

## Magnetite-catalyzed selenium reduction

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Magnetite nanoparticles are widespread mixed-valence iron oxides of industrial and environmental relevance. Among other occurrences, they form during canister steel corrosion in the context of nuclear waste disposal initiatives. Their reactivity towards radionuclides -such as <sup>79</sup>Se- is therefore an important area of research. Here we present a study of the redox reactivity of magnetite nanoparticles towards Se(VI) oxyanions -selenate, evaluating the ability of electrons to be transferred through non-conducting interfacial silica layers. Moreover, the competition for adsorption sites between selenate, silicate and rhenate is also evaluated. Results from potentiometric titration, adsorption isotherms, FTIR spectroscopy and X-ray absorption spectroscopy show that electron transfer is still occurring through thin silica layers, with transfer rates greatly decreased. The reduction of Se(VI) to Se(IV) occurs with initial fast electron exchange at the surface of magnetite which brings first reduction of Se(VI) to Se(IV), and then instantaneous conversion to Se(0) – the most stable insoluble form. A competition between silicate and the sorbed Se(VI) and Se(IV) is described. We conclude that neither partial oxidation nor silica surface coatings block the sorption and redox-catalytic properties of magnetite nanoparticles, a result with important implications to assess the reactivity of mixed-valence phases in environmental settings.