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Rate law for galena dissolution in acidic environment

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Abstract

A dissolution rate law for galena in acidic environment was derived from the steady-state dissolution rates using flow-through experiments. The influence of temperature, dissolved oxygen concentration and pH between 1 and 3 was assessed. This rate law can be used for predicting galena dissolution behavior in a wide range of conditions analogous to Acid Rock Drainage.

For pH below 2, the dissolution rate law can be expressed as:

$$R_{\mathrm{Gn,pH<2}} = 10^{-5.7\pm0.4} e^{\frac{-23\pm3}{\mathrm{RT}}} a_{\mathrm{H^+}}^{0.43\pm0.05}$$

where R_{Gn} is the galena dissolution rate (mol m^{-2} s^{-1}), R is the gas constant (kJ mol^{-1} K^{-1}) , T is the temperature (K) and a_{H^+} is the activity of hydrogen ion in the solution.

Galena dissolution rate law for pH between 2 and 3 can be expressed as:

$$R_{\mathrm{Gn,pH=2-3}} = 10^{-8.5\pm0.4} e^{\frac{-15\pm2}{\mathrm{RT}}} a_{\mathrm{H^+}}^{-0.78\pm0.04} a_{\mathrm{O_{2(aq)}}}^{0.30\pm0.03}$$

where $a_{O_{2(\mathrm{aq})}}$ is the activity of dissolved oxygen.

XPS (X-ray Photoelectron Spectroscopy) examination of the reacted galena samples shows the formation of a lead-deficient and sulfur-rich surface layer, consistent with the observed non-stoichiometry between dissolved sulfur and lead in all the studied solutions.

Based on the S/Pb ratio observed in solution and the reacted surfaces and the pH and dissolved oxygen dependence of the rates, two possible reactions for galena dissolution in acidic aqueous solution are proposed; (1) at pH ≤ 2 the rate seems to be determined by the protonation of surface sulfur atoms, and (2) at pH ≥ 2 the rate seems to be controlled by the attachment of oxygen to surface sulfur atoms.

The values obtained for the activation energies (15±2 kJ mol^{-1} at pH 3 and 23±3 kJ mol^{-1} at pH 1) suggest that galena dissolution is controlled by diffusion processes or mixed-controlled by diffusion of reactants and products between the bulk solutions and the reacting surfaces.

Keywords: Sulfides; Acid mine drainage; Dissolution kinetics; Lead

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1. Introduction

Galena (PbS) is one of the most important sulfide minerals and the only lead mineral with economical interest. Together with other sulfide phases, galena is present in a large number of natural environments and mining sites and its weathering is very often an important source of pollution due to the release of lead to the soils, surface run-off and groundwaters. The mobility and potential toxicity associated to galena dissolution is increased in scenarios undergoing Acid Rock Drainage (ARD), not only because of the enhancement of the solubility of lead aqueous species at low pH but also because galena seems to dissolve faster in acidic aqueous solutions (Hsieh and Huang, 1989; De Giudici et al., 2005).

Owing to its environmental implications, many studies have focused on galena dissolution kinetics in the last years. Most of the earlier works have focused on the galena dissolution behavior in the very beginning of its interaction with solutions (a few hours to a few days) under different conditions of pH, dissolved oxygen and temperature. In one of the first kinetic studies, Hsieh and Huang (1989) studied the dissolution of galena at 20 °C and at pH from 2.5 to 9 and observed that galena dissolution rate was almost independent on the availability of dissolved oxygen but very pH-dependent, decreasing sharply when increasing pH in the studied range. Rimstidt et al. (1994) assessed the role of Fe(III) in galena dissolution at pH around 2 and pointed out that galena dissolution kinetics was substantially different from pyrite. More recently, De Giudici and Zuddas (2001) and De Giudici et al. (2005) studied the dissolution of freshly cleaved galena (001) surfaces at pH from 1 to around 6 and at temperatures ranging from 25 to 75 °C in short experiments (<150 h) and observed that galena dissolution rate increased with decreasing pH. Finally, two recent short batch studies (less than 1 h of interaction between galena and solutions) carried out under acidic conditions proposed that galena dissolution is non-oxidative (Pashkov et al., 2002; Zhang et al., 2004). Moreover, a first order dependence on $[H^+]$ was proposed by (Zhang et al., 2004) for the initial rate of galena dissolution within the pH range from 0.43 to 2.45 and in the presence of 1 mol l^{-1} NaCl solutions.

All these earlier studies have focused on the galena dissolution behavior in the very beginning of its interaction with solutions (a few hours to a few days). A short duration of experiments usually renders much faster dissolution rates than the ones obtained after months (or years) of interaction with solutions because there is no time for true steady state to be achieved. Hence, apparent rates obtained by short experiments are not applicable for predicting mineral dissolution in scenarios where an extended interaction with solutions is expected (e.g. in the pores of mine tailings or in acid streams). In line with this affirmation, galena dissolution rates obtained in earlier long-term dissolution experiments (Domènech et al., 2002; Cama et al., 2005) are up to three orders of magnitude slower than the initial rates.

Even though earlier studies have provided with a very valuable background on galena dissolution kinetics in the initial stages of interaction with solutions, the rates and reactions taking place during galena long-term dissolution remain almost unknown. In fact, within the acidic pH range, the steady-state dissolution rate has only been obtained at pH 3, at 25 °C and in solutions in equilibrium with atmospheric oxygen (Domènech et al., 2002; Cama et al., 2005).

In an attempt to bridge a part of the existing gap between data from short-term dissolution studies and field conditions, this paper is aimed at gaining insight into the galena long-term dissolution behavior. The main innovative aspect of this study with regard to previous works dealing with galena dissolution is that dissolution kinetic data were obtained at steady state. Therefore, the results obtained will be useful for predicting galena dissolution kinetics during extended interaction with acidic solutions, as in environments undergoing ARD. With this goal, the influence of temperature, hydrogen ion and dissolved oxygen concentrations at steady-state dissolution were exhaustively studied. As a result, a rate law accounting for the effects of these environmental factors on galena long-term dissolution was obtained. Moreover, the possible reactions controlling the overall galena dissolution within the range of the studied conditions were discussed, based on the observation of the evolution of solutions and reacting surfaces.

2. Materials and methods

2.1. Sample characterization

The galena sample used in this study was original from El Molar (Catalonian Coastal Range, Spain). X-ray Diffraction (XRD) was performed on thoroughly crushed samples using a Bruker D5005 difractometer with Cu Kα radiation. Powdered samples were scanned from 0 to 60° 2θ with a continuous scan at a rate of 0.083° 2θ per minute. XRD spectra of raw galena showed no evidence of the presence of any other mineral phase. Microprobe analysis was carried out in multiple points of the sample using an accelerating voltage of 20 kV and a beam current of 15 nA. The microprobe results confirmed the high