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Characterization of U(VI)-phases in corroded cement products by micro(μ)-spectroscopic methods

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Abstract. Cementation is an industrial scale conditioning method applied to fix and solidify liquid low and intermediate level radioactive wastes (LLW/ILW) prior to underground disposal in geological formations.To assist prognosis of the long-term safety of cemented waste, alteration of uranium doped cement productswas studied in chloride-rich solutions relevant for final LLW/ILW disposal in rock salt. After long-time exposure of the full-scale LLW/ILW simulates to concentrated NaCl and $MgCl_2$ brines, solid samples were retrieved for chemical and mineralogical analysis with an emphasis on uranium speciation in the corroded cement matrix.Bulk and recent spatially resolved micro(μ) U L3-XAFS measurements point to the occurrence of a diuranate type U(VI) phase forming throughout the corroded cement monoliths. U-enriched hot spots with dimensions up to several tens of μm turn out to be generally X-ray amorphous.

1. Introduction

Cementation of waste solutions containing low to intermediate level concentrations of radionuclidesis considered as an appropriate conditioning method to fix and solidify radioactive wastes with negligible heat production(low-level and intermediate-level waste, LLW and ILW, respectively) prior to disposal. Cementation of LLW/ILW isused in many countries on an industrial scale for treatment of waste streams stemming from basic research, engineering applications, medical treatment or reprocessing activities. Cemented LLW/ILW containing in total some 100 tons of uranium was disposed of in the AsseII[1] and ERAM salt mines in Northern Germany from 1967 to 1978. For safety assessment and evaluation of possible closure concepts, it is mandatory to understand the release and retention reactions of uranium and other radionuclides in case of water intrusion into the disposal caverns. Alteration of radionuclide bearing cement products in dilute aqueous solutions has been studied quite extensively. Yet, in chloride-rich solutions, which are relevant for final disposal of cemented LLW/ILW in rock salt, thermodynamic data and understanding of both the cement corrosion process and radionuclide leaching behaviour are still lacking.Hardened cement paste or concrete consists of a multitude of phases whichcomplicate the investigation of radionuclide leaching andretention mechanisms. As laboratory batch experiments conducted with hardened cement paste

alone may not provide sufficient insight into the complexity of long-term cement chemistry, full-scale leaching and corrosionexperimentswith simulated waste products were performed with U(VI) doped cement monolithsin the Asse II mine. Cement blocks produced by an industrial process simulating relevant LLW/ILW compositions were exposed to NaCl and $MgCl_2$ brines for more than two decades.Solid samples for mineralogical laboratory analysis and synchrotron radiation (SR) based speciation techniques wereobtained after recovery of corroded monoliths from the mine.

Initial bulk powder U L3-XANES, laser spectroscopy and XRD measurements were interpreted as indicating the presence of a Ca-U(VI)-silicate phase, e.g., uranophane, in the corroded waste products [2]. U L3-XANES white line (WL) and multiple scattering (MS, cf. spectra in figure 1) features of the corroded cement samples appeared significantly broadened compared to corresponding features in crystalline reference compound spectra. Coexistence of different U(VI) coordination environments associated with high structural disorder or highly distorted U(VI) coordination environments in the corroded cement were assumed to explain the difference between the corroded cement sample and reference XANES. However, recent μ-Raman spectroscopy data indicate that U-rich aggregates found in the corroded cement matrix with dimensions up to several tens of μm are more likely diuranate phases [3]. The present investigation extends initial SR based investigations to spatially resolved techniques - including μ-XAFS (μ-XANES/μ-EXAFS), μ-XRFand μ-XRD-to better characterize U-rich volumes of the generally heterogeneoussalt brine corroded cement matrices.
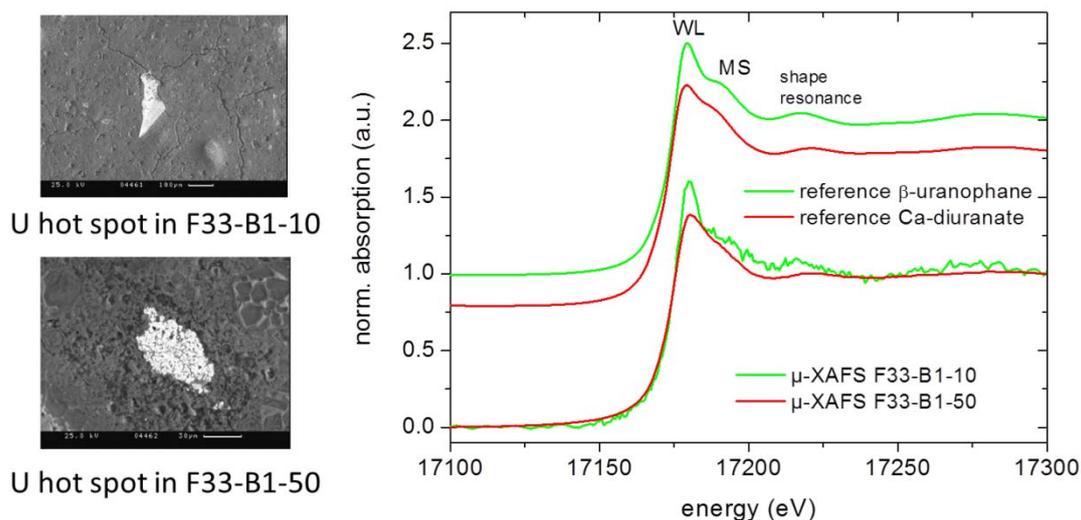

Figure 1. left – SEM images of U-rich hot spots in samples F33-B1-10 ($MgCl_2$ system, top) and F33-B1-50 (bottom, cf. text for nomenclature); right – U L3 μ-XANES spectra recorded at these spots compared to bulk XANES of crystalline U(VI) references Ca-diuranate and β-uranophane(spectra vertically shifted for clarity).

2. Experimental

2.1. Full-scale corrosion experiments

Cemented full-scale LLW/ILW simulateswere fabricated in the 1980sbased onliquid waste compositions simulating thoseresulting from spent nuclear fuel reprocessing in the PUREX process.For monoliths doped with natural uranium, aqueous solutions containing 1.02 kg of U(VI) in the form of $(NH_4)_2U_2O_7$ were added to Ordinary Portland Cement, the water/cement ratios adjusted to 0.5 and the mixtures filled in 200 l steel drums.Details on monolith production and compositioncan be found elsewhere([2] and references therein). After complete hydration, these monoliths (total mass 336 kg) were removed from the drums, immersed in 400 l steel canisters filled with saturated NaCl or $MgCl_2$ brines and stored in the Asse II salt mine at the 490 m level. Two uranium doped monoliths-'F31' corroded in NaCl and 'F33' corroded in $MgCl_2$- were recovered from the leaching vessels after

18 and 17 years, respectively.Several vertical bore holes were cored from the top parallel to the central monolith cylinder axis to probe the degree of corrosive cement degradation and U speciationat varying positions along the cylinder length and surface distances. Samples are identifiedaccordinglyusing the nomenclature 'brine-distance-vertical position', e.g., F33-B1-10 denotes a sample extracted from bore core B1(cored at 21 cm distance from the cylinder surface) in the upper 0-10 cm of the monolith corroded in $MgCl_2$ (cf. details in [2]).

2.2 SR based analysis methods
Thin sectionscut from bore cores F31-B1-10, F31-B1-50, F33-B1-10 and F33-B1-50 mounted on glass slides are used for SR-based characterization.Regions of interest are preselected fromScanning Electron Microscopy (SEM) backscattering images, showing high contrast for U rich aggregates (hot spots) embedded in the corroded cement matrix (figure 1 - left), and identified with a visible light microscope (VLM) at the SR experimental stations.Two beamlines are used for spatially resolved measurements - HASYLAB BL-L at DESY (Hamburg, Germany) and the INE-BL at ANKA located at the KIT North Campus (Karlsruhe, Germany) [4]. At HASYLAB, a small wavelength bandpass from a multilayer monochromator (max. output tuned to 0.70246 Å/17.650 keV) is focused into a spot of <20 µm on the sample surface by a single bounce capillary mounted on a hexapod positioning unit.Sample slidesaremounted on a three-axis positioning stage with the thin section samplesurface at a45° angle to theincident beam. The y and z stage axes (the x-axis determines the focus) are used to scan selected areas and precisely position the samples in the beam path. A silicon drift detector (SDD, SIINT Vortex-90EX)is used for collecting X-ray fluorescence radiation.U hot spots identified in element distribution maps reconstructed from the scanning µ-XRF data are selected for µ-XRD analysis. Diffraction patterns are collected in Laue transmission mode by a CCD camera (MAR CCD, MARUSA Co.) mounted perpendicular to the beam ~15.5 cmdownstream from the sample. XRD geometry parameters are calibrated against a LaB_6 reference sample. At ANKA, a similar setup and single bounce capillary is used for µ-XRD measurements, but diffraction patterns are registered on erasable X-ray sensitive films (PerkinElmer). Apolycapillary optic is used to focus monochromatic radiation delivered by a double crystal monochromator (DCM) equipped with a pair of Ge<422> crystals and reflected on a toroidal focussingmirror to a beam spot-size of 25-30 µm at the sample surface for µ-XRF and µ-XAFS measurements. A SDD (Vortex-60EX) is used here, too. U L3 µ-XAFS spectra, recorded by registering windowed U Lαfluorescence intensity, are normalized to the total flux impinging on the sample measured by a pin-diode mounted behind the polycapillary. The DCM energy is calibrated relative to the first inflection point in the K-XANES of a Y foil defined as 17.038 keV.

3. Results and Discussion
3.1 U L3 µ-XAFS/µ-XRF
The uranium speciation in numerous U hot spots and in the surrounding corroded cement matrix of the four thin section samples are investigated. U-rich hot spots identified in µ-XRF element distribution maps generally exhibit U L3-XANES energy positions characteristic for U(VI) (WL peak position at ~17.180 keV), thus clearly confirming preservation of the hexavalent uranium state in the cement after long-time exposure to NaCl and $MgCl_2$ brines. This finding is also in accordance with previous U speciation results based on bulk XAFS spectra obtained for F31 and F33 monolith drill dust samples [2]. µ-XANES features obtained for most U hot spots and in more diffuse U distributions located nearby are nearly indistinguishable from each other and from previous bulk spectra. These spectra obviously represent a prevalent U(VI) species formedthroughout the corroded cement matrices. The XANES for the F33-B1-50 U hot spot is representative of this major species. The spectra exhibit features significantly different from those typical for U(VI)dioxo-moieties (e.g., theU(VI) mineralβ-uranophaneCa(UO_2)$_2$(SiO_3OH)$_2$•5(H_2O); cf. figure 1). Both µ-XANES WL features and the post-edge 'shape resonance' are moresimilar to a diuranate (CaU_2O_7/$Na_2U_2O_7$•xH_2O) type phase (figure 1 - right, red curves).The U coordination in diuranates is characterized by an elongated axial oxygen distance (1.92 Å vs. 1.79Å for uranophane) and a reduced average equatorial oxygen distance (2.31 Å vs.

2.36Å for uranophane). This coordination results in WLdampening and a decrease in the energy difference between the WL and axial oxygenMS feature observed for diuranates (cf., e.g., [5]). These effects are easily modelled by feff8.4 [6]U L3-XANES calculations. Correspondingly, in bulk U L3-EXAFS measurements of pure Ca/Na-diuranate reference samples the Fourier transformation (FT) magnitude peaks associated with axial and equatorial oxygen neighbours merge into a single broad first shell peak [2]. This same broad FT peak is observed in a μ-EXAFS spectrum recorded at a U hot spot insample F33-B1-50 (not shown). Nevertheless, at least one U-rich area in sample F33-B1-10 (corroded in MgCl₂ brine - thin section taken near the F33 monolith surface) is found, which exhibits distinct features similar to a uranophane-like U(VI) phase (figure 1 - right, green curves).Thermodynamic solubility calculations performed for the U-doped cement/salt brine systems suggest both diuranates and uranophane as possible solubility limiting phases in the cement/MgCl₂ system, while ruling out the formation of schoepite, another mineral with the dioxo moiety U corrdination structure.In contrast, measured U(VI) concentrations in the cement/NaClbrineare only in agreement with a diuranate solubility limiting phase [7]. No XANES spectra similar to the uranophane reference were found in the F31 samples investigated. Note, however, that the total sample volume studied in these spatially resolved experiments is necessarily small and, hence, any exclusion of the presence of such phases cannot be made with great certainty.

In addition to U-rich hot spots anduranium ubiquitously present in diffuse distributions across the thin section samples, a number of other elementsassociated with the cement and its additives are identified in μ-XRF distribution maps. As a general trend, Fe showsa clear anti-correlation with U enriched areas, whereas K, Sr and Rb distributions are correlatedto U in most of these hot spots. Other transition metals (Ti, Mn, Cu, Zn) show no or only weak U correlations (figure 2).
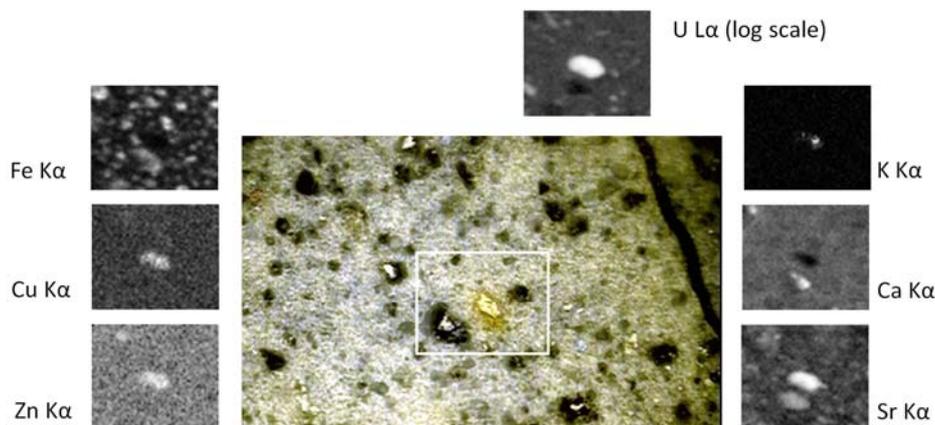

Figure 2. VLM image of area around U hot spot in F33-B1-50 (same hot spot as depicted in SEM image, figure 1 bottom left) and μ-XRF element distribution maps recorded for the marked area (scan area 600μm×500μm, 10μm×10μm steps, beam spot size ~25 μm).

3.2 μ-XRD
μ-XRD measurements of numerous U-rich hot spots,including those depicted on the left hand side of figure 1, performed at both SR sources show these to be generally X-ray amorphous;no evidence is obtained for the presence of any crystalline uranium phase. Weak diffraction patterns identified for some of these hot spots can be attributed to cement corrosion products.

4. Conclusions
It is well-established from multiple scattering XAFS theory that relatively small clusters of some tens of atoms surrounding a chosen absorber are generally sufficient to produce XANES spectral features. However, such nm-sized atomic clusters may be too small – and/or too distorted – to sufficiently

diffract impinging X-rays into detectable XRD patterns. This might explain the absence of any μ-XRD signal from uranium hot spots in the present study. The U-rich areas in the corroded cement matrix, which are clearly discernible in both SEM images and in μ-XRF maps, are X-ray amorphous and therefore not crystalline phases. More likely, they are mere smallatomic clusters or assemblies of small clusters (crystallites) forming under the chemical conditions of the long-time cement corrosion experiments.

Acknowledgement

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