



The interaction of clay minerals and saline water in coarse coal flotation



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HIGHLIGHTS

- A synergistic interaction occurred between saline water and clay minerals in coal flotation.
- Saline water promoted the formation of aggregates of clay platelets.
- These aggregates sustained in the dynamic flotation condition and entered the concentrate.
- They altered the froth property and recovery of coarse coal by true flotation.
- Clay minerals may have a beneficial effect in some flotation scenarios.

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ABSTRACT

In this study the fundamental science underpinning the interaction of saline water and clay minerals was studied under flotation contexts to address important problems confronting the coal industry. For the first time, the beneficial effect of clay minerals in some flotation scenarios was revealed after testing a typical coal sample having a low content of clay minerals and its mixture with another coal sample having a high content of clay minerals in de-ionised water and saline water with medium conductivity. Equipped with a range of techniques including froth stability measurements, modelling true flotation, settling tests and Cryo-SEM analyses, it was found that froth stability was higher in the flotation with a higher concentration of clay minerals in both de-ionised water and saline water, corresponding to increased combustible matter recovery and ash recovery. A synergistic interaction was evident between saline water and clay minerals in stabilising the froth and recovering combustible matter by true flotation. This is because saline water promoted the formation of association of clay platelets that sustained in the dynamic flotation condition, entered the flotation concentrate and altered the froth property and coarse coal flotation behaviour.

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1. Introduction

Clay minerals often associate with valuable minerals in a great range of ore bodies and have a substantial impact on the efficiency of many processes including grinding, pumping and dewatering, etc. when valuable minerals are extracted [1–3]. In mineral flotation, a number of studies have demonstrated that clay slime coatings can occur on mineral surfaces through the electrostatic attraction, reduce surface hydrophobicity and then depress mineral flotation [3]. These studies explore the anisotropic charges on edges and basal faces of clay minerals which are attracted to either negatively or positively charged minerals. In the previous study, we investigated the behaviour of clay minerals in fine coal

flotation and identified their entrainment and entrapment in the flotation process [4]. This study explores the nature of colloid size of clay minerals which promotes their entrainment through water films between air bubbles and entrapment through the aggregation of fine coal particles. However, all previous studies did not take into account another important nature of clay minerals, the formation of network structures of clay platelets in aqueous solutions.

Clay minerals are anisotropic phyllosilicates and have a layer structure comprised of edges (E) and faces (F), and therefore clay platelets can associate in edge–edge (E–E), edge–face (E–F), and face–face (F–F) configurations. It is known that clay minerals have a basal permanent negative charge caused by isomorphous substitution, whilst the charge on the edges is either positive or negative depending on the pH [5–8]. Recent work has reported that the two basal plane surfaces of kaolinite can have positive or negative charges as well [9]. The anisotropic structure and charge properties

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lead to the association of clay platelets. The easy formation of the different types of association depends on the balance of electrostatic interactions (attractive or repulsive), which are controlled by the chemistry of the suspension, and the attractive van der Waals forces between the particles [8,10]. In dispersions with high clay mineral contents and a high negative edge charge density of the particles, the strong repulsion between the faces can also force the particles into adopting a certain parallel orientation promoting edge(-)/edge(-) aggregation and thereby altering the rheology behaviour [9]. In dilute clay mineral suspensions, the viscosity increases with E–E and E–F association whilst the viscosity decreases when the particles become thicker by F–F association. In concentrated clay mineral suspensions, E–E or E–F association leads to the formation of continuous, linked, card-house structures characterized by non-Newtonian flow. If F–F association occurs simultaneously, the number of units building the card-house structures is reduced [6].

The flotation of clayey ores is also complicated by the use of saline water. In Australia, all coal sites have introduced water reuse as a conventional practice due to scarcity of fresh water and stringent policy on the quality of water that can be discharged into local river systems. One of the consequences of increased water reuse is a concomitant increase in salinity on sites and subsequently in flotation. A number of studies have been conducted to investigate the effect of saline water on coal flotation. In general, saline water increases combustible recovery compared to fresh water and three mechanisms have been proposed to explain this phenomenon. Klassen and Mokrousov [11] and Blake and Kitchener [12] proposed that the lowering of electrokinetic potential of coal surfaces by the adsorbed ions reduced the stability of the hydration layers facilitating their disruption. The destabilisation of hydration layers increased the surface hydrophobicity and therefore coal flotation. Secondly, it was proposed that the electrolytes increased the electrical repulsive forces at bubble surfaces, inhibiting bubble coalescence [13–18]. The reduced bubbles increase bubble–particle collision efficiency and the overall flotation efficiency. Thirdly, the compression of the electrical double layer in saline water was attributed to the opening of hydrophobic surface sites enhancing the thinning and rupture of the wetting film between the particles and bubbles which is a critical step in the formation of a stable particle–bubble aggregate leading to an increase in flotation [19]. In the previous study addressing fine coal flotation using saline water, we found that saline water reduced the bubble size increasing the entrainment of clay minerals, and also enhanced the aggregation of fine coal particles exacerbating the entrapment of clay minerals.

It is interesting to know that saline water alters the association of clay platelets. Unlike other colloidal dispersions, well-dispersed clay minerals may be coagulated by very low concentrations of inorganic salts and the critical coagulation concentration varies with clay mineral, electrolyte and pH [20]. It has been found that the edge of clay minerals (e.g., montmorillonite) is small relative to the Debye length at the critical salt concentration and the negative double layer extending from the basal plane surfaces spills over into the edge region [21]. The influence of the negative face charges is significant at the critical salt concentration (e.g., less than 10^{-3} M sodium salt concentration) and coagulation therefore occurs between edges(-) and faces(-) [22]. When the increased salt concentration required for edge(-)/face(-) coagulation approximates the salt concentration for face(-)/face(-) aggregation, the dispersion coagulates face-to-face because the area between two faces is larger than between an edge and a face [20]. Face/face aggregation between two layers or particles might be initiated at surface regions with lower than average charge density because of layer charge heterogeneity [23,24].

The objective of this study is to understand the interaction of clay minerals and saline water and its effect on coarse coal

flotation in parallel with the previous study on the effect of clay minerals on fine coal flotation [4]. The difficulty in floating coarse particles is another challenge confronting the coal and minerals industry. In coal flotation, there is a linear decrease in combustible recovery with increasing the particle size in the range of 127–505 μm [25]. Two main reasons have been attributed to the poor recovery of coarse particles, inefficient collision of coarse particles and bubbles failed to generate stable aggregates, and insufficient buoyancy failed to float the heavy particle aggregates [26,27]. During flotation, effective collecting of the particles occurs when the collision of particles and bubbles generates a stable bubble–particle aggregate that rises to the surface of the pulp. However, for coarse particles, the process of attachment to an air bubble is limited by the acceleration of the bubble–particle complex, because if it exceeds a critical value, the particle will detach [28,29]. The probability of detachment increases as the particle size increases [30]. Besides, coarse particles are too heavy. The downward gravity force component dominates the whole force balance, leading to the settlement of coarse particles through the froth [31].

2. Materials and methods

2.1. Raw materials

A low-clay-content coal (LCC) and a high-clay-content coal (HCC) were supplied from a coal mine at Central Queensland, Australia, and examined in this study. LCC is currently processed in the plant to produce high quality hard coking coal for use in the international and domestic steel industry, whilst HCC cannot be processed economically due to the high clay content. The quantitative XRD analysis of these two samples as flotation feeds is indicated in Table 1. The two samples contain the same clay minerals, kaolinite and illite/smectite which are the major mineral matter. The LCC contains about 83% combustible matter and 7% clay minerals, while HCC contains about 61% combustible matter and 33% clay minerals.

Artificial saline water was prepared and used in this study following the study by Ofori et al. [32] who conducted a survey of Australian coal preparation plants regarding the quality of process and make-up water. They summarised the data by giving the minimum, medium and maximum values of the concentration of major ions to give an indication of variation in composition of process water. In this study saline water with the medium value of the concentration of major ions was made and its compositions are shown in Table 2. The major ions are Na^+ , Mg^{2+} , Ca^+ , K^+ , SO_4^{2+} , Cl^- and HCO_3^- . They were dissolved in de-ionised water. For a comparison, de-ionised water was examined as well throughout the study.

MIBC (Methyl Isobutyl Carbinol) and Diesel, industrial grade, were used as frother and collector, respectively, in coal flotation. They are normally used in coal preparation plants in Australia.

2.2. Flotation

Both LCC and HCC were screened to $-710 \mu\text{m}$ following the bore core procedure of the coal mine. In the coal plant, the particles greater than $710 \mu\text{m}$ are subjected to gravity separation, while the particles smaller than $710 \mu\text{m}$ are floated. Previous studies in the plant indicated that minerals were well liberated in both feeds to gravity and flotation circuits. The cut-off size for gravity and flotation separation was chosen primarily based on the size limit of gravity devices. The particle size distribution of the flotation feed of LCC with 7% clay minerals and HCC with 33% clay minerals is showed in Fig. 1. In the plant, LCC is referred to as coarse coal with about 51% particles greater than $150 \mu\text{m}$, while HCC as “clay” due

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