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Oxidation of Se-bearing iron sulfides and its effect on selenium retention

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The long-lived fission product Se-79 is a significant contributor to radioactivity in geological repositories long after their closure. Se migration can be mitigated via sequestration by iron sulfides like mackinawite, which forms primarily under anoxic conditions. Although metastable, mackinawite can persist as long as anoxic conditions are maintained, serving as a stable, long-term host for contaminants like Se. However, post-closure fluctuations in groundwater conditions, or changes in the geological environment could alter the redox conditions surrounding the repositories. The possible oxidation of mackinawite could potentially remobilize previously immobilized Se in its structure. To date, Se retention during the mackinawite oxidation has not been studied. In this work, we investigated the behavior of Se initially associated with mackinawite, as mackinawite is oxidized at circumneutral conditions.

Powdered Se-bearing mackinawite was dispersed in a MOPS-buffered solution at pH 7 inside a glove box. The suspensions were then taken out of the glove box and stirred in the dark at room temperature. Aliquots were extracted and vacuum-filtered to separate solid and liquid fractions. Se concentrations in solution were measured, and solids were analyzed for phase composition by XRD. Se speciation in the solids was examined by Se *K*-edge XANES and EXAFS.

The Se-mackinawite suspension, which was initially black, gradually turned brown as the reaction proceeded. XRD analyses showed that mackinawite was gradually oxidized to lepidocrocite and elemental sulfur. Se *K*-edge XANES showed that the Se in mackinawite, which was initially in the –II state, was oxidized to Se(0). EXAFS fitting analysis showed the presence of a small number of S atoms in the first coordination shell in addition to Se atoms. These observations indicate that Se was released during mackinawite oxidation then re-sequestered as a S-doped elemental selenium-like compound. The formation of a discrete solid phase suggests that environmental changes (e.g. oxidation) are likely to have a limited impact on Se mobility.

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