Selenium reduction by zero valent iron with real time XANES measurements and accompanying Se stable isotope data

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A flow-through-cell experiment was designed to examine the reduction of Se(VI) by zero-valent iron (ZVI) in real time. X-ray absorption data from the solid phase and samples for Se isotope ratio measurements were simultaneuosly collected during the experiment. ZVI is commonly used in permeable reactive barriers to treat contaminants such as Se.

The experiment was conducted at the APS in order to obtain *in situ* XANES measurements during treatment of Se, using a flow cell with a transparent Kapton® window. The experimental design built on that used for the treatment of Cr and Zn [1,2]. Three different locations were monitored in the cell to determine where and how the Se was accumulating. The influent Se concentration was increased over time to alter the proportion of Se removed from solution in order to investigate changes in Se isotope composition. At the conclusion of the experiment, a Se-free simulated groundwater solution was pumped through the cell to assess the stability of the reaction products.

XANES analysis revealed that reduced Se accumulated on the ZVI over time. A large peak representing Se(VI), which increased as the concentration of Se in solution increased, disappeared when Se was removed from the input, leaving primarily Se(IV) and Fe selenides on the solid phase.

The $\delta^{82/76}$Se values of the effluent fit a straight line, with an isotopic discrimination of 9.6 ‰. In contrast, the isotope data from the effluent samples collected during the Se-free stage fit a Rayleigh curve with an effective fractionation of 2.4 ‰; these samples represent transport of mobile Se remaining in the system. The value for effective fractionation is between the value of < 1.0 ‰, caused by adsorption onto Fe oxide minerals [3], and of 4.3 ‰, the effective fractionation due to reduction by ZVI in a $CaCO_3$ saturated system [4]. The combination of isotopic and XANES techniques applied in this experiment can be used to elucidate the effect of transport on Se isotope behavior.

[1] Jamieson-Hanes *et al.* (2014) *GCA* **142**, 299-313. [2] Jamieson-Hanes *et al.* (2017) *GCA* **203**, 1-14. [3] Mitchell *et al.* (2013) *Chem. Geol.* **342**, 21-28. [4] Shrimpton *et al.* (2015) *ES&T* **49**, 11688-11696.