Research Paper

The mechanism of electrochemical dissolution of sphalerite in sulfuric acid media

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A B S T R A C T

The dissolution of sphalerite concentrate from Angouran mine was studied in 0.5 M sulfuric acid solution by the application of carbon paste electrode at 22 °C. Different electrochemical methods including cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS) were applied to study the behavior of the sphalerite. Results showed that the oxidation of sphalerite proceeds in the anodic potential range of open circuit potential (OCP) to 900 mV vs. Ag/AgCl. At low anodic potential of 400 mV vs. Ag/AgCl a sulfur−rich passive layer forms on the mineral surface. The predominant reaction on the electrode surface at 400 mV vs. Ag/AgCl is oxidative sphalerite dissolution, in which zinc ions and elemental sulfur layer, as a passive layer, form through the electrochemical reaction. By increasing the potential to 550 mV vs. Ag/AgCl the passive layer was partially dissolved. Further increase of the potential to 900 mV vs. Ag/AgCl results in the complete dissolution of the passive film and active dissolution of sphalerite. The electrochemical oxidation of sphalerite and the formation and dissolution of its passive film were also studied by EIS. Afterwards, the EIS spectra were modeled by equivalent electrochemical circuit. Together, the EIS data and Raman spectroscopy results strongly supported the proposed mechanisms for the oxidative sphalerite dissolution through the anodic potential range.

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1. Introduction

Sphalerite is the most important zinc mineral, which contains various impurities. The common impurities in sphalerite are iron, lead, cadmium and copper. Pyrrhotite (FeS) is an important impurity, which is always present at concentrations between 0.3 and >20%. Cadmium can be as high as 1.5% and copper vary from trace to 20%. These impurities are either replacements of zinc in the crystal structure of sphalerite or the formation of emulsions in the mineral itself, as micron inclusion in sphalerite [1,2]. Sphalerite holds the leading position among the zinc minerals, as 90% for zinc is produced via treating this mineral [3]. About 80% of zinc production occurs via roasting−leaching−electrowinning (RLE) of sphalerite. An alternative to RLE process is the atmospheric leaching of sphalerite, which is more attractive from many standpoints such as ability to deal with low−grade materials with higher impurities [4,5]. The critical problem associated with the

zinc sulfide atmospheric leaching processes is the slow dissolution rate of sphalerite due to its surface passivation. Studying the dissolution mechanism of sphalerite in ferric sulfate media would be one of the first steps to shed a light on the atmospheric leaching process mechanism and the reason behind its slow kinetics. The sphalerite leaching process is an electrochemical process in nature, sulfide oxidizing to form elemental sulfur or other oxidized sulfur species such as sulfate. Thus, studying the sphalerite electrochemistry is important for this matter.

Whereas, different electrochemical techniques have been performed to realize the dissolution mechanism of sphalerite [6–11]. Based on the literature review, anodic behavior of sphalerite divided into two separate potential regions, passive region dissolution and active region dissolution. At passive region in which a passive layer is established, sphalerite oxidized to zinc ions and elemental sulfur on the sphalerite surface. While, sphalerite dissolved without formation of any passive layer in active region. Srinivasan et al. [10] have focused on the mechanism of sphalerite dissolution by the application of cyclic voltammetry in 0.5 M sulfuric acid. The obtained voltammograms with compacted sphalerite electrodes showed a broad peak at potential range of 0 to 800 mV vs. Ag/AgCl, which was attributed to ZnS

oxidation to zinc ions and elemental sulfur, referring to passive region. The proposed passive region for sphalerite dissolution introduced in a wide range, seems to be incorrect due to the high concentration of iron in sphalerite mineral. Active dissolution has been connected to the oxidation of the product formed during the anodic dissolution of ZnS at potential higher than 800 mV vs. Ag/AgCl. Srinivasan et al. [10] have showed that higher sulfuric acid concentrations and faster scan sweep rates could increase the sphalerite dissolution kinetics. In Nava et al. [9] study, they have investigated the electrochemical oxidation of a sphalerite concentrate containing several sulfide minerals. They have concluded that sphalerite and galena oxidize in relatively large anodic potential window of 400 to 850 mV vs. Ag/AgCl, whereas covellite and pyrite oxidation occur at potentials greater than 850 mV vs. Ag/AgCl. According to their results, passive oxidative dissolution of sphalerite occurred at potential range of 400 to 615 mV vs. Ag/AgCl and active sphalerite dissolution took place in the range of 615−850 mV vs. Ag/AgCl. Despite formation of elemental sulfur through the passive dissolution of sphalerite, the sulfur oxidation was not reported in potential range of 400 to 850 mV vs. Ag/AgCl.

Ahlberg and Asbjornsson [6] have proposed that the low iron sphalerite minerals do not show any electrochemical activity in perchlorate, chloride and sulfate media in the potential range of −970 to 1030 mV vs. Ag/AgCl, while high iron sphalerite was found to be electrochemically active. A survey in literature showed that leaching of sphalerite is an electrochemical reaction involving oxidation of sphalerite and ferric reduction regardless of its chemical composition [6–11]. In another study, the anodic dissolution of sphalerite electrode was studied at potentials of 300 and 650 mV vs. Ag/AgCl [12], where the potentiostatic studies showed that a sharp drop of current occurred during the first 30 min at 300 mV vs. Ag/AgCl; however, at 650 mV vs. Ag/AgCl the current density was much higher than that of 300 mV vs. Ag/AgCl, and it decreased gradually by time. The current efficiency of sphalerite dissolution at 650 mV vs. Ag/AgCl was lower than that at 350 mV vs. Ag/AgCl, which indicated that the sulfur oxidation was a major co−occurring process at 650 mV vs. Ag/AgCl [12]. Narasa-goudar et al. [12] have concluded that the sphalerite oxidation in sulfuric acid media has both electrochemical and chemical reactions involved.

Urbano et al. [11] have shown that the electrochemical activity of high lead sphalerite increases in 0.1 M NaNO₃, due to the galvanic interaction between sphalerite and galena. It has been proposed that passive dissolution of sphalerite occurs at potential around 800 mV vs. Ag/AgCl, which hinders the sphalerite oxidation. The passive layer could be dissolved at potentials higher than 800 mV vs. Ag/AgCl [11]. Choi et al. [7] studied the sphalerite oxidation by cyclic voltammetry and chronoamperometry measurements in the presence and absence of T. ferrooxidans at potential range of −1000 to 1400 mV vs. Ag/AgCl. The results showed a higher electrochemical activity in the presence of microorganism for sphalerite [7]. It has been reported that sphalerite oxidizes to zinc ions and elemental sulfur at around 20 mV vs. Ag/AgCl. The sulfur oxidation was registered to begin at 500 mV vs. Ag/AgCl, which is lower than that reported in other studies [7]. Elsewhere, Rodriguez et al. [13] have pointed out that the electrochemical reactivity of sphalerite with 1.65% Fe gradually enhances by increasing the temperature from 35 to 68 °C in the presence of microorganisms. As far as the authors are aware, there is no comprehensive study about the anodic dissolution of sphalerite in a wide potential range. In addition, there is no certainty about potential range for passive and active dissolution of sphalerite.

A limited number of published papers have studied the anodic dissolution of high iron sphalerite (marmatite) by electrochemical impedance spectroscopy (EIS) [14–16]. Xiong et al. [16] have suggested that the marmatite dissolution process is a charge

transfer−controlled process in the presence of ferric and ferric−-free electrolytes at open circuit potential (OCP). The oxidation of marmatite is controlled by a two−step charge transfer process in the ferric−containing solutions, and a single−step charge transfer process in the ferric−free solutions [14]. Elsewhere, the EIS measurement for marmatite electrode illustrated two−step charge transfer in the high and medium frequencies and a typical feature of Warburg impedance at lower frequencies, which was attributed to the diffusion process [15]. In these studies [14–16], EIS measurements were applied to high iron sphalerite minerals in the presence of microorganism; however, no EIS studies on the sphalerite dissolution in microorganism−free media are available in the literature. Therefore, it is believed that a systematic electrochemical study is required to shed a light on the sphalerite electrodissolution mechanism, and provide a better understanding of the sphalerite dissolution at different anodic potentials. Besides, the chemically stable and electrically conductive sphalerite electrodes are essential to provide highly reproducible results.

Sphalerite naturally has a very high resistivity of $10^9−10^{12}\,\Omega$ cm [6], and it is fair to consider the mineral as an electrical insulator. To improve the conductivity, fine ground sphalerite particles have been mixed with carbon powder [6,10] to make a carbon paste electrode with higher electrical conductivity. Carbon paste electrodes (CPEs) were first introduced in 1950s for analytical purposes [17].

In this report CPE of Angouran sphalerite (CPE−Angouran), a mine site in Iran, is used to study the mechanism of sphalerite dissolution in 0.5 M sulfuric acid solution by the application of a variety of electrochemical techniques such as chronoamperom-etry, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The specific goals of this study are: (1) to investigate the oxidation and passivation of sphalerite in sulfuric acid solution at different anodic potentials; (2) to combine the EIS and Raman spectroscopy studies with the results of the cyclic voltammetry tests to develop a better understanding of the sphalerite dissolution mechanism; (3) to study the polarized surface of sphalerite electrode at different applied potential by Raman spectroscopy analysis.

2. Experimental

2.1. Sulfide mineral concentrates

The zinc concentrate from Angouran mine was used for the carbon paste electrode fabrication. The mineralogical composition of the concentrate was (wt. %): 73.2% sphalerite (ZnS), 5.4% pyrite (FeS₂) and pyrrhotite (FeS), 4.8% galena (PbS), 1.4% greenockite (CdS), 1.1% arsenopyrite (FeAsS) and 12.3% silica (SiO₂). Addition-ally, two high purity mineral samples of sphalerite (86.0% ZnS and 10.1% SiO₂) and galena (97.0%) were used for carbon paste electrode preparation (CPE-sphalerite and CPE-galena) to compare their electrochemical responses with those of the concentrate sample. The elemental assays of the concentrate and mineral samples are presented in Table 1.

2.2. Working electrodes preparation

The carbon paste electrode of Angouran sphalerite (CPE-−Angouran) electrodes were prepared by mixing 12 g of sphalerite concentrate with 3 g graphite (Aldrich grade, <20 μm). After mixing the concentrate and graphite, 4 g of silicone oil (Aldrich, viscosity 100 kcSt) was added as a non−conducting binder. The resulting homogeneous paste was placed in a 50 mL plastic syringe and a copper wire was immersed in the paste to conduct the electricity to the potentiostat. The CPE−Angouran was pushed out of the tube with the plunger in order to renew the surface after