

Selenite interactions with iron sulfides

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The sorption and redox behavior of selenium is of interest for nuclear waste disposal initiatives. Mackinawite (FeS), a redox-active ferrous mineral, is a phase that can form at interfaces of reinforced cement with pore water, potentially playing a role retarding the transport of oxyanionic radionuclides such as selenite and selenate in cement porous media. However, the reduction mechanisms of selenium by mackinawite in the extreme conditions (high pH) of cement pore water remain unclear. In this work we combine ion chromatography and ICP to measure the concentration of selenite (SeO_3^{2-}) and sulfur species (S^{2-} , SO_3^{2-} and SO_4^{2-}) with Fe and Se K-edge X-ray absorption spectroscopy to identify the reduced species of selenium and mineral composition of Fe. The results showed that after 192h reaction, $\sim 95\%$ of SeO_3^{2-} was reduced to a SeS_2 -like solid product, and $\sim 94\%$ selenium was released to the solution due to the dissolution of FeS and SeS_2 at high pH. The fate of selenium and the solids formed underwent four reaction steps: (1) SeO_3^{2-} was reduced to Se^0 , FeSe and FeSe₂ by the oxidation of sulfite to S^0 within 1h; (2) Zero-valent selenium particles also reacted forming SeS_2 during the reduction of SeO_3^{2-} to Se^0 by sulfite from 1h to 24h. (3) Fe(II) and S(-II) cooperate to reduce SeO_3^{2-} to Se^0 and meanwhile to be oxidised to SO_3^{2-} , S^0 and Fe_2O_3 respectively between 24h and 96h. Meanwhile, mackinawite was transformed to magnetite during the reduction and SeS_2 precipitation started to release to the solution. (4) $\sim 62\%$ magnetite was produced due to phase transformation and $\sim 94\%$ of selenium reduced species as SeS_2 were released to the solution after 192 hours reaction. These results provide valuable information about the reduction mechanisms of selenium in actual field conditions.

