



Effect of Chloride Salt Ions onto Coal Flotation based on Contact Angle and Bubble-Particle Attachment Time

Klorür Tuz İyonlarının Temas Açısı ve Kabarcık-Tane Yapışma Süresi Açısından Kömür Flotasyonuna Etkisi

Can Gungoren ¹, Yasin Baktarhan ^{1,2}, Oktay Sahbaz ³, Ilgin Kursun Unver ¹
Safak Gokhan Ozkan ⁴ Orhan Ozdemir ^{1*}

¹ Istanbul University-Cerrahpasa, Engineering Faculty, Mining Engineering Department, Istanbul, Turkey

² Mineral Research and Exploration General Directorate, Head of Department of Mineral Analysis and Technology, Ankara, Turkey

³ Kutahya Dumlupınar University, Engineering Faculty, Mining Engineering Department, Kutahya, Turkey

⁴ Turkish-German University, The Institute of the Graduate Studies in Science and Engineering, Department of Robotics and Intelligent Systems, Istanbul, Turkey

Sorumlu Yazar / Corresponding Author *: orhanozdemir@iuc.edu.tr

Geliş Tarihi / Received: 10.09.2021

Kabul Tarihi / Accepted: 14.12.2021

Araştırma Makalesi/Research Article

DOI:10.21205/deufmd.2022247119

Atıf şekli/How to cite: GUNGOREN, C., BAKTARHAN, Y., SAHBAZ, O., KURSUN UNVER, I., OZKAN, S.G., OZDEMIR, O. (2022). Effect of Chloride Salt Ions onto Coal Flotation based on Contact Angle and Bubble-Particle Attachment Time. DEUFMD, 24(71), 553-562.

Abstract

This study was aimed to reveal the effect of K^+ , Na^+ , Ca^{2+} , and Mg^{2+} ions on the bubble-particle interactions of high-rank coal with contact angle and bubble-particle attachment time studies. The results for the contact angle experiments indicated that the contact angle of the coal, which was 62° in the absence of ions, increased slightly in the presence of mono- and divalent ions and reached a maximum (67°) in the presence of $1 \cdot 10^{-1}$ mol/dm³ Mg^{2+} , and the effect of K^+ ions on the contact angle was minimal. Furthermore, the results for the bubble-particle attachment time experiments showed that the bubble-particle attachment time of coal, which was measured as 4.5 ms in the absence of ions, decreased as a function of ion concentration from $1 \cdot 10^{-2}$ mol/dm³ to 1 mol/dm³. While the bubble-particle attachment times of coal particles in the presence of K^+/Na^+ and Ca^{2+}/Mg^{2+} at low concentrations were around 2-3 ms and 1-2 ms, respectively, the increase in the concentration slightly changed the attachment time which decreased to less than 1 ms except for K^+ ions. Overall, it can be concluded from this study that the effect of these dissolved ions in water was more prominent on the bubble-particle attachment time of the coal particles rather than the contact angle which showed no significant change. Also, the specific ion effect was determined as " $Mg^{2+} > Ca^{2+} > Na^+ > K^+$ " in terms of the bubble-particle interactions in the presence of these ions.

Keywords: Chloride Salt Ions, Coal, Flotation, Bubble-Particle Attachment Time, Contact Angle

Özet

Bu çalışma, K^+ , Na^+ , Ca^{2+} ve Mg^{2+} iyonlarının yüksek kaliteli kömürün kabarcık-tane etkileşimleri üzerindeki etkisini, temas açısı ve kabarcık-tane yapışma süresi çalışmaları ile ortaya koymayı amaçlamıştır. Temas açısı deney sonuçları, iyon yokluğunda 62° olan kömürün temas açısının, bir ve iki değerlikli iyonların varlığında hafifçe arttığını, $1 \cdot 10^{-1}$ mol/dm³ Mg^{2+} varlığında maksimuma (67°) ulaştığını ve K^+ iyonunun temas açısı üzerindeki etkisinin minimum olduğunu göstermiştir. Ayrıca, kabarcık-tane yapışma süresi deney sonuçları, iyon yokluğunda 4,5 ms olarak ölçülen kömürün kabarcık-tane yapışma süresinin, iyon konsantrasyonunun bir fonksiyonu olarak $1 \cdot 10^{-2}$ mol/dm³ ile 1 mol/dm³ arasında azaldığını göstermiştir. K^+/Na^+ ve Ca^{2+}/Mg^{2+} varlığında düşük

konsantrasyonlarda kömür tanelerinin kabarcık-tane yapışma süreleri sırasıyla 2-3 ms ve 1-2 ms civarındayken, konsantrasyondaki artış yapışma süresini biraz değiştirmiş ve K⁺ iyonları hariç 1 ms'nin altına düşürmüştür. Genel olarak, bu çalışmadan, sudaki bu çözünmüş iyonların etkisinin önemli bir değişiklik göstermeyen temas açısından ziyade, kömür tanelerinin kabarcık-tane yapışma süresi üzerinde daha belirgin olduğu sonucuna varılabilir. Ayrıca bu iyonlar varlığında kabarcık-tane etkileşimleri açısından spesifik iyon etkisi "Mg²⁺ > Ca²⁺ > Na⁺ > K⁺" olarak belirlenmiştir.

Anahtar Kelimeler: Klorür Tuz İyonları, Kömür, Flotasyon, Kabarcık-Tane Yapışma Süresi, Temas Açısı

1. Introduction

Coal contains various amounts of ash, sulfur, moisture, volatile matter, phosphor, and alkali impurities, which are harmful to the environment [1]. Therefore, coals need to be upgraded from these undesirable ingredients by coal preparation methods. Flotation is a physicochemical processing method widely used for the processing of fine coals [2]. Flotation is a separation technique for hydrophobic particles from hydrophilic ones utilizing air bubbles. In this technique, the hydrophobic particles adhere to bubbles and ascend to the surface. Meanwhile, the hydrophilic particles stay in the flotation pulp [3-5]. Low-rank coals are hydrophilic such as most of the minerals. Therefore, there is a need for collectors to make them hydrophobic [6]. On the other hand, high-rank coals have high hydrophobicity. Their particles can attach to air bubbles more easily in the absence of collectors. Meanwhile, it is a well-known fact that the ions dissolved in water affect the solution, interfaces, adsorption, and therefore the colloidal interactions between the bubbles and particles [7-10]. Therefore, the flotation recovery can be enhanced by dissolved ions of salts [11].

In the literature, various researches showed that dissolved ions in a pulp influence the flotation response of minerals [11-13]. Aplan [14] showed that high-rank coals could be floated without any reagent in the presence of ions. On the other hand, the flotation of low-rank coals could not be achieved effectively in the presence of dissolved ions without flotation reagents such as collector and frother [15,16]. In the light of these works, various assumptions have been suggested explaining the effect of dissolved ions in flotation. Klassen and Mokrousov [17] reported that the ions decreased the surface wettability of coal particles by destabilizing the hydrated films around them. Later, Paulson and Pugh [18] classify the salt groups according to their effect on flotation recovery. They reported that di- and trivalent ions including Mg²⁺ and Ca²⁺ give high flotation response even at low concentrations

(0.02 mol/dm³). Several monovalent ions including Na⁺ and K⁺ give an intermediate flotation response beginning at about 0.05 to 0.1 mol/dm³ concentration. Additionally, they reported that the enhancement of flotation in the presence of dissolved ions can be inferred from the decrease in the bubble coalescence and accordingly the decrease in the size and the increase in the number of bubbles. In another study, Harvey et al. [19] stated that there is a relationship between the flotation success of high-rank coal particles and the electrical double layer interaction in the presence of ions. Moreover, they observed nano-bubble formations on coal surfaces that were stabilized by ions using atomic force microscopy (AFM) analysis and emphasized that the generation of these nano-bubbles leads to the coagulation of hydrophobic coal particles which improves their floatability.

As seen from the theories discussed above, the influence of the ions on coal flotation has not been completely understood yet. Therefore, this study aimed to reveal the influence of the ions on the flotation behavior of coal particles along with contact angle and bubble-particle attachment time measurements. Moreover, it is important for the use of water resources containing high amounts of salt or seawater for saving freshwater resources. In this context, the experimental study was carried out in the presence of K⁺, Na⁺, Ca²⁺, and Mg²⁺ ions using their chloride salts which are readily available in the sea or bore waters. The results of this study will contribute to the understanding of the flotation behavior of coal particles in the presence of ions to contribute to the development of flotation technology as well as reducing the flotation cost by decreasing the use of flotation reagents.

2. Material and Method

2.1. Material

For the experimental studies, the high-rank coal specimens were collected from Zonguldak-

Uzulmez, Turkey. Several particles (~10 μm) were chosen for the contact angle measurements. They were prepared using a rock cutting device (Discoplan TS, Struers, Denmark) and polished manually with fine silica carbide particles. The specimens, for the bubble-particle attachment time tests, were crushed using jaw and roll crushers under 1 mm. Then, the sample was ground by a ring grinder to obtain 150 \times 75 μm -sized particles.

The analytical grade ($\geq 99.0\%$ purity) NaCl and KCl salts were obtained from Carlo Erba (Italy) where CaCl_2 and MgCl_2 salts were purchased from Merck (Germany) for this study. All experiments were performed using deionized (DI) water (MilliQ, Germany, the resistivity 18.2 $\text{M}\Omega\cdot\text{cm}$).

Meanwhile, the proximate analysis of the coal is presented in Table 1. As seen in Table 1, the coal is a high-rank (bituminous) coal with a relatively high volatile matter.

Table 1. Proximate analysis results of the coal on air-dry basis.

Fixed Carbon (%)	Ash Content (%)	Volatile Matter (%)	Total S Content (%)	Calorific Value (kcal/kg)
42.51	24.39	33.10	0.45	6150

2.2. Contact Angle Measurements

The polished coal samples were cleaned with analytical grade ethylene alcohol and rinsed with DI water prior to each contact angle measurement carried out with the sessile drop method using an optical measurement device (Attension Theta Lite, Biolin Scientific, Finland).

A salt solution at a definite concentration was dripped on the polished surface of the coal sample employing a glass syringe, and the contact angles at both sides of the droplet were detected by the digital camera and the embedded software according to the change in the droplet shape. The contact angle measurements were performed 10 times, and the average was obtained [20].

2.3. Bubble-Particle Attachment Time Experiments

Contact angle measurements are important indicators of surface wettability. However, the

sessile drop is mostly a static contact angle measurement technique. On the other hand, minerals and air bubbles are always in motion in a real flotation environment. They come into contact only for a short time in milliseconds. Therefore, in some circumstances, the contact angle measurements alone cannot characterize the bubble-particle interactions sufficiently enough. In such circumstances, the bubble-particle attachment possibility should be determined for a restricted time using the equipment made for this purpose [21-23].

Miller et al. [24] also remarked on this issue. In their study on coal flotation, they stated that the improvement in the flotation efficiency with the decrease in dextrin amount was related to the bubble-particle attachment time, which decreased significantly (from 45 ms to under 3 ms) rather than the contact angle values that did not show a significant increase (from 33° to 40°). This finding supports that one of the most important factors in determining the flotation behavior of coal is the required time for the bubble-particle attachment.

In this study, the bubble-particle attachment time was determined with the BKT-100 bubble-particle attachment time measurement device (Bratton Engineering and Technical Associates, LLC, USA). The related experimental setup is shown in Figure 1.

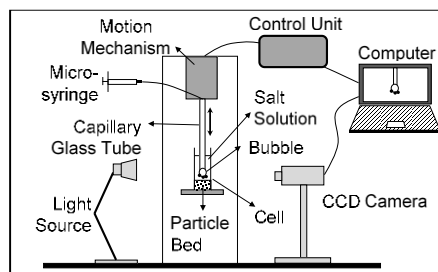


Figure 1. Bubble-particle attachment time measurement experimental setup

In the experiments, the coal sample (0.5 g) was conditioned with a salt solution (50 cm^3) for 5 min by a magnetic stirrer (500 rpm). Then, the measurement cuvette was filled with this suspension and hence a particle bed was formed on the floor of the cuvette. The capillary of the attachment time device was located in the cuvette. An air bubble with a diameter of approximately 2 mm was generated at the end of the capillary by a connected micro-syringe. After

that cuvette and hence the particle bed was approached the bubble properly. The desired contact time was adjusted through the software of the device. Then, the bubble was moved downwards and stayed in touch with the particle bed during the adjusted contact time between 1 and 1000 ms before returning its initial position. The process was observed through a computer screen using a digital camera. If the bubble-particle attachment occurred, the capillary tube was shaken with several slight touches to observe the stability of the bubble-particle aggregate at the end of the capillary. Some attached particles could be detached from the bubble after this process. The bubble-particle aggregates that were remained stable were used in the calculation of the bubble-particle attachment time which was calculated as the time for which 50% of the observations [9,25] resulted in an attachment. This procedure was performed 20 times at various places of the particle bed and the results were recorded.

3. Results

3.1. Contact Angle Measurements

The result of the contact angle measurements is shown in Figure 2 with respect to the ion concentration.

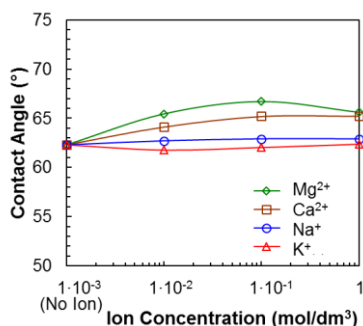


Figure 2. Contact angle results with respect to ion concentration

As seen in Figure 2, the contact angle of the coal was found to be 62° in the absence of ions. The effect of mono and divalent ions caused a slight increase in the contact angle values of the coal samples. While this increase was more pronounced in the presence of divalent ions, and the highest contact angle was obtained in the presence of 1·10⁻¹ mol/dm³ Mg²⁺ as 67°, the effect of K⁺ ions on the contact angle was minimal. It is known that while the contact angle

of low-rank coal particles may show some increase in the presence of dissolved ions (Mg²⁺, Ca²⁺, and Na⁺) [16], the wettability of high-rank coals was not affected by ions significantly as already reported by Laskowski and Iskra [26] and Ozdemir et al. [20].

3.2. Bubble-Particle Attachment Time Experiments

Sequential processes that occur in bubble-particle attachment time experiments are seen in the representative images taken during the measurements (Figure 3).

As seen in Figure 3a and Figure 3b, respectively, the bubble approached the particle bed first and then remained in contact for the specified time. If the particle hydrophobicity and/or contact time were not sufficiently high, the particle attachment did not occur when the bubble returned to its original position at the end of the specified contact time (Figure 3c).

In the case of bubble-particle attachment (Figure 3d), as a result of the subsequent manual shaking process, the attached particles might completely be detached from the bubble (Figure 3e) as a result of the generated tensile stresses, and the bubble might remain unloaded (Figure 3f). On the other hand, if the adhesion force between the bubble and particles was strong enough, the bubble remained laden with the particles even if there were several detached particles (Figure 3g).

In the case of attachment, it is seen that before (Figure 3d) or after (Figure 3g) the shaking process, even when a small number of coal particles adhered to the bubble surface, due to the hydrophobic attraction forces between the coal particles, the coal particles were agglomerated so that a large number of coal particles can be carried with one bubble.

Furthermore, the bubble-coal particle attachment percent as a function of contact time is seen in Figure 4 for various salts. It can be seen from the attachment percentage results in Figure 4 that the attachment percent increases at all conditions with contact time. The attachment increased to 80% when the contact time was 1000 ms in the absence of ions. This showed that the coal particles were hydrophobic. The ion addition increased the attachment percent related to the concentration.

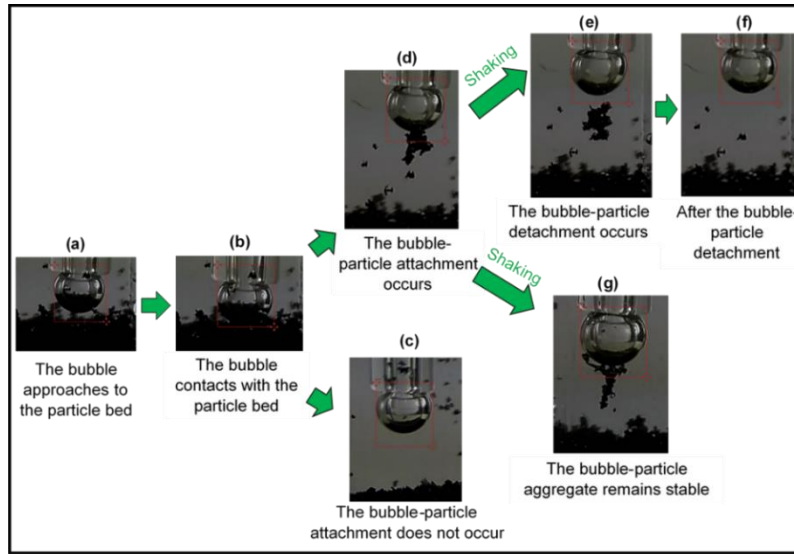


Figure 3. Sequential processes that occur in bubble-particle attachment time experiments

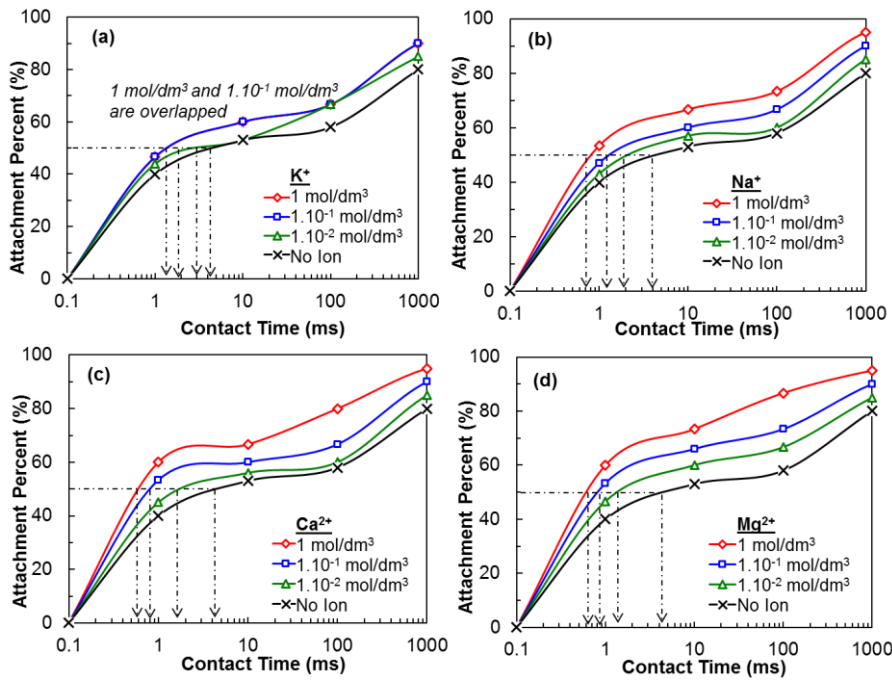


Figure 4. Results for attachment time percent with respect to contact time in the presence of (a) K^+ , (b) Na^+ , (c) Ca^{2+} , and (d) Mg^{2+}

Figure 5 shows the results for bubble-particle attachment time as a function of ion concentration. As seen from Figure 5, the bubble-particle attachment time was found as 4.5 ms in the absence of ions and decrease with

the addition of ions. The attachment time decreased to 2.5 ms and 2.1 ms in the presence of K^+ and Na^+ , respectively. While the attachment time was stable at 1.4 ms after $1 \cdot 10^{-1} \text{ mol/dm}^3$ for K^+ , it decreased to 0.8 ms with Na^+ and 0.6 ms

in the presence of divalent ions (Ca^{2+} and Mg^{2+}) at 1 mol/dm^3 concentration.

Therefore, it can be understood from these results that bubble-particle attachment time was more dominant than the contact angle in terms of the flotation behavior of coal. Furthermore, the ions can be ordered as " $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$ " considering their effects in the bubble-particle interactions.

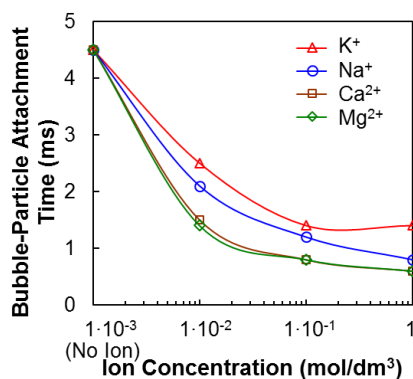


Figure 5. The bubble-particle attachment time results with respect to ion concentration

4. Discussion and Conclusion

4.1. Discussion

The effect of dissolved ions in flotation is diverse. They have a strong effect on gas dispersion, bubble size, and froth stability. They can affect the functional groups on the coal surface [27] and surfactant adsorption [28]. The ions may also interact with each other [29] and flotation reagents [30]. There are also several studies on the mechanism of the influence of salt ions on bubble-particle attachment time which show that the electrical double-layer around a particle is compressed by the ions in water and reduces the repulsive forces between bubbles and particles [12,18,19]. Therefore, the hydrophobic forces will control the system. In parallel, the atomic force microscopy (AFM) results of Ozdemir et al. [20] also showed that the repulsive forces reduced in brines for the bubble and the coal particles. Furthermore, Laskowski [13] stated that the destabilization of the wetting film on coal by the compressed electrical double layer enhanced the coal flotation kinetics.

In a previous study using coal supplied from the same region as the coal used in this study, Ozdemir [31] conducted laboratory-scale

collectorless flotation experiments with 100 g of coal particles ($0.212 \times 0.038 \text{ mm}$) using a 1.5 dm^3 -volume Denver (D-12) flotation cell in the presence of the same ions. Ozdemir [31] reported that the combustible recovery of the coal was 10% in the absence of ions. As found in the present study, although the coal was sufficiently hydrophobic in the absence of ions with a contact angle of 62° , the unsuccessful flotation of the coal can be explained by the lack of a sufficient number of stable bubbles in the flotation environment. However, as a result of decreased attachment time in the presence of ions, the combustible recovery showed an increasing trend with ion concentration [12,32,33] and reached over 90% with Mg^{2+} , Ca^{2+} , and Na^+ and 75% in the presence of K^+ which is in the same tendency with the contact angle values and bubble-particle attachment time results of the present study. In similar, Paulson and Pugh [18] observed an increasing trend in the flotation recovery of graphite with the increasing concentration of a large number of salt types. The importance of salt type was also stated by Ozkan et al. [16]. Their results indicated that MgCl_2 and CaCl_2 were more functional than NaCl in the flotation of low-rank coals.

Moreover, the results for the bubble-particle attachment time were correlated with the combustible recovery results of Ozdemir [31], and the relationship is given in Figure 6.

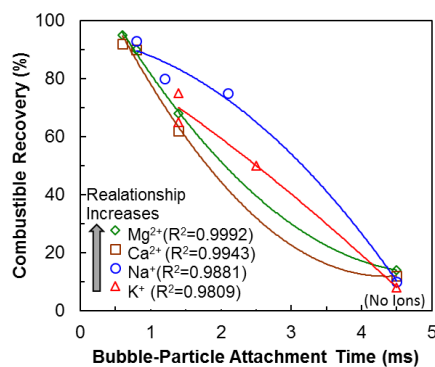


Figure 6. Correlation between the combustible recovery [31] and the bubble-particle attachment time

As shown in Figure 6, the combustible recovery shows an increase when attachment time decreased. While the relationship between the combustible recovery and the attachment time was the lowest for K^+ , higher correlation

coefficients were obtained with Na^+ , Ca^{2+} , and Mg^{2+} , respectively.

As known from the literature, the collecting ability of bubbles is very crucial to perform a successful flotation process [34,35]. However, since the hydrophobic attraction forces between the bubbles are very strong when they are close enough, they coalesce and form a bigger bubble. This process makes the bubble-particle attachment more difficult and also causes the detachment of the previously attached particles [36-39]. As well as frothing agents, several ions can be also employed for the inhibition of bubble coalescence [22].

As known from the literature, the effect of ions on bubble size and coalescence is ion-specific [40] and related to the ion properties such as size and polarizability [33]. Where some ions showed no effect, the presence of some ions in aqueous solutions reduced the bubble size related to the ion concentration [41,42], ionic strength [43], the valence of the ions, and the magnitude of the surface tension [44,45]. In addition to these, Craig et al. [46] and Craig et al. [47] showed that bubble coalescence and the transition concentration which varies according to salt type are strongly related [48]. Sadeghi and Vissers [49] reduced the bubble size to 20-30 μm from 50 μm and 100 μm with the addition of 5 g/dm^3 and 40 g/dm^3 NaCl, respectively. Quinn et al. [43] reported that the critical coalescence concentration (CCC) of NaCl and KCl is 0.31 mol/dm^3 . In another study on salt mixtures, Gungoren [4] investigated the effect of KCl and NaCl salts in bubble coalescence. Their bubble coalescence time measurement results indicated that the time required for bubble coalescence was 650 ms for fully NaCl saturated solution, 270 ms for the 50-50% NaCl and KCl mixture, finally and 100 ms for fully saturated KCl. Several other studies reported that a high bubble population in the presence of salt solutions increased the efficiency of coal flotation [31,33,50]. Various mechanisms have been suggested on the effect of ions on bubble coalescence. Craig [51] and Wu et al. [52] stated that although the ions may not alter the interaction forces between the bubbles, they modify the dynamic processes which lead to the rupture of the thin film. Meanwhile, it was reported by Wu et al. [52] and Wang and Peng [53] that the thinning of the film at high ion concentrations keeps the gas/liquid interface

between coalescing bubbles stable and thus hardens the bubble coalescence.

Meanwhile, in a previous study, Gungoren et al. [54] investigated the effect of Na^+ and Ca^{2+} ions on bubble coalescence with a modified version of the bubble-particle attachment timer used in the present study. The bubble coalescence time is accepted as the time that half of the experiments result in coalescence Figure 7 shows the results of Gungoren et al. [54] for bubble coalescence at 100 ms contact time in the presence of Na^+ ion along with the combustible recovery results of Ozdemir [31] and the results for the bubble-particle attachment time with respect to Na^+ ion concentration.

As shown in Figure 7, the bubble coalescence was inhibited related to the ion concentration and the salt transition concentration was determined as $1.5 \cdot 10^{-1} \text{ mol}/\text{dm}^3$ for Na^+ . Meanwhile, the flotation recovery increased and the bubble-particle attachment time decreased with ion concentration.

Furthermore, to obtain a better comprehension of the effects of ions on the flotation of coal, several representative images on the froth formation, bubble-particle attachment, and bubble size in the presence of Na^+ ion at $1 \cdot 10^{-2}$, $1 \cdot 10^{-1}$, and $1 \text{ mol}/\text{dm}^3$ concentrations are shown in Figure 8.

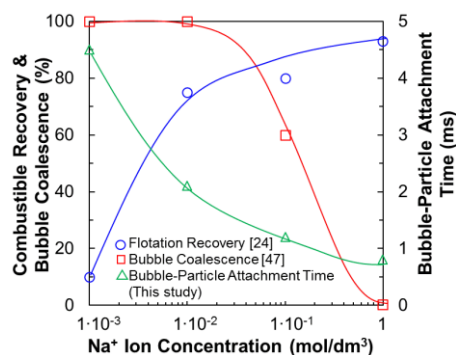


Figure 7. Results for flotation recovery [31], bubble coalescence [54], and bubble-particle attachment time with respect to Na^+ ion concentration

As seen in Figure 8a, considering that the experiments were carried out in the absence of frother, there was a low success in forming a stable froth zone at low Na^+ ion concentrations. However, a more stable froth, laden with hydrophobic coal particles, could be obtained at

higher Na^+ concentrations. Meanwhile, it is seen in Figure 8b that while coal particles had difficulties in attaching to the bubble at low Na^+ concentration, as the concentration increases, a higher number of hydrophobic coal particles could attach to the bubble. Finally, Figure 3c indicated that larger bubbles were generated as a result of high bubble coalescence at low Na^+ concentrations. On the other hand, since the bubble coalescence probability decreased at

high Na^+ concentrations, bubbles became more stable and consequently, bubble sizes decreased.

Therefore, it can be deduced from Figure 7 and Figure 8 that several factors were responsible for the significant increase in the flotation recovery of coal particles in the presence of dissolved ions including the decrease in the bubble coalescence probability (the presence of more stable and smaller bubbles) and the decreased bubble-coal particle attachment time.

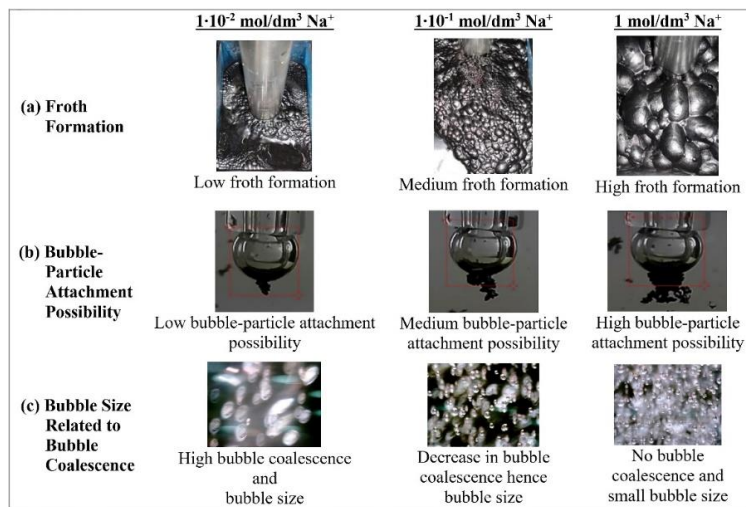


Figure 8. Representative images on the (a) froth formation (with $212 \times 38 \mu\text{m}$ coal particles in 1 dm^3 flotation cell at 10% solids ratio, 1000 rpm stirring speed, and at $10 \text{ dm}^3/\text{min}$ air flow rate), (b) bubble-particle attachment, and (c) bubble size in the presence of Na^+ ion

4.2. Conclusion

In this study, the effects of K^+ , Na^+ , Ca^{2+} , and Mg^{2+} ions on the hydrophobicity and bubble-particle interaction of high-rank coal from Zonguldak-Uzulmez, Turkey was investigated. The contact angle results indicated that the use of Mg^{2+} at $1 \cdot 10^{-1} \text{ mol/dm}^3$ concentration increased the contact angle of coal slightly from 62° to 67° . The main influence of the ions was on the bubble-particle attachment time which was decreased from 4.5 ms to 1.4 ms in the presence of $1 \cdot 10^{-1} \text{ mol/dm}^3 \text{ K}^+$. While 0.8 ms attachment time was obtained at $1 \text{ mol/dm}^3 \text{ Na}^+$, the attachment time decreased to 0.6 ms at the same concentration of Ca^{2+} and Mg^{2+} . The reason for the slightly higher contact angles and distinctly lower bubble-particle attachment time values in the presence of divalent salts than monovalent salts at the same concentration probably can be attributed to the compressing ability of divalent salts to the electrical double layer of coal particle surfaces is

stronger than that of monovalent salts. Therefore, it is obvious that divalent ions would be more useful for the collectorless flotation of coal. As a conclusion, it can be said based on the results obtained from this study that the effects of Mg^{2+} , Ca^{2+} , Na^+ , and K^+ ions in the bubble-particle attachment time of the coal particles were more clear rather than the contact angle to explain the coal flotation behaviour in the presence of these ions. And, a specific effect of these ions can be written as " $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$ " in terms of their interactions onto the bubble-particle attachment.

Acknowledgment

This work is supported by the Research Fund of Istanbul University-Cerrahpasa (Project Number: 38723).

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