Hydrophobic aggregation of fine particles in high muddied coal slurry water
Jun Chen, Fanfei Min, Lingyun Liu, Chenliang Peng and Fangqin Lu

ABSTRACT

The hydrophobic aggregation of fine particles in high muddied coal slurry water in the presence of four quaternary ammonium salts of 1231(dodecyl trimethyl ammonium chloride), 1431(tetradecyl trimethyl ammonium chloride), 1631(cetyl trimethyl ammonium chloride) and 1831(octadecyl trimethyl ammonium chloride) was investigated through the measurement of contact angles, zeta potentials, aggregation observation, adsorption and sedimentation. The results show that quaternary ammonium salts can enhance the hydrophobicity and reduce the electronegativity of particle surface, and thus induce a strong hydrophobic aggregation of slurry fine particles which promotes the settlement of coal slurry water. The adsorption of quaternary ammonium salts on slurry particles increases with the increase of alkyl chain length and reagent dosage, and will reach equilibrium when the dosage reaches a certain value. Weak alkaline conditions also can promote quaternary ammonium salts to be adsorbed on the coal slurry fine particles. In addition, reasonable energy input and a chemical environment of weak alkaline solution are conducive to hydrophobic aggregation settlement of high muddied coal slurry water with quaternary ammonium salts. The main mechanism of hydrophobic aggregation of coal slurry particles with quaternary ammonium salts is ‘adsorption charge neutralization’ and hydrophobic interaction.

Key words | action mechanism, adsorption, coal slurry water, hydrophobic aggregation, quaternary ammonium salt, sedimentation

INTRODUCTION

Coal slurry water is a kind of industrial waste water produced in wet coal separation, and its clarification treatment is an essential link in the processes of coal preparation plants. Due to the mechanization of coal mining and the deterioration of raw coal, lots of high muddied coal slurry water is produced in coal preparation, which has characteristics of extraordinary fine granularity, high clay mineral content, and strong electronegativity of particle surface (Chen et al. 2014). The particles in coal slurry water, especially the clay mineral particles, have strong hydrophilic surfaces which easily attract water molecules to form a strong hydration layer. When the particles approach each other, strong hydration repulsion and a stereo-hindrance effect are produced to make the dispersion system of coal slurry water stable, and avoid the aggregation settlement of the slurry particles (Israelachvili & McGuigan 1988; Israelachvili 1992; Song et al. 2006). In the case, the sedimentation effect of conventional technique by adding electrolyte coagulant and polymeric flocculant is not ideal. Therefore, it is significant to develop an effective settlement technology for coal slurry water.

Min et al. (2014) pointed out that hydrophobic aggregation was an effective process for coal slurry water treatment. And as the main components of coal slurry, clay minerals have a significant influence on dispersion and aggregation of kaolinite particles, and one of the important premises of achieving the effective aggregation of kaolinite is adjusting its surface properties. For the hydrophilic clay minerals in coal slurry water, hydrophobic aggregation could be realized through rendering surface hydrophobicity after the adsorption of surfactants on the surfaces to reduce the hydration repulsive force and enhance the hydrophobic attraction.
The coal slurry water sample was taken from a coking coal preparation plant in Huainan, Anhui, China. And pulp density of the coal slurry water was 21 g/L, pH = 7.9. The size distribution of coal slurry water was measured based on the China Standard of GB/T19093-2003, and the cumulative size distribution of the slurry particles of −0.045 mm was determined using a laser particle size analyzer (SALD-7101, Japan). A scanning electron microscope (SEM) (S3000-N, Japan) was used to observe the morphologies of the slurry particles in different sizes. And the mineral components were analyzed by using a X-ray diffraction meter (XRD-6000, Japan) with Cu Kα radiation.

In this test, a measured dosage of quaternary ammonium salt (1231, 1431, 1631 and 1831, analytical grade, Shanghai Sinopharm Chemical Reagent Co., Ltd, China) was added into the coal slurry water of 500 mL. The pH was adjusted to the predetermined value by 1 mol/L NaOH or HCl. Then, the slurry water was mixed immediately at 750 r/min for 10 min. The contact angle of water on the slurry particles was measured at 25 °C by a contact angle meter (C20, America). About 0.6 g dry slurry particles in different conditions were pressed into a 2 mm thick slice at 30 MPa. The contact angle of the surface was the average of six measurements on two different locations of the surface. Zeta potentials were measured at 25 °C by a Zetaprobe zeta meter (USA), and the average of three measurements was taken in the present results. The microstructure of the aggregations was observed on a glass slide by using a Monocular Zoom Microscope (HSA10, China) when the hydrophobic aggregation was stable.

The adsorption quantity of quaternary ammonium salts on slurry particles was determined using the same spectrophotometric method as Wu et al. (2002) in this study. Firstly, the absorption spectroscopies of quaternary ammonium salts at a series of given concentrations at 616 nm wavelength (Chen et al. 2015) were determined by Ultraviolet Spectrophotometry (UV-2000, China) to obtain the calibration curve. A given concentration of quaternary ammonium salt was added into the 30 g/L slurry water of 500 ml, then the slurry water was mixed at 750 r/min for 10 min with a given pH, and finally settled for 3 hours. After that, the supernatant solution was centrifuged at 5,000 r/min for 30 min. Then centrifugal liquid was next analyzed for the final concentration of quaternary ammonium salts, based on the calibration curve. The adsorption quantity of quaternary ammonium salts on slurry particles was estimated by the following expression:

\[ A = \frac{V(C_0 - C)}{m}, \]

where \( A \) is the adsorption quantity, mg/g; \( C_0 \) and \( C \) are the initial and final concentrations, respectively, mg/L; \( V \) is the solution volume, L; \( m \) is the weight of the particles, g.

In the sedimentation test, a measured dosage of quaternary ammonium salt was added into the slurry water of 500 mL. The pH was adjusted to the predetermined value by 1 mol/L NaOH or HCl. Then, the slurry water was mixed immediately at a predetermined speed for a predetermined time, and finally precipitated in a 500 mL graduated cylinder for 30 min. When precipitating for 15 min, the light transmittance of liquid supernatant was measured by a spectrophotometer. The initial settling velocity was calculated.

\[ \text{Absorption} = \frac{C}{A} \]

where \( A \) is the adsorption quantity, mg/g; \( C \) is the final concentration, mg/L; \( A \) is the surface area of the particles, m².

\[ \text{Settling velocity} = \frac{W}{V} \]

where \( W \) is the weight of the particles, g; \( V \) is the volume of the slurry, L.

\[ \text{Zeta potential} = \frac{V}{I} \]

where \( V \) is the solution volume, L; \( I \) is the current, A; \( V \) is the voltage, V.

\[ \text{Contact angle} = \frac{\sin \theta}{\cos \phi} \]

where \( \theta \) is the contact angle; \( \phi \) is the angle of incidence; \( \theta \) is the angle of reflection.

\[ \text{Surface tension} = \frac{1}{r} \]

where \( r \) is the radius of the sphere, m.

\[ \text{Density} = \frac{\rho}{\rho_0} \]

where \( \rho \) is the density of the particles; \( \rho_0 \) is the density of water.
RESULTS AND DISCUSSION

Characteristics of coal slurry water

The particle size distribution of coal slurry is shown in Table 1, the −0.045 mm grade of coal slurry was 82.30%, and the ash content was 54.42%. And the $d_{50}$ (average particle size) of the slurry particles of −0.045 mm was 2.073 μm, as shown in Figure 1. The SEM images of coal slurry in different particle sizes are shown in Figure 2. The particles of 0.50–0.045 mm have smooth cleavage planes, and the ones of −0.045 mm have irregular cleavage planes. Figure 3 illustrates the X-ray diffraction pattern of the sample. Five minerals, including quartz, kaolinite, smectite, chlorite and calcite could be found in the sample. These minerals can increase the difficulty of coal slurry water treatment because they are all clayed minerals (Cao et al. 2009) and can slime easily. These results show that the coal slurry water sample was a typical high muddied slurry water.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The particle size distribution of coal slurry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size fraction/mm</td>
<td>Productivity/%</td>
</tr>
<tr>
<td>0.5–0.25</td>
<td>1.18</td>
</tr>
<tr>
<td>0.25–0.125</td>
<td>4.20</td>
</tr>
<tr>
<td>0.125–0.075</td>
<td>4.80</td>
</tr>
<tr>
<td>0.075–0.045</td>
<td>7.53</td>
</tr>
<tr>
<td>−0.045</td>
<td>82.30</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Contact angles, zeta potentials and aggregation observation

The wettability of the prepared coal slurry samples was investigated according to the different contact angles on their surfaces. Table 2 shows the contact angles of coal slurry in different conditions at pH 7.9. The contact angles of coal slurry increased with the increase of alkyl chain length and reagent dosage of quaternary ammonium salts.

pH is an important factor which affects the zeta potential of the mineral particle surface (Syed et al. 1996; Yukselen & Aksoy 2011), and zeta potential is an important parameter to reflect the effect of chemicals and mechanisms on the slurry water treatment. Figure 4 illustrated the zeta potential of coal slurry particles as a function of pH with (or without) quaternary ammonium salts. The zeta potentials of coal slurry particles were negative and reduced with the decrease of pH. Meanwhile, the absolute value of zeta potential decreased with the increase of alkyl chain length and reagent dosage of quaternary ammonium salts.

Figure 5 showed the microscopy images of aggregated slurry particles with reagent dosage of 4,000 g/t at pH 7.9. The sizes of the aggregations increased with the increase of alkyl chain length of quaternary ammonium salts, which indicated that aggregating abilities of this quaternary ammonium salts for coal slurry fell in the order of 1831 > 1631 > 1431 > 1231. The sizes of the aggregations were about 0.5–1.8 mm, which were 724–868 times the average particle size (see Figure 1) of coal slurry particles.

These results show that the quaternary ammonium salts can enhance the hydrophobicity and reduce the electronegativity of slurry particle surfaces, and the fine particles strongly aggregated with quaternary ammonium salts by hydrophobic attraction, which is in line with the extended Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. This is consistent with hydrophobic aggregation.

Adsorption and sedimentation

Figure 6 shows the adsorption quantity of quaternary ammonium salts on slurry particles as a function of reagent dosage and pH. The adsorption quantity was on the upward trend with the increase of alkyl chain length and reagent dosage, and it tended to be stable when the dosage reached 8,000 g/t. There was a slight increase of the adsorption along with the increase of pH, but it started to decrease when pH was above 8 due to the interaction between OH− and quaternary ammonium cations.
Figure 7 showed the influence of reagent types and dosage on hydrophobic aggregation settlement of coal slurry water. The initial settling velocity increased with the increase of dosage of 1431, 1631 and 1831 and reached a peak when the dosage was 1,000 g/t, then sharply declined. But it decreased with the increasing dosage of 1231. The light transmittance of supernatant liquid increased with the increase of alkyl chain length and dosage. Figure 8 showed the influence of energy input on hydrophobic aggregation settlement of coal slurry water. With the stirring intensity increasing from 300 r/min to
1,300 r/min, the initial settling velocity presented an obvious rising trend. And the light transmittance of supernatant liquid changed obviously, which first increased and then decreased with the increase of stirring intensity and stirring time. The effect of hydrophobic aggregation settlement was sufficient when the stirring intensity was 750 r/min and stirring time was 10 min, because the settling velocity and light transmittance reached the optimal value at the same time. Figure 9 shows the influence of pH on the hydrophobic aggregation settlement of coal slurry water. When the pH increased from 4 to 12, the initial settling velocity increased steadily, and the light transmittance of supernatant liquid decreased rapidly. As can be seen from Figure 9(a) and 9(b), both the initial settling velocity and light transmittance achieved a high value when the pH was weak alkaline (from 7 to 9) and this was the better condition for slurry water hydrophobic aggregation settlement.
The results of adsorption and sedimentation show that quaternary ammonium salts can adsorb on the slurry fine particles to promote the hydrophobic aggregation settlement of the high muddied coal slurry water. The adsorption of quaternary ammonium salts on slurry particles increases with the increase of alkyl chain length and reagent dosage.
Mechanical energy input has great influence on the hydrophobic aggregation settlement of coal slurry water, because it changes the adsorption quantity of reagents on slurry particles and the collision probability between hydrophobic particles, which impacts the formation and the sizes of hydrophobic aggregations. As a result, the initial settling velocity and the light transmittance of supernatant liquid present significant differences. Thus, the proper stirring intensity and stirring time are very beneficial to hydrophobic aggregation settlement.

As the main clay minerals in coal slurry water, kaolinite and quartz have a significant impact on the settlement of coal slurry water. It is well known that clay minerals have a basal permanent negative charge caused by isomorphous substitution, while the charge on the planes is either positive or negative depending on the pH (Luckham & Rossi 1999; Lagaly & Ziesmer 2003; Bergaya et al. 2006). Liu et al. (2015) indicated that kaolinite is an anisotropic charged body which gets permanent negative charge on the silicon-oxygen tetrahedron (T plane), and gets variable charge on the end (E plane) and alumina octahedron (O plane). When the pH is lower than 5, kaolinite is positively charged because of the protonation, and it is negatively charged when pH is higher than 5 because of deprotonation (Schroth & Sposito 1997). Quartz is an isotropic charged body, whose charge is closely related to the pH due to its low zero isoelectric point, and it is negatively charged in the test pH range. Because the E and O planes of kaolinite are positively charged in coal slurry water at pH < 5, the aggregating process of slurry particles has two main parts, as follows. (1) The T–O, T–E planes of the kaolinite attract each other and produce the aggregate behavior; the O plane and E plane of kaolinite attract quartz particles and other negative electrostatics to form aggregation. The positive charge quantity of the O and E plane of kaolinite increases gradually with the decrease of pH, which enhances the capability of forming aggregations. (2) The reagent molecules adsorbed on the surfaces of slurry particles can reduce the electronegativity of slurry particle surfaces, so that particles attract each other more easily to form hydrophobic aggregations. It can be found that the lower the pH was, the lower the electronegativity was (see Figure 4) and the better the effect of particles forming aggregations for the particles. Under the circumstances, the sizes of slurry aggregations increase with the decrease of the pH, and large aggregations heap up on each other and form a mesh structure to net fine particles during the settlement process, which increases the light transmittance of supernatant liquid. When pH is higher than 5, each planes of
kaolinite is negatively charged. The aggregation of slurry particles is mainly the effect of hydrophobic interaction due to the adsorption of reagent molecules enhanced with the increase of pH. Therefore, when pH ranges from 5 to 8, the hydrophobic interaction between the particles is greater than the electrostatic repulsion, and hydrophobic particles aggregate better. But when the pH is higher than 8, the particle surface electronegativity and OH⁻ ions in solution increase rapidly, and the electrostatic repulsion between the particles is greater than the hydrophobic interaction, resulting in deterioration of the particles aggregate. Small aggregations avoid the particles crowding mutually during the settlement process, which increases settling velocity. However, the light transmittance of supernatant liquid reduces due to the lack of complete mesh structure. In summary, in alkaline conditions the settling velocity and the light transmittance can reach satisfactory values to adapt to the sedimentation of coal slurry water.

**Action mechanism of hydrophobic aggregation**

The flocculation mechanism of cationic flocculant for negatively charged particles was the result of the combination of ‘adsorption charge neutralization action’ and ‘adsorption bridging flocculation’ (Tian et al. 2007). Quaternary ammonium salts used as cationic surfactants which have long alkyl chain could not only be adsorbed on the surfaces of negatively charged particles by electrostatic attraction, but also have a slight flocculation on slurry particles. However, because the quaternary ammonium cation compound was a small molecule, which only had one active group, it can be adsorbed on slurry particles to produce a single point adsorption rather than simultaneously capturing two or more particles, the action of ‘adsorption bridging flocculation’ was very weak and could be ignored. Adsorption bridging theory (Wandrey et al. 1999; Matsumoto 2001) indicated that, only adding the proper dosage of flocculant, i.e., the colloid particle surface is partly covered, can have an effective adsorption bridging role between colloidal particles, and have the best flocculation effect. Therefore, when the dosage of quaternary ammonium salts is enough to be fully adsorbed on the particle surface and mechanical energy input is provided to produce high collision probability between particles, reagent molecules have a weak ‘adsorption bridging flocculation effect’ due to the hydrophobic association of the carbon chain. So, the action mechanism of hydrophobic aggregation of coal slurry particles with quaternary ammonium salts is predominantly the effect of ‘adsorption charge neutralization action’. Namely, the absorption of quaternary ammonium cations on the surface of single particles is consistent with the pattern of aggregation for ‘adsorption charge neutralization action’ (as shown in Figure 11). A large amount of cationic groups of quaternary ammonium salt molecules was adsorbed and covered on the particle surfaces by electrostatic interaction, resulting in the reduced electronegativity of the slurry particle surface and the decreased electrostatic repulsion between particles to make the particles aggregate more easily.

After hydrophobic modification by quaternary ammonium salts, the slurry particles aggregated by hydrophobic attraction, which is in line with the extended DLVO theory. Extended DLVO theory indicates that particle interface energy should include interactions of DLVO and non-DLVO. When the particle spacing is less than 20 nm, hydrophobic interaction between particles tends to be significant. Due to the presence of hydrophobic interaction energy, hydrophobic interactions show strong attraction which is found to be 10–100 times stronger than van der Waals force (Min et al. 2014), and the total interaction energy is essentially provided by hydrophobic interaction energy. Thus, if coal slurry particles are fully hydrophobically modified by quaternary ammonium salts, hydrophobic attraction can overcome the electrostatic repulsion and make the hydrophobic particles form aggregates even in the case of higher zeta potential.

In summary, the action mechanism of hydrophobic aggregation with quaternary ammonium salts should be the result of ‘adsorption charge neutralization’ action and hydrophobic attraction, and the strength of the two interactions depended not only on the reagent types and dosage of

![Figure 11](https://iwaponline.com/wst/article-pdf/73/3/501/463792/wst073030501.pdf)
quaternary ammonium salts, but also on the characteristics of the slurry water system, such as pH and pulp density.

CONCLUSION

1. Fine particles in high muddied coal slurry water strongly aggregated with quaternary ammonium salts, which can enhance the hydrophobicity and reduce the electronegativity of particle surfaces. This phenomenon was in line with extended DLVO theory, and closely correlated with the adsorption of quaternary ammonium salts on particles and thus the hydrophobicity of particle surfaces. Accordingly, it belongs to hydrophobic aggregation. The aggregating abilities of the four quaternary ammonium salts for coal slurry fall in the order $1831 > 1631 > 1431 > 1231$.

2. Quaternary ammonium salts can adsorb on the slurry fine particles to promote the hydrophobic aggregation settlement of the high muddied coal slurry water. With the increase of alkyl chain length and reagent dosage, the adsorption quantity of quaternary ammonium salts on the slurry particles tends to increase. And it reaches equilibrium when the reagent dosage is about $8,000$ g/t. Weak alkaline conditions also can promote quaternary ammonium salts to be adsorbed on the coal slurry particles. In addition, reasonable energy input and a chemical environment of weak alkaline solution are conducive to hydrophobic aggregation settlement of high muddied coal slurry water.

3. The main mechanism of the hydrophobic aggregation of coal slurry particles under the action of quaternary ammonium salts is ‘adsorption charge neutralization’ and hydrophobic interaction.

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