



Understanding different roles of lignosulfonate in dispersing clay minerals in coal flotation using deionised water and saline water



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HIGHLIGHTS

- A small lignosulfonate addition mitigated clay surface coatings in deionised water.
- Electrostatic repulsion between coal and clay was enhanced in deionised water.
- In saline water, electrostatic repulsion was minimised.
- Steric repulsion was not sufficient to mitigate clay coatings at a low addition.
- A high lignosulfonate addition depressed coal flotation regardless of water quality.

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ABSTRACT

This study aims to understand the fundamental mechanism underpinning the different behaviour of ionic dispersants in fresh water and saline water observed in coal and mineral flotation and many other disciplines dealing with particles. Lignosulfonate D748 (LS), an anionic dispersant was used in this study to mitigate the clay slime coating in coal flotation using deionised water, and saline water of high ionic strength. In deionised water, the addition of a small amount of lignosulfonate enhanced coal flotation in the presence of clay minerals, but this beneficial effect was not observed in saline water. The addition of a large amount of lignosulfonate depressed coal flotation in both deionised water and saline water. The underlying mechanism was investigated by a range of techniques including flotation of pure coal, adsorption tests, and atomic force measurements (AFM). It was found that the enhanced electrostatic repulsion induced by a small amount of lignosulfonate in deionised water was responsible for the mitigation of clay coatings on the coal surface, resulting in improved coal flotation. In saline water, a low amount of lignosulfonate could not disperse clay minerals from the coal surface due to insufficient steric repulsion, and flotation improvement was therefore unable to achieve. The depression of coal flotation at a high lignosulfonate concentration in deionised water and saline water was attributed to the high adsorption on the coal surface, rendering it strongly hydrophilic regardless of the removal of clay coatings.

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1. Introduction

The Australian coal industry is facing the challenge of processing clayey coals as a result of the depletion of high quality coal deposits. Clay particles, usually less than 2 μm , may coat the coal surface, make it hydrophilic, prevent the adsorption of collectors and therefore depress coal flotation [1,2]. Oats et al. proposed that clay coatings occurred mainly as a result of strong van der Waals attraction, whilst the double-layer interaction played a secondary role [3]. In fact, clay minerals, such as kaolinite and bentonite,

are phyllosilicates which contain a continuous tetrahedral and octahedral layer. They usually have a complicated surface chemistry because of heterogeneity of charged edges and faces. The basal surface carries a permanent pH-independent negative charge, while the edge surface possesses a pH-dependent charge [4]. Although zeta-potential measurements suggest that at flotation conditions of pH 8, both coal and clay particles are negatively charged and hence the double-layer force between them is repulsive, calculation results based on colloid stability theory have suggested that van der Waals attraction is strong enough to overcome double-layer repulsion [3]. Recently, Wang et al. [5] detected the presence of clay coatings on coal surfaces by Cyro-SEM (scanning electron microscopy) and ascribed the low combustible recovery to clay coatings in coal flotation.

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To mitigate the adverse effect of clay minerals on mineral flotation, dispersants have been introduced to modify the colloidal interactions by creating electrostatic and/or steric repulsion. Seaman et al. [6] and Wei et al. [7] demonstrated that lignosulfonate improved copper and gold recovery by dispersing clay minerals in flotation using fresh water. Recently, we also found that a small amount of lignosulfonate improved coal flotation in the presence of clay minerals in deionised water [8]. However, the mechanism responsible for mitigating clay coatings on mineral surfaces by lignosulfonate has not been studied.

On the other hand, it is interesting to find that lignosulfonate displayed a different behaviour in coal flotation in the presence of clay minerals when saline water was used. As demonstrated by Liu and Peng, lignosulfonate depressed coal flotation in saline water in comparison to its beneficial effect in deionised water [8]. In fact, a number of studies have revealed a similar phenomenon that anionic polymeric dispersants behave differently in flotation using fresh water and saline water. For instance, Peng and Seaman [9] examined the dispersion effect of carboxymethyl cellulose (CMC) in pentlandite flotation in the presence of serpentine minerals, and found that the effective use of CMC to mitigate the coating of serpentine minerals on pentlandite surfaces in the laboratory failed to be transferred into the plant. They attributed this disparity to water of different ionic compositions used in the laboratory and the plant. In the laboratory, fresh water was used while in the plant, saline water was applied. Wellham et al. [10] also demonstrated that CMC required an uneconomically high dosage to achieve satisfactory nickel flotation by dispersing serpentine slime particles in high ionic water.

According to Vincent [11], the dispersion behaviour of polymers is strongly linked to their adsorption on colloidal particles, which is ionic strength dependent. Besides, polymer conformation can also be affected by salts [12], which may result in a structure change of adsorbed polymer layers formed on mineral surfaces, leading to a different dispersion and stabilisation mechanism. Studies on lignosulfonate conformation indicates that lignosulfonate takes a microgel model in solutions, with free charges on the surface and charge-free aromatic groups built up as the interior [13]. Yan et al. [14] pointed out that sulfonic groups and phenolic groups were mainly distributed on lignosulfonate surface, and carboxyl groups existed in the core. Meanwhile, lignosulfonate molecules are easy to aggregate in solutions [15,16]. The association among lignosulfonate molecules happens as a result of hydrogen bonding between carboxylic acid and phenolic hydroxyl groups [17]. The conformation of lignosulfonate used in this study was also investigated in the previous work by dynamic light scattering measurements [8]. It was found that at a low concentration, few lignosulfonate molecules aggregated in deionised water at weak alkaline conditions. With an increase in ionic strength, more and bigger lignosulfonate aggregates were formed in saline water at a same concentration. Apparently, saline water compressed the diffuse double layer around lignosulfonate molecules and facilitated randomly branched molecules to fold and associate with each other to form more and larger spherical aggregates. The change of lignosulfonate conformation in saline water may contribute to the different behaviour of lignosulfonate in coal flotation, which is the subject of this study.

In this study, the dispersion effect of lignosulfonate on clay minerals was investigated in coal flotation and correlated with interfacial studies to establish the underlying dispersion mechanisms in deionised water and saline water. This study will help provide a new insight into understanding the role of anionic polymeric dispersants in dispersing clay minerals in the flotation process.

2. Materials and methods

2.1. Raw materials and reagents

A problematic coal sample was obtained from a mine in the Bowen Basin in the state of Queensland, Australia. This is typically a low quality coal sample which is high in ash due to it being in a thinner section of the seam. The combustible feed grade of the coal is 82.9%. X-ray diffraction (XRD) analysis of the coal showed 3.9% kaolinite, 2.8% muscovite and 3.4% smectite as the main clay minerals [5]. In the laboratory, the coal sample was screened to $-150\ \mu\text{m}$ for flotation following the plant procedure. In the previous study, the slime coating of clay minerals on coal surfaces was detected by Cryo-SEM and was considered to be responsible for the low combustible recovery in the flotation [5]. In addition, a pure coal sample was obtained by hand-picking the coarse coal sample supplied from the same mine site. XRD analysis suggests that the purity of the coal sample is about 95%, containing no clay minerals. This pure coal sample was also crushed and sieved to below $-150\ \mu\text{m}$ for flotation tests and adsorption measurements to determine how lignosulfonate affected the surface property of coal and therefore coal flotation behaviour in the absence of clay minerals.

Kaolinite was selected to represent the main clay mineral for the adsorption tests. It was purchased from Sibelco, Australia Limited Company, South Australia. Quantitative XRD analysis shows that this kaolinite sample contains 85 wt.% kaolinite with 11 wt.% muscovite and 4 wt.% quartz [18]. Other chemical reagents such as different salts (analytical grade) were purchased from Sigma-Aldrich.

Deionised water and process water with a high salt content from the mine site were used in flotation tests. The composition of process water assayed by inductively coupled plasma mass spectrometer (ICP-MS) was listed in Table 1. The major ions are Na^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , Cl^- , and CO_3^{2-} . The pH and conductivity of the water are 8.5, and 9.32 mS/cm, respectively. Since traces of impurities such as residue collector and frother were present in the process water and may interfere with fundamental understanding for the flotation of the pure coal sample, adsorption measurements and AFM analyses, synthetic saline water with the same salt compositions of the process water by adding salts in deionised water was used.

MIBC (Methyl Isobutyl Carbinol), 100% laboratory grade, and fresh Caltex diesel were used as frother and collector, respectively. Commercial lignosulfonate D748 was supplied by Borregaard-Lignotech USA and used in this study. The chemical properties of the lignosulfonate was well characterized by Ma and Pawlik [19]. It was reported that the average molecular weight of the lignosulfonate is 45 kDa and the proportion of Na, total sulphur, sulfonate sulphur, HPLC sugars, and Carboxylic groups in lignosulfonate is 7.0%, 6.5%, 6.2%, 1.0%, and 3.1% respectively. Fresh stock solutions of lignosulfonate were prepared at a concentration of 1 g/L daily.

2.2. Flotation tests

After screening, the coal slurry was transferred to a $2.5\ \text{dm}^3$ JK batch flotation cell and then conditioned with or without lignosulfonate, and collector (160 mL/t) for 7 min at 900 rpm of agitation. The flotation was then conducted following the addition of frother (110 mL/t). The solid percentage in the flotation cell was about 5% as used in the plant. In flotation, four concentrates were collected after a cumulative time of 1, 2.5, 5, and 10 min. Flotation was operated at an air flow rate of $3.0\ \text{dm}^3/\text{min}$. Flotation froth was scraped every 15 s. The chosen deionised water, process water, or synthetic saline water was utilized in all stages of screening and flotation.

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