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Sorption and reduction of uranium at the surface of anoxically produced steel corrosion products

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In the high level nuclear waste repository concept, spent nuclear fuel is designed to be encapsulated in iron steel canisters. Besides constituting a physical barrier for an eventual groundwater intrusion to the repository, the steel canister can, due to its chemical behaviour, provide an effective chemical trap for the release of several of the radionuclides present in the fuel. Under the conditions expected to prevail in an underground repository, the corrosion of steel, if any, is going to be produced anoxically. Under anoxic conditions Fe corrodes in a first step, to produce $\text{Fe}(\text{OH})_{2(s)}$ which, in turn, can experiment the Schikorr reaction to transform into magnetite, $\text{Fe}_3\text{O}_{4(s)}$.

The semiconductor characteristics of magnetite points out its potential redox capacity in the system and leads us to consider its role as mediator in the reduction of actinides which results in an immobilisation of these elements via precipitation of the more insoluble Actinide(IV) solid phases.

We have studied experimentally the role of the anoxic corrosion products of steel on the retention of uranium. Experiments included the analyses of the sorption properties of magnetite as well as the eventual reduction that hexavalent uranium may suffer after interacting with the surface of the solid. The experiments have been conducted with commercial magnetite as well as with an steel coupon that had been anoxically corroded under 7 atm of hydrogen overpressure.

The effect of the hydrogen overpressure on the system has been tested and we have observed an important effect of this parameter on the extent of reduction of the aqueous uranium concentration. On the other hand, the comparison between the results obtained by using commercial magnetite and those obtained when working with the anoxically corroded steel coupon highlight the role of metallic iron under the surface of magnetite in accelerating the reduction process.

Solution and surface analyses indicate that the surface of magnetite is able not only to retain uranium via sorption, but also to reduce hexavalent to tetravalent uranium providing, thus, an effective retardation to the migration of this actinide out of the repository system.

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Uranium and other trace element incorporation into tufa calcite

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An integrated petrographic (phosphor imaging, fission-track mapping, cathodoluminescence) and spectroscopic (X-ray diffraction, synchrotron X-ray absorption spectroscopy, X-ray fluorescence) study of tufas from the middle Miocene Barstow Formation, California relates sample morphology, mineralogy, and geochemical composition. The tufas, composed mainly of calcite that formed at the interface between an ancient alkaline lake and ground- or springwaters, have textures similar to those of microbially mediated terrestrial stromatolites and travertines. The tufas have highly variable concentrations of a number of trace elements including Mn, Fe, Sr, and U on a very fine scale. Synchrotron X-ray fluorescence (XRF) analyses show U concentrations can exceed 500 ppm. X-ray absorption near edge spectroscopy (XANES) indicates that U in these samples is incorporated as U(IV).

The highly variable trace element incorporation in tufa calcite and negative correlation between such elements as U and Sr suggests mixing of fluids and/or conditions. One of the fluids was the lake water which was most likely alkaline, analogous to modern alkaline lakes in the Great Basin that have elevated U/Ca. Because Ca is limited in these lakes, tufa calcite forms where groundwater or (in the case of the Barstow Fm tufas, possibly epithermal) springs bring in Ca and trace elements such as Sr, accounting for the negative correlation observed between U and Sr concentrations in the tufa deposits. Rapid, and possibly microbially mediated, precipitation of calcite allows for incorporation of high concentrations of trace metals. More work is needed to understand how these elements are complexed in the fluids from which they precipitated and to understand if the U and other trace metals were incorporated into the calcite structure, as micron to sub-micron scale inclusions, or sorbed to the surface of organic matter or an inorganic phase. Concordant U-Pb dating of these samples shows that Barstow Fm tufas sequestered U for millions of years.