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Stibnite (Sb_2S_3) oxidative dissolution kinetics from pH 1 to 11

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Abstract

The kinetics of oxidative dissolution of natural stibnite (Sb_2S_3) under environmentally relevant conditions is investigated. The effects of hydrogen ion activity (pH 1.08–10.63), dissolved oxygen saturation ($p(O_2)$ from 0 to 80% of atmospheric pressure), and temperature (25–48 °C) on the reaction rate were studied using a mixed flow reactor. Trivalent cations (Fe^{3+}, Al^{3+}, Ce^{3+}) in acidic solution, and divalent cations (Mg^{2+}, Ca^{2+}) in basic solution were found to accelerate the rates, with the effect being related to ionic radius. In both acid and basic domains, the stibnite dissolution rate was found to be proportional to fractional powers of hydrogen ion and dissolved oxygen activities. The rate dependence on dissolved oxygen could also be described in terms of Langmuir adsorption, with saturation predicted to occur at oxygen partial pressures in excess of 3.5 atm in acid solution and 15.5 atm in basic solution. The empirical rate equations are given by:

$$r = k' \mathrm{a}(\mathrm{H}^+)^{\alpha}\theta = k' \mathrm{a}(\mathrm{H}^+)^{\alpha}\frac{K\mathrm{a}(\mathrm{O}_2)}{1+K\mathrm{a}(\mathrm{O}_2)}$$

where $k' = 1.25 \times 10^{-10} \pm 0.02 \times 10^{-10}$; $\alpha = 0.133 \pm 0.005$; $K = 2.22 \times 10^4 \pm 0.16 \times 10^4$ mol^{-1} l in acid solution (pH 3.0) and $k' = 8.88 \times 10^{-12} \pm 0.62 \times 10^{-12}$; $\alpha = -0.133 \pm 0.008$; $K = 5.01 \times 10^3 \pm 1.24 \times 10^3$ mol^{-1} l in basic solution (pH 9.8), both at 25 °C. Activation energies are 7.4 ± 0.5 kJ mol^{-1} (pH 3.0, between 25 °C and 40 °C) and 56.1 ± 5.0 kJ mol^{-1} (pH 9.9, between 25 °C and 48 °C), suggesting diffusion control in acidic solution and surface control in basic solution. Ferric iron in acidic solution strongly catalyzes the dissolution, with an acceleration of the rate by approximately an order of magnitude for $\mathrm{a}(Fe^{3+}) = 4.03 \times 10^{-4}$ M at pH 2.0. Aluminum ion, which has an ionic radius (54 pm) almost identical to that of ferric iron (55 pm), produces a similar rate enhancement. The effect of cationic radius on the dissolution rate of stibnite in the acid domain was evaluated using Ce^{3+} (114 pm), which increased the rate even more. In basic solution, Mg^{2+} and Ca^{2+} increased the dissolution rate; the effect was stronger with the larger of the two cations (Ca^{2+}). Stibnite dissolution was incongruent to varying degrees, with elemental sulfur forming a residual surface layer, in both acid and basic solution. In the presence of high concentrations of ferric iron, the dissolution became highly incongruent, with a substantial accumulation (7–13 atomic layers) of elemental sulfur. In contrast to Fe^{3+}, neither Ce^{3+} nor Al^{3+} had an effect on the formation of elemental sulfur, clearly demonstrating the important role played by Fe^{3+} in the oxidation of sulfide to elemental sulfur. In the case of iron catalyzed dissolution, the elemental sulfur formed at the reacting surface accounts for a very significant proportion of the stoichiometric total reactive sulfur, so that reaction rates may not be assessed by measuring the concentration of dissolved sulfur species.

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