International Journal of Mineral Processing 154 (2016) 16–23

Contents lists available at ScienceDirect

International Journal of Mineral Processing

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

Evaluation of collector adsorption by electrochemical impedance spectroscopy

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ARTICLE INFO

Article history:
Received 9 October 2015
Received in revised form 22 June 2016
Accepted 28 June 2016
Available online 29 June 2016

Keywords:
Pyrite
Collectors
Electrochemical impedance spectroscopy
Surface enhanced Raman spectroscopy

ABSTRACT

Laboratory bench-scale flotation test is generally used as a standard method to investigate effects of different flotation reagents on flotation performance. A comprehensive test program requires large amount of representative samples, takes long time and could be costly. Hence, developing alternative cost effective, fast and low cost methods have recently been in the subject of many research studies. Microflotation, induction time measurement, electrochemical methods, etc. have been used to measure adsorption of flotation reagents and derive a proxy to correlate with flotation behaviors of sulfide minerals. In this study, Electrochemical Impedance Spectroscopy (EIS) method was used to measure rate of collector adsorption on two different pyrite rich samples from flotation plants processing Carlin and Yanacocha Verde ores. Eight different types of collectors were selected based on their chemistry and applications in flotation operations. Adsorption of the collectors were also measured by using Surface Enhanced Raman Spectroscopy (SERS) technique and correlated with EIS results. The results showed clearly that Carlin pyrite was more electrochemically reactive than Verde pyrite. Rate of adsorption of the collectors was related to coating resistance (R_c), which was calculated using an equivalent electrical circuit model fitted to the EIS data. Based on R_c values, order of adsorption of the collectors for Carlin and Verde samples were discussed. It is therefore shown that preliminary reagent selection for a specific ore can be done using EIS technique, which is considerably faster and low cost compared to the other techniques.

1. Introduction

Laboratory bench-scale flotation test methodology is generally used as a standard technique to assess ore flotability, i.e. effects of ore type, flotation reagents, chemical conditions, etc. Approximately 1–2 kg of ore sample is used in each test and a large number of tests are usually required to screen potential reagents, determine optimal grind size, circuit design, etc. Therefore, a comprehensive testing program requires large amount of ore samples, time and also budget, especially for complex ores which require selective flotation. Hence, test programs, particularly for screening flotation reagents, are usually planned to minimize the number of tests based on literature and historical data of similar ore types, recommendation of reagent manufacturers, etc. This means that the test program will always has deficits in terms of investigation of all possible combinations of flotation reagents.

Alternative methods, such as microflotation, EMDEE Microflot (Bıçak et al., 2011; Chudacek, 1992), bubble induction time measurements (Verrelli and Albijanic, 2015), electrochemical techniques (Ekmekçi et al., 2011), etc. are developed to estimate flotability of an ore using small amount of sample. These techniques are considered to be less time-consuming and less costly than bench scale flotation tests. In spite of a large number of research studies, however, the bench scale flotation test method is still used as the most reliable technique for determination of flotation characteristics of ores.

Electrochemical techniques have been used to provide valuable information about surface reactivity of sulfide minerals and interaction between various flotation reagents and sulfide minerals. Open circuit potential (OCP) (also referred to as rest potential) measurement, steady-state polarization, voltammetry, galvanostatic polarization, chronoamperometry, electrochemical impedance spectroscopy are the common methods used for this purpose (Tadie et al., 2015; Parker et al., 2012; Niu et al., 2014; Woods, 2003; Abramov and Avdohin, 1997; Hu et al., 2009). Especially, electrochemical impedance spectroscopy (EIS) has recently been widely used for surface characterization of sulfide minerals, assessment of adsorption mechanisms of flotation reagents on sulfide minerals and also identifying surface products in absence and presence of flotation reagents (Velasquez et al., 2000; Pang and Chander, 1990; Venter and Vermaak, 2008; Bevilaqua et al., 2009; Ekmekçi et al., 2010a; Ekmekçi et al., 2010b; Ekmekçi, 2011).

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http://dx.doi.org/10.1016/j.minpro.2016.06.012
0301-7516/

Pyrite is found in almost all of the sulfide ore deposits as a major sulfide gangue mineral. In most flotation applications, depression of pyrite could be the most challenging part of flotation chemistry. But, in some ore deposits pyrite may contain precious metals, such as Au, Ag and PGE, in the form of association or inclusion, and becomes an economic mineral (Dunne, 2005; Allan and Woodcock, 2001; Marsden and House, 2006). In either case, surface chemistry of pyrite particles has crucial importance for success of the flotation.

Pyrite is a semiconductor with variable electrochemical properties, which mainly depends on ore genesis, surface defects and also association with other sulfide minerals (Abramov and Avdohin, 1997). Pyrite surface chemistry, as a complex system, has been extensively studied and when oxygen and other oxidizing ions are present, electrochemical oxidation may occur. Therefore, electrochemical techniques are suitable for investigating surface chemistry, adsorption of flotation reagents and thus flotability of pyrite under various flotation conditions. Outcome of such studies may not be used to directly estimate flotation behaviour of sulfide minerals in a flotation cell, but as a proxy to evaluate effects of various reagents and flotation conditions as a fast and cost effective ways.

The electrochemical techniques require small amount of materials compared to bench-scale flotation tests. A large number of parameters can be tested in a relatively short time and at relatively low cost. For most of the sulfide minerals, a direct correlation between collector adsorption and electrochemical response could be observed (Allison et al., 1972; Goold and Finkelstein, 1972; Ekmekçi et al., 2010a). Therefore, it is possible to use an electrochemical measurement as a proxy to estimate adsorption of flotation reagents (collectors, activators, depressants) and hence correlate with flotation behaviour.

In this study, use of electrochemical impedance spectroscopy (EIS) for measurement of collector adsorption was investigated by using two pyrite samples from different sources (Carlin and Yanacocha Verde). The samples were products of flotation plants and in the form of fine particle size material. Therefore, a novel mineral electrode fabrication method was employed to prepare the mineral electrodes (Ekmekçi et al., 2011). Cyclic voltammetry and EIS were used to identify the surface products formed after oxidation/reduction reactions. Raman spectroscopy was also used to determine chemical bonds of collectors on pyrite electrodes and direct analysis of collector adsorption to support results of EIS measurements.

2. Experimental

2.1. Pyrite ore samples

Two pyrite samples, from Carlin and Yanacocha Verde provided by Newmont, were used in the tests. The samples were not fresh pure samples taken from the ore deposit but products of flotation plants. Carlin sample was taken from final pyrite concentrate and the Verde sample from pyrite scavenger concentrate. Chemical composition of the samples is given in Table 1. Sulfide mineral content of Verde sample was considerably higher than Carlin sample. XRD analysis of the samples showed that the major minerals in Verde pyrite scavenger concentrate were pyrite (70%), quartz (19%) and pyrophyllite (11%) (Lopez, 2013). High As content in Carlin pyrite concentrate indicates presence of arsenopyrite and arsenian pyrite. Modal mineralogical analysis of Carlin sample showed that the major minerals were 48% quartz, 27% pyrite, 10% illite, 2.38% arsenian pyrite and 1.44% arsenopyrite. Both samples contain gold and hence recovery of sulfide minerals, mainly pyrite is essential to maximize gold recovery.

Table 1
Chemical composition of Carlin pyrite concentrate and Verde pyrite scavenger concentrate.

Sample	S %	Au ppm	Ag ppm	As ppm	Fe %	Al %	Cu ppm	Zn ppm	Ca ppm
Verde	40.02	1.103	14.3	794	34.23	1.94	3204	107	207
Carlin	12.26	9.111	6.3	6527	12.84	4.42	612	4541	7644

Sulfide mineral content of a mineral sample should be as high as possible for electrode fabrication to obtain a high surface area and thus better electrochemical response. Pyrite content of Verde sample was 70% and suitable for mineral electrode fabrication. However, Carlin sample contained only 27% pyrite and was not adequate to get strong electrochemical response. Thus, it was upgraded to about 70% pyrite using dry electrostatic separation technique. Finally, the ratio of surface area of pyrite in both electrodes was increased to 30%, which is suitable for electrochemical experiments.

2.2. Fabrication of mineral electrodes

As it was explained above, the samples used in this study were flotation concentrates. The surface of the particles were, therefore, coated with flotation reagent and most likely oxidized to some extent. In order to remove any oxidation products and organic species from the surface of the pyrite particles, both samples were washed first by diluted HCl and subsequently acetone, and then rinsed with distilled water. The washed samples were dried in a vacuum desiccator to prevent surface oxidation. The mineral electrode is composed of pyrite sample, graphite and a conductive binder (conductive polymer polyaniline) (Ekmekçi et al., 2011). This mixture is homogenized and pressed to produce a pellet. Then, the mineral electrode is fabricated by mounting the pellet in an electrochemical inert epoxy resin (Fig. 1). The pellet (1.3 cm diameter) is prepared in a way that the epoxy resin is diffused into the pores and cracks in the pellet and hardens the structure without affecting the electrical conductivity. This methodology allows polishing the surface of mineral electrode with alumina paste to create fresh surface for the electrochemical experiments. The polished electrode surface of both samples is illustrated in Fig. 2. Surface area of pyrite particles was

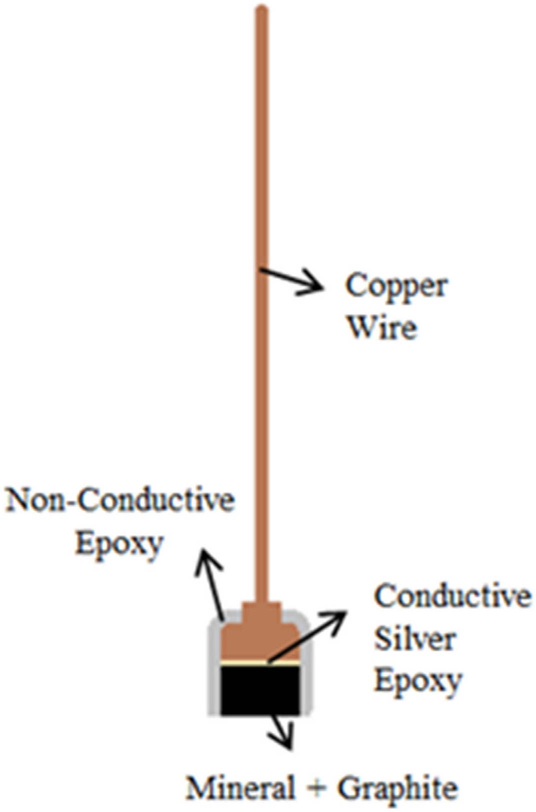

Fig. 1. Schematic view of the mineral electrode.