

Experimental and Modeling Study of the Interaction between Uranium(VI) and Magnetite

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Magnetite has been identified as a corrosion product of the carbon steel canister intended to be used in the final deep repository of high level nuclear waste (HLNW). The results of uranium/magnetite interaction found in the literature are scarce. (Grambow, 1996) studied the sorption and subsequent reduction of U(VI) onto canister corrosion products (iron(II) hydroxide and magnetite) and observed that the reduction of U(VI) to U(IV) was lower than expected. (El Aamrani, 1998) have shown a decrease of the U(VI) aqueous concentration in the presence of magnetite but the authors did not identify the process responsible of this decrease. Finally, (Sagert, 1989) observed that the sorption of U(VI) onto magnetite in carbonate medium is similar to the one obtained in the presence of hematite. In this work, we have studied the sorption of the U(VI) onto the surface of commercial magnetite and also the potential heterogeneous reduction of U(VI) to U(IV) on the magnetite surface by using X-Ray Photoelectron Spectroscopy (XPS).

Experimental Part

20cm³ of 0.1M (Na)ClO₄ + (Na)HCO₃ ionic medium at pH=8.0 were put in contact, at 25°C, in stoppered glass tubes, with weighed amounts of magnetite of particle size (dp) < 5µ. The tubes were continuously shaken in a rotary mixer. After the contacting period, samples of the supernatant solution were withdrawn, filtered through a 0.22µ pore size SARTORIUS filter and analysed for their uranium content by means of an SCINTREX UA-3 laser fluorimeter.

Sorption Results and Analysis of the Data

The values of the distribution coefficient obtained decreased with the carbonate concentration, as expected from the formation of very stable uranium-carbonate complexes, which prevent the sorption onto the surface of the solid. The sorption extent increases when increasing the surface area to volume ratio, and these results indicate that no saturation of the surface of the solid is achieved in the experiments. The results have been treated by

applying a non-electrostatic surface co-ordination model and the best agreement between measurements and model have been obtained by assuming the formation of the following surface complexes with their associated stability constants: $>FeOH + UO_2^{2+} = >FeO-UO_2^+ + H^+$; $K_a = 139 \pm 0.45$ $>FeOH + UO_2^{2+} + 2H_2O = >FeO-UO_2(OH)_2^- + 3H^+$; $K_b = (2.76 \pm 0.32) 10^{-15}$

XPS RESULTS Magnetite was examined by XPS before and after uranium(VI) attachment. Spectra were recorded on a PHI Perkin Elmer ESCA Multianalyser 5500 using an Al-K α X-ray source (1486.6eV). The error in the determination of the electron energies was ± 0.2 eV.

The XPS results obtained from pure commercial magnetite rendered a Fe(II)/Fe(III) ratio of 0.49, which was kept constant when the solid was contacted with a carbonate solution under atmospheric conditions. However, when the solution was contacted with air without carbonate, the Fe(III) produced by the oxidation of Fe(II) was not released to the solution, and the ratio Fe(II)/Fe(III) was observed to decrease to values around 0.35.

When adding uranium to an anoxic carbonate solution in contact with magnetite, the ratio Fe(II)/Fe(III) decreased to values around 0.45 after 120 days of contact. During the same period of time we observed a shift in the U 4f peak from 382.0meV to 381.7meV, what may be attributed to a reduction of uranium due to the oxidation of Fe(II) from magnetite.

Grambow B, Smailos E, Geckeis H, Müller R & Hentschel H, *Radiochim. Acta*, **74**, 149-154, (1996).

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