THE MECHANISMS OF THE PASSIVATION OF SULFIDE MINERALS IN OXIDATIVE LEACHING PROCESSES

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1. Abstract

A number of sulfide minerals of copper, nickel and iron can only be effectively leached by methods that require elevated temperatures in acidic solutions. While suitable for concentrates, these processes are not applicable to tank or heap leaching of low grade ores. It is now generally accepted that many of these minerals are subject to so-called passivation under oxidising conditions. However, the mechanisms involved in this passivation are not well understood and this study will review some of these mechanisms and show that the passivation of several of these important minerals appears to follow similar trends.

Electrochemical measurements using millerite, covellite and chalcopyrite electrodes were used to study the similarities of leaching and passivation processes taking place in oxidative acidic media. Thus, potentiostatic current-time transient experiments have demonstrated the resemblance with selective dissolution of metals from alloy systems. A model will be proposed which involves depletion of metal from outer layers of the minerals and the limiting step being diffusion of the metal ions through sulfur sub-lattice in these minerals. Potential step polarization experiments have enabled estimates to be made of the self-diffusion coefficients of copper, nickel and iron which were in the range of published values extrapolated from higher temperatures. The well known parabolic leaching behaviour of these minerals is supported by solid state diffusion as the rate limiting step.

2. Introduction

Sulfide minerals are the main sources of non-ferrous metals (Vaughan, 2006). Pyrometallurgical treatment of these minerals has been traditionally used in industrial practice. Although these methods have many advantages, they are associated with substantial capital costs and atmospheric pollution. Progressive lowering of ore grades with simultaneous tougher environmental regulations has resulted in the search for alternative hydrometallurgical treatment of sulfides. Because of the generally refractory nature of these materials towards leaching, processes at elevated temperatures and pressures were introduced.

From the thermodynamic analysis of systems involving many of the sulfide minerals, two main pathways of dissolution in acidic media were suggested (see for example Peters, 1976) namely acidic or non-oxidative (1) and oxidative (2, 3) reactions. These can be described by the following reactions for a divalent metal sulfide
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MeS(s) + 2H^+(aq) = Me^{2+}(aq) + H_2S(aq)  \hspace{1cm} (1)
MeS(s) + 2Ox(aq) = Me^{2+}(aq) + S(s) + 2Ox^-(aq) \hspace{1cm} (2)
MeS(s) + 8Ox(aq) + 4H_2O(l) = Me^{2+}(aq) + HSO_4^-(aq) + 8Ox^-(aq) + 7H^+(aq) \hspace{1cm} (3)

In some cases, the Eh-pH diagrams show that thermodynamic non-oxidative dissolution is not favourable. On the other hand, although thermodynamically favourable, many sulfides oxidative dissolution was found to be retarded under ambient conditions. Parabolic kinetics which is commonly observed in leaching experiments was said to be caused by passivation which set in after initial rapid dissolution.

Initially the term *passivation* was introduced for the description of this phenomenon in the dissolution of metals and alloys and only later was transferred to the field of leaching. It describes the situation in which the metal or mineral surface is covered with an inhibiting layer of an oxide or other insoluble species which is formed at a particular, so-called critical potential. Of the mineral sulfides, the most well studied is chalcopyrite and for this mineral several different passivating species have been suggested (Klauber, 2008), namely elemental sulfur, polysulfides, metal-deficient sulfides, jarosite and jarosite-like compounds.

It is generally accepted that sulfur is not responsible for passivation and consensus has not been achieved about the role and nature of these passivating layers despite many electrochemical and surface analytical studies.

This work is a comparative study of the behaviour of chalcopyrite, covellite and millerite under similar conditions in an attempt to demonstrate the common nature of passivation of these mineral surfaces.

3. Experimental

For all electrochemical experiments, a water jacketed conventional three electrode cell of 125 ml with accessories was used. In the case of chalcopyrite and millerite, high purity nitrogen (>99.99%) was purged through the solution for 30 minutes prior to and during the experiments. In case of covellite, the solutions were not deoxygenated. Platinum wire and silver silver chloride (KCl saturated), calomel (KCl saturated) or mercury mercurous sulfate (K_2SO_4 saturated) electrodes were used as counter and reference electrodes respectively. All potentials are quoted with respect to the standard hydrogen electrode.

Chalcopyrite and millerite electrodes were prepared by cutting an appropriate size piece of natural mineral and attaching it to a brass holder with conductive silver epoxy resin. The holder and mineral were subsequently imbedded in non-conductive epoxy resin and a surface of the mineral exposed by grinding. A covellite electrode was constructed as a 1 mm in diameter sintered rod of covellite. The mineral itself was synthesized by a conventional high temperature technique from the elements as described by Dutrizac and MacDonald (Dutrizac and MacDonald, 1974). Surfaces of the electrodes were investigated by SEM and mineral purity confirmed by XRD.
All electrochemical measurements were performed with either a Potentiostat/Galvanostat Model 273A (EG&G), using 352 SoftCorr III Measurement software Version 3.06 for operation and recording of results or with an EG&G Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat together with an EG&G PAR Model 175 Universal programmer. In this case data from the potentiostat were collected using a National Instrument data acquisition board controlled by Labview software.

All chemicals used were either analytical or laboratory grade. Concentrations of acids in the solution were confirmed by acid base titration. Concentrations of metals were confirmed by AAS.

The main electrochemical method employed was potential step polarization in acid solutions. This involves application of a potential close to the measured mixed potential in a typical lixiviant solution with ferric ions as the oxidant to the working (mineral) electrode and monitoring of the subsequent current-time transient. The mixed potentials in the absence of an oxidant are not well poised and therefore variable. The mixed potentials in the presence of ferric ferrous couple in the solution were in the ranges indicated in the table below. Most of the electrochemical measurements were conducted using rotating disc electrode at 200 rpm.

All experiments presented in this work were conducted under the conditions presented in Table 1.

<table>
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<th>Table 1 Conditions of minerals oxidation.</th>
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<td>Mineral</td>
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<td>Chalcopyrite</td>
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4. Results and discussion

The shape of a current-time transient can be generally separated to two limiting cases (Bard and Faulkner, 1980). The first limiting case is when the rate of the process is limited by an electrochemical step on the surface of the electrode, the current remains substantially constant with time, whereas in the second case the current decays with time after application of the potential step indicating diffusion limitation. The typical observed current time transients are presented in Figures 1a, 2a and 3a. It is clear that for chalcopyrite, covellite and millerite a rapid decay of the current is observe at potentials that are appropriate to oxidative leaching (Figures 1b, 2b and 3b).
Figure 1 Results of electrochemical experiments for chalcopyrite (CuFeS₂) at 25°C in 1M H₂SO₄.

650 mV

650 mV

Figure 1 Results of electrochemical experiments for chalcopyrite (CuFeS₂) at 25°C in 1M H₂SO₄.
Figure 2 Results of electrochemical experiments for covellite (CuS) at ambient temperature in 0.2M HCl.
Figure 3 Results of electrochemical experiments for millerite (NiS) at 60 °C in 1M H$_2$SO$_4$. 
In all cases, steady-state was not achieved even after extended polarization times. It should be noted that, in all cases, the current transients were unaffected by changes in agitation of the solution which eliminates diffusion in the aqueous phase as the rate determining step.

For a diffusion controlled process at a planar surface, the current time transient should follow the Cottrell equation:

\[ i(t) = \frac{nFD^{0.5}C_b}{\pi^{0.5}t^{0.5}}, \]

in which \( i(t) \) – current density at time \( t \).
\( n \) - number of electrons transferred to or from the diffusing species;
\( D \) - diffusion coefficient of the limiting rate species;
\( C_b \) - bulk concentration of diffusing species;
\( F \) - Faraday constant;
\( t \) - time.

In Figures 1c, 2c and 3c current density is plotted as a function of \( t^{0.5} \) for each mineral respectively, in each case this is done at one of the applied potentials. It is apparent that the predicted linear relationship is observed. The diffusion coefficients for diffusion of the metal ions in the solid phase (from the bulk of the mineral) to the electrode-electrolyte interface through the sulfur sublattice can be estimated from the slopes of the graphs. It was assumed that there is partial depletion of metals from the outer layers of the mineral as a result of dissolution. The diffusion coefficients were found to be in the range \( 10^{-15} \) to \( 10^{-14} \) cm\(^2\)/s for CuFeS\(_2\), \( 10^{-14} \) to \( 10^{-12} \) cm\(^2\)/s for CuS and \( 10^{-15} \) to \( 10^{-14} \) cm\(^2\)/s for β-NiS.

In case of chalcopyrite the estimated diffusion coefficient is a combination of diffusion coefficients for Cu\(^{2+}\) and Fe\(^{2+}\) according to the formula:

\[ D_{Me} = (D_{Cu}^{0.5} + D_{Fe}^{0.5})^2; \]

where \( D_{Me} \) - diffusion coefficient determined from current-time transient;
\( D_{Cu} \) – self-diffusion coefficient of Cu in CuFeS\(_2\);
\( D_{Fe} \) – self-diffusion coefficient of Fe in CuFeS\(_2\).

These estimated values were found to be comparable with literature values extrapolated from higher temperature data. For example for chalcopyrite based on data of Chen and Harvey (1975), the diffusion coefficients \( D_{Me} \) at 25 and 60 °C can be estimated as \( 2.1*10^{-15} \) and \( 1.5*10^{-14} \) cm\(^2\)/s respectively. In case of covellite a literature value of \( 2.3*10^{-12} \) to \( 3.3*10^{-12} \) cm\(^2\)/s can be found in (Cassaignon et al., 1999) for ambient temperature. The literature data for β-NiS is not available except just one value for synthetic material at 50 °C given by Price and Davenport (1982) which is \( 2.36*10^{-8} \) cm\(^2\)/s. This value appears to be unacceptably high due to possible involvement of migration at the very high overpotentials used. The material used by these authors was synthetic and was possibly not stoichiometric, which would impact on the defect density in the lattice increasing the rate of intercrystalline diffusion.
Extrapolation of the data of Fueki et al. (1968) and Klotsman et al. (1963, 1964a, 1964b) to ambient temperature gives self-diffusion coefficients of Ni in α-NiS to be in the range $10^{-18}$ to $10^{-20} \text{cm}^2/\text{s}$. These values are lower than those found in our work for self-diffusion of Ni in β-NiS. This is not unexpected since data in the literature (Sowa et al., 2004) indicates the volume per formula unit for NiS at ambient temperature for the high temperature phase is approximately 27.35 Å$^3$ whereas for the low temperature phase is approximately 28.00 Å$^3$. Generally it can be expected that diffusion in the denser phase would be slower.

Diffusion control of the overall rate of the electrochemical process can also be confirmed by constancy of the function $t^{0.5}$ with time (Kissinger and Heineman, 1996). In Figures 1d, 2d and 3d this constancy is evident in all cases, all three minerals as well as all the different applied potentials, for polarization times longer than approximately 30 s.

Higher values of $t^{0.5}$ at shorter polarization times for higher applied potentials for chalcopyrite (< 30 s) and covellite (< 10 s) may be due to the decrease with time of the Cu and Fe diffusion coefficients due to compaction of the partially depleted metal outer layers or possibly by recrystallization with formation of a less penetrable sulfur phase. Figures 1e, 2e and 3e present data which are based on the average current densities from 55-60 s after the application of the applied potential step. It is evident that in none of the three data sets there is the predicted independence of the current to the applied potential. This could be related to the involvement of migration in addition to diffusion in the transport process and to the very high concentration of metal in the solid phase. These effects are assumed to be absent in the derivation of the Cottrell equation. In spite of this fact, the rate limiting step in the oxidative dissolution of these minerals appears to be solid state diffusion.

The process of dissolution for these minerals can be summarized in terms of the following sequence of steps:
- dissolution of the outer (surface) layer of the mineral results in initial relatively rapid rates, observed as high anodic dissolution currents;
- diffusion of Cu, Fe and Ni from the bulk mineral to the depleted surface with the thickening of a metal depleted layer in the solid phase;
- possible consolidation and/or recrystallization of the depleted metal layer with a decrease in the effective metal diffusion coefficients;
- continuing thickening of the diffusion layer into the bulk of the mineral.

5. Conclusions

Potential step polarization experiments conducted for chalcopyrite, covellite and millerite showed that the most probable limiting step in oxidative dissolution of these minerals in sulfate and chloride media is solid state diffusion of the corresponding metal ions in the sulfur sublattice of the mineral. Subsequent steps of consolidation and/or recrystallization of the sulfur product layer on the surface of the mineral are possible in the case of chalcopyrite and covellite.
The estimated metal diffusion coefficients obtained from the current-time transients are $10^{-15}$ to $10^{-14}$ cm$^2$/s for CuFeS$_2$, $10^{-14}$ to $10^{-12}$ cm$^2$/s for CuS and $10^{-15}$ to $10^{-14}$ cm$^2$/s for \(\beta\)-NiS. These values are in a good agreement with available and extrapolated literature data.

6. Acknowledgement

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7. Literature


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Dmitry Pugaev is a PhD student at Murdoch University, Australia. His project is devoted to the investigation of passivation and dissolution of base sulfide minerals using electrochemical and leaching techniques. He obtained his undergraduate degree from D.I. Mendeleyev University of Chemical Technology of Russia, with a focus on solvent extraction technology. Dmitry has co-authored one patent, several journal and conference articles.