Comparison between chalcopyrite and sphalerite dissolution kinetics under ARD conditions

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Chalcopyrite ($CuFeS_2$) has a very similar structure to sphalerite (ZnS). Both are soluble in aqueous media and their dissolution is the main source responsible for the release of copper and zinc, respectively, to groundwaters and surface run-off in environments undergoing Acid Rock Drainage (ARD).

Steady-state dissolution rates under far-from-equilibrium conditions were obtained by means of long-term stirred flow-through experiments. Examination of the effect of environmental variables (such as pH, temperature, dissolved oxygen availability and sulfate content) on the dissolution of both sulfides was assessed.

Under highly acidic conditions ($1< \text{pH} <3$) the chalcopyrite dissolution rates are slightly dependent of pH, increasing when pH decreases, whereas sphalerite dissolution rates are significantly dependent on pH. Dissolution rates of sphalerite and chalcopyrite are DO independent. This is relevant because both sulphides can dissolve within the entire column of groundwater although oxygen is not present. The main dissolution reaction for both phases is non-oxidative but proton promoted, leading to the release of sulphur as H_2S(aq) and not as sulfate or other intermediate oxygenated species.

Dissolution does not yield stoichiometric metal/sulphur ratios in solution compared with the bulk mineral stoichiometry. Solutions are generally enriched in the metal or metalloid in relation to sulphur due to partial volatilization of the released sulphur as H_2S(g) and to the formation of a sulphur-rich surface layer onto the reacting mineral. In the light of the activation energy values obtained, the presence of this surface layer seems to be rate-limiting in the case of sphalerite, but not in the case of chalcopyrite.