive charge, which suggested the synergistic flocculation mechanism of charge neutralization by Al(OH)3 colloid particles and bridge adsorption by the stretched PAM chains (Alagha et al. 2011)

The inorganic-organic hybrid polymers are usually employed to overcome the electrostatic repulsion among tailing particles with negative charge by inorganic colloids and bring the particles into polymer bridging adsorption (Alamgir et al. 2012). In recent studies, Al-PAM has been used as flocculant or filtration aid in mature fine tailings (Lee et al. 2012; Wang et al. 2014a). Al-PAM could flocculate fine, negatively-charged particles to produce large and compact flocules to separate the particles from the tailing suspensions rapidly and effectively, thus generating large quantity of high quality recycled water. The integration of Al(OH)3 colloids into the PAM matrix contributes to reducing the electrostatic repulsion between tailing particles by partially or completely neutralizing negative charges and thus provides the driving force for the adsorption of negatively-charged particles on the Al-PAM surface (Sun et al. 2008; Alagha et al. 2013). Therefore, Al-PAM has great potential to be used in solid-liquid separation of suspensions containing negatively-charged particles. Table 1 summarizes the flocculation performance of Al-PAM reported by Yang et al. (2004), Alagha et al. (2011) and Alamgir et al. (2012).

Al-PAM polymerization was mostly carried out in water solution (Yang et al. 2004; Alamgir et al. 2012; Alagha et al. 2013; Wang et al. 2014c). Nevertheless, solution polymerization methods have great difficulty in heat dissipation due to gelation or high viscosity, so the concentration of monomer is usually low, the molecular weight of the product is of wide dispersion, and the dry product hard to dissolve during application (Qiu et al. 2016). Inverse microemulsion polymerization is a favorable method to prepare water soluble polymers such as PAM, because the viscosity and heat dissipation of the system is easy to control as the polymerization mainly occurs in microemulsion droplets. To our knowledge, no attempt has been made to prepare Al-PAM in a water-in-oil (W/O) microemulsion. The objective of this study is to provide a new approach for the preparation of an inorganic-organic hybrid Al-PAM polymer with narrow molecular weight distribution via inverse microemulsion polymerization. The flocculation effect of Al-PAM was investigated in 10 wt% (w/w) cyanide tailing suspensions with silica as its major component to accelerate dewatering in the gold extraction industry, which saves water resources as well as reducing the threat of hazardous components entering the environment in mineral processing wastewater. In order to better describe the enhanced performance of Al-PAM in flocculation, commercial non-ionic GG was used to compare the flocculation performance.

### MATERIALS AND METHODS

#### Synthesis of Al-PAM

The inverse microemulsion used for polymerization consists of Al(OH)3 colloidal suspension-acrylamide mixture dispersed in

<table>
<thead>
<tr>
<th>Suspensions</th>
<th>Solid content (wt%)</th>
<th>ISR (m/h)</th>
<th>Turbidity removal efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>0.25</td>
<td>0.84</td>
<td>98%</td>
<td>Yang et al. (2004)</td>
</tr>
<tr>
<td>Silica</td>
<td>5</td>
<td>13</td>
<td>/</td>
<td>Alagha et al. (2011)</td>
</tr>
<tr>
<td>Mature fine tailings</td>
<td>5</td>
<td>6.2</td>
<td>/</td>
<td>Alamgir et al. (2012)</td>
</tr>
</tbody>
</table>
cyclohexane and stabilized by hexadecyltrimethylammonium bromide (CTAB) and 1-pentanol. 9 mL of 15 wt% ammonium carbonate solution was dropped into 20 mL of 8 wt% aluminum chloride solution slowly at an agitation speed of 1,500 rpm to acquire an Al(OH)₃ colloidal suspension. 4.5 g acrylamide was added to 12 mL Al(OH)₃ colloidal suspensions with different Al(OH)₃ content as shown in Table 2. The aqueous phase was dispersed into a CTAB-1-pentanol-cyclohexane solution to form a W/O (water in oil) microemulsion. The microemulsion was stirred and heated to 40 °C in a water bath under nitrogen for 30 min. To initiate the polymerization of acrylamide on aluminum hydroxide colloids, 2 mL of NH₄S₂O₈/NaHSO₃ at a mass ratio of 2:1 was added slowly to the microemulsion. The reaction was kept for 3.5 h under agitation and nitrogen gas flow at 100 mL/min. The Al-PAM polymer was obtained by precipitating with excess alcohol and thoroughly washing with acetone to remove Al(OH)₃ colloids, acrylamide, and other impurities. The resultant solid was dried at 55 °C under vacuum until there was no change in weight. The properties of polymers used in this study are shown in Table 2. Al-PAMM₁, Al-PAMM₂, and Al-PAMM₃ were synthesized by inverse microemulsion polymerization with different molecular weight and Al(OH)₃ content. Besides, Al-PAMS, synthesized by solution polymerization, and GG were also listed for comparison.

**Characterization of Al-PAM**

**Infrared spectroscopy analysis**

Infrared (IR) spectroscopy analysis was used to characterize the functional groups in the polymer molecular structure. A mixture of methanamide and acetic acid (1:1, v/v) was used to remove homopolymer polyacrylamide in Al-PAM. The IR spectra of PAM and Al-PAM over 4,000–300 cm⁻¹ were recorded using a Fourier transform infrared (FTIR) spectrometer (Spectrum GX, Perkin Elmer, USA) with a measurement resolution of 4 cm⁻¹. Sample powders were mixed well with KBr (1:100, w/w) and pressed into a wafer shape.

**Thermogravimetric analysis**

The mass loss at different temperatures was given by thermogravimetric analysis (TGA) to investigate the components and thermal stability of the polymer. The thermal degradation test was conducted in a TGA device (STA449 F3, Germany) with a maximum weight of 35 g. The data were collected every 15 s. The heating rate was 10 °C/min under air from 35 °C to 900 °C.

**Transmission electron microscopy imaging**

Transmission electron microscopy (TEM) was applied to demonstrate the morphology of the hybrid polymer and the distribution of Al(OH)₃ particles in polyacrylamide. 200 μL of 100 ppm Al-PAM solution was dropped on a carbon-coated copper grid and stabilized for 10 min. The extra solution was removed by filter paper, followed by staining with 3% phosphotungstic acid for 2 min. Then the sample was rinsed with Milli-Q water to remove the residual stain. The sample was blow-dried with pure nitrogen for TEM (JEM-2100, Japan) imaging.

**Scanning electron microscopy imaging**

The morphology and microstructure of the flocules was obtained on a thermal field emission scanning electron microscope (JSM-7001F, Japan). Figure 1 gives the X-ray diffraction pattern of cyanide tailings, from which we can see quartz was the major ingredient. Therefore, a monodispersed nano-size silica suspension was chosen to substitute for the cyanide tailing suspension for scanning electron microscopy (SEM) imaging, which was performed using flocules in the supernatant after a settling test of nano-size silica suspensions with the addition of polymers. A total of 50 μL of supernatant was placed on a foil surface and blow-dried with pure nitrogen. The sample was coated with gold in order to be conductive, and subjected to scanning electron microscope analysis.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Details of polymers used in this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>Initiator (g/L)</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Al-PAMM₁</td>
<td>2.25</td>
</tr>
<tr>
<td>Al-PAMM₂</td>
<td>0.75</td>
</tr>
<tr>
<td>Al-PAMM₃</td>
<td>0.75</td>
</tr>
<tr>
<td>Al-PAM₅</td>
<td>2.25</td>
</tr>
<tr>
<td>GG</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Mw: weight average molecular weight; Mn: number average molecular weight; PDI: Mw/Mn, polydispersity index; Initiator: NH₄S₂O₈/NaHSO₃.
Gel permeation chromatography analysis

The molecular weight distribution of Al-PAM was obtained by gel permeation chromatography (GPC, Waters, 1515, USA) analysis, which was carried out in an aqueous solution at 25 °C with a flow rate of 0.5 mL/min. Samples were prepared by dissolving Al-PAM in 0.1 M sodium chloride (NaCl) solution for a final polymer concentration of 1 mg/mL. 100 μL of the sample was injected into the GPC apparatus. NaCl solution was used as an eluent and the system was calibrated with polysaccharide standard.

Flocculation behavior

Settling experiments

Flocculation performance of Al-PAM or GG was evaluated by settling experiments of cyanide tailing suspensions prepared through dispersing the tailing particles in plant circulating water taken from the Zhaoyuan gold mine in Shandong Province. The characterization of the suspensions is given in Table 3, including the standard deviation in three replicates. 1,000 ppm of polymer solution was prepared with Milli-Q water as flocculant. The tailing suspensions were put in a jar and agitated at 500 rpm for 1 min as various doses of flocculant solution ranging from 0.1 mg/L to 6 mg/L were added. After the addition of polymer, the stirring rate was adjusted to 300 rpm lasting for 2 min. Then the tailing suspensions were diverted to a 1,000 mL graduated cylinder. The height of a clear interface between the water and the solid bed was read over time with the settlement of tailing particles and plotted against settling time. After the first 5 min of settling, the turbidity of supernatant, which was removed from the top of the cylinder, was determined by a photoelectric turbidimeter (WZT-3, China). In the settling experiment, polymer dosages were expressed with reference to the volume of tailing suspension.

RESULTS AND DISCUSSION

Characterization of Al-PAM

IR spectroscopy analysis

As shown in Figure 2, Al-PAM$_S$ and Al-PAM$_M$ demonstrate the nearly alike IR absorption bands with PAM other than

![Figure 1](https://example.com/f1.png)

**Figure 1** The X-ray diffraction pattern of cyanide tailings.

**Table 3** Characteristics of cyanide tailing suspensions

<table>
<thead>
<tr>
<th>pH</th>
<th>Total solids (g/L)</th>
<th>COD (mg/L)</th>
<th>DOC (mg/L)</th>
<th>Fe (mg/L)</th>
<th>Zn (mg/L)</th>
<th>CN (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.7 ± 0.1</td>
<td>100 ± 2</td>
<td>6,460 ± 50</td>
<td>1,250 ± 30</td>
<td>12 ± 0.6</td>
<td>8.6 ± 0.2</td>
<td>28 ± 1</td>
</tr>
</tbody>
</table>

DOC: dissolved organic carbon.
the peak of 538 cm$^{-1}$, 736 cm$^{-1}$, 1,358 cm$^{-1}$. According to the literature and IR standard spectrum of Al(OH)$_3$, absorbance bands at 538 cm$^{-1}$, 736 cm$^{-1}$ and 1,358 cm$^{-1}$ can be assigned to Al-O stretching vibration and -OH bending vibration respectively (Music´et al. 1999; Yang et al. 2004). In addition, Al-PAMS with 6.94% Al(OH)$_3$ exhibited stronger absorbance than Al-PAMM with 3.47%. So the inorganic Al(OH)$_3$ group was successfully incorporated into PAM and the organic-inorganic hybrid Al-PAM polymer was confirmed by IR (Yang et al. 2004).

TGA measurement

The TGA curves of Al-PAM hybrid polymers, PAM/Al(OH)$_3$ blend and PAM are demonstrated in Figure 3. Compared with Al-PAMS and PAM/Al(OH)$_3$, PAM was weakly resistant to heat and its thermal degradation behavior was consistent with Silva et al. (2000) and Tang et al. (2009). Four steps were observed in the thermal degradation process of Al-PAMs and PAM/Al(OH)$_3$. In the first step, about 10% weight lost between 40 °C and 150 °C was owing to the evaporation of absorbed moisture (Wang et al. 2014b). The degradation of structure units in PAM chains and decomposition of aluminum hydroxide began with the temperature increasing to 250 °C, which caused the slight drop in the second step of the TGA curve (Tang et al. 2009; Cao et al. 2015). The TGA curve showed a significant drop at the third step of 330 °C, which was probably attributed to a thermal process involving both aluminum hydroxide decomposition and cleavage of the weak and unstable linkages in PAM, such as the side chain of acylamino producing NH$_3$ (Silva et al. 2000). With further increase of temperature in the fourth step, the polymer backbone broke down completely to generate low molecular gases, i.e. CO$_2$ and H$_2$O, leading to rapid weight loss (Silva et al. 2000; Tang et al. 2009). Al-PAM and PAM/Al(OH)$_3$ started degradation of the fourth step at 450 °C and 420 °C respectively. Because the end of the PAM chain in the hybrid polymer was attached with Al(OH)$_3$, the thermal motion of the polymer chains was weakened and the thermal stability of the hybrid polymer was improved (Ramesh et al. 2015; Lal et al. 2016). The major difference in the fourth step between Al-PAM and PAM/Al(OH)$_3$ indicated that Al-PAM is not a simple composite of PAM and Al(OH)$_3$ but a hybrid polymer (Yang et al. 2004).

TEM imaging

Compared with organic PAM without inorganic nanoparticles in a polymer matrix, the TEM image of the inorganic-organic hybrid Al-PAM$_M$ revealed that the aluminum hydroxide nanoparticles had a spherical morphology (Figure 4), which were homogeneously dispersed in the polymer matrix with an average particle size of about 10 nm to 20 nm. This indicated that no agglomeration of inorganic particles existed in the bulk of the polymer, suggesting polymerization of acrylamide monomer was initiated at the surface of a single aluminum hydroxide particle. As a result, the nanoparticle was encircled by PAM chains, and acted as a core linking the chains. Each Al(OH)$_3$ core had a couple of PAM arms, showing a ‘star-like’ structure (Sun et al. 2008).

SEM imaging

The flocculated nano-silica suspensions with Al-PAM$_M$ and PAM are shown in Figure 5. As demonstrated in Figure 5(a),
there were a few floccules existing in the supernatant, and the residual floccule was always a single one which was not bridging with others. The image of the floccule in the supernatant of nano-silica suspensions treated by Al-PAM showed a ‘star-like’ shape which may further confirm the structure of Al-PAM as mentioned by Sun et al. (2008), that an Al(OH)₃ core had some PAM side chains as arms, presenting a ‘star-like’ feature. The silica nanospheres were monodispersed or slightly aggregated in supernatant without the addition of flocculant, as shown in the upper right corner of Figure 5(a) and 5(b). However, the floccules in the supernatant of nano-silica suspensions flocculated by PAM in Figure 5(b) demonstrate the long chain characteristic in correspondence with the structure of homo-polymer PAM. In terms of molecular structure, the ‘star-like’ structure of Al-PAM has easier accessibility to suspended particles compared with the linear chain molecules of PAM, which is favorable to the bridging process to form large and dense floccules (Sun et al. 2008).

Flocculation study

Settling test

Different doses ranging from 0.1 mg/L to 6 mg/L of the as-synthesized Al-PAMₐ₁, Al-PAMₐ₂, Al-PAMₐ₃ and the commercial GG were added to the 10 wt% cyanide tailing suspensions, and the settling curves are demonstrated in Figure 6. All polymers exhibited a remarkable positive effect on settling fine tailing particles in comparison to the control experiment without flocculant. It was observed that either high molecular weight (Al-PAMₐ₁ vs Al-PAMₐ₂) or high aluminum content (Al-PAMₐ₂ vs Al-PAMₐ₃) contributed to the flocculation of suspended particles, demonstrated by the faster sedimentation of fine particles in suspension. For a given aluminum content, the higher molecular weight of Al-PAM led to more rapid settlement of particles, owing to more adsorption sites of polymer chains and stronger bridging being provided by the larger Al-PAM molecules (Alamgir et al. 2012; Xu et al. 2015). On the other hand, for a specific molecular weight of Al-PAM, the increase of aluminum content increased binding sites and promoted charge neutralization of negatively charged particles in the suspensions (Jankolovits et al. 2016; Li et al. 2016). Additionally, the clarified height of suspensions at a corresponding time did not increase or even decrease when the addition of Al-PAMₐ₁ exceeded the optimum dosage.
5 mg/L, demonstrating that an overdose of polymer with high molecular weight led to steric stabilization (Alamgir et al. 2012; Wang et al. 2014c). The overdose of Al-PAMM1 indicated that the surface of particles was fully covered by the tightly adsorbed long polymer chains, which prevented further bridging flocculation to the particles, while the low molecular weight Al-PAMM2 and Al-PAMM3 had not reached the optimum concentrations of flocculating the particles in cyanide tailing suspensions with the equal dosage to Al-PAMM1. Commercial GG attained its maximum performance at 5 mg/L, the overdose of which led to the functional adsorption sites being enwrapped by GG chains (Kee et al. 2015). The Al-PAMs all demonstrated better flocculation than the commercial GG.

**Turbidity of supernatant**

Supernatant turbidity of cyanide tailing suspensions after flocculation, shown by bar chart (Figure 7), was measured after 5 min of settlement. The initial settling rates (ISR) curve of each polymer at different dosages in Figure 7 was defined by the slope calculated from the settling curve in Figure 6. As can be clearly seen in Figure 7, the supernatant turbidity decreased with increasing polymer concentration until the optimum dosage, which varied inversely with the ISR of the tailing slurry. The lowest supernatant turbidity of suspensions flocculated with 5 mg/L Al-PAMM1, 5 mg/L Al-PAMM2, and 6 mg/L Al-PAMM3 was achieved at 35 ± 2 NTU, 61 ± 2 NTU, and 51 ± 2 NTU respectively, compared to 353 ± 2 NTU for the control, demonstrated by the green bar. The lowest supernatant turbidity treated by GG was 221 ± 2 NTU at 5 mg/L, which was much higher than that of Al-PAM. The better flocculation performance of Al-PAM could be attributed to the synergism of two components of Al(OH)₃, colloidal particles and PAM chains. The positive Al(OH)₃ colloidal particles reduce the electrostatic repulsion among the negatively-charged tailing particles, especially for fine particles with high stability, which contributed to a higher supernatant turbidity, and...
then PAM chains at an adequate dose of 5 mg/L bridge tailing particles through hydrogen bonding to form large and dense flocules. The electrostatic repulsion hinders the close approximation between fine particles with a negative charge, thus weakening the bridge flocculation of GG (Sun et al. 2008; Wang et al. 2014c).

In addition, Al-PAMM1 was observed to have a higher ISR of 6.60 m/h and lower supernatant turbidity of 35 ± 2 NTU compared with 6.36 m/h and 41 ± 2 NTU flocculated by Al-PAMs at the same dosage of 5 mg/L, even though it has a lower molecular weight. This could be attributed to the narrower molecular weight distribution of Al-PAMM1, as indicated by a small polydispersity index (PDI) of 1.29 for Al-PAMM1 and a large one of 4.03 for Al-PAMs as shown in Table 1. PDI is the molecular weight distribution index, and a small value of PDI indicates a narrow and uniform distribution of molecular weight. Generally, a better flocculation performance is achieved with a higher molecular weight. Al-PAM with higher PDI shows a higher proportion of low molecular weight, which may weaken the flocculation efficiency (Alagha et al. 2011). The ISR of Al-PAMM2 was 4.68 m/h and supernatant turbidity was 72 ± 2 NTU at 5 mg/L, which is mainly attributed to its low molecular weight, because fewer adsorption sites were supplied by the lower molecular weight polymers, which was unfavorable to forming larger flocules for quicker precipitation. GG had an ISR of 2.4 m/h and a supernatant turbidity of 221 ± 2 NTU at 5 mg/L, which exhibited a poor sedimentation effect on cyanide tailing suspensions, in contrast with the Al-PAM. Compared with uncharged GG, the superior flocculation behavior of Al-PAM could be primarily owing to the electrostatic attraction of positive Al(OH)3 cores and negative tailing particles (Jankolovits et al. 2016; Li et al. 2016).

Flocculation behavior determined by FBRM

The chord size distribution of particles and flocules were measured by FBRM probe, ranging from 0.5 μm to 2,000 μm. The proportion of chord length at higher values increases with increasing concentration of polymers (Figure 8). When the dosage of Al-PAMM1 was 5 mg/L, the d50 of flocules’ chord length reached its maximum 60 μm in contrast to 6 μm in the blank. What’s more, the size of the flocules stopped increasing but decreased with further increase of dosage to 6 mg/L because of the steric stabilization (Alamgir et al. 2012; Wang et al. 2014a). Therefore, the optimum dosage of Al-PAMM1 was 5 mg/L, at which the maximum sedimentation was achieved by the largest flocules. In addition, fine particles aggregated with the addition of floculants, reducing the particle residue in the supernatant, which was shown by the decrease of supernatant turbidity. This was in accordance with the result of the settling experiment. Therefore, flocule size was a critical parameter for estimating the flocculation effect of polymers.

A similar variation of flocule sizes was found in Al-PAMM2, Al-PAMM3 and GG, and the optimum dosage of each floculant corresponded with the result obtained from the settling experiment. Table 4 gives the FBRM results of Al-PAMM1, Al-PAMM2, Al-PAMM3, and GG in comparison with the blank experiment without the addition of floculant. The maximum d50 of 45 μm, 35 μm and 15 μm were acquired by Al-PAMM2, Al-PAMM3 and GG respectively. Compared with Al-PAMM1, a high proportion of chord length at lower values was observed in Al-PAMM2 and Al-PAMM3 at equal dosage, which was caused by lower molecular weight or Al(OH)3 content, thus leading to poorer performance in the settling experiment, as shown in Figure 6 (Alamgir et al. 2012; Xu et al. 2015; Jankolovits et al. 2016; Li et al. 2016).

The chord length distribution of flocules treated by GG was between 0 μm and 100 μm, indicating poorer flocculation performance than the Al-PAM, the flocule sizes of which was between 0 μm and 300 μm.

Flocculation behavior studied by PVM

Rapid formation of large and compact flocules contributed to fast sedimentation of tailing particles, which indicated excellent performance of a floculant. PVM (Particle Video Microscope), which provides high-quality images in dark environments such as tailing suspensions, was applied to monitor the flocculation process. After adding Al-PAMM1 at the optimum concentration of 5 mg/L, the images of flocule formation at different
times was taken and demonstrated in Figure 9. Well-distrib-
uted solid particles as circled in red (see online) were
observed with no flocculant at 0 s (Figure 9(a)). At 10 s
after adding Al-PAMM1, the particles gathered gradually
to be absorbed onto the chains of PAM through hydrogen
bonds to form chain-like floccules surrounding Al(OH)₃
cores, circled in red (Figure 9(b)) linked by the arrow
from 0 s (Alagha et al. 2014). Then the floccules grew
bigger quickly by adsorption bridging among polymer
chains when the time extended to 30 s (Figure 9(c)) and
finally stabilized at 1 min (Figure 9(d)) (Sun et al. 2008).

Table 4 | FBRM results of different polymers used in this study

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Maximum d₅₀/μm</th>
<th>Range of chord length/μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>6</td>
<td>0–70</td>
</tr>
<tr>
<td>Al-PAMM₁</td>
<td>60</td>
<td>0–300</td>
</tr>
<tr>
<td>Al-PAMM₂</td>
<td>45</td>
<td>0–300</td>
</tr>
<tr>
<td>Al-PAMM₃</td>
<td>35</td>
<td>0–300</td>
</tr>
<tr>
<td>GG</td>
<td>15</td>
<td>0–100</td>
</tr>
</tbody>
</table>

The images of stable floccules of Al-PAMM₁, Al-PAMM₂
and Al-PAMM₃ demonstrated that increasing molecular
weight and aluminum content provided more adsorption

Figure 8 | The chord length distribution of floccules-aggregates in tailing suspensions at different dosages of polymers: (a) Al-PAMM₁, (b) Al-PAMM₂, (c) Al-PAMM₃ and (d) GG.

Figure 9 | Images of floccules in suspensions flocculated with 5 mg/L Al-PAMM₁ at (a) 0 s, (b) 10 s, (c) 30 s and (d) 60 s respectively. The full color version of this figure is available in the online version of this paper, at http://dx.doi.org/10.2166/wst.2017.422.
surface and binding sites, which contributed to the generation of larger and denser flocs and the firm attachment of particles on the polymer (Figure 10). Contrary to that, smaller and looser flocs were formed by adding GG, and part of the unadsorbed particles remained in suspension (Figure 10), possibly owing to the electrostatic repulsion between particles. As for the Al-PAM, the positively charged Al(OH)₃ cores diminished the electrostatic repulsion between oppositely-charged particles by charge neutralization and achieved much greater and denser adsorption. Besides, the ‘star-like’ structure brings great convenience to the interaction between PAM chains in Al-PAM and tailing particles because of the easy approachability. Accordingly, larger quantities of particles were adsorbed onto the PAM chains through hydrogen bonding between the solid surface hydroxyls and polymer carbonyl groups, bringing about the formation of larger and denser flocs (Music´ et al. 1999; Alagha et al. 2013; Lu et al. 2016).

**Interaction of Al-PAM with silica by ζ potential measurement**

The interaction of the Al-PAM with 0.02 wt% nano-silica suspensions was investigated by measuring the ζ potentials of silica particles before and after adding different concentrations of polymer. Figure 11 shows a gradual decrease in the negative value of the ζ potential with increasing addition of Al-PAM, more efficient for Al-PAM of higher aluminum content (Al-PAMM₁ and Al-PAMM₂ vs Al-PAMM₃). The average ζ potential of nano-silica particles was −40 mV without adding Al-PAM, while it increased gradually from −40 mV to −1 mV with the increasing dosage of 30 ppm Al-PAMM₁. For Al-PAMM₁ and Al-PAMM₂, no significant increase in the ζ potential of silica particles was observed when the polymer dosage exceeded 30 ppm, probably suggesting the surfaces of the silica particles were saturated with Al-PAM molecules (Wang et al. 2014c). The higher ζ potential values of silica particles treated with equal amounts of Al-PAMM₁ and Al-PAMM₂ compared to Al-PAMM₃ indicate higher aluminum contents are more effective in neutralizing the negatively-charged silica particles, which confirmed the charge neutralization of negatively-charged silica particles by positively charged Al-PAM. The more efficient effect of a higher aluminum content on neutralizing the negative charge of the silica particle just explains the enhanced flocculation of the Al-PAM observed in the settling experiment of cyanide tailing suspensions.

**Flocculation mechanism of Al-PAM**

On the basis of the above experimental results, a synergistic mechanism is put forward to illuminate the superior performance of the hybrid polymer Al-PAM (Figure 12): (1) charge neutralization by positively charged Al(OH)₃ core particles and (2) bridge adsorption by the stretched PAM arm chains. The cationic ‘star-like’ Al-PAM reduces the electrostatic repulsion among the oppositely-charged tailing particles by Al(OH)₃ particles and allows the particles to achieve a closer approximation, which facilitates PAM chains to bridge many more particles. The dosage of cationic Al-PAM plays a key role in the flocculation effect, both insufficient and superfluous polymers cannot aggregate or flocculate the residual fine particles or small flocs. If
insufficient Al-PAM is used, part of the particles will aggregate in the suspensions and some fines will be left in the supernatant. Therefore, a small size of flocules will form at a low concentration of flocculant, leading to a low ISR and high supernatant turbidity of the tailing suspensions. In addition, if the Al-PAM is applied in excess, the superfluous Al-PAM will cause steric stabilization, prohibiting polymer bridging and resulting in formation of smaller flocules, which leads to lower ISR and higher supernatant turbidity. Only moderate or optimal dosage of Al-PAM will be of great benefit in forming large and compact flocules. As a result, the settling experiment exhibits a rapid ISR and a low solids content in the supernatant.

**CONCLUSIONS**

Enhancement of cyanide tailing suspensions dewatering requires destabilization of particles with a negative charge and particle aggregation through polymer bridging adsorption. An ideal flocculant of Al-PAM is capable of accomplishing these objectives, with the conclusions as follows:

1. An inorganic-organic hybrid flocculant, Al-PAM, was prepared by inverse microemulsion polymerization. TEM images and flocule morphology observed with SEM indicated that the Al-PAM molecule had a ‘star-like’ structure with the core Al(OH)₃ colloidal particles linking PAM arm chains.
2. Flocculation of the Al-PAM to fine particles in cyanide tailing suspensions was greatly superior to that of commercial flocculant GG. Al-PAM M₁ at 1.5 mg/L could get an equal effect in flocculating cyanide tailing suspensions to GG at 5 mg/L. Furthermore, Al-PAM M₁ exhibited 17.5 times the ISR increasing ratio, about 3.1 fold higher than GG, and 90.0% removal efficiency of supernatant turbidity, compared with GG, which had 5.7 times and 37.2% at the same dosage of 5 mg/L.
3. The molecular weight and Al(OH)₃ content determined the flocculation performance of the Al-PAM for tailing suspensions. For Al-PAM with a given Al(OH)₃ content, higher molecular weight showed a stronger adsorption bridge and thus formed larger and denser flocules. For Al-PAM with a given molecular weight, higher Al(OH)₃ content showed more effective charge neutralization to the negatively-charged particles. The flocculation mechanism of Al-PAM for cyanide tailing suspensions was charge neutralization by Al(OH)₃ colloidal particles and bridge adsorption by the extended PAM chains.

**REFERENCES**


