

Sulfate coordination shifts during the organic acid-induced dissolution of Tooeleite. A sulfur K-edge XAS study

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Sulfate plays a crucial environmental role in acid mine drainage (AMD) areas, where it facilitates formation of arsenic iron hydroxy-sulfate phases, such as Tooeleite (Zhu et al., 2014). In post-AMD systems, the presence of organic matter, microbial activity, and plant root exudates can alter the speciation of both iron and arsenic through various reaction pathways and molecular structural changes (Chen et al., 2023; Mikutta et al., 2010). However, the structural stability of sulfate in iron oxyhydroxide sulfate minerals in post-AMD environments remains poorly resolved. This study explores the transformation processes of sulfate ions (SO_4^{2-}) originating from the organic acid dissolution of tooeleite using sulfur K-edge X-ray absorption spectroscopy. Citric acid was used at C: Fe ratios of 0, 2 or 10 with the solution pH maintained at 3, 6 or 8. The initial and reacted minerals were characterized using XRD, FTIR, TEM, XPS, and Raman spectroscopy. After 80 days of reaction, there was a substantial transformation of tooeleite into ferrihydrite mineral phases, with As(III) being oxidized to arsenate. Notably, sulfur K-edge X-ray absorption near edge spectroscopy (XANES) analysis demonstrated the formation of SO_4^{2-} -bound with ferrihydrite, which was greatly influenced by pH. XANES analysis distinguished between co-precipitated ferrihydrite and adsorbed ferrihydrite based on white line position and intensity. The linear combination fitting results indicated that up to 85% of sulfate was present as co-precipitated ferrihydrite at pH 6, further confirmed by bright field TEM images and selected area electron diffraction pattern. While citric acid influenced the release of As, Fe, and S in solution, high citrate-high pH reaction systems appeared to inhibit the formation of ferrihydrite. These findings illuminate the geochemical interactions of a structural sulfate complex within AMD-affected environments and, thus, our understanding of sulfate chemistry for the remediation of arsenic-contaminated sites.

Chen, C., Dong, Y., Thompson, A., 2023. Environmental Science & Technology 57(29), pp.10696-10707.

Mikutta, C., Frommer, J., Voegelin, A., Kaegi, R., Kretzschmar, R., 2010. Geochimica et Cosmochimica Acta 74(19), 5574-5592.