

# Effect of electrolytes on the flotation of copper minerals in the presence of clay minerals



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## ABSTRACT

Clay minerals have a deleterious effect on flotation. In a previous study (Peng and Zhao, 2011), the authors found that the flotation of secondary copper minerals such as chalcocite was more affected by clay minerals than the flotation of primary copper minerals such as chalcopyrite due to stronger surface oxidation resulting in an electrostatic attraction to clay particles. In this current study, the intention was to use electrolytes to mitigate the adverse effect of clay minerals on chalcocite flotation. A copper ore mainly containing chalcocite was examined. In fresh tap water, kaolinite significantly depressed chalcocite flotation. However, with an increase in the electrolyte concentration, the recovery of chalcocite was increased. It is concluded that the electrolytes reduce the electrostatic attraction between kaolinite and chalcocite so that the surface coating of kaolinite on chalcocite surfaces may be mitigated leading to improved chalcocite flotation. It is interesting to find that anions and cations with a greater atomic size had a more beneficial effect which may be associated with their tendency to modify surface hydrophobicity.

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## 1. Introduction

The mining industry is well aware of the difficulty in treating copper ores in the presence of clay minerals. In a previous study, Peng and Zhao (2011) investigated the effect of bentonite on the flotation of chalcopyrite (a primary copper sulfide mineral) and chalcocite (a secondary copper sulfide mineral) in terms of slime coating. They found that as a result of the different extent of mineral surface oxidation, chalcopyrite remained negatively charged but chalcocite became positively charged after grinding leading to the different interactions of copper minerals with bentonite particles. The surface of chalcocite after grinding was electrostatically attracted to bentonite resulting in bentonite slime coating and the depressed flotation of chalcocite. Unlike chalcocite, chalcopyrite exhibited an electrostatic repulsion to bentonite. Zhao and Peng (2012) confirmed the occurrence of bentonite slime coating on chalcocite but not on chalcopyrite by Cryo-SEM measurements.

Other researchers have also reported clay slime coating on galena, coal and bitumen surfaces through the electrostatic attraction reducing surface hydrophobicity and then depressing the flotation significantly (Arnold and Aplan, 1986; Gaudin et al., 1960; Liu et al., 2005a,b). In pentlandite flotation, serpentine minerals also depress flotation due to slime coating. Edwards et al. (1980) found that pentlandite flotation was depressed in the presence of lizardite or chrysotile. By using electrophoresis and Scanning Electron Microscopy (SEM) measurements, they identified slime coating of serpentine minerals on the pentlandite surfaces which contributed to pentlandite flotation depression. This mechanism was also identified by Bremmell et al. (2005) using flotation, zeta potential measurements, SEM and Atomic Force Microscope (AFM) analysis on a mineral system consisting of pentlandite and lizardite. A similar phenomenon was observed by Peng and Bradshaw (2012) when they floated pentlandite in the presence of lizardite in de-ionised water. However, Peng and Bradshaw (2012) found that bore water with a high ionic strength increased pentlandite flotation recovery. They proposed that the reduction of electrical double layer forces between particles in bore water mitigated the coating of lizardite particles on pentlandite surfaces resulting in the improved pentlandite flotation. For the same reason, the clay slime coating on copper mineral surfaces may be mitigated by electrolytes.

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The effect of electrolytes on mineral flotation has been studied by other researchers from a different perspective. Paulson and Pugh (1996) investigated the flotation of model hydrophobic graphite particles in a series of electrolytes. Based on flotation recovery, they classified the electrolytes into three distinct groups as shown in Fig. 1. Group A electrolytes (LaCl<sub>3</sub>, MgCl<sub>2</sub>, MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, etc.) gave high flotation and group B electrolytes (NaCl, LiCl, KCl, CsCl, NH<sub>4</sub>Cl, etc.) gave intermediate flotation, but group C electrolytes (NaAc, NaClO<sub>4</sub>, HClO<sub>4</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, LiClO<sub>4</sub>, etc.) produced low flotation. Paulson and Pugh (1996) proposed that the increased flotation performance of the hydrophobic graphite in electrolytes was linked with the dissolved gas concentration gradients in the electrolyte solutions. Higher flotation recoveries were attributed to an increase in the collision probability with higher concentration of smaller non-coalescing bubbles and a reduction in the electrostatic interactions between particles and bubbles.

In fact, Craig et al. (1993) studied the inhibition of bubble coalescence in electrolyte solutions. By empirically assigning ions a value of either  $\alpha$  or  $\beta$  an electrolyte's coalescence inhibition behaviour could be described using simple combining rules as shown in Table 1. A cation or an anion is assigned as  $\alpha$  or  $\beta$ . Only  $\alpha\alpha$  or  $\beta\beta$  electrolytes result in a bubble coalescence inhibition (indicated by a tick) and  $\alpha\beta$  or  $\beta\alpha$  electrolytes result in no inhibition (as indicated by a cross). Researchers have not found any exceptions to these simple predictive rules. Currently it is unclear precisely what properties make an ion  $\alpha$  or  $\beta$  ion.

In addition, Hancer et al. (2001) classified certain ions as “structure breaking” ions. These ions are large inorganic ions, such as Cs<sup>+</sup> and I<sup>−</sup>. On the other hand, small inorganic ions, such as Li<sup>+</sup>, Mg<sup>2+</sup>, F<sup>−</sup>, and Cl<sup>−</sup> are referred to as “structure making” ions. Table 2 shows some structure maker and breaker ions. Hancer et al. (2001) proposed that for a collector molecule to adsorb at the salt interface it had to displace interfacial water or penetrate through the structure of water. If the structure of water was strongly hydrogen bonded due to the presence of structure making anions and cations, then collector molecules could not reach the surface and be adsorbed. Those ions that had a tendency to destroy the structure of water could create a condition for the adsorption of collector molecules and subsequently allow the flotation of soluble salt minerals.

In this study, the effect of clay minerals on chalcocite flotation was examined in electrolyte solutions. It is expected that electrolytes may mitigate slime coating and therefore improve chalcocite flotation. Meanwhile, electrolytes may also affect flotation through

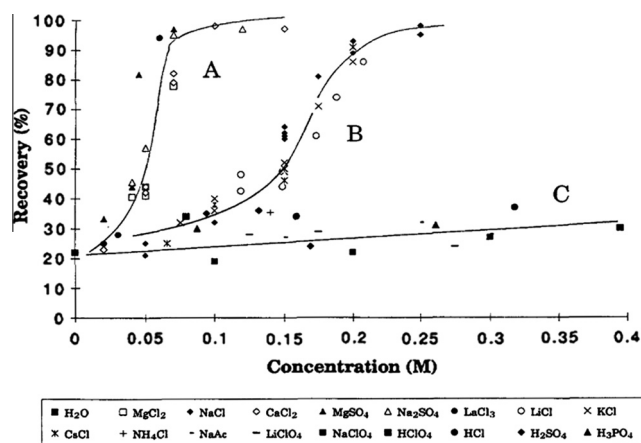


Fig. 1. Flotation recovery of model hydrophobic graphite in different groups of electrolytes (Paulson and Pugh, 1996).

Table 1

Combining rules for effects of electrolytes on bubble coalescence inhibition Craig et al. (1993).

	$\beta$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\beta$	$\alpha$
Anions	H <sup>+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Cs <sup>+</sup>	Me <sub>4</sub> N <sup>+</sup>	Li <sup>+</sup>
$\alpha$ OH <sup>−</sup>	×	I.Sol		I.Sol	✓				
$\alpha$ Cl <sup>−</sup>	×	✓	✓	✓	✓	✓	×		✓
$\alpha$ Br <sup>−</sup>	×		✓	✓	✓		✓		
$\alpha$ NO <sub>3</sub> <sup>−</sup>	×		✓	✓	✓	✓			✓
$\beta$ ClO <sub>3</sub> <sup>−</sup>			×	I	I.Sol		I.Sol		
$\alpha$ SO <sub>4</sub> <sup>2−</sup>	×	✓	✓	I.Sol		✓			✓
$\beta$ ClO <sub>4</sub> <sup>−</sup>	✓	×	×		I.Sol	×	I.Sol		
$\beta$ CH <sub>3</sub> COO <sup>−</sup>	✓	×	×		×	×	×	✓	
$\alpha$ Oxlate <sup>2−</sup>	×	I.Sol	I.Sol	I.Sol	✓	I.Sol			

Table 2

Structure makers and breaker ions (Hancer et al., 2001).

	F	Cl	Br	I
Li	F	NF	NF	NF
Structure makers				
Na	NF	NF	NF	NF
K	NF	F	F	F
Cs	NF	F	F	F
Structure makers				
Rb	NF	F	F	F

the inhibition of bubble coalescence and modification of surface hydrophobicity which were examined in this study as well.

## 2. Experimental

### 2.1. Materials and reagents

A copper ore sample obtained from an Australian copper plant was crushed to a size of −1.70 mm and stored in a freezer before grinding and flotation. The copper grade of the ore is about 2.9%. Quantitative XRD analysis indicates that the copper ore contains 0.1% chalcocite, 0.4% cuprite, 4.7% chalcocite, 40.6% hematite, 16.4% muscovite, 33.8% quartz. About 91% Cu originates from chalcocite. A kaolinite sample was purchased from Sibelco Australia Limited Company to study the effect of clay minerals on chalcocite flotation. It contains 70.3% kaolinite, 18.8% muscovite and 6.8% quartz based on quantitative XRD analysis.

Tap water was used throughout the study. Table 3 shows the chemical compositions of the water analysed by ICP. The pH of the water was 7.0.

Potassium amyl xanthate (PAX) and methyl iso-butyl carbinol (MIBC) of industrial grade were used as collector and frother, respectively.

To investigate the effect of electrolytes on the flotation of chalcocite in the presence of kaolinite, sodium chloride (NaCl), lithium chloride (LiCl), sodium fluoride (NaF), potassium chloride (KCl) and sodium iodide (NaI) of analytical grade were used to make different strengths of solutions. These electrolytes vary in both anion and cation size.

### 2.2. Grinding and flotation

600 g Crushed copper ore was ground in a laboratory stainless steel ball mill at 60% solids to obtain 80% particles passing 38  $\mu$ m. The mill discharge was then transferred to a 2.5 L Agitair

Table 3

Chemical compositions of tap water used in this study (mg/L).

TDS	EC	Cl <sup>−</sup>	SO <sub>4</sub> <sup>2−</sup>	CO <sub>3</sub> <sup>2−</sup>	Ca	Mg	K	Na
52	110	11	7	24	7.9	0.6	2.8	7.4

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