Minerals Engineering 23 (2010) 903–907

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

An impedance study of the adsorption of $CuSO_4$ and SIBX on pyrrhotite samples of different provenances

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ARTICLE INFO

Article history:
Received 14 December 2009
Accepted 11 February 2010
Available online 29 March 2010

Keywords:
Sulfide ores
Froth flotation
Redox reactions
Electrochemical impedance analysis

ABSTRACT

The non-stoichiometric sulfide mineral pyrrhotite ($Fe_{(1-x)}S$), common to many nickel ore deposits, occurs in differing crystallographic forms and compositions. The processing of pyrrhotite from these ores through froth flotation is based on the surface properties of the sulfides and since pyrrhotite is a metallic conductor, it is of interest to characterise the surface properties of pyrrhotite with respect to its electrochemical state. In this study, a series of pyrrhotite samples derived from Canada, South Africa, and Botswana whose mineralogy is well characterised, were used for electrochemical impedance spectroscopy (EIS). The behaviour of the different pyrrhotite samples were compared in terms of the effect of pH (7 and 10), collector addition (SIBX) and copper activation and the results correlated with microflotation tests. The EIS results were then used to interpret and understand the differences in flotation performance of the pyrrhotite samples under the different reagent conditions and provide some answers as to why the success of copper activation on pyrrhotite is so variable.

1. Introduction

Understanding flotation behaviour of pyrrhotite is of vital importance as it is considered as a valuable mineral in PGM ores or a gangue mineral in Ni–Cu ores. A variety of chemical reagents such as collectors, activators, depressants, and modifiers are used to manipulate the flotation of pyrrhotite. In general, xanthate type collectors, such as sodium isobutyl xanthate (SIBX) and sodium normal propyl xanthate (SNPX) are used in the flotation of pyrrhotite. Dixanthogen is generally considered as the commonly occurring collector species responsible for rendering pyrrhotite its hydrophobicity during flotation (Allison et al., 1972; Fornasiero et al., 1995; Bozkurt et al., 1998). The rate of adsorption and consequent dixanthogen formation is dependent on pH; and decreases with an increase in pH of the mineral solution.

In some cases, the flotation of pyrrhotite is very low even in the presence of long chain xanthates and mixtures of collectors. In order to improve the efficiency of adsorption of collectors to sulfide minerals during flotation, activators, such as Cu, Pb, and Ag, are used. However, Cu^{2+} appears to have been the most widely used activator for pyrrhotite flotation in PGM ores. Early studies of the copper activation mechanism for pyrrhotite suggested ion exchange between copper and iron at the pyrrhotite surface (Buswell and Nicol, 2002). More recently it has been proposed that the copper activation of pyrrhotite is not through direct ion exchange, but rather an ion adsorption mechanism similar to that for pyrite (Gerson and Jasieniak, 2008). This mechanism involves direct adsorption of Cu^{2+} onto the pyrite surface followed by the in situ reduction of Cu^{2+} to Cu^{+} (Weisener and Gerson, 2000). Following the reduction of copper to Cu^{+}, an overlayer of $Cu(OH)_2$ formed when the reaction occurred at alkaline conditions.

Although, the activation of pyrrhotite by copper ions is generally accepted, there have been discrepancies in the results of some studies indicating copper activation may potentially be related to the nature of the pyrrhotite sample in terms of its degree of oxidation or crystallography. In the work of (Wiese et al., 2005) which compared the flotation performance of pyrrhotite from different mines of the Merensky Reef, it was shown that the effect of copper activation was quite different between the ores. For one of the ores, the addition of copper caused relatively little improvement in pyrrhotite recovery whereas for the other ore, there was a 50% improvement in pyrrhotite recovery with copper activation.

Similar discrepancies have been observed by Becker et al. (2008) with pyrrhotite samples of different origins. Therefore, the aim of this work was to investigate adsorption of $CuSO_4$ and SIBX on four pyrrhotite samples having different crystallography by using electrochemical impedance spectroscopy.

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doi:10.1016/j.mineng.2010.02.007

2. Materials and experimental methods

2.1. Pyrrhotite samples

The pyrrhotite samples used in this study were obtained from a variety of nickel ore deposits located within South Africa, Canada, and Botswana (Table 1). The mineralogy of the pyrrhotite samples was characterised using optical microscopy, X-ray diffraction (XRD) and electron microprobe analysis (Becker et al., 2008; Becker, 2009; de Villiers et al., 2009. The determination of magnetic (monoclinic 4C) versus non-magnetic (orthorhombic NC) pyrrhotite was performed with the use of the magnetic colloid method as described by Craig and Vaughan (1981).

Two samples were obtained from the Sudbury ore deposit in Canada, namely a massive sulfide ore from the Copper Cliff North (CCN) mine and a semi-massive to massive sulfide ore from the Gertrude West mine. The mineralogical characterisation showed that the CCN pyrrhotite is non-magnetic of composition Fe_9S_{10}, whereas the Gertrude West is almost entirely magnetic pyrrhotite of composition Fe_7S_8. Pyrrhotite from the Phoenix deposit in Bostwana is also magnetic pyrrhotite of composition Fe_7S_8. The pyrrhotite derived from the massive sulfide body (MSB) at Nkomati mine in South Africa was mixed and consisted of inter grown magnetic (Fe_7S_8) and non-magnetic pyrrhotite (Fe_9S_{10}).

2.2. Electrode preparation

Working electrodes of the pyrrhotite samples in this study were manufactured by mounting a ~2 × 2 mm slice of pyrrhotite into an epoxy resin, connected by a copper plate and wire. In order to confirm the purity of the pyrrhotite electrodes, BSE images and elemental maps of the electrodes were taken on an EVO50SEM with Bruker Xflash 3001 energy dispersive detectors at Hacettepe University.

2.3. Impedance spectroscopy

The experiments were performed using a conventional three electrode electrochemical cell at pH 7 and pH 10. Impedance spectra measurements were taken in the absence of dissolved oxygen. The DC voltage (the starting potential) was taken as the open circuit potential. The AC voltage (amplitude) was 7 mV. The initial and final frequencies were 100,000 Hz and 0.01 Hz, respectively.

EIS experiments were performed in the absence and presence of 8×10^{-6} M $CuSO_4$ and 10^{-3} M SIBX, individually and in combination.

3. Results and discussion

The EIS was performed to observe the adsorption of SIBX with and without copper activation. Bode plots of the EIS data are

Table 1
Mineralogical characteristics of the pyrrhotite samples used in this study (Becker et al., 2008).

Pyrrhotite sample	Crystallography	Composition
Sudbury Copper Cliff North (CCN; Canada)	Non-magnetic orthorhombic pyrrhotite	Fe_9S_{10}
Sudbury Gertrude West (Canada)	Magnetic monoclinic pyrrhotite	Fe_7S_8
Phoenix (Botswana)	Magnetic monoclinic pyrrhotite	Fe_7S_8
Nkomati MSB (South Africa)	Inter grown magnetic monoclinic and non-magnetic (orthorhombic) pyrrhotite	Fe_7S_8 and Fe_9S_{10}

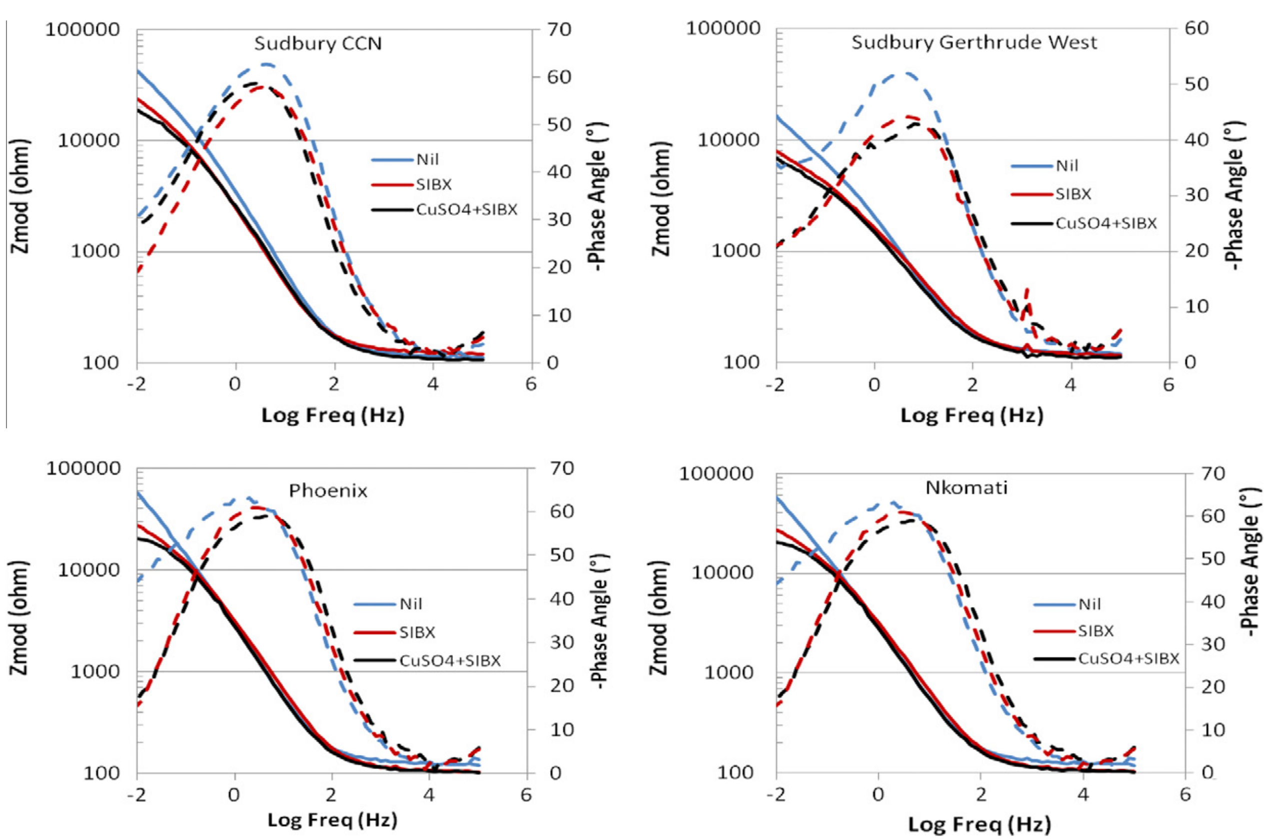

Fig. 1. Bode plots for the pyrrhotite samples in the absence and presence of SIBX and $CuSO_4$ + SIBX at pH 7.