



	Experiment title: Uranyl speciation in cement phases using XAS	Experiment number: ME-308
Beamline: BM20	Date of experiment: from: 24-01-2002 to: 31-01-2002	Date of report: 26-08-2002
Shifts: 18	Local contact(s): Christoph HENNIG	<i>Received at ESRF:</i>
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While the speciation of U(VI) in alkaline solution is relatively well known, the interaction of U(VI) with cement and cement phases remains poorly understood. Some authors have reported inner-sphere complexation between uranyl and hydrothermally altered concrete in the pH range 9-12. However the chemical phase responsible for this process has not been identified. Moreover the identification of the U solubility limiting phase in cementitious systems is subject to debates. To deepen our knowledge on the U(VI)/cement system, a XAS study was initiated and measurements at the U L₃ edge (17.17 keV) carried out. Selected XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Spectroscopy) spectra are presented in Figure 1. For oversaturated conditions with respect to the precipitation of the U-solubility limiting phase(s), the spectra of HCP-Ov are similar to those of the UO₂-Ca reference (synthesized at pH=13.3 in the presence of Ca(II)). Some complementary experiments are on the way to identify UO₂-Ca solid but it most likely corresponds to becquerelite (Ca[(UO₂)₆O₄(OH)₆].8H₂O). For undersaturated conditions, the spectra of HCP-Und display some marked differences with those of UO₂-Ca but are similar to those of CSH-0.7, which may reveal that CSH phase is the U(VI) uptake-controlling phase in cementitious systems. Data fitting are currently undertaken to identify the U(VI) coordination mode in the CSH and HCP solids.

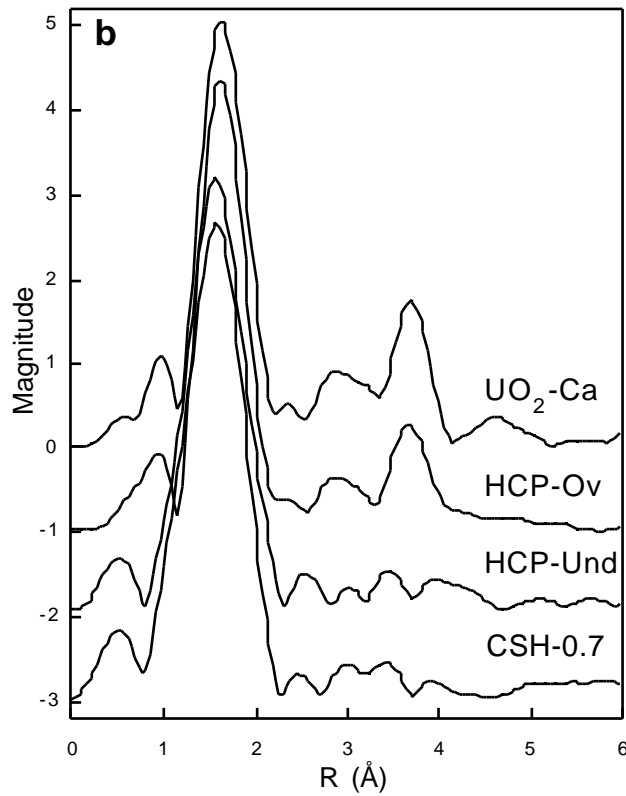
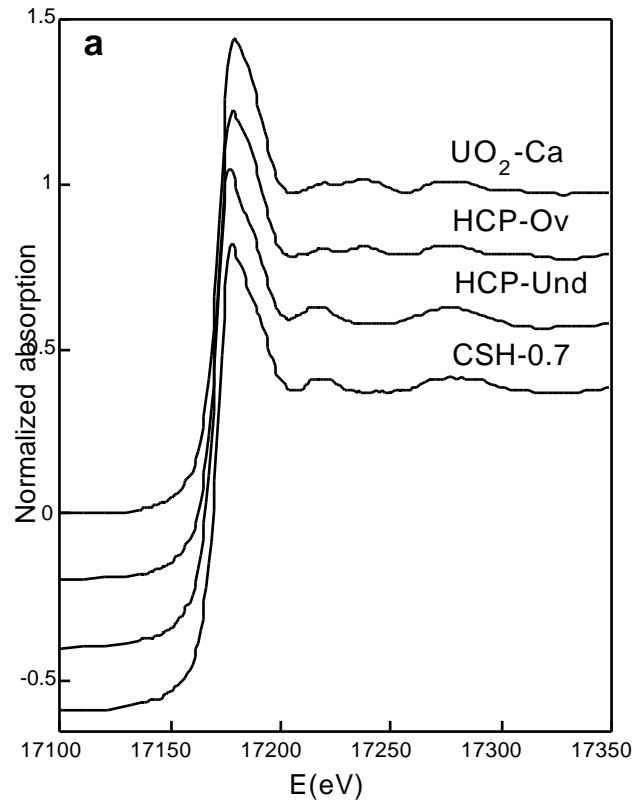


Figure 1: XANES (*a*) and PRDF (*b*) spectra of UO₂-Ca (reference compound), U(VI) immobilized on HCP (HCP-Ov: Oversaturated conditions; HCP-Und: Undersaturated conditions) and on CSH (CSH-0.7)