SPECIFIC ION EFFECT OF CHLORIDE SALTS ON COLLECTORLESS FLOTATION OF COAL

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Abstract. Separation of naturally hydrophobic particles, such as coal, by flotation is known to be enhanced with the addition of salt solutions into the system. In this study, the flotation of bituminous coal in the presence of NaCl, KCl, CaCl₂ and MgCl₂ without use of any flotation chemicals was investigated in detailed. In addition, zeta potential and foam stability tests were performed. The results from this study showed that the flotation behaviour of coal was influenced by these dissolved salts, and determined by the specific effect of these ions, while MgCl₂ and KCl solutions showed the highest and the lowest flotation performance improvements, respectively. The ash content of the products also increased with the salt concentration. This can be attributed to the entrainment of the ash minerals in the salt solutions, particularly at higher salt concentrations. Meanwhile, the froth stability tests at 1 M salt concentration also indicated that there is a correlation between the flotation recovery and stability profile of the froth. These results also clearly indicated that Na⁺, K⁺, Ca²⁺, Mg²⁺ ions have a strong ion specific effect on the flotation recovery of the coal particles, and there is an optimum salt concentration to produce a clean coal in these salt solutions.

Key words: flotation, coal, salt, froth stability, ion-specific effect

Introduction

High salt concentration has a significant effect on bulk and interfacial water structure, and colloidal interactions between bubbles and particles hence affect flotation of minerals. There are several studies in the literature indicating that dissolved ions in flotation system have a significant effect on the flotation of minerals such as potash, trona and borax in brine solutions, and coal in saline water (Yoon and Sabey 1989; Laskowski 1994; Celik et al. 2002; Ozdemir et al. 2010). Several experimental and modelling techniques for determining solution viscosity and surface tension, bubble-particle attachment time, contact angle, atomic force microscopy, sum-frequency vibrational spectroscopy and molecular dynamics simulation have been used to
provide further information on air-solution and solid-solution interfacial phenomena, especially the interfacial water structure due to the presence of dissolved ions (Ozdemir et al. 2007; Schreithofer and Laskowski 2007; Cheng et al. 2008; Du et al. 2008; Burduková et al. 2009).

Several flotation plants in the world use process water with high salt content. Meanwhile, the use of process and saline waters in coal flotation has also attracted great interest for many years as the process water can be re-used and the accumulated salt ions available in water can enhance coal flotation. Since the researchers (Majer et al., 1934) discovered in 1934 that that coal could be floated with the increase in salt concentration without use of flotation chemicals (Ratajczak and Drzymala 2003), a number of theories have been proposed to explain the flotation behaviour of coal in salt solutions.

- Klassen and Płaksin 1954 hypothesized that salt ions destabilize the hydrated layers surrounding the coal and hence reduce the surface hydration of the coal (Ratajczak and Drzymala 2003). The destabilization makes the coal more hydrophobic and enhances the bubble-particle attachment. They also concluded that high salt concentration causes a decrease in the hydrophobicity of coal and thus decreases flotation.
- Charlamow 1957 later hypothesized that flotation in salt solutions is only possible for naturally hydrophobic minerals (Ratajczak and Drzymala 2003). Salt flotation significantly depends on the nature of the anions and cations in the salt solution used.
- Klassen and Kovatchev (1959) demonstrated that salt flotation increases with decreasing in zeta potential of particles (Ratajczak and Drzymala 2003).
- First time in the literature, Klassen and Mokrousov 1963 confirmed the discovery of flotation enhancement of naturally hydrophobic particles in salt solutions.
- Laskowski (1962 and 1963) proposed that the salt flotation is an electrochemical phenomenon; therefore the presence of electrolytes compresses the electrical double-layer (EDL) between bubbles and particles which corresponds to the reduction of zeta potential of both bubble and particle (Ratajczak and Drzymala 2003).
- Laskowski and Mielecki (1964) later showed that salt flotation is a kinetic phenomenon (Ratajczak and Drzymala 2003).
- Marrucci and Nicodemo (1967) found that the presence of electrolytes in aqueous solution reduced bubble size in the pulp phase when the electrolyte concentration was increased. They proposed that the reduction of bubble coalescence depends upon the valence of the electrolytes as well as the magnitude of the surface tension (dγ/dC).
- Laskowski and Iskra (1970) illustrated that contact angle does not change with increasing concentration of salt.
- Li and Somasundaran (1991) showed that efficiency of flotation depends on the degree of bubble coalescence. They later confirmed that while coal flotation decreases at low salt concentration, flotation increased at higher salt
concentrations. For example their studies showed that above 0.1 M NaCl any increase in salt concentration increased the coal floatability. Their studies also showed that the coal flotation decreased with an increase in the salt concentration up to 0.1 M (Li and Somasundaran 1993).

- Reduction of bubble coalescence in salt solutions was also investigated by Craig et al. (1993). Test results showed that there is a definite correlation between the valence of the electrolytes and the transition concentration, where bubble coalescence is reduced by 50%.
- Laskowski (1994) proved that salt ions in the solution destabilize the layer of water around the hydrophobic place as the bridge between the hydrophilic sites.
- Pugh et al. (1997) showed that salt flotation may result from the evolution of hydrophobic micro bubbles on the mineral surfaces. They proposed that salty water contains less dissolved air and thus less cavitations occurs (Paulson and Pugh 1996).
- Ratajczak (2002) also showed that a salt flotation kinetic and thermodynamic phenomenon. And, there is a relationship between contact angle and the energy state of the phase boundaries (Ratajczak and Drzymala 2003).
- Although the studies mentioned above showed that the flotation recovery has a maximum at minimum zeta potentials other studies indicated that the flotation recovery has a maximum at pH values both above and below the isoelectric point (Celik and Somasundaran 1980; Li and Somasundaran 1993).
- However, Harvey et al. (2002) showed that the reduction of zeta potential cannot solely explain the floatability of coal in electrolyte solutions.
- Recently, a study performed by Ozdemir et al. (2009) found that the enhancement of coal flotation in hypersaline water (1 M NaCl) cannot be entirely attributed to the surface chemistry aspects as previously proposed. Their results also proved the previous results by Laskowski and Iskra (1970) that the contact angle of coal in saline water did not change compared with that in de-ionized (DI) water. The atomic force microscopy (AFM) results also indicated that the repulsive force between the bubble and the coal particle was reduced in saline water.

There also have been many studies investigating this mechanism in seawater and saline waters (Yoon 1982; Yoon and Sabey 1989). These studies have brought several mechanisms to explain coal flotation in inorganic electrolyte solutions, and several theories have been suggested to explain the enhancement of coal flotation by salt ions, but the bubble coalescence in salt solutions seems to be a significant factor in coal flotation in saline water. Other available studies have shown that salt ions play an important role in the flotation of soluble minerals and coal (Miller et al. 1992; Hancer et al. 2001; Harvey et al. 2002; Ozdemir et al. 2007). In fact, it is an important issue of using waters containing high salt or sea water due to lack of fresh water in the world. This will also eliminate using flotation chemicals, and therefore, reduce the cost of flotation process. Therefore, it is important to understand how the dissolved ions behave in solutions and at the interfaces.
The literature review shows that little work has been done on investigating the effect of salt ions on the ash content of the coal products in the presence of salt solutions. There has been a significant work on the effect and control of various surfactants used in flotation, on bubble size and particle hydrophobicity, however the effect of electrolytes on coal flotation has not been thoroughly investigated in term of ash content of the products. Therefore, the objective of this study is to investigate the effect of various ions (Na⁺, K⁺, Ca²⁺, Mg²⁺) on flotation of coal along with the behaviour of ash minerals in the salt solutions. In this matter, laboratory scale conventional flotation (Denver) experiments were carried out in NaCl, KCl, CaCl₂, MgCl₂ solutions as a function of salt concentration. Additionally, flotation mechanism of coals in these salt solutions was investigated using zeta potential and froth stability tests.

Materials and methods

Materials

The coal sample used in this study was obtained from Zonguldak, Turkey. The sample was first crushed using jaw and roll crushers to reduce the particle size less than 1 mm. The particle size distribution and ash content of the sample is shown in Fig. (a) and (b). Then, the sample size was reduced down to 212 µm using a ring mill. Finally, the sample was sieved from a 38 µm sieve, and the flotation sample -212+38 µm was obtained. In the case of zeta potential measurements, the sample size was reduced to less than 38 µm using an automatic mortar and pestle.

![Fig. 1. (a) Particle size distribution, and (b) ash content of the raw coal sample](image-url)

The flotation studies and the froth stability tests were carried out with analytical grade (> 99%) salts (NaCl, KCl, CaCl₂, MgCl₂), and they were used without further purification. The salt concentrations used in the experiments were 0.01 M, 0.1 M, 1.0 M, and prepared with mono-distilled water (GFL, Germany). All salt solutions were freshly prepared and used. Additionally, the zeta potential and froth stability tests were performed in de-ionized (DI) water (18 MΩcm) (Milli-Q plus Millipore Ultra Pure...
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Water system, Millipore Ltd, Molsheim, France). The surface tension of the DI water was measured, and found to be about 72.0 mN/m at 23 °C.

Methods

Zeta potential measurements

The zeta potential measurements of coal particles were carried out using a ZetaPlus instrument (Brookhaven Instruments, Holtsville, NY) to determine the electrophoretic mobility of charged suspensions. First, about 7 g of the sample was dry ground for 15 min using a mortar and pestle. Then, the ground sample was screened through a 38 µm sieve, and the undersize fraction was conditioned in the DI water (solid ratio 1%) using a magnetic stirrer at 500 rpm for 15 min. For pH adjustments, the suspension was mixed for about 5 min in order to reach equilibrium after adding the desired amount of 0.1 M HCl or 0.1 M NaOH. Before each experiment, the suspensions were kept for 5 min to allow the coarse particles to settle down. Then, a small amount of suspension was taken from the top of the suspension, and transferred to the measurement cell. Finally, ten measurements at each pH value were performed, and the average value of the measurements was obtained for the coal particles. An average error of these measurements was about 3%. The experiments were carried out at room temperature (23 °C).

Flotation experiments

The flotation experiments were carried out with 212×38 µm size fraction using a small laboratory Denver flotation cell (1.5 dm³). For each flotation experiment, 100 g of a coal sample was added into the cell and mixed with salt solutions at 1000 rpm for 3 min without reagent addition. After 3 min conditioning, air was introduced at a flow rate of 10 dm³/min into the cell and froth was collected at 1, 3, 7, and 15 min. The impeller speed was kept at 1000 rpm. Feed solid concentration was 10% by weight. After flotation, completed concentrates and tailing were filtered, dried at 80 °C, and weighted for further processing and analysis. For the ash analysis, an about 5 g of dried sample from each product was first ground using a mortar and pestle. Then, approximately 2 g of a ground sample from each product was burned in an oven at 815 °C for 2 hr. The ash left over was weighed to calculate the ash content.

Equation 1 was used to calculate the combustible recovery of the flotation experiments:

\[
\text{Combustible Recovery (\%) } = \left[ \frac{M_C(100 - A_C)}{M_F(100 - A_F)} \right] \cdot 100
\]

where \(M_C\) is weight of the concentrate (%), \(M_F\) is weight of the feed (%), \(A_C\) is the ash content (wt.%) of the concentrate and \(A_F\) is the ash content of the feed by weight (%).

Froth stability tests

The froth stability tests were carried out using a 125 cm³ micro-flotation column cell which was mounted on a magnetic stirrer, and a magnetic stirrer bar was used for
agitation. In this study, 1 g sample (212×38 µm) was used for each test. A suspension of 1% by weight was prepared, and mixed at 500 rpm for 10 min. Finally, the suspension was transferred into the micro-flotation cell, and the froth stability tests were performed at a flow rate of 25, 50, and 100 cm³/min. The froth height was recorded as a function of time at a constant airflow rate until the froth reached to a determined level, and the height was used to calculate the dynamic froth stability.

Dynamic froth stability values were determined using the Bikerman equation, as calculated by Eq. 2 (Johansson and Pugh 1992; Paulson and Pugh 1996; Gourram-Badri et al. 1997; Barbian et al. 2003)

$$DFS = \frac{V_f}{Q} = \frac{H_{\text{max}} A}{Q}$$

(2)

where DFS is the dynamic froth stability, $V_f$ is the foam volume, $H_{\text{max}}$ is the equilibrium height of the froth, $A$ is the cross-section area of the cell, and $Q$ is the gas volumetric flow rate.

Results and discussion

Results

Zeta potential measurements

Electrokinetic properties of minerals as revealed from zeta potential measurements provide important information for understanding of flotation separation processes. In this regard, zeta potential measurements for the coal were performed to determine the electrophoretic mobility of the sample. Figure 2 presents the zeta potential results of the coal as a function of pH. As seen from Fig. 2, the pzc (point of zero charge) values for the sample were found to be between pH 7 and 8, which agrees with the literature.

![Fig. 2. Zeta potential-pH profile for the coal sample used in this study](image-url)
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data. According to Aplan (1976), the rank of coals can be classified based on their pzc which decreases from bituminous coal to lignite coal. The pzc for low and medium volatile bituminous coals is about pH 8 which indicates that the coal sample used in this study is very hydrophobic.

**Flotation experiments**

Flotation of coal was carried out in chloride halide salt solutions as a function of salt concentration without a frother or collector, and the results are shown in Figs 3–6. According to the results obtained from coal flotation in NaCl salt solutions, it is possible to produce a coal product with an ash content of 11.17% from the coal sample with an ash content of 52.16% in $10^{-2}$ M salt concentration in 1 min. If the products are combined after completion of 15 min flotation time, a coal product with an ash content of 17.85% can be obtained with a recovery of 75.6%. With further increase in the salt concentration, the flotation recovery increased to 81.8% and 96.0% for $10^{-1}$ M and 1 M NaCl, respectively. On the other hand, an increase in salt concentration significantly increased the ash content of the products. For example, it was obtained a coal product with an ash content of 22.35% in $10^{-1}$ M NaCl, however the ash content of the product at 1 M dramatically increased up to 41.82% for 1 M NaCl. These results clearly indicate that the salt concentration plays an important role in the coal flotation in the salt solutions.

Additionally, a coal product with an ash content of 18.13% was obtained with a recovery of 51.1% after completion of 15 min flotation time in $10^{-2}$ M KCl salt concentration. An increase in the salt concentration from $10^{-2}$ M to $10^{-1}$ M and 1 M increased the flotation recovery to 73.7% and 88.5%, respectively. However, the ash content of the products also increased 31.68% and 41.60% for $10^{-1}$ M and 1 M KCl, respectively.

![Fig. 3. Coal flotation in NaCl salt solutions](image-url)
The flotation results with CaCl₂ showed that a coal product with an ash content of 15.84% was obtained with a recovery of 62.5% after completion of 15 min flotation time in $10^{-2}$ M salt concentration. A further increase in the salt concentration, the flotation recovery increased to 93.3% and 95.1% for $10^{-1}$ M and 1 M CaCl₂, respectively. An increase in salt concentration also increased the ash content of the products from 34.30% in $10^{-1}$ M CaCl₂ up to 41.24% for 1 M CaCl₂.

Finally, the flotation results with MgCl₂ indicated that a coal product with an ash content of 18.23% was obtained with a recovery of 68.1% after completion of 15 min flotation time in $10^{-2}$ M salt concentration. Additional increase in the salt concentration increased the flotation recovery to 92.5% and 96.9% for $10^{-1}$ M and 1 M
MgCl₂, respectively. An increase in salt concentration also significantly increased the ash content of the products from 34.16% in 10⁻¹ M up to 46.83% for 1 M MgCl₂.

Cumulative combustible flotation recovery versus salt concentration shown in Fig. 7 indicates that the flotation recovery increases with increasing salt concentration. As seen from Fig. 7 the increase continues up to 10⁻¹ M from 10⁻² M, then reaches a plateau. According to these results, while MgCl₂ produced the highest flotation recovery, KCl gave the lowest flotation recovery. Based on these results, the following trend can be written:

$$\text{MgCl}_2 \geq \text{CaCl}_2 \geq \text{NaCl} > \text{KCl}.$$
Froth stability tests

The bubble size distribution of the froth phase is an important performance measure for the flotation system. The experimental results from the froth stability in salt solutions indicated that the same trend can be obtained as shown in Fig. 8

\[
\text{MgCl}_2 > \text{CaCl}_2 > \text{NaCl} > \text{KCl}.\]

While MgCl\(_2\) shows the highest froth stability, KCl gave the lowest stability. Fig. 7 along with Fig. 8 clearly highlights that increased salt concentration solutions to the flotation system can be considered as promoters in the absence of frother as more stable froths form in the system.

![Fig. 8. Dynamic froth stability for coal suspensions in 1 M salt solutions as a function of amount of air](image)

**Discussion**

The flotation results suggest that under the present test conditions the coal product can be recovered in chloride salts without using any frother or collector. The coal recovery increases with increasing salt concentration as a function salt concentration. These results also agree with the previous studies (Yoon and Sabey 1989; Li and Somasundaran 1993; Kurniawan et al. 2011).

An inorganic electrolytes, particularly cations such as Na\(^+\) and Mg\(^{2+}\), show a significant influence on the electrokinetic behaviour of the bubbles and particles and reduce the magnitude of zeta potential of bubble and particle (Li and Somasundaran 1991; Paulson and Pugh 1996). In this case, the electrical double-layer is compressed, and hence it will reduce the repulsive interaction between bubbles and particles. For this reason, the hydrophobic force will dominate the system (Yoon and Sabey 1989; Paulson and Pugh 1996; Harvey et al. 2002). The previous experiments also showed
that the flotation recovery reaches maximum at minimum zeta potential (Paulson and Pugh 1996). The atomic force microscopy (AFM) results also indicated that the repulsive force between the bubble and the coal particle was reduced in saline water (Ozdemir et al. 2009). Meanwhile, the results from this study also showed that the contact angle of coal in saline water did not change when compared with that in DI water.

According to the DLVO theory repulsion between bubbles result form a balance of attractive (Van der Waals or dispersive) and repulsive (electrostatic due to negative charge) forces. However, the presence of electrolytes in aqueous solution is known to reduce the occurrence of this process, and a bubble size is reduced in the pulp phase when the electrolyte concentration was increased (Marrucci and Nicodemo 1967). Meanwhile, Craig et al. 1993a; Craig et al. 1993b also showed that there is a definite correlation between the valence of the electrolytes and the transition concentration where bubble coalescence is reduced by 50%. According to this study, the bubble coalescence was inhibited in the presence of some salts such as NaCl, KCl, MgCl₂ etc. Transition concentration for each salt is quite different for each salt. For example, the transition concentration of MgCl₂ and CaCl₂ is 0.02 M, and that of NaCl and KCl is 0.08 and 0.1 M, respectively (Craig et al. 1993a; Craig et al. 1993b). The increase in the flotation recovery from KCl to MgCl₂ can be easily attributed to the decrease in bubble coalescence. The previous studies showed that the high number of the bubbles in the system increased the flotation efficiency of coal particles in salt solutions (Kurniawan et al. 2011). These results show the importance of the effect of ion specificity (size and polarizability) at high salt concentrations on bubble coalescence.

The attachment of the coal particles on bubbles depends on the long-range hydrophobic interaction between them. It is well known that a stable froth has a tendency to result in greater recovery values since it holds the mineral particles together for a longer time. It is also noted that liberation of coal particles from gangue increases with decreasing particle size and, therefore, small coal particles are likely more hydrophobic than large particles. Thus, the strong and long-range hydrophobic attraction occurs between the small coal particles and the bubble in salt solutions. As seen from Fig. 9, while salt solutions significantly increased flotation of coal, the ash content of the products also increased. And, this can be attributed to the entrainment of the ash minerals in the salt solutions, particularly at higher salt concentrations. The reason for this is inhibition of bubble coalescence in salt solutions. Hence smaller bubbles occur in the system and cause more stable froth. This also can be linked to the effect of salt type and concentration. For example, in the case of 10⁻² M salt concentration, which is lower than the transition concentrations for each salt, there is no significant difference among the salts in terms of flotation recovery and ash content of the products (Fig. 9a). However, with increase in salt concentration up to 10⁻¹ M, which is higher than the transition concentration of MgCl₂ and CaCl₂ but lower for NaCl and KCl, the flotation recovery vs. ash content of the products in MgCl₂ and CaCl₂ solutions exactly shows the same trend compared to NaCl and KCl (Fig. 9b). At
1 M salt concentration which is higher than the transition concentration for each salt the bubble coalescence was completely decreased and eventually prevented, and therefore no significant variation in the flotation recovery was observed for each salt as seen from Fig. 9c. These results clearly indicates that Na⁺, K⁺, Ca²⁺, Mg²⁺ ions have a strong ion specific effect on the flotation recovery of the coal particles, and there is an optimum salt concentration to produce a clean coal in these salt solutions.

![Graphs](image)

Fig. 9. Cumulative combustible recovery vs. ash content of the products as a function of salt concentration (a) $10^{-2}$ M, (b) $10^{-1}$ M, and (c) 1 M

**Conclusions**

In this study, selected chloride salts, MgCl₂, CaCl₂, NaCl, and KCl, were used in the experimental program to clarify the mechanism of coal flotation enhancement by ions of inorganic salts. The results from this study showed that the effect of salt on coal recovery depends on the type and the concentration of the electrolyte which significantly affected the froth flotation performance. The experiments also showed
that while the combustible recovery increased with increasing salt concentration, the ash content of the coal products also increased significantly. These results suggest that a coal product with low ash content can be beneficiated with a higher recovery depending on the salt type and concentration.

The results obtained from this study will help to understand the flotation behaviour of many minerals in salt solutions. Furthermore, this will be a fundamental basis for development of improved flotation technology for mineral processing industry.

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