

Spectroscopic study on the local structure of sulfate (SO_4^{2-}) incorporated in scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) lattice: Implications for understanding the Fe(III)-As(V)- SO_4^{2-} -bearing minerals formation

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ABSTRACT

The incorporation of sulfate (SO_4^{2-}) into the scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) lattice is an important mechanism during arsenic (As) fixation in natural and engineered settings. However, spectroscopic evidence of SO_4^{2-} speciation and local structure in scorodite lattice is still lacking. In this study, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), sulfur *K*-edge X-ray absorption near edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) spectroscopic analyses in combination with density functional theory (DFT) calculations were used to determine the local coordination environment of SO_4^{2-} in the naturally and hydrothermally synthesized scorodite. The SO_4^{2-} retention in natural scorodite and the effect of pH value and initial Na^+ concentration on the incorporation of SO_4^{2-} in synthetic scorodite were investigated. The results showed that trace amounts of SO_4^{2-} were incorporated in natural scorodite samples. Scanning electron microscopy (SEM) results revealed that SO_4^{2-} was homogeneously distributed inside the natural and synthetic scorodite particles, and its content in the synthetic scorodite increased slightly with the initial Na^+ concentration at pH of 1.2 and 1.8. The FTIR features and XANES results indicated that the coordination number (CN) of FeO_6 octahedra around SO_4^{2-} in scorodite lattice is four. The DFT calculation optimized interatomic distances of S-O were 1.45, 1.46, 1.48, and 1.48 Å with an average of ~ 1.47 Å, and the interatomic distances of S-Fe were 3.29, 3.29, 3.33, and 3.41 Å with an average of ~ 3.33 Å. EXAFS analysis gave an average S-O bond length of 1.47(1) and S-Fe bond length of 3.33(1) Å with a $\text{CN}_{\text{S-Fe}} = 4$ for SO_4^{2-} in the scorodite structure, in good agreement with the DFT optimized structure. The results conclusively showed that SO_4^{2-} in the scorodite lattice may be in the form of a $\text{Fe}_2(\text{SO}_4)_3$ -like local structure. The present study is significant for understanding the formation mechanism of scorodite in natural environments and hydrometallurgical unit operations for waste sulfuric acid treatment.

Keywords: Arsenic, scorodite, sulfate, incorporation, local environment