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## **EFFECT OF ELECTROLYTE ADDITION ON FLOTATION RESPONSE OF COAL**

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**Abstract:** In this study, the flotation of naturally hydrophobic coal particles in salt solutions with different cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Al}^{3+}$ ) was investigated to clarify the flotation enhancement mechanism. The surface chemistry aspects were examined using the zeta potential measurements and bubble-particle attachment time experiments. The results of the flotation experiments showed that the presence of electrolytes in the flotation system clearly enhanced the flotation performance in a manner dependent on the type and concentration of the electrolytes. In the experiments, the  $\text{AlCl}_3$  and  $\text{NaCl}$  solutions showed the highest and the lowest flotation performance improvements, respectively. The zeta potential measurements showed that  $\text{AlCl}_3$  had a stronger influence on the surface charge of coal particles than  $\text{CaCl}_2$  or  $\text{NaCl}$  did. The induction time measurements indicated that the attachment decreased with increasing salt concentration and ionic valency state. In addition, abundant fine bubbles were generated in higher concentration salt solutions, particularly for the  $\text{AlCl}_3$  solutions, which prevented from the bubble coalescence and increased froth stability. It is concluded that the addition of salt solutions to a flotation system enhances the coal flotation performance, particularly for high-valence electrolyte solutions, which is attributed to the abundance of finer bubbles in the froth phase, depending on the type and concentration of the electrolyte.

**Keywords:** *coal flotation, salt solutions, zeta potential, induction time, froth stability*

### **Introduction**

Flotation, undoubtedly the most important and versatile mineral processing technique, is a physico-chemical separation process that utilises the difference in surface properties of particles of various minerals (Arnold and Aplan, 1989; Nguyen et al., 1998; Subrahmanyam and Forssberg, 1988). Since researchers first discovered that the electrolyte ions could enhance the flotation of naturally hydrophobic particles, there has been an intense interest in the study of mineral flotation in the seawater and electrolyte solutions (Hampton and Nguyen, 2009; Kurniawan et al., 2011; Wellham et al., 1992; Yoon, 1982). Several theories have been proposed to explain the

enhancement of coal flotation in salt solutions, which can be divided into three categories: i) the inorganic electrolytes destabilise the hydrated layers surrounding the mineral particles and reduce the surface hydration of particles, which in turn increases the attachment efficiency of the valuable mineral particles to air bubbles (Dishon et al., 2009), ii) the inorganic electrolytes compress the electrical double-layer between and reduce the zeta potential of bubbles and particles, which corresponds to the reduction of the electrostatic force between bubbles and particles (Paulson and Pugh, 1996; Yoon and Sabey, 1989), and iii) the inorganic electrolytes decrease the coalescence of bubbles, which produces an abundance of fine bubbles and increases froth stability (Bournival et al., 2012; Craig et al., 1993; Marrucci and Nicodemo, 1967).

However, these theories only partially explain the mechanism of coal flotation in salt solutions, which is very complex. There is undoubtedly a correlation among the flotation recovery, flotation kinetics, bubble size distribution, and froth stability profile with the addition of salt solutions (Marrucci and Nicodemo, 1967; Harvey et al., 2002; Marcelja, 2006; Pugh et al., 1997; Weissenborn and Pugh, 1996). Paulson and Pugh (1996) proposed that the improved flotation of hydrophobic graphite in electrolytes was related to the dissolved gas concentration gradient in the electrolyte solutions. Ozdemir et al. (2009) investigated the surface chemistry aspects of coal flotation. The results indicated that the enhancement of coal flotation in hypersaline water was not entirely due to surface chemistry aspects, as previously proposed. Recently, a study performed by Kurniawan et al. (2011), showed that the addition of salt solutions to a flotation system produced smaller bubbles in the froth phase and that the bubble size decreased with increasing salt concentration, improving the coal flotation performance. Bournival et al. (2012), also investigated the coalescence behaviour of bubbles with NaCl using high-speed video imaging compared with a similar system using 4-methyl-2-pentanol. The results showed that NaCl had no surface-restoring effect, even at high concentration, whereas MIBC prevented the bubble surface from the deformation during coalescence at relatively high concentrations. Ozdemir (2013), investigated the flotation of bituminous coal in the presence of NaCl, KCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> without use of any flotation chemicals. The results clearly indicated that the Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> ions had a strong ion specific effect on the flotation of bituminous coal, and there was an optimum salt concentration to produce a clean coal in these salt solutions.

A review of the literature shows that the previous studies mainly focused on the enhancement of a coal flotation performance in salt solutions. Therefore, to further understand the role of electrolytes in coal flotation, three salt solutions with different cations (Na<sup>+</sup>, Ca<sup>2+</sup>, and Al<sup>3+</sup>) were compared in terms of the coal flotation enhancement using the micro-flotation experiments, zeta potential measurements, and bubble-particle attachment time experiments.

## **Materials and Methods**

### **Materials**

The pure coal sample used in this study was obtained from Alberta, Canada, and was naturally hydrophobic. The volatile matter content for the coal was less than 10%. The  $-250+212\ \mu\text{m}$  particle size fraction was selected for all tests. Analytical grade ( $>99\%$ ) electrolytes (NaCl,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$ ) were used in the experiments. The electrolyte concentrations used in the tests were 0.01 M, 0.05 M, 0.1 M, 0.15 M, and 0.2 M. Analytical grade hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the pH level. For all experiments, the pH value was kept at  $\sim 6.4$ .

### **Methods**

#### **Micro-flotation experiments**

The coal samples taken from the  $-250+212\ \mu\text{m}$  fraction were used for the micro-flotation, which was performed in a Hallimond tube equipped with an air flowmeter and magnetic stirrer. In each test, 1 g of the coal sample was mixed with 150 ml of a given salt solution, and the mixture was placed in a 250 ml beaker agitated for 5 min. The slurry was then transferred to the tube followed by a stream of  $\text{N}_2$  at a flow rate at 45 ml/min. A constant stirrer speed of 250 rpm and a constant water level were maintained within the tube during each experiment. All tests were performed at room temperature. The flotation time was 3 min for each test. Finally, the flotation products were filtered, dried, and weighed.

#### **Zeta potential measurements**

The zeta potential measurements were performed using Brookhaven ZetaPALS. The coal samples taken from the  $-250+212\ \mu\text{m}$  fraction were further ground to a  $-45\ \mu\text{m}$  particle size for zeta potential measurements. For each experiment, 0.05–0.1 wt.% suspensions of the ground coal particles were prepared using the desired salt solutions. The suspensions were allowed to stand for 12 h prior to the measurement. The pH value was adjusted using either acid (HCl) or alkali (NaOH). The zeta potential was measured 6 times during each experiment, and the average value was reported. The measurements were performed at  $22\ ^\circ\text{C}$ .

#### **Induction time measurements**

Induction time measurements between coal particles and air bubbles were performed with a homemade induction time device (Gu et al., 2003), as shown in Fig. 1. The coal samples taken from the  $-250+212\ \mu\text{m}$  fraction were used to measure the bubble-particle attachment time. For each measurement, 1 g of coal was conditioned in a given salt solution for 5 min. Next, the conditioned particles together with the solution were transferred to the measurement vessel under the bubble holder. The bubble generated from a glass capillary was brought into contact with the particle bed at a set contact time.

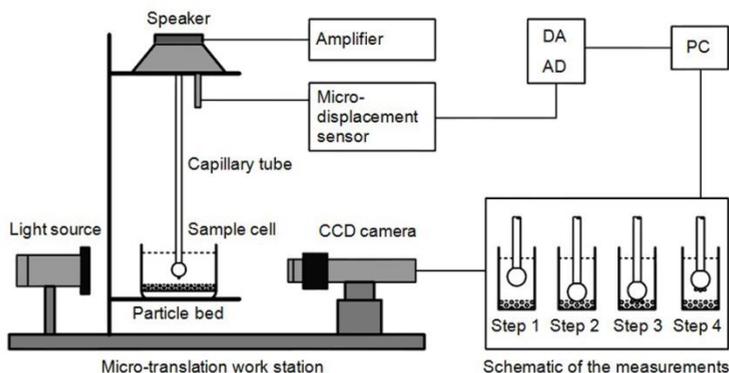


Fig. 1. Schematic of the bubble-particle attachment time measurement device (Gu et al., 2003)

Each experiment was repeated 20 times at different locations in the particle bed. The induction time was characterised as the contact time, at which the pickup probability was 50%. The approach and attachment processes were recorded by a CCD camera. The initial distance between the bubble pole and particle bed (0.40 mm), the amplitude of the bubble motion (5 volt), the approach and retraction velocities of bubbles (40 ms), the bubble size (1.2 mm), were all kept constant during the measurements. The measurements were carried out at room temperature.

## Results and discussion

### Micro-flotation experiments

Coal flotation was carried out in three salt solutions without a frother or collector. The coal recovery as a function of salt concentration is plotted in Fig. 2. The results show that the coal recovery increased with an increasing salt concentration under the

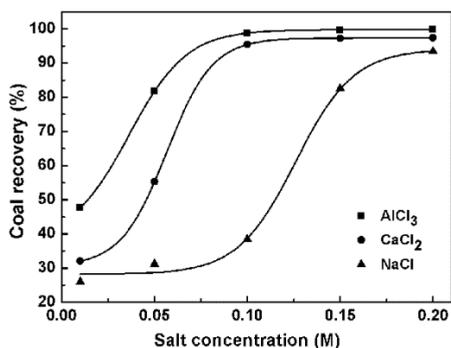


Fig. 2. Effect of salt concentration on coal recovery

test conditions. The coal recovery plateaued when the salt's concentration exceeded 0.1 M for  $\text{AlCl}_3$  and  $\text{CaCl}_2$  and 0.2 M for  $\text{NaCl}$ . The results indicated that  $\text{AlCl}_3$  produced the highest coal recovery, followed by  $\text{CaCl}_2$  and  $\text{NaCl}$ . These results were in agreement with the findings of Li and Somasundaran, 1993, who investigated the flotation of bituminous coal in the  $\text{NaCl}$  solutions using a modified Hallimond tube and concluded that the flotation of coal increased significantly upon the addition of inorganic electrolytes. Ozdemir et al., 2009, also indicated that coal particles could float in bore water, which contained mostly  $\text{Na}^+$  and  $\text{Mg}^{2+}$ , without using any frother or collector, obtaining a coal concentrate recovery of 85%.

### Zeta potentials

The zeta potential of the coal particles as a function of a salt type and concentration were measured. The results for the measurements are given in Fig. 3. As seen in this figure, similarly to the flotation recovery response, the mean value for the zeta

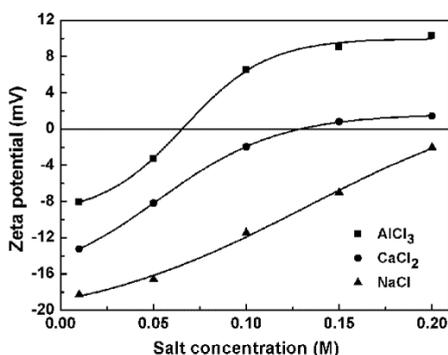


Fig. 3. Effect of salt concentration on zeta potential

potentials were becoming less negative with an increasing salt concentration at constant pH. The  $\text{AlCl}_3$  and  $\text{NaCl}$  solutions showed both the lowest and the highest salt concentration for the point of zero charge of the coal particles, respectively. The results indicated that  $\text{AlCl}_3$  had the strongest influence on the zeta potential at a given salt concentration, followed by  $\text{CaCl}_2$  and  $\text{NaCl}$ . The changes in the zeta potential can be linked with the difference in charge and radius among  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Na}^+$ . Li and Somasundaran (1993), studied the reversal of bubble charge in multivalent inorganic salt solutions and also concluded that the charge of gas bubbles can even be reversed in the electrolyte solutions of multivalent metal ions. In addition, a study performed by Li et al. (1993), showed that trivalent metal cations had the strongest effect on the surface charge of particles, followed by divalent and monovalent metal cations.

### Bubble-particle attachment time measurements

Minerals are separated by their attachment to rising air bubbles in the flotation system. The floatability of the coal particles can be measured using the bubble-particle attachment time (Ye et al., 1989). The bubble-particle attachment time experiments were carried out to measure the flotation of the coal particles as a function of the salt's type and concentration. The results for attachment time are shown in Fig. 4. As seen from Fig. 4, an increase in the salt concentration led to a decrease in the bubble-particle attachment time over the entire tested salt concentration range, which was consistent with the results of the micro-flotation experiments. The shortest induction time was obtained for  $\text{AlCl}_3$ , followed by  $\text{CaCl}_2$  and  $\text{NaCl}$ . In the case of  $\text{NaCl}$ , the result was consistent with the findings of Yoon and Sabey (1989), who concluded that the attachment time was reduced in the  $\text{NaCl}$  solutions. However, this effect is not yet conclusive. For example, according to the bubble-particle attachment time results from Ozdemir et al. (2009), the bubble-particle attachment in bore water was significantly longer than that in the distilled water. Thus, the coal particles would be more floatable in distilled water than in bore water, which contained mostly  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . The flotation tests showed the opposite results, indicating that the induction time experiments could not be precisely correlated with the flotation behaviour of the coal particles in bore water.

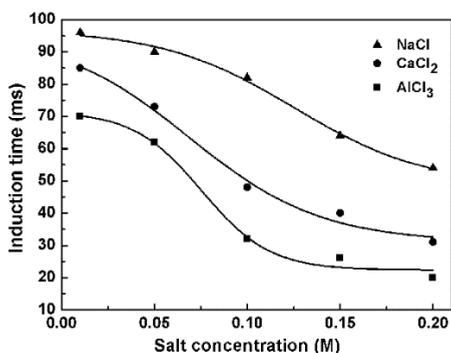


Fig. 4. Effect of salt concentration on bubble-particle attachment time

### Discussion

It has been reported that the flotation of naturally hydrophobic coal can be increased significantly by the addition of the inorganic electrolytes (Hampton and Nguyen, 2009; Kurniawan et al., 2011; Wellham et al., 1992; Yoon, 1982; Li and Somasundaran, 1993). The overall results of this study showed that the effect of the

salt on the coal recovery depends on the salt type and concentration. Under the test conditions used in this study, the coal can be recovered from salt solutions without using flotation reagents.  $\text{AlCl}_3$  showed the best flotation recovery response, followed by  $\text{CaCl}_2$  and  $\text{NaCl}$ . This result was consistent with other researchers' earlier findings that the flotation of naturally hydrophobic materials increased significantly upon the addition of inorganic electrolytes (Kurniawan et al., 2011; Yoon, 1982; Yoon and Sabey, 1989; Li and Somasundaran, 1993; Laskowski, 1965).

The zeta potential measurements indicated that the salt solutions had a strong influence on the reduction of the zeta potential due to the compression of the electrical double layers (Paulson and Pugh, 1996; Yoon and Sabey, 1989). Therefore, the electrostatic repulsion between bubbles and particles decreased. Some previous studies on the coal particles and bubbles indicated that the soluble cations significantly reduced the magnitude of the zeta potential of particles and bubbles (Paulson and Pugh, 1996; Li and Somasundaran, 1993). The results of our study contradict those of Paulson and Pugh, 1996, who demonstrated that the flotation recovery was the highest for the lowest zeta potential, which can be attributed to the fact that the surface charge of the coal particles would change from negative to positive in the salt solutions under some certain conditions, whereas the bubbles would remain negatively charged. For this reason, the electrostatic attraction would most likely dominate the bubble-particle attachment, which further corresponds to an improvement in the flotation response.

It has been previously indicated that the inorganic electrolytes can destabilise the hydrated layers surrounding particles and reduce the surface hydration of particles, which corresponds to a reduction of the induction time between bubbles and particles (Dishon et al., 2009; Yoon and Sabey, 1989). According to the bubble-particle attachment measurements, it is evident that the induction time of coal particles in the  $\text{NaCl}$  solutions was longer comparing to those in the  $\text{CaCl}_2$  and  $\text{AlCl}_3$  solutions. As for the bubble-particle attachment time results, the coal particles would be more floatable in the  $\text{AlCl}_3$  solutions. Therefore, the decrease in bubble-particle attachment time for coal particles in the  $\text{AlCl}_3$  solutions could have a significant effect on the coal flotation in the  $\text{AlCl}_3$  solutions, which was further supported by the results of micro-flotation tests. These results clearly indicated that the induction time results could be precisely correlated with the micro-flotation behaviour of the coal particles in the salt solutions.

In addition, the flotation efficiency also depends on the bubble size distribution and on the degree of the bubble coalescence because fine bubbles are generally more effective at capturing the particles (Li and Somasundaran, 1991). Figure 5 shows the snapshots of the bubbles in the salt solutions in a  $1 \text{ dm}^3$  Denver cell. An abundance of smaller bubbles was produced with the electrolyte addition, particularly at the higher salt concentrations, which agrees with the literature. It is known that the bubble size is reduced, the bubble coalescence was decreased, and the froth stability increased with the increase of the electrolyte concentration (Ozdemir, 2013; Marrucci and Nicodemo, 1967). It should be noted that the electrolytes used in this study were not purified, which would affect size of the bubbles formed because of surface active contaminants

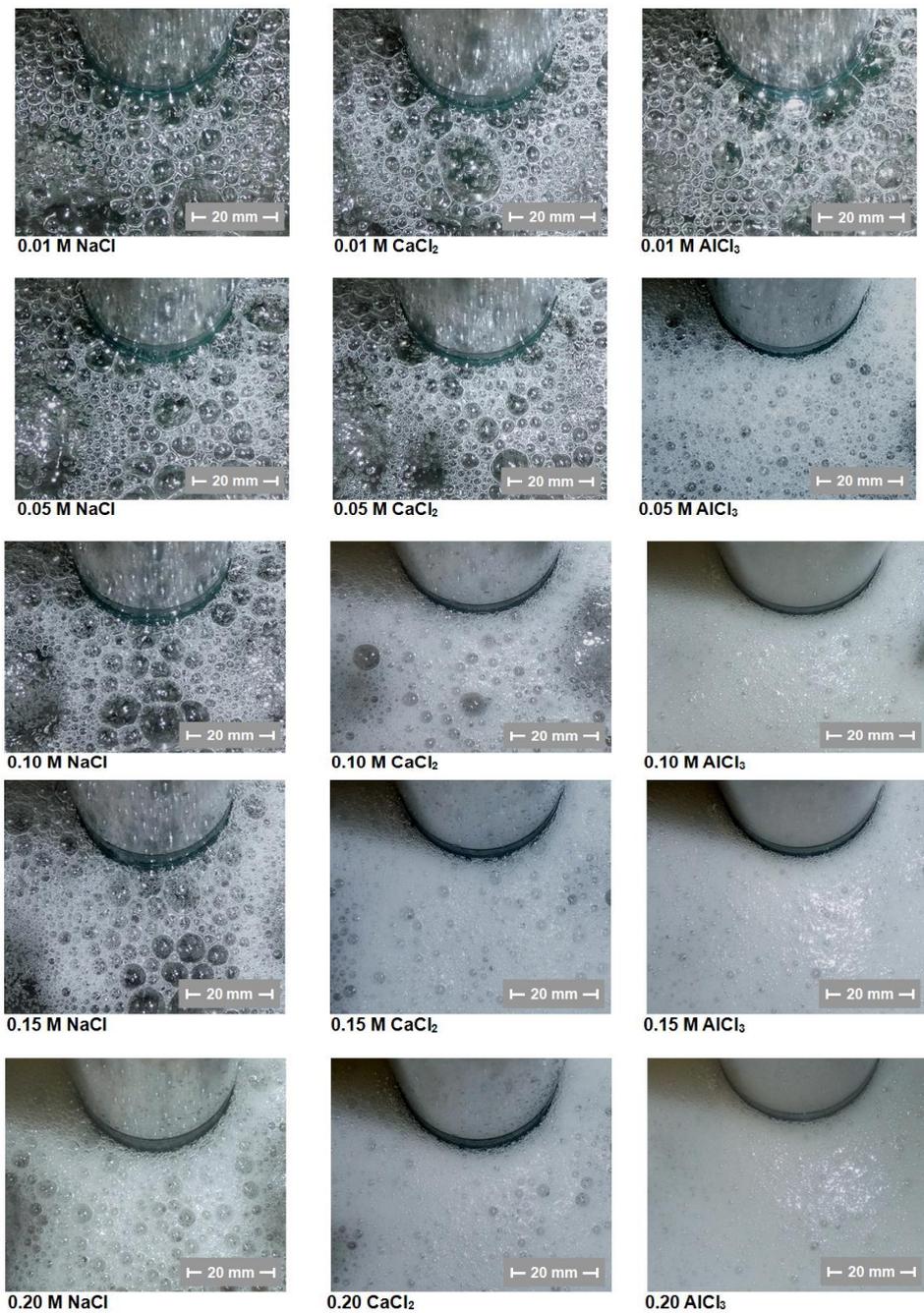


Fig. 5. Snapshots of the bubbles in salt solutions ( $1 \text{ dm}^3$  Denver cell, impeller speed 1500 rpm, air flow rate  $1.25 \text{ dm}^3/\text{min}$ )

at higher electrolyte concentration. But it is undeniable that the addition of salt would increase the froth stability of the system. Accordingly, the coal recovery was significantly improved in the presence of an abundance of fine bubbles. The results indicated that the type and the concentration of the salt solutions significantly affected the froth properties. This phenomenon was consistent with the previous findings (Kurniawan, 2011; Craig et al., 1993). Kurniawan et al. (2011), suggested that there was a correlation between the coal recovery and the stability profile of the froth and concluded that the coal recovery and the bubble size distribution of the froth phase were directly correlated. Recently, Bournival et al. (2012), also concluded that NaCl, albeit at a higher concentration, could be as effective as MIBC in preventing bubble coalescence in a dynamic environment and that the bubbles became more stable with an increasing salt concentration. The reduction of bubble coalescence decreases bubble size and increases froth stability, which is affected by the type and the concentration of the salt (Bournival et al., 2012; Craig et al., 1993; Marrucci and Nicodemo, 1967).

## **Conclusions**

The results of the naturally hydrophobic coal flotation experiments in the presence of salt solutions with different cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Al}^{3+}$ ) showed that the inorganic electrolytes enhanced the flotation performance, depending on the type and the concentration of the salt.  $\text{AlCl}_3$  showed the highest flotation recovery response with increasing salt concentrations, whereas  $\text{CaCl}_2$  showed a moderate increase, and NaCl showed the lowest increase. The zeta potential and bubble-particle attachment time were affected by the type and the concentration of the salt. Similar to the flotation recovery response,  $\text{AlCl}_3$  produced the highest zeta potential at a given salt concentration, followed by  $\text{CaCl}_2$  and NaCl. The results indicated that trivalent metal cations had the strongest effect on the surface charge of the particles. The induction time measurements indicated that the attachment decreased with increasing salt concentration and ionic valency state. In addition, abundant fine bubbles were generated in higher-concentration salt solutions, particularly for the  $\text{AlCl}_3$  solutions, which prevented bubble coalescence and increased froth stability. It is concluded that the addition of salt solutions to a flotation system enhances the coal flotation performance, particularly for high-valence electrolyte solutions, which is due to the abundance of smaller bubbles at the froth phase, depending on the type and concentration of the electrolyte.

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