Electrochemical and XPS surface analytical studies on the reactivity of enargite

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Abstract: Enargite, a copper arsenic sulfide having the formula Cu3AsS4, is a source of arsenic and may cause environmental problems owing to the release of toxic elements upon oxidation, especially in acid mine effluents. In this work the oxidative dissolution of enargite has been studied on freshly cleaved samples exposed to distilled water, sulfuric acid solution at pH 4 and acidic FeCl₃ or Fe₂(SO₄)₃ solutions at pH ca. 2 with 0.025 M Fe³⁺ simulating abiotic acid mine drainage environments. The open-circuit potential of the acidic solutions with ferric ions achieved stabilization at +0.72 ± 0.02 V NHE thus, according to the mixed potential theory, the redox couple Fe³⁺/Fe²⁺ strongly polarizes the enargite surface towards positive potentials. Solution analyses showed that in these conditions about 10–14 μg copper are released every 24 h into solution from approximately 0.5 cm² enargite surface. Based on the amount of dissolved copper, the thickness of the dissolved enargite has been calculated to be about 60–130 nm. XPS analyses of the reacted enargite surfaces revealed no changes in the binding energy of copper Cu₂p₃/₂ found at 932.4 ± 0.2 eV, arsenic As₃d₅/₂ found at 43.3 ± 0.2 eV and of sulfur, S₂p₃/₂ at 161.9 ± 0.2 eV compared to the pristine surface, whereas a prominent sulfur signal appeared at ca. 163.5 ± 0.2 eV, assigned to sulfur in a copper-deficient layer. The XPS quantitative analysis performed by applying a three-layer model revealed the presence of a metal-deficient layer of ca. 0.7 nm thickness on the enargite surface. The interface beneath this layer (estimated thickness 5–10 nm) was slightly enriched in sulfur and depleted in copper. Based on these complementary data from solution analysis and XPS surface analysis, a model similar to the dissolution of binary metallic alloys is here proposed for enargite dissolution under oxidizing conditions.

Key-words: redox potential, mixed potential theory, XPS surface analysis, dissolution, sulfide minerals.

Introduction

Enargite is a copper arsenic sulfide having the formula Cu₃AsS₄. It is found in significant amounts in the so-called epithermal “high sulfidation” volcanic hosted deposits (Arribas, 1995; Lattanzi et al., 2007). Enargite is sometimes used as a minor ore of copper. It is of environmental concern on account of its potential release of toxic arsenic species upon oxidation. Hence, understanding the surface reactivity of enargite is important in environmental issues, as well as in copper mining and ore processing, e.g. by flotation (McCarron et al., 1990). Indirect information may be obtained, as shown in a review by Lattanzi et al. (2007) from data obtained from natural assemblages. However these are difficult to interpret in terms of specific understanding of enargite oxidation. More information can be obtained from laboratory studies of enargite oxidation or dissolution (Dutrizac & Macdonald, 1972; Escobar et al., 1997; Velasquez et al., 2000; Asbjörnsson et al., 2004). Several papers deal with ore processing in alkaline solutions (Cordova et al., 1997; Pauporté & Schuhmann, 1996) using electrochemically altered enargite. These papers are not significant as far as the reactivity of enargite in natural environments or mine effluents is considered.

Early, comprehensive work was performed applying corrosion potential measurements and anodic polarization to sulfide minerals (Venkatachalam & Mallikarjunan, 1970; Nicol & Lazaro, 2002; Rossi, 1990 and literature cited therein). Another, more frequent application of electrochemistry to hydrometallurgical systems is the measurement of the redox-potential of electrolytes (or synonym Eh) (Natarajan & Iwasaki, 1974). In both cases, the mixed potential theory, first proposed by Wagner & Traud (1938), has to be applied in interpreting the measured potentials because several oxidation (anodic) or reduction (cathodic) processes may take place both on the mineral surface and on an inert platinum electrode (Li et al., 1992).

Several papers have been published recently on enargite surface chemistry (Fullston et al., 1999; Velasquez et al., 2002; Pratt, 2004; Viñals et al., 2003). In previous papers our research group reported some results on the X-ray photoelectron spectroscopy (XPS) characterization of synthetic and natural enargite (Rossi et al., 2001a; 2001b). A more precise determination of the chemical state of the