

Combined wet chemistry and EXAFS studies on the radionuclide immobilisation by cement and calcium silicate hydrates

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Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of low- and intermediate level radioactive wastes. Cement is used to condition the waste materials and for the construction of the engineered barrier. Understanding the binding mechanisms in the cement matrix thus enable us to assess the long-term mobility and fate of radionuclides in cementitious repositories.

The potential of hardened cement paste (HCP) to immobilize radionuclides originates from specific interactions of metal cations and anionic species with cement minerals, e.g., calcium silicate hydrates (CSH), portlandite and calcium aluminates. CSH phases ($\text{CaOSiO}_2 \cdot z\text{H}_2\text{O}$) are the most abundant components of HCP (~40-670 wt %), have a large capacity for ion uptake and are thus a prime candidate for heavy metal binding. In this study we present results from combined macroscopic (wet chemistry) and spectroscopic (extended X-ray absorption fine structure (EXAFS) spectroscopy) studies on Sn(IV) and U(VI) uptake by HCP and CSH.

The similarities in their speciation under high pH conditions (pH 13.3) allows a detailed comparison between Sn(IV) and U(VI) immobilisation by HCP. Further, it was expected that sorption and solubility processes control the uptake of both elements by HCP, depending on their inventories in the system. Macroscopic studies were undertaken to measure uptake kinetics and sorption isotherms on HCP and CSH. Uptake of Sn(IV) was found to be stronger than U(VI) binding on both solids. On HCP it was observed that sorption is linear up to a maximum equilibrium concentration of about $8 \cdot 10^{-7}$ M in the case of Sn(IV) and about $6 \cdot 10^{-6}$ M in the case of U(VI). Above these concentrations, the immobilisation of both elements is due to the formation of precipitates; that is Ca-stannate in the case of Sn(IV) and Ca-uranate in the case of U(VI).

EXAFS spectroscopy was used to determine structural parameters of the precipitates and the species sorbed on HCP and CSH. This micro-scale information enabled us to assess the role of CSH as the potentially uptake-controlling mineral phase for Sn(IV) and U(VI) in HCP and to propose structural models of the binding mechanisms in the cement matrix.

Performance characteristics of a new multi-ion-counting system for a TIMS multicollector: Nd and U

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In the past, instrumental improvements were the key to improving the precision of isotope ratio measurements. In particular, this is true for magnetic sector TIMS instruments with the change from single collectors to multicollector arrays. Today, multicollector instruments using arrays of Faraday detectors are the instruments of choice for high precision isotope ratio measurements. However, with decreasing sample sizes, the noise level of the Faraday detectors becomes the limiting factor for high precision isotope ratio measurements. Today's multicollector instruments are equipped with a single ion counting channel and thus very small samples have to be measured in this single collector by peak jumping procedures. Because this is a sequential method, it is both a time consuming and a sample consuming procedure. It would seem to be obvious that a multi-ion-counting approach would give benefits in sample utilization, speed and precision. However, space constraints of a multicollector array are stringent; the width of the standard Faraday detectors is typically ≤ 3 mm, severely limiting the implementation of conventional discrete dynode SEMs in a true multicollector array. In order to overcome this limitation, we have developed special miniaturized SEMs identical in size to and interchangeable with Faraday cups. Up to eight ion counting channels can be installed simultaneously.

The linearity and the stability of the ion counters have to be excellent to meet the demanding requirements for high precision isotope ratio measurements. In particular the ion counters in the array need to be properly cross-calibrated against each other.

We will report on performance characteristics of these new detectors for the measurement of ultra-small neodymium and uranium samples on the ThermoFinnigan Triton. Different strategies for taking full advantage of the characteristics of the new detection system will be discussed.