

## Uptake of U(VI) by hydrated and degraded cement

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The use of cement in engineered barrier systems of radioactive waste repositories emphasize the proper understanding of uranium interaction with hardened cement paste. This study presents experimental and modelling results on uptake of U(VI) in batch experiments by hydrated and degraded cement in contact with MilliQ and aged cement pore water respectively.

Kinetic experiments show that equilibrium between cement and U(VI) is reached in less than two days. Equilibrium uranium concentration denotes a high uranium uptake by cement phases (up to 99% in some cases).  $R_d$  values for hydrated cement (with S/L ranging between 0.05 and 10 g/L) vary between 7 and 65 m<sup>3</sup>/kg (for initial uranium concentrations of 1·10<sup>-6</sup>M) and between 5 and 30 m<sup>3</sup>/kg (for initial uranium concentrations 1·10<sup>-8</sup>M). Regarding degraded cement,  $R_d$  values (with S/L ranging between 0.1 and 20 g/L) are in the range 10-25 m<sup>3</sup>/kg for [U]<sub>0</sub>= 1·10<sup>-6</sup>M. At [U]<sub>0</sub>=1·10<sup>-8</sup>M, the aqueous concentration of U(VI) at the equilibrium falls below the detection limit of the used analytical technique.

A surface complexation model has been used to explain the experimental results on uranium interaction with hardened cement paste. This model takes into account both, aqueous U(VI) speciation and speciation of silanol sites in the typical C-S-H phases of cement. The possible precipitation of solid uranium phases has been also assessed in this work.

## Hydrogen solubility in synthetic rutile

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Hydroxyl solubility in rutile was determined as a function of pressure, temperature, and  $fO_2$  (buffered with nickel-nickel oxide NNO, or magnetite-hematite, MH). Pure, synthetic rutile and H<sub>2</sub>O were sealed in a Pt or Pd/Ag inner capsule and placed within a Au outer capsule containing an  $fO_2$ -buffering assemblage. Experiments employed a piston-cylinder apparatus and NaCl-graphite furnaces. OH concentrations were determined using FTIR spectroscopy and the calibration of Maldener *et al.* 2001. The [OH] in rutile increases from 108 to 956 ppm H<sub>2</sub>O at 1 GPa over the range 500-900°C at the NNO buffer; a fit to the data produces the relationship [OH] (ppm H<sub>2</sub>O wt.) = 4.73 e<sup>0.006T</sup>, R<sup>2</sup>= 0.96. The higher  $fO_2$  of the MH-buffered experiments produced a similar T dependence, but lower overall [OH]; at 1 GPa, [OH] increases from 84 to 267 ppm H<sub>2</sub>O from 600-900°C ([OH] (ppm H<sub>2</sub>O wt.) = 7.28e<sup>0.0039T</sup>, R<sup>2</sup>= 0.97). The effect of pressure on the [OH] in rutile is less pronounced than the temperature effect. At the MH buffer and 800°C, [OH] (ppm H<sub>2</sub>O wt.) = 79±13 x P(GPa) + 88±15 from 0.5-2 GPa. For the experiments conducted at NNO and 800°C, [OH] (ppm H<sub>2</sub>O wt.) = 169±31 x P(GPa) + 409±33 from 0.5 to 2 GPa. Over the 25 seconds it takes to quench the experiments, loss of OH from rutile along the *c* crystallographic axis is significant — a 33% decrease in [OH] over a distance of 0.35 mm for an unbuffered experiment at 1000°C and 1 GPa was observed. Measurements of OH concentration should be obtained in the center of rutile grains at least 0.5 mm in diameter along the *c*-axis to obtain equilibrium values.

### References

Maldener, J., Rauch, F., Gavranic, M., and Beran, A. (2001), *Min. Pet.* **71** 21-29.