

Effect of surface oxidation on the flotation response of enargite in a complex ore system



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ABSTRACT

In previous study, the selective separation of enargite from complex ore samples in a batch flotation system under controlled pulp potential was investigated (Tayebi-Khorami et al., 2017b). It has been found that it is possible to make a separation between enargite and the other copper minerals in a real ore system using pulp potential control. In this study, the effect of the surface chemistry on the floatability of enargite and pyrite in complex ore systems were investigated. Based on flotation behaviour, EDTA (Ethylenediaminetetraacetic acid) extraction, pulp potential measurement and pure mineral study, it was found that the galvanic interactions between sulphide minerals, and pulp potential conditions, determined the flotation performances of the ore samples. It was also concluded that enargite had the lowest rest potential compared to the other sulphide minerals, which caused strong galvanic interaction between enargite and pyrite. This study has an important implication in sulphide flotation where enargite is present in the ore samples.

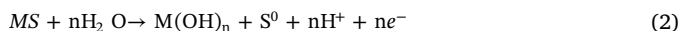
1. Introduction

Sulphide minerals are readily oxidised in the presence of aerated aqueous conditions due to the electrochemical interactions that occur between sulphide minerals and the solution species. Oxidation of their surfaces is an important phenomenon, especially in the flotation process, as the floatability of sulphide particles is controlled by the level of surface oxidation (Fullston et al., 1999c; Peng and Zhao, 2011; Jacques et al., 2016). Slight surface oxidation can increase the floatability of sulphide minerals by forming elemental sulphur or polysulphides (reactions (1) and (2)).

In acidic conditions:



In alkaline conditions:



where M is metal ion (Rao et al., 1992; Ralston et al., 2005). Any of these equations can cause the mineral surface to become hydrophobic to a certain degree, which is the basis of collectorless flotation (Heyes and Trahar, 1984; Rao et al., 1992). The oxidation of chalcopyrite, for

instance, causes the dissolution of Cu and Fe ions and produces a polysulphide layer on the mineral surface in alkaline conditions. The collectorless floatability of chalcopyrite is attributed to the presence of this polysulphide layer (Walker et al., 1989; Woods, 1976; Smart et al., 1998; Smart, 1991).

However, under highly oxidative conditions, sulphate or thiosulphate would be formed (reactions (3) and (4)) which causes a lack of hydrophobicity and reduces the floatability of sulphide minerals and their selectivity (Senior and Trahar, 1991; Rao et al., 1992; Kant et al., 1994; Clarke et al., 1995; Rumball and Richmond, 1996; Ekmekçi and Demirel, 1997; Greet and Smart, 2002).



and/or



Several surface chemistry techniques are available for the study of the oxidation of sulphide minerals such as ToF-SIMS (Time of Flight Secondary Ion Mass Spectroscopy), XPS (X-ray Photoelectron Spectroscopy), and EDTA (Ethylenediaminetetraacetic acid) extraction technique. EDTA has been used to determine the extent of oxidation of

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minerals in the flotation pulps. It has the ability to extract metal oxidation products from the surfaces of minerals (Rao and Leja, 2004).

Previous researchers have mentioned the ability of EDTA to solubilise surface oxidised products, such as oxides/hydroxides, sulphates, and carbonates, without dissolving the metal sulphide (Kant et al., 1994; Rumball and Richmond, 1996; Greet and Smart, 2002). Shannon and Trahar (1986) found that the removal of surface species by EDTA increased the floatability of chalcopyrite. Senior and Trahar (1991) studied the effect of the addition of EDTA on the interactions of lead and zinc hydroxide with chalcopyrite in the absence and presence of xanthate. They showed that the precipitated metal hydroxides on the surface of chalcopyrite prevented its collectorless flotation and reduced its recovery in collector-induced flotation. They also observed that the effect of xanthate on the floatability of chalcopyrite depends on the type of metal hydroxide. Rumball and Richmond (1996) studied the extent of oxidation of the sulphide minerals by leaching slurries with an EDTA solution. They suggested that chalcopyrite released iron but not copper (Rumball and Richmond, 1996). Kant et al. (1994) used the EDTA extraction technique in a study of sulphide mineral surfaces and found also that EDTA did not extract copper from chalcopyrite.

Previously, Tayebi-Khorami et al. (2017a,b) investigated the separation of enargite from other copper sulphide minerals in real ore systems by controlling the potential of the pulp. Two ore samples were selected from the Tampakan copper-gold deposit located in the Philippines. A composite of several high arsenic-containing drill core intersections for a high arsenic sample (HAS) and a composite of some low arsenic-containing drill core intersections for a low arsenic sample (LAS), were selected to provide a range of arsenic levels (Tayebi-Khorami et al., 2017a).

Comprehensive size-by-size chemical and mineralogical analyses were performed on the HAS and the LAS samples. It was observed that enargite was the only arsenic-copper mineral present in both samples and arsenic in the HAS sample was two times higher than that for the LAS, assaying about 230 ppm. The other non-enargite copper minerals (NECu) were bornite and chalcopyrite. The amount of copper in other non-enargite copper minerals (NECu) was similar in both samples (circa 0.56%) (Table 1). The sulphide gangue mineral was pyrite with practically two times higher in the HAS sample than that for the LAS sample. Gangue mineralogy mainly comprised of quartz, diaspore, muscovite, pyrophyllite, and kaolinite. The size-by-size mineral distributions in the ground product showed that the amounts of fine ($-11\ \mu\text{m}$) particles were noticeably greater for enargite than for NECu, indicating that the enargite tends to be ground more readily than the other copper sulphide minerals. The mineral grain size data showed that enargite had a finer grain size distribution compared to the other copper minerals in both samples. Moreover, it was observed from the mineral locking data that enargite was more associated with pyrite in the HAS sample compared to the LAS sample. More information regarding the mineralogy characteristics of the HAS and the LAS samples is available in Tayebi-Khorami et al. (2017a).

Flotation tests were performed at several pulp potential values (-200 , 0 , $+200$, and $+400$ mV SHE) on both the HAS and the LAS samples. The flotation data were analysed to determine the floatability of enargite, NECu, and pyrite under these controlled pulp potential conditions (Fig. 1). For the LAS sample, the results confirmed that it is possible to separate enargite from non-enargite copper minerals (NECu) at a reducing potential (-200 mV SHE) and pH 11. For the HAS sample no separation between enargite and NECu was observed at reducing

potentials and enargite in the HAS sample showed very low recovery variations as the Eh was changed. It was observed that even for liberated enargite, its recovery was still low for all Eh ranges in the HAS sample. In addition, it was observed that pyrite showed high recovery at pH 11 and Eh values below $+400$ mV SHE, while it was highly depressed at Eh $+400$ mV SHE in both samples without the addition of any chemical depressant. More details about the selective flotation of enargite from copper sulphides in the HAS and the LAS ore samples can be found in Tayebi-Khorami et al. (2017b).

One possible reason for the different response of enargite in the HAS sample could be the presence of oxidation products on the surface of the particles. In the present paper, surface chemistry studies were undertaken using an EDTA extraction technique for both the HAS and the LAS samples to evaluate the amount and type of metal ions on the mineral surface and the possible reasons for different flotation results.

2. Experimental procedure

2.1. Sample preparation

Similar to the previous papers by Tayebi-Khorami et al. (2017a,b) the high arsenic sample (HAS) and the low arsenic sample (LAS) from Tampakan deposit were selected for this study. A Roclabs laboratory jaw crusher followed by a roll crusher in closed circuit with a sieve was used for crushing the HAS and the LAS drill cores to 100% finer than 1.7 mm. The crushed drill cores were blended to form a composite HAS and LAS sample, and then split into sub-samples of 500 g by a rotary splitter using standard methods and stored in a dry cupboard to prevent further oxidation. For each test, the sub-sample of 500 g crushed ore (HAS or LAS) was mixed with Brisbane tap water in an iron ball mill at a solid-liquid ratio of 2:1, i.e. 67% solids by weight and ground using stainless steel balls to achieve the P_{80} of 90 μm . The mill was cleaned by grinding a sample of quartz for 5 min before each test.

2.2. EDTA extraction tests

Ethylenediaminetetraacetic acid tri-sodium salt (Na_3EDTA) as an AnalaR product was used to solubilise metal sulphide oxidation products from the surface of particles and to determine the type and amount of oxidation species formed on the minerals surface.

Two sets of EDTA extraction tests were conducted. The schematic of the experimental procedure is shown in Fig. 2:

- The first set of tests was conducted on the HAS and the LAS samples, which were ground to P_{80} of 90 μm (Mill discharge).
- The second set of tests was performed on the conditioning stage of the flotation tests (Flotation feed).

For the first set of tests, after grinding the sample of the HAS or the LAS to P_{80} of 90 μm , the sample was weighed and leached by 5% solution Na_3EDTA for 10 min using an electrical stirrer. The slurry was filtered using a Whatman number 40 filter paper and then fine filtered using a 0.45 μm Millipore filter. The solubilised metals were determined by Inductively Coupled Plasma (ICP) Atomic Emission Spectrophotometry (AES).

For the second set of tests, as details described in Tayebi-Khorami et al. (2017b), four different pulp potential (Eh) values of -200 , 0 , $+200$, and $+400$ mV SHE were selected and the experiments were conducted at these Eh values for both the HAS and the LAS samples in a 3 dm³ modified laboratory stainless steel Denver cell. This cell was fitted with pulp level control, an automatic titration control unit for control and monitoring pH and pulp potential, and a gas on/off control. The pH was measured with a Radiometer glass electrode, and calibrated using standard pH 7 and pH 10 buffer solutions before each test. The pulp potential was measured with a high impedance differential voltmeter using polished platinum electrode and an Ag/AgCl reference

Table 1
The head assays of HAS and LAS samples.

Sample	Cu (%)	As (ppm)	S (%)	Fe (%)	NECu (%)
HAS	0.64	233	2.96	2.91	0.58
LAS	0.57	114	1.91	1.87	0.54

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