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Marcasite oxidation in low-temperature acidic (pH 3.0) solutions: Mechanism and rate laws

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Abstract

Marcasite surfaces were analyzed using X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES). XPS data of a pristine marcasite surface are used as a template to examine the characteristics of a marcasite surface after exposure to vigorous cleaning procedures and after reaction in oxygenated and mildly acidic (pH 3.0) solution.

Minor changes are observed to the Fe($2p_{3/2}$) spectrum after cleaning the surface with concentrated HCl. A new species is observed at approximately 709 eV, representing 10–15% of the total Fe spectrum. Chloride was detected by XPS broadscans and OH^- was observed in the O(1s) spectrum. The new Fe species at 709 eV may be associated with either OH^- or Cl^-.

XPS sulfur spectrum of the surface exposed to oxygenated, HCl solution (pH = 3.0) indicates that polysulfide increases at the expense of disulfide. The Fe species observed at 709 eV is also present and represents 10–15% total Fe. XPS broadscan analyses indicate trace amounts of chloride. Oxide O^{2-} is absent from the O(1s) spectrum but OH^- is present. AES depth profiles reveal no compositionally distinct zones after reaction.

Leach rates for the aqueous oxidation of marcasite were determined at 25 °C in O-saturated chloride solution at pH 3.0. Two rate experiments were performed on crushed and sieved size fractions of marcasite: one sample was vigorously cleaned to investigate fundamental aspects of marcasite leaching and the other was untreated to simulate conditions found in natural environments. The oxidative leach rate of Fe(aq) from pristine marcasite is 4.25×10^{-5} mmol/(m^2·s). Analyses of aqueous S speciation reveal fluctuations in S content of oxidation state lower than SO_4^{2-}. The XPS results suggest that the fluctuation may result from periodic release of polysulfide to solution, after accumulation on the reactive marcasite surface.