Radionuclide uptake by calcium silicate hydrates: Case studies with Th(IV) and U(VI)

Nuclear Energy and Safety Research Department
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Jan Tits¹, Tomonari Fujita², Messaoud Harfouche¹, Rainer Dähn¹, Masaki Tsukamoto², Erich Wieland¹

1 Paul Scherrer Institut, Villigen PSI, Switzerland
2 Central Research Institute of the Electric Power Industry, Tokyo, Japan
Preface

The Laboratory for Waste Management of the Nuclear Energy and Safety Research Department at the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of the Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the partial financial support of, the National Cooperative for the Disposal of Nuclear Waste (Nagra).

The present study has been undertaken in cooperation with and with financial support of the Central Research Institute of the Electric Power Industry (CRIEPI), Japan.
Abstract

The immobilization of Th(IV) and U(VI) by C-S-H phases has been investigated under conditions relevant to the cementitious near field of a nuclear waste repository. To this end, C-S-H phases were synthesized using two different procedures: the “direct reaction” method and the “solution reaction” method. The solids were characterized with respect to their solid and equilibrium solution compositions and specific surface area.

The solubility limits of Th(IV) and U(VI) in alkaline solutions (presence of precipitates or colloidal material) were studied, and the outcome was compared with the results of speciation and solubility calculations assuming the presence of combinations of different solid Th(IV) and U(VI) phases. The solid phases controlling Th(IV) and U(VI) solubility were found to be ThO₂(s) and CaUO₄(s), respectively.

The Th(IV) and U(VI) sorption and co-precipitation kinetics on C-S-H phases with different CaO:SiO₂ ratios were determined. Furthermore, in the case of U(VI), sorption and co-precipitation isotherms on C-S-H phases were measured under various chemical conditions. Both radionuclides were found to sorb fast and very strongly on C-S-H phases with sorption distribution ratios (R_d values) ranging between 10⁵ L kg⁻¹ and 10⁷ L kg⁻¹ in the case of Th(IV) and between 10⁴ L kg⁻¹ and 10⁶ L kg⁻¹ in the case of U(VI). Both sorption and co-precipitation experiments resulted in similar R_d values, thus indicating that no additional sorption sites for Th(IV) and U(VI) had been generated in the co-precipitation process. C-S-H synthesis procedures did not have a significant influence on the Th(IV) and U(VI) sorption behaviour. The U(VI) sorption- and co-precipitation isotherms were found to be non-linear, and further, increasing Ca concentrations gave rise to increasing U(VI) uptake. The latter observation suggests that U(VI) uptake is controlled by a solubility-limiting process, while the former observation indicates that this process is non-stoichiometric (solid solution formation).

EXAFS measurements performed on U(VI) sorbed on C-S-H phases revealed a coordination environment with a split equatorial oxygen shell similar to that reported for U(VI) in uranophane. This structural model was found in all sorption samples regardless of the synthesis procedure used. The coordination environment of U(VI) co-precipitated with C-S-H phases using the “direct reaction” method revealed a coordination environment similar to U(VI) in the sorption samples. By contrast, the split equatorial oxygen shell could not be resolved for U(VI) co-precipitated with C-S-H phases using the “solution reaction” method. This finding suggest that the method used for the preparation of the co-precipitation samples could have an influence on the structural arrangement of U(VI) bound in C-S-H.
Zusammenfassung


Die durch die Anwesenheit von Ausfällungen oder kolloidalem Material bestimmten Löslichkeitslimiten von Th(IV) und U(VI) wurden experimentell in alkalischen Lösungen bestimmt. Diese Daten wurden mit den Resultaten aus Speziationen- und Löslichkeitsberechnungen verglichen, in denen die Anwesenheit verschiedener, löslichkeitslimitierender Th(IV) und U(VI) Festphasen berücksichtigt wurde. ThO2(s) und CaUO4(s) wurden als diejenigen Festphasen identifiziert, welche die Th(IV) und U(VI) Löslichkeit unter den gegebenen Bedingungen kontrollieren.

Die Kinetik der Th(IV) und U(VI) Sorptions- und Ko-Präzipitationsprozesse wurde an C-S-H Phasen mit unterschiedlichen CaO:SiO2 Verhältnissen bestimmt. Zusätzlich wurden U(VI) Sorptionsisothermen unter verschiedenen chemischen Bedingungen ermittelt. Die Ko-Präzipitationstests wurden ebenfalls unter den gleichen Bedingungen mit unterschiedlichen U(VI) Konzentrationen (“Ko-Präzipitationsisotherme”) durchgeführt. Es wurde beobachtet, dass Th(IV) und U(VI) sehr schnell und stark sorbieren, wobei Sorptions-Verteilungsverhältnisse (Rd Werte) zwischen 10^5 L kg^{-1} und 10^7 L kg^{-1} für Th(IV) und 10^4 L kg^{-1} und 10^6 L kg^{-1} für U(VI) gemessen wurden. Sowohl die Sorptions- wie auch die Ko-Präzipitationsexperimente ergaben ähnliche Rd Werte bei beiden Radionukliden, was darauf hinweist, dass bei der Ko-Präzipitation keine zusätzlichen Plätze für die Einbindung von Th(IV) und U(VI) gebildet werden. Die beiden unterschiedlichen Methoden der C-S-H Synthese hatten keinen messbaren Einfluss auf das Sorptionsverhalten von Th(IV) und U(VI). Die Sorptions- und Ko-Präzipitationsisothermen für U(VI) waren nicht linear. Zudem wurde beobachtet, dass die Aufnahme von U(VI) durch C-S-H Phasen mit steigender Ca Konzentration ansteigt. Diese Beobachtung könnte bedeuten, dass die Aufnahme von U(VI) durch einen löslichkeitslimitierenden Prozess kontrolliert wird, während die Nicht-Linearität der Sorptions- und Ko-Präzipitationsisothermen darauf hindeutet, dass der Prozess der U(VI) Aufnahme nicht stöchiometrisch erfolgt (Bildung einer festen Lösung).

EXAFS Messungen an C-S-H Phasen mit sorbiertem U(VI) zeigten eine Aufspaltung der äquatorialen Sauerstoffschale und eine Koordinationsumgebung von U(VI), die derjenigen von U(VI) in Uranophan gleicht. Eine dem Uranophan ähnliche Koordinationsumgebung wurde für alle Sorptionsproben unabhängig des für die Synthese verwendeten Verfahrens beobachtet. Auch in Ko-Präzipitationsproben eingebundenes U(VI), die mit der “direkten Reaktions-Methode” hergestellt worden waren, zeigte die gleiche Koordinationsumgebung wie sie für die U(VI) Sorptionsproben beobachtet worden war. Im Gegensatz dazu konnte die Aufspaltung
Resume

La rétention du thorium (IV) et de l’uranium (VI) par les phases de C-S-H a été étudiée en conditions pertinentes pour un site de stockage de déchets radioactifs en milieu cimentaire. Dans ce contexte, les phases de C-S-H ont été préparées selon deux voies de synthèses : une première dite de « réaction directe » et une seconde dite de « réaction en solution ». Les solides produits par ces réactions ont été caractérisés en termes de surfaces spécifiques et en termes de composition élémentaire pour le solide lui-même et pour la solution d’équilibre qui lui est associée.

Les limites de solubilités du Th(IV) et de l’U(VI) ont été étudiées en solutions alcalines (en présence éventuelle de précipités ou de colloïdes). Ces résultats expérimentaux ont alors été comparés aux résultats obtenus par calculs de spéciation et de solubilité, prenant en compte la présence de différentes phases solides de Th(IV) et d’U(VI). Le solide ThO$_2$(s) s’avère être la phase solide contrôlant la solubilité de Th(IV) et CaUO$_4$(s) celle contrôlant la solubilité de l’U(VI).

Une étude de cinétique de rétention et de co-précipitation de Th(IV) et U(VI) par les phases de C-S-H a été menée pour différents rapports CaO/SiO$_2$. De plus, dans le cas de l’U(VI), des isothermes de rétention et de co-précipitation par les phases de C-S-H ont été déterminées en fonction de conditions chimiques variables. L’étude montre que les deux radionucléides étudiés sont retenus significativement par les phases de C-S-H selon une cinétique rapide et il en résulte des valeurs de rapport de distribution ($R_d$) s’échelonnant de $10^5$ L.kg$^{-1}$ à $10^7$ L.kg$^{-1}$ pour le Th(IV) et de $10^4$ L.kg$^{-1}$ à $10^6$ L.kg$^{-1}$ pour l’U(VI). Les valeurs obtenues de $R_d$ sont comparables pour les expériences de sorption et pour celles de co-précipitation, ce qui indique alors, qu’aucun site de sorption supplémentaire pour l’U(VI) et pour le Th(IV) n’a été généré lors du processus de co-précipitation. De plus, la voie de synthèse des phases de C-S-H n’engendre aucun effet sur le comportement de l’U(VI) et du Th(IV) vis-à-vis de la rétention. Les isothermes de rétention et de co-précipitation de l’U(VI) par les phases de C-S-H ne sont pas linéaires. De plus, l’augmentation de la concentration en calcium (en solution) est directement liée à l’augmentation de la rétention de l’U(VI). Ces observations suggèrent d’une part que la rétention de l’U(VI) dans les phases de C-S-H est contrôlée par un processus limitant la solubilité et d’autre part, que ce processus est non-stœchiométrique (de type formation de solution-solide).

L’analyse des spectres EXAFS des échantillons d’U(VI) retenus par les phases de C-S-H a permis par l’étude des couches de coordinations de distinguer 2 types de liaisons équatoriales U(VI)-oxygène, le même environnement a été reporté pour l’U(VI) dans l’uranophane. Ce modèle de structure a pu être appliqué à tous les échantillons U(VI)/C-S-H, quelque soit la voie de synthèse utilisée. La coordination de l’U(VI) co-précipité aux phases de C-S-H via la méthode de « réaction directe » s’apparente à celle de l’U(VI) des échantillons retenus par les phases de C-S-H. Cependant, pour les échantillons d’U(VI) co-précipité aux phases de C-S-H via la méthode de « réaction en solution », les liaisons équatoriales U(VI)-oxygène n’ont pu être différenciées par manque de résolution des spectres. Ces observations montrent que la voie de synthèse utilisée pour préparer les échantillons de co-precipitation a un effet sur l’arrangement structural de l’U(VI) dans les phases de C-S-H.
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1 Introduction

Cementitious materials are common use world-wide in immobilization strategies for radioactive waste (e.g., Chapman & McCombie 2003). The immobilization of radionuclides by the cementitious materials of a repository for radioactive waste takes place both in the waste containers and in the construction materials, such as backfill, liners etc. To date, a great number of studies have demonstrated the waste loading potential of cementitious materials and their performance in leaching tests (e.g., Connor 1990; Batchelor 2006). On the atomic/molecular scale, however, the chemical mechanisms governing waste ion immobilization are not well understood. Nevertheless, a mechanistic understanding of the chemical processes by which waste ions become immobilized in cement-based matrices, is important in conjunction with long-term assessments of the performance of repositories for radioactive waste.

Cement is a complex mixture of different cement phases. From a mineralogical standpoint cement consists mainly of calcium (aluminium) silicate hydrates (C-(A)-S-H phases, ~50 wt%, portlandite (~20 wt%) and calcium aluminates (~18 wt %), i.e., AFm (Al2O3-Fe2O3-mono)-type and AFt (Al2O3-Fe2O3-tri)-type phases, and ~9 wt % minor phases (e.g., hydrotalcite, hydrogarnet, ferrite) that can expose highly reactive surface sites for sorption and act as storage minerals for waste ions (e.g., Taylor 1997). The immobilization potential of cement originates from the selective binding properties of these phases for metal cations and anionic species (e.g. see reviews in Macphee & Glasser 1993; Cocke & Mollah 1993; Gougar et al. 1996). Calcium aluminates and calcium silicate hydrates (C-S-H phases) are considered to be among the most important cement phases governing immobilization processes. In particular C-S-H phases may control the release of many radionuclides from a cementitious near field because of their long-term stability and high immobilization potential for cations.

The pool of sorption data available for uranium and thorium on cementitious systems originates primarily from batch-type sorption experiments on dispersed systems. Batch-type experiments allow the uptake of radionuclides in cementitious systems to be quantified in terms of distribution ratios between the liquid and solid phase. Therefore, to a large extent, assessment of the safe disposal of cementitious uranium/thorium-containing radioactive waste is presently based on state-of-the-art knowledge of the interaction of uranium and thorium with cementitious materials as obtained from wet chemical and radiotracer studies. Several studies have been undertaken into the immobilization of uranium and thorium by cementitious materials at ambient (Allard 1985; Höglund et al. 1985; Brownsword et al. 1990; Berner 1990; Kienzler et al. 1998; Holgersson et al. 1998; Wieland et al. 1998; Tits et al. 2000, Wieland et al. 2002; Sutton et al. 2003; Pointeau et al. 2004) and elevated temperature (Matzen et al. 2000). In the case of Th(IV) a strong uptake was reported with distribution ratios (Rd) typically ≥ 10^5 L kg^{-1}. Rd values were found to be about one to two orders of magnitude lower in the case of U(VI), indicating that the interaction of hexavalent uranium with the cement matrix is weaker but still significant. U(VI) and Th(IV) uptake by cementitious materials has been interpreted in terms of inner-sphere complexation with surfaces of cement (Wieland et al. 2002; Sutton et al. 2003; Pointeau et al. 2004). The cement phase(s) responsible for Th(IV) and U(VI) binding, however, has not been identified to date. The studies of Tits et al. (2000) and Pointeau et al. (2004) suggest that C-S-H
phases could play an important role in the uptake of Th(IV) and U(VI) by cementitious materials.

Several sorption processes may control the interaction of radionuclides with C-S-H phases. Besides adsorption, which accounts for the binding of an anion or cation on the surface of the solid material, co-precipitation (or incorporation) processes with C-S-H phases may take place and, thus, enhance radionuclide retardation in the cementitious near field (e.g., Cocke & Mollah 1993; Gougar et al. 1996). Co-precipitation is a process by which two or more chemical components are simultaneously and permanently incorporated into a single non-stoichiometric solid phase during precipitation from solution. The compound formed may be either amorphous or crystalline. Considerable evidence has been presented that co-precipitation with amorphous and crystalline C-S-H phases is a possible retardation mechanism (e.g., Lieber & Gebauer 1969; McCulloch et al. 1985; Cartledge et al. 1990; Moroni & Glasser 1995; Johnson & Kersten 1999). Co-precipitation of radionuclides with C-S-H phases in a repository environment can occur under the following conditions:

1) Co-precipitation takes place during the solidification of radioactive waste with cement in the canister. The initial hydration of the cement clinker is a rapid process whereby C-S-H phases precipitate under supersaturated conditions due to the rapid dissolution of the components of the clinker minerals, i.e., mainly Ca$_3$SiO$_5$ (C$_3$S), Ca$_2$SiO$_4$ (C$_2$S), Ca$_3$Al$_2$O$_6$ (C$_3$A) and Ca$_4$Al$_2$Fe$_2$O$_{10}$ (C$_4$AF) (Cocke & Mollah 1993).

2) During the service life of a cement-based repository the cementitious materials degrade caused by the interaction with groundwater. The alteration of the C-S-H phases during this degradation process may also provide necessary conditions for co-precipitation processes to occur.

3) Co-precipitation also takes place if conditions are such that the formation of secondary C-S-H-type minerals occurs. Such conditions may exist in the near field of a repository, e.g., when a quartz-rich material is used as backfill or in the far field due to the interaction of hyperalkaline near field pore water with the host rock. Under these conditions, the formation of C-S-H phases may be driven by the dissolution of the silica-containing minerals, which allows C-S-H phases to be formed under weakly oversaturated conditions (Tits et al. 2004).

4) Radionuclide uptake by co-precipitation may take place during in-situ formation of cementitious colloids in the near field of a repository. The colloidal material is of the C-S-H-type and may act as carrier phase for radionuclides (Ramsay et al. 1991; Wieland 2001; Fujita et al. 2003; Wieland et al. 2004). Thus, studies on the co-precipitation of radionuclides with C-S-H phases are important to assess the impact of in-situ formed C-S-H-type colloids on radionuclide mobility.

To date structural information on uranium and thorium uptake by cementitious materials on the molecular level is still scarce, and the speciation of the sorbing and dissolved species as well as the binding mechanisms involved are still poorly known. The use of advanced synchrotron-based spectroscopic techniques opens up the possibility of closing this gap in our knowledge explaining the growing interest of the scientific
community in this field (see e.g., Rose et al. 2000; Scheidegger et al. 2000; Rose et al. 2001; Ziegler et al. 2001; Bonhoure et al. 2002; Bonhoure et al. 2003; Bonhoure et al. 2006; Harfouche et al. 2006; Vespa et al. 2006a and b; Macé et al. 2013). X-ray absorption fine structure (XAFS) spectroscopy investigations of U(VI) interactions in cementitious systems have previously been reported by Sylvester et al. (2000a) and Zhao et al. (2000). In these studies the coordination environment of U(VI) loaded on untreated and hydrothermally treated concrete was probed in the alkaline pH range (pH = 9.3 - 12.3). The uranium XAFS results showed the preservation of the [O=U=O]^{2+} structure in all samples with axial oxygens (U-O_{ax} = 1.81 - 1.83 Å) and a split equatorial shell (U-O_{eq1}: R = 2.23 - 2.30 Å; N = 2.5 - 4.3; U-O_{eq2}: R = 2.39 - 2.53 Å; N = 1.4 - 2.2). Splitting of the equatorial shell was considered to be consistent with inner-sphere surface complexation and/or the formation of an U(VI) precipitate. The U(VI) samples equilibrated on hydrothermally altered concrete further revealed U-U interactions indicative of oligomer formation or surface precipitation. The studies of Sylvester et al. (2000a) and Zhao et al. (2000), however, did not yield further information on the cement phases that may be responsible for U(VI) uptake by treated and non-treated concretes nor the U-bearing solids that may be controlling U(VI) solubility in these systems.

Macé et al. 2013 carried out XAFS investigations on U(VI)-doped cementitious materials prepared under varying conditions, such as samples from sorption and diffusion experiments, and using different cementitious materials such as crushed hardened cement paste (HCP) and synthetic C-S-H phases. The authors showed that, at low loading, U(VI) is bound to the C-S-H phases in HCP, while at high U(VI) loading, the immobilisation of U(VI) in cementitious materials is mainly controlled by the precipitation of a calcium uranate type phase. These observations were confirmed by Tits et al., 2015).

XAFS studies of potentially solubility-controlling U-bearing phases have been reported by Allen et al. (1996) Reich et al. (1996), and Thompson et al. (1997). Reich et al. (1996) present XAFS data for uranyl orthosilicate, (UO_{2})_{2}SiO_{4}·2H_{2}O, which exists as the mineral soddyite (U/Si ratio = 2) in nature, and UO_{2}^{2+} sorbed on silica gel. The bond length of the axial oxygen (R = 1.79 Å) in uranyl orthosilicate as determined by Reich et al. (1996) is consistent with literature data. Furthermore, the authors found no split equatorial shell (U-O_{eq}: R = 2.38 Å; N = 5.4). Third and fourth coordination shells were associated with U-Si and U-U interactions (U-Si: R = 3.16 Å; N = 0.9; U-U: R = 3.88 Å; N = 1.2). In contrast, a split equatorial shell was observed for UO_{2}^{2+} sorbed on silica gel (U-O_{eq1}: R = 2.29 Å; N = 4; U-O_{eq2}: R = 2.5 Å; N = 1.6) whereas the bond distance of the axial oxygen was found to be identical to uranyl orthosilicate (R = 1.78 Å). Allen et al. (1996) report a XAFS study of schoepite (UO_{2}(OH)_{2}·H_{2}O) samples prepared at varying pH (pH = 7.2, 8.4, 11.4). The authors found an increase in the axial oxygen bond length from 1.80 Å (pH = 7.2) to 1.86 Å (pH = 11.4). In addition, a concomitant decrease in the bond lengths of the equatorial oxygen and the nearest-neighbour uranium was found with increasing pH. Thus, the linear uranyl [O=U=O]^{2+} structure becomes elongated and the equatorial bonds contract with increasing pH. The authors concluded that the precipitate formed at pH = 7.2 resemble that of schoepite or a similar hydrated hydroxide, whereas the structural parameters of the precipitate formed at pH = 11.4 are more closely related to those of an alkali metal uranate. Thompson et al. (1997) investigated the coordination environment of UO_{2}^{2+} in an uranophane
(Ca(UO₂)₂(SiO₃OH)₂·5H₂O) of unknown origin. A multi-shell fit allowed an excellent reproduction of the oscillatory features of the EXAFS spectrum. The authors determined the axial oxygen bond length to be 1.82 Å and observed a split equatorial shell (U-Oₑq₁: R = 2.32 Å; N = 3; U-Oₑq₂: R = 2.49 Å; N = 2). Additional coordination shells were attributed to U-Si and U-U nearest neighbours (U-Si: R = 3.17 Å; N = 1; U-U: R = 3.96 Å; N = 2). According to the authors, however, the fit did not require inclusion of additional Si at short distances (R = 3.63 Å, 3.75 Å, and 3.78 Å), which are parameters expected from crystallographic characterizations (Ginderow 1988). This finding was ascribed to destructive interference of the backscattering waves, which precludes detection of all but the closest Si atom. Furthermore, the authors suggested multiple scattering resonances to intersperse with single scattering to Si atoms although their contribution was considered to be small due to the low symmetry of the U sites in uranophane.

The objective of the present study, which was carried out in the frame of a joint research project between the Central Research Institute of the Electric Power Industry (CRIEPI), Japan, and the Laboratory for Waste Management (LES) of the Paul Scherrer Institute (PSI), was to investigate the interaction modes of Th(IV) and U(VI) with C-S-H phases under conditions relevant to the cementitious near field of a repository for radioactive waste, to distinguish adsorption from co-precipitation (incorporation) processes on C-S-H phases, and to assess the relevance of these processes for performance assessment. XAFS studies on U(VI) doped C-S-H systems were undertaken with the aim to gain molecular-level information on the coordination environment of UO₂²⁺ bound to C-S-H phases, which were prepared using two different methods for C-S-H synthesis. No detailed XAFS investigations were conducted on Th(IV) doped C-S-H systems due to limited Th(IV) loadings that were achievable and constrained by the low solubility of Th(OH)₄ under strongly alkaline conditions.

The present study was undertaken in close co-operation with, and with the financial support of the National Cooperative for the Disposal of Radioactive Waste (Nagra), Switzerland.
2 Materials and Methods

2.1 General

The pore water in the cementitious near field of a repository for radioactive waste is strongly influenced by the degradation of the cementitious material causing significant changes of its composition during the service life of a repository. The cement pore water evolves from a NaOH/KOH dominated solution with a pH of approximately 13.3 in the first stage of the cement degradation to a Ca(OH)₂ saturated solution of pH=12.5 (Berner 1990). It should be noted that the pore water composition significantly influences the composition of the C-S-H phases in cement. In fresh cement paste C-S-H phases incorporate significant amounts of Na and K, whereas in the second degradation stage of a cementitious system, Na and K are absent in the C-S-H phases (e.g. Tits et al. 2006a). Furthermore, the higher Ca concentration in the pore water in the second stage of cement degradation may significantly influence the CaO:SiO₂ (C:S) ratio of the C-S-H phases, which further may affect sorption properties. C-S-H phases with different compositions have been prepared with the aim of assessing the influence of the solid phase composition and the solution composition on Th(IV) and U(VI) uptake. To this end purpose C-S-H phases were synthesized in an artificial cement pore water (ACW) containing high Na and K concentrations and having a constant pH of 13.3, and in pure Milli-Q water. In the latter case the equilibrium solution composition contains only Ca and Si and the pH varies as function of the C:S ratio of the C-S-H phases (pH range ~10.0 to 12.5). Ca and Si concentrations and pH are controlled by the solubility of the C-S-H phases at equilibrium. The solubility of C-S-H phases synthesized in water has been extensively studied in the past (see e.g., Fujii & Kondo 1981; Gartner & Jennings 1986; Jennings 1986; Richardson & Groves 1992; Thomas & Jennings 1998; Chen et al. 2004), whereas the solubility of C-S-H phases synthesized in the presence of NaOH and KOH is poorly known.

Throughout this study the solutions were prepared using Fluka or Merck “pro analysis” chemicals. Milli-Q water generated by a Millipore water purification system was used for the preparation of solutions and for sample dilution. The sorption experiments were carried out in 40 mL polyallomere centrifuge tubes (Beckman Instruments, Inc.), which were washed, left overnight in a solution of 0.1 M HCl, and thoroughly rinsed with deionized water. For C-S-H synthesis and storage of the alkaline solutions flasks made from perfluoralkoxy-copolymers (PFA) were used. Furthermore, all experiments were carried out in a glove box under a nitrogen atmosphere (CO₂, O₂ ≤ 2 ppm).

2.2 Wet chemistry experiments

2.2.1 Synthesis of C-S-H phases

In the present study C-S-H phases were synthesized using two different preparative methods: The first type of C-S-H phases was prepared using an adapted version of the so-called "direct reaction" method (Atkins et al. 1991, 1993) by mixing silica fume (AEROSIL 300, Degussa-Huls AG, Baar, Switzerland) with CaO in Milli-Q water or ACW ([Na]=0.11 M, [K]=0.18 M) at room temperature at ratios corresponding to the
target C:S ratios of the C-S-H phases. The masses of CaO and Aerosil 300 used were
chosen in such a way that the final solid-to-liquid (S:L) ratio of the mixture (based upon
the dry mass of CaO + SiO₂) was 5.0 g L⁻¹ for the sorption experiments with U(VI) and
2.0 g L⁻¹ for the Th(IV) sorption experiments. Details of this preparative method as well
as a detailed characterization of the C-S-H material are given in Tits et al. (2006a).

The composition of ACW is given elsewhere (Wieland et al. 1998). The C-S-H
suspensions were either used without further pre-treatment after 2 weeks ageing
(“fresh” C-S-H phases), or they were filtered through Whatman ashless 541-grade filter
paper and aged in a desiccator at a relative humidity of 30% until required for use in the
sorption tests (“aged” C-S-H phases). The filtrates were analysed using inductively
coupled plasma optical spectrometry (ICP-OES) to determine the composition of the
equilibrium solution of each C-S-H phase. A dry weight of each “aged” C-S-H phase
was determined with the aim of knowing the amount of C-S-H phases used in the
sorption tests. To this end ~0.5 g C-S-H material of each C-S-H phase was transferred
into porcelain crucibles and weighed. The measurements were carried out in triplicates.
The samples were dried at 105ºC until their weight remained constant. The samples
were then heated at 1000ºC until the weight remained constant. The dry weight of the
residual material corresponds to the mass of CaO and SiO₂ of the C-S-H phases. Note
that the sorption values reported in the following sections will be given relative to the
dry weight of the C-S-H phases. This further allows comparisons with sorption values
from experiments with “fresh” C-S-H phases to be made. In the latter experiments the
dry weight of “fresh” C-S-H phases is based on the amount of CaO and SiO₂ used in the
in-situ synthesis.

For the second method C-S-H phases were prepared using starting solutions with the
aim of avoiding the presence of solid reactants. The C-S-H phases were prepared by
mixing calcium hydroxide (Ca(OH)₂) solutions with sodium metasilicate solutions
(Na₂SiO₃·9H₂O). In the following this method is denoted as “solution reaction” method,
and a detailed description is given elsewhere (Sugiyama & Fujita 2006). Briefly, 20 mL
aliquots of a 0.015 M Ca(OH)₂ solution were mixed with Na₂SiO₃ solutions of
appropriate concentrations to give target C:S ratios between 0.66 and 1.8. For the
preparation of the latter solutions appropriate amounts of Na₂SiO₃ solutions of
Milli-Q water or in a solution containing 0.228 M NaOH and 0.36 M KOH. The Na
and K concentrations of the latter solution are twice the concentrations in ACW. Prior to
use, the Ca(OH)₂ solutions were filtered using a membrane filter with a molecular
weight cut-off of 3000 Dalton to remove any remaining calcium hydroxide colloids.

2.2.2 Analytical methods

Carrier-free ²²⁸Th was purchased from Isotopendienst Blasek GmbH, Waldenburg,
Germany. ²²⁸Th source solutions were diluted in 50 mL 5% HCl to produce a stock
solution. Small aliquots (0.1-1 mL) of the stock solution were further diluted with 0.1 M
HCl to give tracer solutions with the required concentrations. ²²⁸Th activities were
determined on untreated 5 mL samples with the help of a Canberra Packard Tri-carb
2250 CA liquid scintillation analyser (LSA) or a Canberra Packard Tri-carb A3170 TR
LSA, respectively, using the energy window between 6 keV and 350 keV. The
background activities measured in this window were typically between 30 cpm and 35
pcpm in 5 mL sample volume for the experiments in alkali-rich ACW and between 2 cpm and 7 cpm in 5 mL sample volume for the experiments performed in the alkali-free solutions. The difference in background activity originates from the presence of $^{40}$K in ACW. The $^{228}$Th activities in suspensions were determined with the help of a Packard Cobra 5003 auto gamma counter using an energy window between 55 keV and 125 keV. The background activity measured in this window was typically between 4 cpm and 15 cpm in 5 mL sample volume for all the experiments. Prior to $^{228}$Th activity measurements, the solutions were stored for at least one month to allow secular equilibrium of $^{228}$Th with the daughters to be established. This secular equilibrium was disturbed after uptake of the tracer by the solid due to the much higher sorption of $^{228}$Th ($R_d = \sim 10^5 \text{ L kg}^{-1}$) compared to its daughter $^{224}$Ra ($10^2 < R_d < 10^4 \text{ L kg}^{-1}$, Tits et al. 2006a). The $^{228}$Th solutions were prepared for analysis by mixing 5 mL aliquots with 15 mL scintillator (Ultima Gold XR, Packard Bioscience S.A.) prior to counting.

The high pH of the samples gave rise to sorption of $^{228}$Th on the walls of the beta vials resulting in a reduction of the measured beta activity by approximately 10% compared to samples which were acidified prior to radio assay. Radionuclides sorbed on the walls of the beta vials have a reduced probability that their radiation interacts with the scintillator, resulting in a lower detection efficiency. Test experiments revealed that the reduction was linear over the range between 1000 cpm and 50000 cpm. As a consequence, all $^{228}$Th activity measurements presented in this report are relative measurements in which the activities in unknown samples are compared to activities in standard solutions of known $^{228}$Th activity. With this it is considered that measurements of standards and samples have been subjected to the same effects.

Tracer solutions for uptake experiments with $^{233}$U were prepared as follows: A $^{233}$U(VI) source solution was diluted in 50 mL 5% HCl to produce a stock solution. Small aliquots (0.1-1 mL) of the stock solution were further diluted with 0.1 M HCl to give tracer solutions with the required concentrations. $^{233}$U(VI) activity was determined on the Canberra Packard Tri-carb 2250 CA LSA using the energy window between 100 keV and 200 keV. The background activity measured in this window was typically 21 cpm in 5 mL sample volume. The $^{233}$U(VI) sample solutions for analysis were prepared by mixing 5 mL aliquots with 15 mL scintillator (Ultima Gold XR, Packard Bioscience S.A.) prior to counting. Sorption on the walls of the beta vials was found to be negligible. Hence, no reduction of the measured activity due to wall sorption had to be taken into account in this case. Furthermore, the long half-life of $^{233}$U ($1.6 \cdot 10^5$ y) implies that the activities of its daughters are always negligible.

2.2.3 Characterization of the C-S-H phases

C-S-H suspensions prepared as described above were filtered through Whatman ashless 541-grade filter paper using a Buchner funnel with a vacuum pump. The Na, K, Ca, Si and Sr concentrations in the filtrates were determined using ICP-OES. The solids were quickly washed with deionised water and dried in the glovebox. The elemental compositions of the C-S-H phases were obtained by acid dissolution with HF, dissolution of the metal fluorides with H$_3$BO$_3$ and analysis of the resulting solution with ICP-OES. This method was adapted from Lim & Jackson (1982).
The specific surface area of some of the C-S-H phases was determined using the N₂-BET method (e.g. Kantro et al. 1967) by measuring multipoint N₂ sorption isotherms with a Micrometrics Gemini 2360 surface area analyser. Note that the value for the specific surface area obtained with this method only gives an estimate of the real surface area of the C-S-H phases due to severe treatment of the samples (drying at 80°C under vacuum) prior to the measurement.

X-ray diffraction (XRD) measurements of the powders were performed between 1.5° and 96.99° 2θ using a Bragg-Brentano diffractometer (Bruker AXS D8, Cu-Kα radiation, automatic divergence slit, graphite monochromator). The step width was 0.03° 2θ and step counting time was 4 s.

Thermal gravimetry (TG) with evolved gas analysis (EGA) was performed on a thermal balance (Mettler TGA/SDTA 851e) coupled through a capillary to a quadrupole mass spectrometer (Balzers ThermoStar). 50 mg of finely ground material was heated in a platinum crucible at a rate of 10°C min⁻¹ and an N₂ gas flow of 50 mL min⁻¹. The evolved gas was analyzed for water and carbon dioxide using the most abundant fragments of the two components, CO₂⁺ (m/e = 44) and H₂O⁺ (m/e = 18). The portlandite content was determined from both XRD pattern fitting and TG/EGA determination of the amount of water released from decomposing portlandite (Müller 2005). Prior to each XRD measurement a known amount of an internal standard (CaCO₃, Fluka) was added to the C-S-H powder material. This mixture was gently homogenised by grinding. Only the XRD lines of the internal standard and the portlandite were fitted with the program BGMN® (Bergmann et al. 1998). The resulting portlandite contents were then recalculated with the known content of the internal standard. The portlandite contents of the C-S-H powders were determined by TG-EGA based on the decomposition of portlandite with increasing temperature and determination of the associated release of H₂O between 370° and 500°C. The portlandite content was calculated from the loss of water mass multiplied by the molar mass ratio of portlandite and water.

2.2.4 Presentation of the sorption and co-precipitation data

The sorption data are presented in terms of a distribution ratio, R_d, thus relating the concentration of radionuclide sorbed per kg solid. The R_d value is used to describe the partitioning of a radionuclide between the liquid and the solid phase as follows:

\[
R_d = \frac{\{M_s\}}{[M_l]} = \frac{[M_{\text{susp}}] - [M_l]}{[M_l]} \cdot \frac{V}{m} \quad \text{(L kg}^{-1})
\]

{M_s}: radionuclide concentration on the solid phase (mol kg⁻¹),
[M_l]: radionuclide concentration in the liquid phase (mol L⁻¹),
[M_{susp}]: total concentration of radionuclide in suspension (= total concentration added and corrected for wall sorption) (mol L⁻¹),
V: volume of the liquid phase (L),
m: mass of solid phase, corresponding to the dry weight after calcination of C-S-H phases (kg).
In this study, $R_d$ values have been determined from batch-type experiments using radiotracers. They were calculated from the ratio of the activity of the radionuclide on the solid phase and its activity in the aqueous solution. The activity on the solid phase was obtained by subtracting the activity in the aqueous phase after centrifugation from the total activity measured in the suspension before centrifugation.

\[ R_d = \frac{A_s}{A_l} = \left( \frac{A_{\text{susp}} - A_l}{A_l} \right) \cdot \frac{V}{m} \quad (L \ kg^{-1}) \]  

(2.2)

$A_s$: radionuclide activity on the solid phase (cpm kg$^{-1}$),

$A_{\text{susp}}$: radionuclide activity in the suspension (cpm L$^{-1}$),

$A_l$: radionuclide activity in the equilibrium solution (cpm L$^{-1}$).

The radionuclide concentration in solution, $[M_l]$, was calculated by dividing the activity determined in solution, $A_l$, by the specific activity of the tracer solution, $A_{\text{spec}}$:

\[ [M_l] = \frac{A_l}{A_{\text{spec}}} \quad (mol \ L^{-1}) \]  

(2.3)

$A_{\text{spec}}$ is defined as follows:

\[ A_{\text{spec}} = \frac{A_{\text{std}}}{[M_{\text{std}}]} \quad (cpm \ mol^{-1}) \]  

(2.4)

$A_{\text{std}}$: measured activity of the standard solution (cpm L$^{-1}$),

$[M_{\text{std}}]$: cation (stable isotope + radioisotope) concentration in the standard solution (mol L$^{-1}$).

Thus, $A_{\text{spec}}$ was obtained by measuring the activity of the standard solution. The latter solution was prepared from an aliquot of the tracer solution.

The quantity of a radionuclide sorbed $\{M_s\}$, expressed in mol kg$^{-1}$, was calculated as follows:

\[ \{M_s\} = \left( \frac{A_{\text{susp}} - A_l}{A_{\text{spec}}} \right) \cdot \frac{V}{m} \quad (mol \ kg^{-1}) \]  

(2.5)

2.2.5 Experimental methods

2.2.5.1 Preliminary stability experiments

The solubility of Th(IV) and U(VI) was tested in alkaline solutions with different chemical compositions. The compositions were chosen in a fashion to represent
variations in pH and cation concentrations expected in the sorption tests. The solubility tests were carried out as follows: Small volumes (< 1 mL) of Th(IV) or U(VI) (U-nat) solutions of known concentrations and prepared in 0.1 M HNO₃, labelled with ²²⁸Th(IV) or ²³³U(VI) tracer solutions were diluted with the solutions listed in Table 2.1. The total concentrations varied in the range between 4.3·10⁻¹¹ M and 10⁻⁶ M in the case of Th(IV) and between 2.1·10⁻⁸ M and 10⁻⁴ M in the case of U(VI). These solutions were shaken end-over-end for 1 day, 7 days or 30 days, respectively. After equilibration, the radionuclide activities were determined in the homogeneous bulk solution and in the supernatant obtained after centrifugation (1 hour at 95000 g(max)). Calculations using Stokes law suggested that any colloidal material with a diameter larger than ~ 15 nm should settle during centrifugation. With the above procedure it was possible to distinguish the radionuclide fraction in "true" solution from the radionuclide fraction present as colloidal material. Furthermore, in one stability test with U(VI), the supernatant solution obtained after centrifugation was discarded, and the residual dissolved adding 0.1 M HCl to the centrifuge tube. From this procedure the amount of radiotracer precipitated during centrifugation could be directly determined which further allowed the mass balance to be checked.

Tab. 2.1: Composition of the solutions used in the stability tests.

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Si</th>
<th>Na</th>
<th>K</th>
<th>pH calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACW</td>
<td>1.6·10⁻³</td>
<td>5·10⁻⁵</td>
<td>0.118</td>
<td>0.18</td>
<td>13.3</td>
</tr>
<tr>
<td>Calcium hydroxide solution</td>
<td>1.5·10⁻²</td>
<td>10⁻⁵</td>
<td>0</td>
<td>0</td>
<td>12.2</td>
</tr>
<tr>
<td>Solution in equilibrium with a C-S-H phase with a high C:S ratio (max. [Ca] and min. [Si])</td>
<td>3·10⁻³</td>
<td>1·10⁻⁴</td>
<td>1·10⁻²</td>
<td>0</td>
<td>12.1</td>
</tr>
<tr>
<td>Solution in equilibrium with a C-S-H phase with a low C:S ratio. (min. [Ca] and max. [Si])</td>
<td>5·10⁻⁵</td>
<td>2·10⁻³</td>
<td>2·10⁻²</td>
<td>0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

2.2.5.2 Sorption kinetic tests

Sorption kinetic experiments were performed using “fresh” and “aged” C-S-H phases that had been prepared using both methods for C-S-H synthesis. The target C:S mol ratios were 0.65, 0.9, 1.1 and 1.65 in case of the C-S-H phases prepared using the “solution reaction” method and 0.75, 1.07, 1.29, 1.5 and 1.82 in case of the C-S-H phases prepared using the “direct reaction” method. The detailed set-ups for all the sorption kinetic experiments are listed in Tables 2.2a and 2.2b and Tables 2.3a through 2.3d. It should be noted that the target C:S ratios of the C-S-H phases prepared using the “direct reaction” method cannot be directly deduced from the stoichiometric ratios of CaO and SiO₂ used to synthesize the C-S-H phases under alkali-free conditions (Tables 2.3a through 2.3c).
For some cases it should be considered that additional amounts of CaO or SiO$_2$ were added to account for Ca and Si dissolved in the equilibrium solutions. On the other hand, the actual C:S ratios of the C-S-H phases prepared using the “solution reaction” method do not necessarily agree with the target C:S ratios because small fractions of Ca(OH)$_2$ and Na$_2$SiO$_3$·9H$_2$O added for the C-S-H synthesis remained dissolved in the equilibrium solution.

The final S:L ratio of the suspensions with “fresh” C-S-H phases made following the “direct reaction” method was 1 g L$^{-1}$ in case of the Th(IV) experiments and 5 g L$^{-1}$ in case of the U(VI) experiments (based upon the dry mass of CaO and SiO$_2$ used in the synthesis procedure). The final S:L ratio of the suspensions with “aged” C-S-H phases (based upon a dry weight measured after firing at 1000°C) varied between 2 g L$^{-1}$ and 5 g L$^{-1}$. The final S:L ratio of the suspensions made following the “solution reaction” method varied between 0.8 g L$^{-1}$ and 2.4 g L$^{-1}$ in all sorption experiments.

Prior to the addition of the radiotracers, the suspensions were shaken end-over-end in a glove box under a nitrogen atmosphere for two weeks to reach equilibrium between solid and liquid phase. All samples were then spiked with 0.4 mL 4.28·10$^{-9}$ M $^{228}$Th tracer solution (in 0.1 M HNO$_3$; changes in pH caused by the addition of the acidic tracer were found to be negligible) or 0.1 mL 2.16·10$^{-5}$ M $^{233}$U tracer solution (in H$_2$O). The final total $^{228}$Th and $^{233}$U concentrations were 1.07·10$^{-10}$ M and 5.40·10$^{-7}$ M, respectively. The centrifuge tubes were again shaken end-over-end in the glove box for additional 1, 7, 20, 40, and 120 days. Sampling was carried out as described in section 2.2.5.6.

Tab. 2.2a: Set-up of the Th(IV) sorption kinetic tests with C-S-H phases synthesized under low alkali conditions and in ACW following the “solution reaction” method (20 mL Ca(OH)$_2$ solution mixed with 20 mL Na$_2$SiO$_3$ solution).

<table>
<thead>
<tr>
<th>Target C:S mol ratio</th>
<th>Ca(OH)$_2$ solution (M)</th>
<th>Na$_2$SiO$_3$ concentration (M)</th>
<th>Th(IV) tracer solution 4.28·10$^{-9}$ M (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>1.50·10$^{-2}$</td>
<td>2.31·10$^{-2}$</td>
<td>0.4</td>
</tr>
<tr>
<td>0.90</td>
<td>1.50·10$^{-2}$</td>
<td>1.67·10$^{-2}$</td>
<td>0.4</td>
</tr>
<tr>
<td>1.1</td>
<td>1.50·10$^{-2}$</td>
<td>1.36·10$^{-2}$</td>
<td>0.4</td>
</tr>
<tr>
<td>1.65</td>
<td>1.50·10$^{-2}$</td>
<td>9.00·10$^{-3}$</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Tab. 2.2b: Set-up of the U(VI) sorption kinetic tests with C-S-H phases synthesized under low alkali conditions and in ACW following the “solution reaction” method (20 mL Ca(OH)$_2$ solution mixed with 20 mL Na$_2$SiO$_3$ solution).

<table>
<thead>
<tr>
<th>Target C:S mol ratio</th>
<th>Ca(OH)$_2$ concentration (M)</th>
<th>Na$_2$SiO$_3$ concentration (M)</th>
<th>U(VI) tracer solution 2.16·10$^{-5}$ M (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>1.50·10$^{-2}$</td>
<td>2.31·10$^{-2}$</td>
<td>0.1</td>
</tr>
<tr>
<td>0.90</td>
<td>1.50·10$^{-2}$</td>
<td>1.67·10$^{-2}$</td>
<td>0.1</td>
</tr>
<tr>
<td>1.1</td>
<td>1.50·10$^{-2}$</td>
<td>1.36·10$^{-2}$</td>
<td>0.1</td>
</tr>
<tr>
<td>1.65</td>
<td>1.50·10$^{-2}$</td>
<td>9.00·10$^{-3}$</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Tab. 2.3a: Set-up of the Th(IV) sorption kinetic tests with C-S-H phases synthesized under alkali-free conditions following the “direct reaction” method. The S:L ratio of the CaO and Aerosil 300 suspensions was 1.0 g L⁻¹.

<table>
<thead>
<tr>
<th>Target C:S mol ratio</th>
<th>CaO suspension in H₂O (mL)</th>
<th>Aerosil 300 suspension in H₂O (mL)</th>
<th>H₂O (mL)</th>
<th>Th(IV) tracer solution 4.28·10⁻⁹ M (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>9.36</td>
<td>11.76</td>
<td>18.88</td>
<td>0.4</td>
</tr>
<tr>
<td>1.07</td>
<td>13.30</td>
<td>10.00</td>
<td>16.70</td>
<td>0.4</td>
</tr>
<tr>
<td>1.29</td>
<td>16.67</td>
<td>9.10</td>
<td>14.23</td>
<td>0.4</td>
</tr>
<tr>
<td>1.82</td>
<td>24.06</td>
<td>7.14</td>
<td>8.80</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Tab. 2.3b: Set-up of the Th(IV) sorption kinetic tests with C-S-H phases synthesized in ACW following the “direct reaction” method. The S:L ratio of the CaO and Aerosil 300 suspensions was 1 g L⁻¹.

<table>
<thead>
<tr>
<th>Target C:S mol ratio</th>
<th>CaO suspension in H₂O (mL)</th>
<th>Aerosil 300 suspension in H₂O (mL)</th>
<th>H₂O (mL)</th>
<th>Th(IV) tracer solution 4.28·10⁻⁹ M (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>16.5</td>
<td>23.5</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>1.07</td>
<td>20.0</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tab. 2.3c: Set-up of the U(VI) sorption kinetic tests with C-S-H phases synthesized under alkali-free conditions following the “direct reaction” method. The S:L ratio of the CaO and Aerosil 300 suspensions was 5 g L⁻¹.

<table>
<thead>
<tr>
<th>Target C:S mol ratio</th>
<th>CaO suspension in H₂O (mL)</th>
<th>Aerosil 300 suspension in H₂O (mL)</th>
<th>H₂O (mL)</th>
<th>U(VI) tracer solution 2.16·10⁻⁵ M (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>8.42</td>
<td>12.14</td>
<td>19.44</td>
<td>0.1</td>
</tr>
<tr>
<td>1.07</td>
<td>11.30</td>
<td>10.00</td>
<td>18.70</td>
<td>0.1</td>
</tr>
<tr>
<td>1.29</td>
<td>13.21</td>
<td>9.10</td>
<td>17.69</td>
<td>0.1</td>
</tr>
<tr>
<td>1.82</td>
<td>17.08</td>
<td>7.40</td>
<td>15.52</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Tab. 2.3d: Set-up of the U(VI) sorption kinetic tests with C-S-H phases synthesized in ACW following the “direct reaction” method. The S:L ratio of the CaO and Aerosil 300 suspensions was 1 g L⁻¹.

<table>
<thead>
<tr>
<th>Target C:S mol ratio</th>
<th>CaO suspension in H₂O (mL)</th>
<th>Aerosil 300 suspension in H₂O (mL)</th>
<th>U(VI) tracer solution 2.16·10⁻⁵ M (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>16.50</td>
<td>23.50</td>
<td>0.1</td>
</tr>
<tr>
<td>1.07</td>
<td>20.00</td>
<td>20.00</td>
<td>0.1</td>
</tr>
<tr>
<td>1.29</td>
<td>21.82</td>
<td>18.18</td>
<td>0.1</td>
</tr>
<tr>
<td>1.50</td>
<td>23.33</td>
<td>16.67</td>
<td>0.1</td>
</tr>
</tbody>
</table>

2.2.5.3 Set-up of the co-precipitation kinetic tests

Co-precipitation kinetics tests with Th(IV) and U(VI) were performed using procedures similar to those in the sorption kinetic experiments. The main difference is related to tracer addition: In the co-precipitation tests, the ²²⁸Th tracer or the ²³³U tracer were added immediately (within one minute) after mixing the chemicals used for the C-S-H synthesis instead of allowing the C-S-H suspensions to equilibrate for 2 weeks prior to tracer addition.

2.2.5.4 U(VI) sorption isotherms

In a first series of preliminary experiments U(VI) sorption isotherm measurements were carried out using different experimental set-ups in order to assess whether or not the large variation previously observed in replicate measurements of sorption kinetics, using the “direct reaction” method for C-S-H preparation, could be attributed to specific conditions in the experimental set-up. In particular the influence of C-S-H ageing on U(VI) sorption was tested by comparing a sorption isotherm on a C-S-H phase aged for more than four years with an isotherm on a fresh C-S-H phase. The experiments were performed both under alkali-free conditions, low alkali conditions (“solution reaction” method) and in ACW. Sampling was carried out as described in the following section 2.2.5.6.

The main series of U(VI) sorption isotherm measurements were carried out using C-S-H phases with target C:S ratios of 0.65 and 1.1, synthesized following the “solution reaction” procedure, and using C-S-H phases with target C:S ratios of 0.75 and 1.07 synthesized following the “direct reaction” procedure. The suspensions were equilibrated end-over-end for two weeks prior to the addition of U(VI) tracer. One isotherm was determined using a C-S-H phase aged for 4 years. The experimental set-up was similar to that for the sorption kinetic tests. The required U(VI) concentrations in all the suspensions were adjusted by adding appropriate volumes of a 10⁻² M UO₂(NO₃)₂ solution covering a concentration range between 5.4·10⁻⁸ M and 2.5·10⁻⁴ M. Subsequently, the mixtures were spiked with 0.1 mL 2.16·10⁻⁵ M ²³³U tracer solution (prepared in 0.1 M HNO₃). To the samples with the lowest total U(VI) concentration,
only $^{233}$U tracer solution (0.025 mL – 0.5 mL) was added. The spiked solutions were equilibrated on an end-over-end shaker for 1 month.

### 2.2.5.5 Desorption experiments

In some Th(IV) experiments the sorption test was followed by a desorption test to gain information on the reversibility of the sorption process. Desorption tests were carried out on C-S-H phases synthesized following the “direct reaction” method. After the sorption process had been completed, the samples were centrifuged for 1 hour at 9500 g, and 35 mL aliquots of the supernatant solutions were carefully sampled. The supernatant solutions were kept for radio assay of the tracer concentration. 35 mL Th(IV)-free alkaline solution, which had a composition similar to the solution in equilibrium with the C-S-H phase used in the sorption experiment, was added to each tube. The equilibrium solutions were obtained from a series of samples prepared in the same way as those used in the sorption tests. The suspensions were mixed, homogenised with a shear mixer and equilibrated end-over-end for three days. After equilibration, solid/liquid phase separation was performed by centrifugation, and 35 mL aliquots of the supernatant solutions were carefully removed and radio assayed as described below. A total of three replacements were carried out for each sample.

### 2.2.5.6 Sampling and radio assay

Sampling was conducted in a similar fashion for all sorption and co-precipitation samples: After equilibration, duplicate samples of the vigorously stirred Th(IV) or U(VI) spiked suspensions were withdrawn from centrifuge tubes. The total activity involved in the sorption reaction was determined from the aliquots by gamma counting in the case of $^{228}$Th samples and beta counting in the case of $^{233}$U samples. Note that measuring the radionuclide activity in the suspension allowed artefacts caused by wall sorption of the tracers on centrifuge tubes to be avoided. Phase separation was achieved by centrifugation (1 hour at 95000 g). After centrifugation, duplicate samples were withdrawn from the supernatant solution for radio assay.

The $^{228}$Th containing samples withdrawn from the suspensions and from the supernatant solutions were stored for one month to allow the secular equilibrium of $^{228}$Th with its daughters to be established. Standards for radio assay were prepared as follows: 0.1 mL aliquots of each tracer solution ($^{228}$Th, $^{233}$U) were pipetted into counting vials. The vials were filled up to 5 mL using ACW or a 0.01 M Ca(OH)$_2$ solution. 15 mL scintillator (Ultima Gold XR, Packard Bioscience S.A.) was added to the standards used for liquid scintillation counting. The samples were analysed together with the standards using liquid scintillation (beta) counting and gamma counting. Blanks containing 5 mL ACW or 5 mL 0.01 M Ca(OH)$_2$ were placed between the samples to check the background activity.

The $^{228}$Th containing suspensions were measured with a gamma counter because the presence of the C-S-H gel in the samples was found to cause quenching in beta counting. No quenching effect was observed with the $^{233}$U containing suspensions. The $^{228}$Th activities determined with gamma counting were corrected for further use in the
calculations of the distribution ratios. The activities determined with gamma counting were multiplied with a correction factor, which is the ratio of the activities of a standard solution measured in the gamma counter and the activities of the same standard solution measured in the LSA, to replace gamma by beta activities in the calculations.

In the case of the sorption tests using the C-S-H phases prepared with the “solution reaction” method for C-S-H synthesis, the weight of C-S-H phases formed was determined after sampling for radio assay. With this, the S:L ratio of each sample could be determined. The following procedure was applied to determine the amount of C-S-H phase formed: After centrifugation and sampling for radio assay, the remaining supernatant solution was removed. The solid phase was dried in a desiccator using silica gel until the weight remained constant (within 1 mg uncertainty). The dry weights obtained in this way were converted to the weight after calcination by multiplication with a weight conversion factor determined in a preliminary test experiment, in which both the weight loss in a desiccator and after calcination were measured and compared.

2.3 EXAFS investigations with U(VI) doped C-S-H samples

2.3.1 Preparation of the EXAFS samples

The U(VI) sorption samples used for the EXAFS measurements were prepared by adding appropriate aliquots of a 0.1 M UO₂(NO₃)₂ solution (pH = 3) to the C-S-H materials to achieve U(VI) loadings on wet C-S-H of about 1100 ppm (~0.005 mol kg⁻¹) and 3400 ppm (~0.014 mol kg⁻¹), respectively (Table 2.4). C-S-H phases were prepared as outlined above following the two different methods for C-S-H synthesis. Prior to U(VI) addition the C-S-H phases were aged for two weeks in ACW. For the co-precipitation samples, an aliquot of the 0.1 M UO₂(NO₃)₂ solution was added during synthesis of the C-S-H phases to obtain the same U(VI) loadings as for the sorption samples. After adding U(VI), the U(VI) doped C-S-H samples obtained from the sorption and co-precipitation experiments were equilibrated for 1 day and 30 days, respectively. The samples were kept in the glove box under nitrogen atmosphere and shaken continuously on an end-over-end shaker. Solid and liquid phase were separated by centrifugation (20 min at 10000 g), and the supernatant solution decanted. The residual wet C-S-H pastes were packed into sample holders made from acrylic glass and sealed with Kapton tape. The U(VI) doped C-S-H samples were stored in tightly closed tubes to avoid carbonation of the material and water loss before use in the EXAFS measurements.

2.3.2 EXAFS data collection and reduction

Uranium L_{III}-edge (17166 eV) EXAFS spectra were recorded at the Rossendorf beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France (Matz et al. 1999). The beamline is equipped with a water-cooled Si(111) double crystal monochromator between Pt coated mirrors for beam focusing and rejection of higher order harmonics in the monochromatic beam. The monochromator position was calibrated by assigning the first inflection point of the K-absorption edge of the Y foil to 17038 eV. Several scans were averaged to improve the signal-to-noise ratio (reference
samples ~3 scans; dilute samples ~6 scans). The spectra were measured at room temperature in transmission (ionization chambers) mode for the reference samples (UO$_2$(NO$_3$)$_2$, U nitrate solution) and in fluorescence mode (4-element Ge solid-state detector) for the U(VI) doped C-S-H samples.

EXAFS data reduction was performed using the WinXAS 97 2.3 software package following standard procedures (Ressler 1998). The collected raw data were dead-time corrected. After background subtraction, the energy was converted to photoelectron vector wave units (Å$^{-1}$) by assigning the ionization energy of the U L$_{\text{III}}$ edge, $E_0$, to the first inflection point of the absorption edge. Radial structural functions (RSFs) were obtained by Fourier transforming $k^2$-weighted $\chi(k)$ functions between 2.6 and 11 Å$^{-1}$ (“solution reaction” samples) and 2.6 and 12 Å$^{-1}$ (“direct reaction” samples) using a Bessel window function with a smoothing parameter of 4. Theoretical scattering paths for the fit were calculated with FEFF8.0 (Rehr & Albers 2000) using the $\beta$ uranophane structure (Ca(UO$_2$)$_2$(SiO$_3$OH)$_2\cdot$5H$_2$O) as a model compound. The fit approach was checked on the reference spectra for UO$_2$(NO$_3$)$_2$.

A multi-shell approach was employed for data fitting. Non-linear least square curve fitting was performed in real space. The total number of fitting parameters was estimated to range between 28 and 32, depending on the R range over which the fit was made (Stern 1993). In order to reduce the number of free parameters, some parameters were fixed such as the coordination number (N) for the first shell, simulating the axial oxygen atoms ($N_{\text{Oax}} = 2$). Floating parameters on the first shell were the Debye-Waller factor $\sigma$ and bond length (R). Floating parameters on further shells were N, $\sigma$ and R. Furthermore, some parameters were linked to avoid correlation problems between N and $\sigma^2$, e.g. $\sigma^2$ of the two shells were linked in the case of a split equatorial oxygen shell. In addition, for each fit, the shift in the threshold energy ($\Delta E_0$) was linked for all the shells, which considerably reduced the number of free parameters. As a consequence, the number of free parameters was estimated to range between 16 and 18 in the R-space of interest for each multi-shell fit ($\Delta R = 0.7 - 5.5$ Å). All single-scattering (SS) and multiple-scattering (MS) paths modelled in the fits were based on the model compound $\beta$ uranophane and derived from FEFF8.0. The relevant paths included U-O (axial), U-O (equatorial), U-Si and U-Ca backscattering paths for the C-S-H samples, and in addition, SS U-U backscattering paths for those samples where the formation of U bearing phases was envisaged (co-precipitation samples). The MS U-O$_1$-U-O$_2$-U (4 legged axial path) backscattering path was included in the fits as described elsewhere (Hudson et al. 1996). The coordination number for each O$_{\text{ax}}$ MS path was linked directly to that of the SS axial oxygen path, while the Debye-Waller factor and path length for each MS path were assumed to be twice that of the SS axial oxygen path ($R_{\text{MS}} = 2R_{\text{SS}}$; $\sigma_{\text{MS}}^2 = 2 \sigma_{\text{SS}}^2$). For all shells at distances longer than 3.7 Å (mainly Si and Ca) the Debye-Waller factors were linked to each other, which allowed variation independently of those of the oxygen shells at shorter distances. The other MS paths were rejected due to their small backscattering contributions. The amplitude reduction factor, $S_0^2$, was held fixed at 1.0 for all fits. The shift in the threshold energy, $\Delta E_0$, was allowed to vary as a global parameter. As indicated above, $\Delta E_0$ of the different shells were linked within each fit.
Tab. 2.4: Chemical conditions of U(VI)/C-S-H sample preparation for EXAFS measurements\(^a\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C-S-H(^b) (g L(^{-1}))</th>
<th>[U](_0) (mM)</th>
<th>[U](_\text{sorbed}) (mol kg(^{-1}))</th>
<th>Equilibration (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>“solution reaction” samples</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-S-H0.65-1d(_\text{ads})</td>
<td>2.2</td>
<td>0.25</td>
<td>4.72·10(^{-3})</td>
<td>1</td>
</tr>
<tr>
<td>C-S-H0.65-30d(_\text{ads})</td>
<td>2.2</td>
<td>0.25</td>
<td>4.72·10(^{-3})</td>
<td>30</td>
</tr>
<tr>
<td>C-S-H0.65-30d(_\text{cop})</td>
<td>2.2</td>
<td>0.25</td>
<td>4.72·10(^{-3})</td>
<td>30</td>
</tr>
<tr>
<td>C-S-H1.1-30d(_\text{ads})</td>
<td>2.3</td>
<td>0.25</td>
<td>4.72·10(^{-3})</td>
<td>30</td>
</tr>
<tr>
<td>C-S-H1.1-30d(_\text{cop})</td>
<td>2.3</td>
<td>0.25</td>
<td>4.72·10(^{-3})</td>
<td>30</td>
</tr>
<tr>
<td><strong>“direct reaction” samples</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-S-H0.75-30d(_\text{ads})</td>
<td>17.5</td>
<td>2.5</td>
<td>1.46·10(^{-2})</td>
<td>30</td>
</tr>
<tr>
<td>C-S-H1.07-30d(_\text{ads})</td>
<td>17.5</td>
<td>2.5</td>
<td>1.46·10(^{-2})</td>
<td>30</td>
</tr>
<tr>
<td>C-S-H1.29-1d(_\text{ads})</td>
<td>17.5</td>
<td>2.5</td>
<td>1.46·10(^{-2})</td>
<td>1</td>
</tr>
<tr>
<td>C-S-H1.29-30d(_\text{ads})</td>
<td>17.5</td>
<td>2.5</td>
<td>1.46·10(^{-2})</td>
<td>30</td>
</tr>
<tr>
<td>C-S-H1.29-30d(_\text{cop})</td>
<td>17.5</td>
<td>2.5</td>
<td>1.46·10(^{-2})</td>
<td>30</td>
</tr>
</tbody>
</table>

\(^a\) Designation of the samples (e.g., C-S-H0.65-1d\(_\text{ads}\)) includes the target C:S mol ratios (0.65, 0.75, 1.07, 1.1, 1.29), the equilibration time (1d, 30 d) and modes of interaction (ads = adsorption, cop = co-precipitation).

\(^b\) The C-S-H mass corresponds to dry C-S-H. The water content was determined to be about 90 wt % upon drying wet C-S-H at 100° C until constant weight was achieved.

\(^c\) The concentrations are estimated values and refer to wet C-S-H samples.
3 Results

3.1 Characterization of the C-S-H phases

3.1.1 Structure

The structure of C-S-H phases is related to 14 Å tobermorite and jennite. C-S-H phases with low C:S ratios resemble 14 Å tobermorite. They have a layered structure consisting of central Ca-O sheets with sevenfold coordinated calcium atoms, where all oxygen atoms are shared with silica atoms arranged in a “dreierketten” formation. The latter formation corresponds to silica dimers connected by bridging silica tetrahedra on both sides of the CaO$_2$ sheets (e.g. Chen et al. 2004; Richardson 2004; Bonaccorsi et al. 2005). The C:S ratio of the C-S-H phases can vary between 0.66 (Fig. 3.1a) and 1.5 (Fig. 3.1b). This is achieved basically by progressively replacing the interlayer protons neutralising the negative charges on the bridging tetrahedra by interlayer calcium atoms (e.g. Nonat 2004; Richardson 2004; Bonaccorsi et al. 2005). C-S-H phases with C:S ratios above 1.5 are envisaged to have either a tobermorite-like structure interstratified with layers of Ca(OH)$_2$ or to have elements of a tobermorite-like structure intermixed with others of the jennite-like structure (Chen et al. 2004; Richardson 2004). Jennite is another layered crystalline calcium silicate hydrate consisting of edge-sharing Ca octahedra and dreierketten silicate chains but with much higher C:S ratios due to the presence of Ca-OH groups in the structure (Bonaccorsi et al. 2004; Richardson 2004).

XRD patterns collected from the samples revealed that, in all cases, the dominant component in the synthesized C-S-H phases is a tobermorite-like material.

Fig. 3.1a: Schematic diagram of the tobermorite-based structure of a C-S-H phase with a C:S ratio of 0.66 and a maximum degree of protonation of the silica chains (adapted from Richardson 2004).
3.1.2 Identification of the sorption sites on C-S-H phases

The “dreierketten” structures of C-S-H phases with low C:S ratios consist of non-bridging silica tetrahedra connected by bridging silica tetrahedra (Fig. 3.1a). The Si in each non-bridging silicate tetrahedron shares all its oxygens with other Si ions or with Ca in the octahedral plane. The Si in the bridging silica tetrahedra, however, have two unshared oxygen atoms neutralised by H⁺, thus forming a silandiol (Si(OH)₂) group. Furthermore, the silicate end-groups, silicates connected to only one other silicate group (Si[Q₁]), also carry an unshared oxygen. With increasing pH the “silandiol” groups in the interlayers and the silanol end-groups at the edges become dissociated and form potential sorption sites for Ca²⁺ or other cations. In this study two types of uptake mechanisms for cations are envisaged: 1) Binding to the silandiol groups in the interlayers, and 2) sorption to silanol end-groups at the surface of C-S-H particles.

A great number of studies have indicated that divalent cations with a radius smaller than Ca²⁺, such as Ni²⁺, Co²⁺, Pb²⁺ or Mg²⁺, can replace Ca²⁺ in the 11 Å tobermorite interlayers (Shrivastava & Glasser 1985; Komarneni et al. 1986; Shrivastava & Glasser 1986). Komarneni et al. (1986) report irreversible exchange of Ca²⁺ by Co²⁺ and Ni²⁺ without noticeable amorphisation of tobermorite for cation exchange capacities corresponding to up to 50% of Ca²⁺ replacement in the interlayer. Further, the stronger binding of Mg²⁺ compared to Sr²⁺ and Ba²⁺ on 11 Å tobermorite suggests that divalent cations with ionic radii larger than Ca²⁺ are unable to replace Ca²⁺ in the interlayer (Shrivastava & Glasser 1986; Komarneni & Tsuji 1989). Based on these observations it is expected that silandiol sites in the interlayer of C-S-H phases are not accessible to U(VI) binding due to the large ionic radius of the UO₂²⁺ cation. Thus, the sites
presumably available for sorption of U(VI) comprise solely the edge and planar silanol groups of C-S-H phases. The latter consideration may also be true for Th(IV) as the bulky neutral species, Th(OH)₄, is the dominant species under highly alkaline conditions.

The cation-exchange capacity (CEC) of the edge and planar silanol groups of C-S-H phases can be estimated approximately based on the measured BET surface area (~148 m² g⁻¹) and by assuming a surface site density of 5 sites per nm². The latter site density corresponds to the density of surface hydroxyl groups on amorphous SiO₂ reported by Schindler (1984). From this, a CEC of 1.2 eq kg⁻¹ is derived. Note that this is only based on simplified assumptions. Amorphous quartz surfaces are not a very good model for the surface of C-S-H phases and the sample treatment applied prior to a BET measurement (2 hours under vacuum at 200°C) can change the C-S-H structure dramatically. Note, however, that Sr²⁺ and Ra²⁺ uptake by C-S-H phases with varying C:S ratios was successfully modelled using the above CEC (Tits et al. 2006a and b).

3.1.3 Solid phase composition

C-S-H phases with C:S ratios above 1.07 and synthesized in ACW contained detectable amounts of portlandite. Below a C:S ratio of 1.07, no portlandite could be detected. In absence of ACW, portlandite was only detected in the C-S-H phases with a target C:S ratio of 1.82. The portlandite contents determined with quantitative XRD are listed in Table 3.5. The detection limit for portlandite was estimated to be approximately 0.5 wt%, and the uncertainties on the portlandite measurements are estimated to be approximately ±20%.

Data from TG/EGA analysis of the C-S-H phases support the findings from the XRD measurements. The portlandite contents determined with TG/EGA are also listed in Table 3.5. Note, however, that the portlandite contents determined with this method were found to be significantly higher than those obtained from quantitative XRD. This finding is in line with previous observations reported by several authors (see review in Taylor 1997). The difference is attributed to the presence of portlandite adsorbed on the C-S-H phases or present in the C-S-H interlayers. Therefore, quantitative interpretation of the TG/EGA measurements is difficult, and further, it is assumed that uncertainties on the TG/EGA data are large (approximately ±50%). Hence, it is believed that XRD measurements are more reliable, and therefore, only the XRD data were used for the following estimate of the actual C:S ratios of C-S-H phases.

The actual C:S ratios of the different C-S-H phases synthesized in ACW can be calculated from the target C:S ratios (in wt%) and the portlandite concentration of each C-S-H phase (in wt%) using the following equation:
\[ C:S^* = (C:S)^\text{Target} - f_{\text{Ca(OH)}_2} \left[ (C:S)^\text{Target} + 1 \right] \]  

(3.6)

- \( C:S^* \): actual C:S ratio (wt%)
- \( (C:S)^\text{Target} \): target C:S ratio of the C-S-H phase (wt%)
- \( f_{\text{Ca(OH)}_2} \): weight fraction of portlandite in the C-S-H phase.

The C:S weight ratio as obtained from Eq. 3.6 can be converted into a mol ratio by multiplying with (60/56).

The results are given in Table 3.5. Uncertainties on C:S* and C:S are calculated following the rules of error propagation assuming that the uncertainty on \( f_{\text{Ca(OH)}_2} \) is 20% and that the uncertainty on \( C:S^\text{Target} \) is 2%. The C:S ratios used in the following discussion correspond to actual C:S mol ratios unless otherwise mentioned.

The bulk chemical compositions of the C-S-H phases prepared using the “direct reaction” method, as obtained from the dissolution in HF, are given in Table 3.6. Most of the measured C-S-H compositions agree reasonably well with the target compositions, indicating that all the CaO and Aerosil 300 were consumed in the reaction. Note, however, that the measured C:S ratios are higher than the actual C:S ratios as the values were not corrected for portlandite content. All C-S-H phases synthesized in ACW had significant amounts of Na and K bound to C-S-H (see Table 3.6). Alkali incorporation reached a maximum at the lowest C:S ratios and decreased with increasing C:S ratio.

In the case of the C-S-H phases synthesized following the “solution reaction” method, the actual C:S ratio may differ significantly from the target C:S ratios because part of the Ca(OH)\(_2\) and Na\(_2\)SiO\(_3\) used in the synthesis remained in the aqueous phase to make up the equilibrium solutions. The composition of the equilibrium solutions with respect to Ca and Si, together with the target and actual C:S ratios, are shown in Table 3.7 for those samples for which measurements are available. The portlandite content in these samples was not determined. Nevertheless, the content can be estimated from the C-S-H phases prepared following the “direct reaction” method. The presence of portlandite is only expected in the C-S-H phases up to a target C:S = 1.65 prepared in ACW.
Tab. 3.5: Portlandite content in C-S-H phases as determined with XRD and TG/EGA and the actual C:S ratio of C-S-H phases (C:S ratios are expressed as mol ratios). The C-S-H phases were synthesized following the “direct reaction” method.

<table>
<thead>
<tr>
<th></th>
<th>Portlandite concentration:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TG/EGA (wt%)</td>
</tr>
<tr>
<td>Portlandite</td>
<td>Quantitative XRD (wt%)</td>
</tr>
<tr>
<td>Actual C:S ratio calculated with Eq. 3.6 (mol/mol)</td>
<td></td>
</tr>
<tr>
<td>C-S-H 0.64/ACW</td>
<td>-</td>
</tr>
<tr>
<td>C-S-H 0.75/ACW</td>
<td>6</td>
</tr>
<tr>
<td>C-S-H 1.07/ACW</td>
<td>9</td>
</tr>
<tr>
<td>C-S-H 1.29/ACW</td>
<td>12.7</td>
</tr>
<tr>
<td>C-S-H 1.50/ACW</td>
<td>17.3</td>
</tr>
<tr>
<td>C-S-H 1.82/ACW</td>
<td>17.1</td>
</tr>
<tr>
<td>C-S-H 0.75/H₂O</td>
<td>0</td>
</tr>
<tr>
<td>C-S-H 1.07/H₂O</td>
<td>0</td>
</tr>
<tr>
<td>C-S-H 1.29/H₂O</td>
<td>0</td>
</tr>
<tr>
<td>C-S-H 1.50/H₂O</td>
<td>0</td>
</tr>
<tr>
<td>C-S-H 1.82/H₂O</td>
<td>7.7</td>
</tr>
</tbody>
</table>

1 Estimated uncertainties on the measurements is ±50%.
2 Estimated uncertainties on the measurements is ±20%.
Table 3.6: Bulk compositions of C-S-H phases and the composition of equilibrium solutions for C-S-H phases synthesized in H₂O (alkali-free systems) and in ACW following the “direct reaction” method.

<table>
<thead>
<tr>
<th>Target C:S ratio (mol/mol)</th>
<th>Medium</th>
<th>C:S ratio measured ¹</th>
<th>Na² (mol kg⁻¹)</th>
<th>K² (mol kg⁻¹)</th>
<th>Sr (mol kg⁻¹)</th>
<th>[Ca] (M)</th>
<th>[Si] (M)</th>
<th>[Na] (M)</th>
<th>[K] (M)</th>
<th>[Sr] (M)</th>
<th>pH calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.64</td>
<td>ACW</td>
<td>0.72</td>
<td>1.7±0.2</td>
<td>2.8±0.3</td>
<td>(4.0±0.4)·10⁻⁴</td>
<td>3.9·10⁻⁵</td>
<td>8.1·10⁻³</td>
<td>0.094</td>
<td>0.162</td>
<td>2.3·10⁻⁷</td>
<td>13.3</td>
</tr>
<tr>
<td>0.75</td>
<td>ACW</td>
<td>0.80</td>
<td>1.9±0.2</td>
<td>3.2±0.3</td>
<td>(6.2±0.6)·10⁻⁴</td>
<td>4.7·10⁻⁵</td>
<td>2.2·10⁻³</td>
<td>0.107</td>
<td>0.170</td>
<td>2.9·10⁻⁷</td>
<td>13.3</td>
</tr>
<tr>
<td>1.07</td>
<td>ACW</td>
<td>1.10</td>
<td>1.0±0.1</td>
<td>1.5±0.2</td>
<td>(6.3±0.6)·10⁻⁴</td>
<td>3.2·10⁻⁴</td>
<td>1.8·10⁻⁴</td>
<td>0.113</td>
<td>0.182</td>
<td>6.8·10⁻⁷</td>
<td>13.3</td>
</tr>
<tr>
<td>1.29</td>
<td>ACW</td>
<td>1.32</td>
<td>1.2±0.1</td>
<td>1.8±0.2</td>
<td>(5.3±0.5)·10⁻⁴</td>
<td>1.3·10⁻³</td>
<td>5.1·10⁻⁵</td>
<td>0.112</td>
<td>0.186</td>
<td>2.1·10⁻⁶</td>
<td>13.3</td>
</tr>
<tr>
<td>1.50</td>
<td>ACW</td>
<td>1.53</td>
<td>0.8±0.1</td>
<td>1.2±0.1</td>
<td>(5.2±0.5)·10⁻⁴</td>
<td>1.5·10⁻³</td>
<td>4.5·10⁻⁵</td>
<td>0.114</td>
<td>0.190</td>
<td>2.6·10⁻⁶</td>
<td>13.3</td>
</tr>
<tr>
<td>1.82</td>
<td>ACW</td>
<td>1.79</td>
<td>0.5±0.1</td>
<td>0.8±0.1</td>
<td>(4.8±0.5)·10⁻⁴</td>
<td>1.6·10⁻³</td>
<td>4.4·10⁻⁵</td>
<td>0.117</td>
<td>0.191</td>
<td>2.9·10⁻⁶</td>
<td>13.3</td>
</tr>
<tr>
<td>0.75</td>
<td>H₂O</td>
<td>0.82</td>
<td>-</td>
<td>-</td>
<td>(8.2±0.8)·10⁻⁴</td>
<td>7.9·10⁻⁴</td>
<td>1.6·10⁻³</td>
<td>-</td>
<td>-</td>
<td>1.0·10⁻⁶</td>
<td>10.1</td>
</tr>
<tr>
<td>1.07</td>
<td>H₂O</td>
<td>1.04</td>
<td>-</td>
<td>-</td>
<td>(1.1±0.1)·10⁻³</td>
<td>5.8·10⁻³</td>
<td>4.4·10⁻⁵</td>
<td>-</td>
<td>-</td>
<td>8.0·10⁻⁷</td>
<td>12.0</td>
</tr>
<tr>
<td>1.29</td>
<td>H₂O</td>
<td>1.29</td>
<td>-</td>
<td>-</td>
<td>(8.8±0.8)·10⁻⁴</td>
<td>1.03·10⁻²</td>
<td>9.8·10⁻⁶</td>
<td>-</td>
<td>-</td>
<td>1.0·10⁻⁶</td>
<td>12.2</td>
</tr>
<tr>
<td>1.50</td>
<td>H₂O</td>
<td>1.40</td>
<td>-</td>
<td>-</td>
<td>(5.1±0.5)·10⁻⁴</td>
<td>1.77·10⁻²</td>
<td>5.5·10⁻⁶</td>
<td>-</td>
<td>-</td>
<td>1.9·10⁻⁶</td>
<td>12.4</td>
</tr>
<tr>
<td>1.82</td>
<td>H₂O</td>
<td>1.65</td>
<td>-</td>
<td>-</td>
<td>(4.3±0.4)·10⁻⁴</td>
<td>2.01·10⁻²</td>
<td>4.3·10⁻⁶</td>
<td>-</td>
<td>-</td>
<td>2.0·10⁻⁶</td>
<td>12.5</td>
</tr>
</tbody>
</table>

¹ C:S ratios determined from acid decomposition of the C-S-H phases.
² Calculated per unit weight of CaO and SiO₂ in the C-S-H phase.
³ Uncertainties on the concentrations are ±10%.
Tab. 3.7: Overview of the solid and solution compositions of C-S-H phases synthesized following the “solution reaction” method.

<table>
<thead>
<tr>
<th>Chemical conditions</th>
<th>Target C:S mol ratio (mol/mol)</th>
<th>Ca in solution¹ (M)</th>
<th>Si in solution¹ (M)</th>
<th>pH (calculated)</th>
<th>Actual C:S mol ratio (mol/mol)</th>
<th>Estimated C:S mol ratio from eq. 3.6²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low alkali</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.65</td>
<td>0.90</td>
<td>6.0·10⁻⁵</td>
<td>2.5·10⁻³</td>
<td>11.9</td>
<td>0.73±0.01</td>
<td>0.73±0.01</td>
</tr>
<tr>
<td>1.1</td>
<td>1.65</td>
<td>nd</td>
<td>1.7·10⁻⁴</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>ACW</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.65</td>
<td>0.90</td>
<td>4.5·10⁻⁵</td>
<td>2.7·10⁻³</td>
<td>13.3</td>
<td>0.74±0.01</td>
<td>0.74±0.01</td>
</tr>
<tr>
<td>1.1</td>
<td>1.65</td>
<td>3.9·10⁻⁴</td>
<td>2.5·10⁻⁴</td>
<td>13.3</td>
<td>1.10±0.02</td>
<td>1.10±0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6·10⁻³</td>
<td>4.5·10⁻⁵</td>
<td>13.3</td>
<td>1.47±0.02</td>
<td>1.23±0.10</td>
</tr>
</tbody>
</table>

¹ Uncertainties on the concentrations are ±10%.
² Estimated from the portlandite content in C-S-H phases prepared with the “direct reaction” method. No portlandite formation is expected except in one sample (C:S=1.65, Ca(OH)₂ content = 15.4 wt%; i.e. in between the Ca(OH)₂ content for C:S=1.5 and C:S=1.82 in ACW in Table 3.5)

nd = not determined.

3.1.4 Solution composition

The solution compositions in equilibrium with C-S-H phases with different C:S ratios, synthesized both in Milli-Q water and in ACW, and using both procedures for C-S-H synthesis have been described in detail elsewhere (Tits et al. 2006a; Sugiyama & Fujita 2006). Generally, an increase of the Ca solubility and a decrease of the Si solubility with increasing C:S ratio was observed in agreement with literature data (e.g. Chen et al. 2004 and references therein). In case of the C-S-H phases synthesized following the “direct reaction” method (Table 3.6) it was observed that the equilibrium aqueous Si concentrations and the equilibrium aqueous Ca concentrations in absence of alkalis show a dependence similar to that reported by Chen et al. (2004). These authors interpreted their “curve A” (Fig. 2 in Chen et al. 2004) as the solubility curve for C-S-H(I), which was considered to have a tobermorite-like structure without Ca-OH groups. This implies that the C-S-H phases with high C:S ratios (> 1.2) synthesized in the present study may have structures similar to that of 14 Å tobermorite rather than jennite. Note that the latter phase has a theoretical Ca-OH content of 33% (Bonaccorsi et al. 2004). The pH of the C-S-H suspensions in the absence of alkalis was found to correlate with the C:S ratio of the C-S-H phases (Table 3.6) and varied between 10.1 and 12.5. The pH in the C-S-H suspensions prepared following the “solution reaction” method was calculated to be approximately 11.9 in absence of ACW. The Ca solubility of C-S-H phases synthesized in ACW at pH 13.3 is approximately a factor 10 lower than the Ca solubility of C-S-H phases with the same C:S ratio synthesized in H₂O. However, Si solubilities in both media are very similar. In case of the C-S-H phases synthesized in ACW, the Ca concentrations in solution remain constant at 1.6·10⁻³ M above a target C:S ratio of 1.29. The latter concentration corresponds to that determined by portlandite solubility in ACW (Table 3.6). This could be an indication that, above the target C:S ratio of 1.29, CaO is only partially incorporated in C-S-H phases. The
remaining portion might be present as Ca(OH)$_2$, which controls the Ca concentration in solution. With this, the actual C:S ratios of the C-S-H phases and, as a consequence of that the Si concentration in solution, are fixed.

### 3.2 Speciation calculations with Th(IV) and U(VI) under alkaline conditions

The speciation of Th(IV) under alkaline conditions between pH 10.0 and pH 13.3 is determined by the formation of one dominant hydrolysis product, Th(OH)$_4$(aq). The stability constants for the hydroxyl complexes were taken from Hummel et al. (2002). The solubility of Th(IV) under alkaline conditions was calculated using the solubility products for ThO$_2$(s) (Hummel et al. 2002). All constants involving reactions with Th(IV) are listed in Table 3.8. Constants for all other reactions needed in the calculations were taken from the core dataset in Hummel et al. (2002). Extrapolation to $I = 0.3$ was done using the Davies equation ($b = 0.3$). The maximum concentration of dissolved Th(IV) in ACW at pH 13.3 was estimated to be $3.0 \cdot 10^{-9}$ M on the assumption that ThO$_2$(s) controls the solubility.

**Tab. 3.8**: Relevant thermodynamic formation constants for Th(IV)-hydroxo species and Th(IV) solubility products (Hummel et al. 2002).

<table>
<thead>
<tr>
<th>Species</th>
<th>$\log_{10} \beta_0$ (I = 0)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th(OH)$_4$</td>
<td>-18.4±0.6</td>
<td>$\text{Th}^{4+} + 4\text{H}_2\text{O} \Leftrightarrow \text{Th(OH)}_4^0$(aq) + 4H$^+$</td>
</tr>
<tr>
<td>ThO$_2$(s)</td>
<td>9.9±0.8</td>
<td>$\text{ThO}_2$(s) + 4H$^+$ $\Leftrightarrow \text{Th}^{4+} + 2\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

The speciation of U(VI) under the alkaline conditions of the present study is dominated by the formation of hydrolysis products and silicate complexes at high Si concentrations. The concentration of U(VI)-carbonate complexes is not significant due to the low carbonate concentration in solution ($1.5 \cdot 10^{-8}$ M in ACW and $\leq 6 \cdot 10^{-4}$ M at pH 12.5, based upon the maximum concentration of CaCO$_3$ impurities in the chemicals given by the supplier). The relevant complexation constants involving reactions with U(VI), summarized in Table 9, were taken from Grenthe et al. (1992), Hummel et al. (2002) and Guillaumont et al. (2003). Constants for all other reactions needed in the calculations were taken from the core dataset in Hummel et al., 2002. The formation of silica polymeric species has been considered in the speciation calculations using the complexation constants reported in Grenthe et al. (1992) and the measured Si concentrations listed in Table 3.6. Nevertheless, the results showed that the concentration of these species is negligible in the systems relevant to the present study.

Selection of the solubility-limiting U(VI) phases for speciation calculations in the C-S-H systems needs to be discussed in more detail. Data for various oxides and hydroxides as well as alkali and alkaline-earth uranates and uranium silicates have been reported in the literature. The minerals listed in Table 3.9 have been considered due to
availability of well-established thermodynamic data. The solubility constants were taken from Grenthe et al. (1992) and Guillaumont et al. (2003) and include data derived from solubility experiments. Data based solely on thermochemical investigations have not been taken into account as suggested by Hummel et al. (2002).

Tab. 3.9: Relevant thermodynamic complexation constants for U(VI)-hydroxy complexes (Hummel et al. 2002; Guillaumont et al. 2003).

<table>
<thead>
<tr>
<th>Species</th>
<th>$\log_{10} \beta^0_0$</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{UO}_2(\text{OH})_2 (aq)$</td>
<td>-12.0±0.5</td>
<td>$\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_2 (aq) + 2\text{H}^+$</td>
</tr>
<tr>
<td>$\text{UO}_2(\text{OH})_3^{-}$</td>
<td>-19.2±0.4</td>
<td>$\text{UO}_2^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_3^{-} + 3\text{H}^+$</td>
</tr>
<tr>
<td>$\text{UO}_2(\text{OH})_4^{2-}$</td>
<td>-33±2</td>
<td>$\text{UO}_2^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_4^{2-} + 4\text{H}^+$</td>
</tr>
<tr>
<td>$\text{(UO}_2\text{)}_3(\text{OH})_7^{-}$</td>
<td>-31±2</td>
<td>$3\text{UO}_2^{2+} + 7\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_7^{-} + 7\text{H}^+$</td>
</tr>
<tr>
<td>$\text{(UO}_2\text{)}_4(\text{OH})_7^{+}$</td>
<td>-21.9±1.0</td>
<td>$4\text{UO}_2^{2+} + 7\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_4(\text{OH})_7^{+} + 7\text{H}^+$</td>
</tr>
<tr>
<td>$\text{UO}_2\text{SiO(OH)}_3^{+}$</td>
<td>-1.8±0.1</td>
<td>$\text{UO}_2^{2+} + \text{Si(OH)}_4 \rightleftharpoons \text{UO}_2\text{SiO(OH)}_3^{+} + \text{H}^+$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>$\log_{10} K_{s,0}^0$</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Na}_2\text{U}_2\text{O}_7 (cr)$</td>
<td>22.6±1.0</td>
<td>$\text{Na}_2\text{U}_2\text{O}_7(s) + 6\text{H}^+ \rightleftharpoons 2\text{UO}_2^{2+} + 2\text{Na}^+ + 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Schoepite</td>
<td>5.96±0.18</td>
<td>$\text{UO}_3 \cdot 2\text{H}_2\text{O} + 2\text{H}^+ \rightleftharpoons \text{UO}_2^{2+} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Becquerelite</td>
<td>40.5±1.6</td>
<td>$\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8\text{H}_2\text{O} + 14\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + 6\text{UO}_2^{2+} + 18\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Compreignacite</td>
<td>40.2±1.2</td>
<td>$\text{K}_3\text{U}<em>6\text{O}</em>{19} \cdot 11\text{H}_2\text{O}(cr) + 14\text{H}^+ \rightleftharpoons 2\text{K}^+ + 6\text{UO}_2^{2+} + 18\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Soddyte</td>
<td>6.2±1.0</td>
<td>$(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O} + 4\text{H}^+ \rightleftharpoons 2\text{UO}_2^{2+} + \text{Si(OH)}_4 + 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Uranophane</td>
<td>9.42±0.48</td>
<td>$\text{Ca}(\text{UO}_2)_2(\text{SiO}_4\text{OH})_2 \cdot 5\text{H}_2\text{O} + 6\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + 2\text{UO}_2^{2+} + 2\text{Si(OH)}_4 + 5\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

In the first series of speciation calculations, the concentration of U(VI) in solution was calculated with respect to the solubility of each single U(VI) solid phase for six selected solution compositions (Table 3.10 and 3.11). The six systems are considered to cover the wide range of chemical solution compositions that can be achieved in the different C-S-H systems used in the present study (Table 3.6 and Table 3.7). Hence, all systems contain Ca and Si. Na is present in the ACW systems as well as in those systems where C-S-H phases were prepared using the “solution reaction” method. In the latter systems,
the pH was adjusted to ~11.9 using NaOH. K is only present in the ACW systems and its concentration is fixed by the ACW composition (Table 3.6). The Si concentration is assumed to be $10^{-5}$ M in ACW and in the pure Ca(OH)$_2$ solutions. The latter concentration corresponds to the background Si concentration in ACW caused by Si impurities of the chemicals. In all calculations it is further assumed that the total U(VI) concentration is $10^{-4}$ M, which corresponds to the maximum U(VI) concentration used in the wet chemistry experiments. The dominating aqueous U(VI) species are calculated to be UO$_2$(OH)$_3^-$ in the systems with pH values ranging between 10.0 and 12.5, while both UO$_2$(OH)$_3^-$ and UO$_2$(OH)$_4^{2-}$ species are present in ACW at pH 13.3. Table 3.10 and Table 3.11 summarise the total equilibrium U(VI) concentrations determined from the speciation calculations for the selected geochemical conditions.

The U(VI) solubility limit with respect to schoepite is not reached in any system. The presence of becquerelite was found to depend on the aqueous U(VI) concentration as well as on the aqueous Ca concentration and pH: Assuming a Ca concentration of 1.6·$10^{-3}$ M in ACW (pH 13.3), the solubility limit of U(VI) with respect to becquerelite is not reached. The solubility of U(VI) controlled by becquerelite in Ca(OH)$_2$ solutions increases with increasing Ca concentration. Thus, in a 2·$10^{-5}$ M Ca(OH)$_2$ solution becquerelite forms at an U(VI) concentration of ~2·$10^{-5}$ M while at a Ca concentration of 2·$10^{-2}$ M, the system is undersaturated with respect to becquerelite at total U(VI) concentrations below 10$^{-4}$ M. The speciation calculations further show that the formation of negatively charged U(VI) hydroxyl complexes in solution increases with increasing pH, which further causes undersaturation of the system with respect to becquerelite. Furthermore, becquerelite is not expected to form in solutions used in the “solution reaction” method for C-S-H synthesis.

Na$_2$U$_2$O$_7$·xH$_2$O(c) is expected to form under ACW conditions and in the Na containing solutions used for C-S-H preparation following the “solution reaction” method. In ACW the solubility of this Na uranate is estimated to be 2.5·$10^{-7}$ M. The main hydrolysis species in equilibrium with the solid are UO$_2$(OH)$_3^-$ and UO$_2$(OH)$_4^{2-}$ under the latter conditions. In the Na containing solutions of pH 12 the U(VI) solubility with respect to Na$_2$U$_2$O$_7$·xH$_2$O(c) is estimated to be approximately 2·$10^{-6}$ M with the main U(VI) species in solution being UO$_2$(OH)$_3^-$ and the lower pH of the latter systems. Compreignacite is expected to form only in ACW systems. However, the U(VI) solubility with respect to this solid is too high (~4·$10^{-4}$ M) and therefore, the solubility limit cannot be reached under the experimental conditions used in the present study.
Tab. 3.10: Solubilities of various U(VI) solids for selected solution compositions relevant in conjunction with C-S-H preparation using the “direct reaction” method. (-) means that the solid does not form under the given experimental conditions.

<table>
<thead>
<tr>
<th>Solid</th>
<th>U(VI) solubility in:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ACW ([Ca] = 1.6·10^{-3} M, [Na] = 0.114 M, [K] = 0.18 M, [Si] = 10^{-5} M pH = 13.3)</td>
</tr>
<tr>
<td>Schoepite</td>
<td>-</td>
</tr>
<tr>
<td>Becquerelite</td>
<td>-</td>
</tr>
<tr>
<td>Na₂U₂O₇·xH₂O</td>
<td>2.5·10^{-7} M</td>
</tr>
<tr>
<td>Compreignacite</td>
<td>4·10^{-4} M</td>
</tr>
<tr>
<td>Soddyite</td>
<td>-</td>
</tr>
<tr>
<td>Uranophane</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.11: Solubilities of various U(VI) solids for selected solution compositions relevant in conjunction with the C-S-H preparation using the “solution reaction” method. (-) means that the solid does not form under the given experimental conditions.

<table>
<thead>
<tr>
<th>Solid</th>
<th>U(VI) solubility in:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.5·10^{-2} M Ca(OH)₂ [Si] = 10^{-5} M pH = 12.18</td>
</tr>
<tr>
<td>Schoepite</td>
<td>-</td>
</tr>
<tr>
<td>Becquerelite</td>
<td>-</td>
</tr>
<tr>
<td>Na₂U₂O₇·xH₂O</td>
<td>-</td>
</tr>
<tr>
<td>Compreignacite</td>
<td>-</td>
</tr>
<tr>
<td>Soddyite</td>
<td>-</td>
</tr>
<tr>
<td>Uranophane</td>
<td>10^{-5} M</td>
</tr>
</tbody>
</table>
Two uranium silicate minerals have been considered in the speciation calculations: Soddyite and uranophane. The calculations indicate that soddyite cannot precipitate in any system used in the present study. Uranophane, however, may form in some systems except in ACW solution, where undersaturation is predicted.

In a second series of speciation calculations the distribution of U(VI) species and the solubilities of potentially forming U(VI) minerals were calculated as a function of the U(VI) concentration in the alkaline systems. The U(VI) concentration was assumed to vary between $10^{-6}$ M and $10^{-4}$ M. The results of the speciation calculations are shown in Figs. 3.2a – 3.2f. Uranophane appears to be the potentially solubility-controlling solid phase, except in the ACW system, where $\text{Na}_2\text{U}_2\text{O}_7\cdot x\text{H}_2\text{O}$ seems to control the U(VI) concentration in solution. Under the chemical conditions corresponding to the “direct reaction” method, the U(VI) concentrations are estimated to be $5\cdot10^{-7}$ M in ACW (pH 13.3), $3\cdot10^{-7}$ M in a Ca(OH)$_2$ solution at pH 10.0 and $4.5\cdot10^{-5}$ M in a Ca(OH)$_2$ solution at pH 12.5.

The speciation calculations show that U(VI) minerals could form in the C-S-H systems above total U(VI) concentrations of about $10^{-7}$ M. The nature of the U(VI) solid formed, however, depends on the solution composition of the C-S-H suspensions.
Fig. 3.2 a-c: Speciation calculations with U(VI) under alkaline conditions (for details see text). All potentially forming U(VI) solid phases are considered.
Fig. 3.2 d-f: Speciation calculations with U(VI) under alkaline conditions (for details see text). All potentially forming U(VI) solid phases are considered.
3.3 Experimental investigations of the solubility limits of Th(IV) and U(VI) at high pH

3.3.1 Solubility limits of Th(IV) and U(VI) in ACW

The review of the existing thermodynamic data for Th(IV) and U(VI) as given in Hummel et al. (2002) showed that an unambiguous interpretation of the hydrolysis data is still missing and that, especially in the case of U(VI), thermodynamic data on the solubilities of most of the alkali and alkaline earth compounds are lacking. Due to this missing information it was decided to experimentally check the stability of Th(IV) and U(VI) tracer solutions prior to performing the sorption experiments.

The results of Th(IV) and U(VI) solubility tests carried out in ACW are displayed in Figs. 3.3a and 3.3b and Figs. 3.4a and 3.4b. The figures show the ratio of the radionuclide concentration determined in solution to the total added radionuclide concentration (Figs. 3.3a and 3.3b) and the solution concentrations of the radionuclides as a function of the added radionuclide concentration in solution (Figs. 3.4a and 3.4b). The data refer to measured concentrations before centrifugation (1 hour at 95000 g) and after centrifugation. Note that particles with diameter larger than ~15 nm are expected to settle during centrifugation. Thus, the concentration determined after centrifugation represents the concentration of dissolved radionuclides plus the concentration of radionuclides associated with colloidal material smaller than ~15 nm. The error bars indicate 95% confidence intervals (1.96σ) calculated from 5 replicates.

In the case of Th(IV), the reduction in the concentration was found to range in value between 40% and 80% of the initial Th(IV) concentration added to ACW. This reduction determined before centrifugation and over the entire concentration range was caused by wall sorption. The percentage of the solution concentration before centrifugation was found to be consistently lower after 30 days than after 1 day equilibration. This indicates that Th(IV) sorption onto the container walls is a slow process. Centrifugation for 1 hour at 95000 g caused an additional reduction in solution concentrations at the highest Th(IV) concentrations. In Fig. 3.3b the continuous line with slope 1 represents the case where the initial concentration in solution (corrected for wall sorption) is completely recovered in solution. The data obtained before centrifugation fall on this line.

At starting Th(IV) concentrations ≥ 10⁻⁸ M, a constant Th(IV) concentration in solution of approximately 5·10⁻⁹ M was determined after centrifugation. This can be explained by the formation of Th(IV) radiocolloids or a Th(IV) solid phase, which formed in ACW and settled during centrifugation. Note that the observed solution concentration is close to the Th(IV) concentration in equilibrium with ThO₂(s) in ACW (shaded area in Fig. 3.3b). Based on these measurements it was concluded that the initial Th(IV) concentration added to ACW should be below 10⁻⁹ M to avoid the formation of colloidal ThO₂(s).
Fig. 3.3: Solubility limits of Th(IV) in ACW. a) Percentage of the Th(IV) inventory measured in solution before (open symbols) and after (closed symbols) centrifugation as function of the total Th(IV) inventory. b) Th(IV) concentration measured in solution before (open symbols) and after (closed symbols) centrifugation as function of the total Th(IV) inventory. Equilibration times were 1 day and 30 days. The curves in a) only serve as a guide to the eye. The shaded area in b) represents the calculated Th(IV) solubility limit with its uncertainty in ACW with respect to ThO₂(s). The line with slope +1 represents 100% recovery in solution.
Fig. 3.4: Stability of U(VI) solutions in ACW. a) Percentage of the U(VI) inventory measured in solution before (open symbols) and after (closed symbols) centrifugation as function of the total U(VI) inventory. b) U(VI) concentration measured in solution before (open symbols) and after (closed symbols) centrifugation as function of the total U(VI) inventory. Equilibration times were 1 day and 30 days. The curves in a) only serve as a guide to the eye. The horizontal line in b) represents the calculated Na₂U₂O₇(s) solubility limit in ACW. The line with slope +1 represents 100% recovery in solution.
In the case of the U(VI)-ACW system no reduction in the U(VI) concentration due to wall sorption was observed. Furthermore, the difference in the concentrations after equilibration for 1 day and 30 days was negligible. No reduction in the solution concentrations were observed before and after centrifugation up to starting concentrations of about $2 \cdot 10^{-6}$ M (Fig. 3.4b). The data fall on the line with slope = 1 in Fig. 3.4b. Above this concentration threshold, however, the portion of added U(VI) that remained in solution after equilibration was found to decrease presumably due to the formation of a U(VI) solid phase. This decrease was more pronounced after centrifugation (Fig. 3.4a). The U(VI) concentration in solution was found to be constant at about $7 \cdot 10^{-6}$ M. Note that this concentration is about a factor of 30 above the solubility limit of Na$_2$U$_2$O$_7$ (~$2.6 \cdot 10^{-7}$ M) (Fig. 3.4b). Thus, the speciation calculations indicate that the latter phase could limit U(VI) solubility in ACW. Based on the above findings it was concluded that the initial U(VI) concentration in ACW should not exceed $7 \cdot 10^{-6}$ M.

### 3.3.2 Solubility limits of Th(IV) and U(VI) at pH < 13.3

The solubility limits for Th(IV) in alkaline solution of pH < 13.3 was not investigated in detail as no major changes in the speciation distribution was expected with decreasing pH. Th(OH)$_4$ is the dominating species and the formation of Th-Si complexes and Th-carbonate complexes is negligible.

The results of the solubility tests with U(VI) in solutions of pH $\leq 12$, having compositions typically found in equilibrium with C-S-H phases, are shown in Figs. 3.5 - 3.11. The solution compositions account for increasing Ca concentrations and decreasing Si concentrations.

Figs. 3.5 and 3.7 show that the U(VI) concentrations determined in solution before and after centrifugation were between 10% and 20% lower than the initial U(VI) concentration in a 0.015 M Ca(OH)$_2$ solution below a total U(VI) concentration of $2 \cdot 10^{-6}$ M. This difference between added and solution concentrations is retained over the concentration range between $2 \cdot 10^{-8}$ M and $2 \cdot 10^{-6}$ M, indicating sorption on the walls of the centrifuge tubes. In the measurements taken after 7 days equilibration, the centrifuge tubes were washed with 0.1 M HCl to remove U(VI) sorbed on the walls. U(VI) was recovered in the acidic solution after the treatment, which confirms that wall sorption took place (Fig. 3.6).

Significant activity reduction was observed above a total U(VI) concentration of $2 \cdot 10^{-6}$ M both in the samples measured before and after centrifugation. This reduction in the U(VI) concentration is attributed to the formation of colloidal U(VI) solid phases. The observed reduction before centrifugation is due to the formation of larger U(VI) colloids, which already settled before centrifugation. The activity reduction observed after centrifugation, however, is attributed to the presence of smaller colloids suspended in solution, which settled during centrifugation. Based on these tests it was concluded that U(VI) solutions containing 0.015 M Ca are stable up to an U(VI) concentration of about $2 \cdot 10^{-6}$ M.
Fig. 3.5: Percentage of the total U(VI) recovered in 1.5·10⁻² M Ca(OH)₂ solution (pH 12.18) before (□, ○) and after (■, ●) centrifugation shown as a function of the total U(VI) concentration. Equilibration times were 1 day and 7 days.

Fig. 3.6: Mass balance for U(VI) in the stability test carried out in 1.5·10⁻² M Ca solution after 7 days equilibration.
Fig. 3.7: U(VI) concentration in $1.5 \times 10^{-2}$ M Ca(OH)$_2$ solution (pH 12.18) before (□, ○) and after (■, ●) centrifugation as a function of the total U(VI) concentration. Equilibration times were 1 day and 7 days.

Figs. 3.8 and 3.9 show that in an U(VI) solution with a Ca concentration of $3 \times 10^{-3}$ M no activity reduction was observed before and after centrifugation up to the total U(VI) concentration of $10^{-5}$ M. Above this concentration threshold, a small reduction was observed before centrifugation. However, the reduction was more pronounced after centrifugation ($\geq 60\%$), suggesting the presence of colloidal U(VI) solid phase. Fig. 3.10 further indicates that U(VI) solutions were stable in the presence of $3 \times 10^{-3}$ M Ca, $10^{-4}$ M Si and $10^{-2}$ M Na, up to a total U(VI) concentration of approximately $10^{-5}$ M.

The results from the solubility test carried out in the presence of $5 \times 10^{-5}$ M Ca, $2 \times 10^{-3}$ M Si and $2 \times 10^{-2}$ M Na (Figs. 3.10 and 3.11) finally showed that no activity reduction occurs neither by wall sorption nor by precipitation after centrifugation under these conditions. The U(VI) solutions were stable in the concentration range covered in the experiments, i.e. up to a total U(VI) concentration of $10^{-4}$ M.

The above tests show that the solubility limit of U(VI) in the pH range between 12 - 12.5 depends on the ionic composition of the solutions. However, the data further show a clear trend: The stability of the U(VI) solution increases with decreasing Ca concentration and increasing Si concentration (compare Figs. 3.7 ([Ca] = 0.015 M, [Si] = $10^{-5}$ M), Fig. 3.9 ([Ca]=3$\times 10^{-3}$ M, [Si]=1$\times 10^{-4}$ M, [Na]=1$\times 10^{-2}$ M) and Fig. 3.11 ([Ca]=5$\times 10^{-5}$ M, [Si]=2$\times 10^{-3}$ M, [Na]=2$\times 10^{-2}$ M)), indicating that U(VI) is more soluble in the C-S-H-type solutions at low Ca concentration and high Si concentration. The speciation calculations discussed in section 3.2 (Figs. 3.2a – 3.2f) performed using exactly the same Ca and Si concentrations as in the solubility tests, suggest that U(VI) solubility could be controlled by a Ca-U(VI) silicate phase, i.e. uranophane, under these conditions. From these calculations it is anticipated that U(VI) should be more soluble in the solutions with low Si concentrations than at high Si concentrations. Note that the
availability of Si is considered to be the limiting factor for uranophane formation in these systems (excess Ca). The experimental observations, however, clearly contradict the results from the speciation calculations. U(VI) was found to be more soluble with increasing Si concentration (compare Figs. 3.7 and 3.11). Thus, we can exclude that uranophane is the solubility-limiting phase under the given conditions.

Fig. 3.8: Percentage of total U(VI) dissolved in a synthetic solution ([Ca] = 3·10⁻³ M, [Si] = 10⁻⁴ M, [Na] = 10⁻² M, pH 12.09) before (□, ○) and after (■, ●) centrifugation as function of the total U(VI) concentration. Equilibration times were 1 day and 7 days.

Fig. 3.9: U(VI) concentration in a synthetic solution ([Ca] = 3·10⁻³ M, [Si] = 10⁻⁴ M, [Na] = 10⁻² M, pH 12.09) before (□, ○) and after (■, ●) centrifugation as a function of the total U(VI) concentration. Equilibration times were 1 day and 7 days.
Fig. 3.10: Percentage of total U(VI) dissolved in a simulated solution ([Ca] = 5 \times 10^{-5} \text{ M}, [Si] = 2 \times 10^{-3} \text{ M}, [Na] = 2 \times 10^{-2} \text{ M}, pH 11.96) before (□, ○) and after (■, ●) centrifugation as a function of the total U(VI) concentration. Equilibration times were 1 day and 7 days.

Fig. 3.11: U(VI) concentration in a synthetic solution ([Ca] = 5 \times 10^{-5} \text{ M}, [Si] = 2 \times 10^{-3} \text{ M}, [Na] = 2 \times 10^{-2} \text{ M}, pH 11.96) before (□, ○) and after (■, ●) centrifugation as a function of the input U(VI) concentration. Equilibration times were 1 day and 7 days.
Ca-uranate comprises the other category of potentially solubility-limiting U(VI) solid phases, which could limit the U(VI) concentration in these systems. Becquerelite is the only well-characterized Ca-uranate for which sufficiently detailed solubility measurements have been performed (Guillaumont et al. 2003). In the present systems (pH ≥ 12), however, the U(VI) solubility controlled by becquerelite is estimated to be above 10⁻⁴ M, suggesting that the observed formation of U(VI) precipitates in the solubility experiments cannot be attributed to becquerelite formation. For the other Ca-uranates listed in Guillaumont et al. (2003) solubility constants were mainly obtained from calorimetric experiments. Hummel et al. (2002) concluded that solid phases identified and characterized in calorimetric experiments at high temperature may often not be representative for aqueous systems. CaUO₄(s) is the only Ca-uranate given in Guillaumont et al. (2003) for which solubility data were deduced from wet chemistry experiments. The phase has been identified and characterized by Moroni & Glasser (1995). Macé et al., 2013 and Tits et al., 2015 showed that U(VI) species having a structure similar to CaUO₄(s), are present as surface precipitates in U(VI) loaded C-S-H phases and HCP. Using the experimental data reported in the latter work, Guillaumont et al. (2003) estimated the solubility product for the following reaction:

\[
CaUO_4(s) + 4H^+ ⇔ Ca^{2+} + UO_2^{2+} + 2H_2O \quad \log_{10} K_{s,0}^0 = 23.1
\]  

(3.7)

Conversion of the estimated solubility product into a Gibbs energy of formation, \( \Delta_f G_m^0 \), as given in Guillaumont et al. (2003), results in a value of -1848 kJ mol⁻¹. This value is significantly different from the Gibbs energy of formation for CaUO₄(s) of -1888.7 kJ mol⁻¹ determined from thermochemical measurements (Grenthe et al. 1992).

In the frame of this study, speciation calculations were carried out using the solubility product of CaUO₄(s) as derived by Guillaumont et al. (2003). With this approach excellent agreement between predicted and experimental data was achieved for all relevant solution compositions used in the present study (Table 3.12). Note that for the latter speciation calculations all other U(VI) solids were ignored. Additional speciation calculations performed by including all U(VI) solid phases resulted in the species distributions shown in Figs. 3.2a – 3.2f in which uranophane and Na₂U₂O₇·xH₂O appear to be the solubility-limiting phases. Note that CaUO₄(s) is more soluble than the other U(VI) solid phases taken into account. In view of the excellent agreement between modelled and experimental U(VI) concentrations it was concluded that a CaUO₄-type phase may be the phase controlling U(VI) solubility in C-S-H systems. The solubility of this phase can be described based on the thermodynamic data deduced in Guillaumont et al. (2003) (log₁₀ \( K_{s,0}^0 = 23.1 \)) for the CaUO₄(s) phase identified by Moroni & Glasser (1995). Nevertheless, the speciation calculations further show that the solubility limits of the other U(VI) solid phases that could form under the given experimental conditions are significantly lower. This could suggest that CaUO₄(s) is a metastable phase in these systems, and that Na₂U₂O₇·xH₂O, becquerelite or uranophane, respectively, could control the U(VI) concentration in cementitious systems in the long term.
Tab. 3.12: Comparison of the calculated CaUO₄(s) solubility with the experimentally determined U(VI) concentrations for the relevant solutions compositions used in this study.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>U(VI) solubility calculated with ( \log_{10} K_{s,o}^{0} = 15.9 )</th>
<th>U(VI) solubility calculated with ( \log_{10} K_{s,o}^{0} = 23.1 )</th>
<th>Experimental U(VI) solubility in solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACW</td>
<td>2 \cdot 10^{-13} M</td>
<td>7 \cdot 10^{-6} M</td>
<td>(1 \pm 0.2) \cdot 10^{-5} M</td>
</tr>
<tr>
<td>1.5 \cdot 10^{-2} M Ca(OH)₂, pH 12.18</td>
<td>1.6 \cdot 10^{-13} M</td>
<td>3 \cdot 10^{-6} M</td>
<td>(4 \pm 1) \cdot 10^{-6} M</td>
</tr>
<tr>
<td>3 \cdot 10^{-3} M Ca, 10^{-2} M Na, 10^{-4} M Si, pH 12.09</td>
<td>9 \cdot 10^{-13} M</td>
<td>2 \cdot 10^{-5} M</td>
<td>(3 \pm 0.5) \cdot 10^{-5} M</td>
</tr>
<tr>
<td>5 \cdot 10^{-5} M Ca, 2 \cdot 10^{-2} M Na, 2 \cdot 10^{-3} M Si, pH 11.96</td>
<td>10^{-10} M</td>
<td>No precipitation</td>
<td>No precipitation</td>
</tr>
</tbody>
</table>

1 Selected by Grenthe et al. (1992) and retained by Guillaumont et al. (2003)
2 Derived by Guillaumont et al. (2003) using the data of Moroni & Glasser (1995)

3.4 Th(IV) sorption and co-precipitation experiments

3.4.1 Th(IV) uptake by C-S-H phases prepared using the “solution reaction” method

The results from the Th(IV) sorption and co-precipitation kinetic experiments with C-S-H phases prepared using the “solution reaction” method are shown in Fig. 3.12 (pH = 13.3) and Fig. 3.13 (pH ~ 12). The error bars indicate the 95% confidence interval (1.96\(\sigma\)) calculated from four replicates. Note that the actual C:S ratio of the C-S-H phase with a target C:S ratio of 0.65 is 0.73 because a significant portion of Si was dissolved in the equilibrium solution. For the other C-S-H phases, however, target and actual C:S ratios agree.

The \( R_d \) values determined in all sorption and co-precipitation tests were found to be very high (\( R_d > 5 \cdot 10^4 \) L kg\(^{-1}\)) both in ACW and at pH ~12. Furthermore, sorption and co-precipitation kinetics were fast and equilibrium was reached within one day. The \( R_d \) values were found to be constant within the uncertainty for the investigated time period (up to 120 days). Note, however, the very large scatter in the data caused by the large uncertainty on the measurements. This large uncertainty is attributed to the high \( R_d \) values measured in these experiments. Equation 2.1 shows that the \( R_d \) value is the ratio of the amount of Th(IV) sorbed (mol kg\(^{-1}\)) and the equilibrium Th(IV) concentration in solution (M). When the sorption is high, the solution concentration is very small and the
smallest C-S-H particles (with high Th(IV) loading) remaining in solution after centrifugation have a significant influence on the measured $R_d$ value.

Concerning dependence on the solid phase composition it was observed that the $R_d$ values are the same for all C-S-H phases irrespective of the C:S ratios. Note that the $R_d$ values determined in the co-precipitation experiments tended to be slightly higher than those obtained from the sorption experiments, although the difference is hardly significant within the experimental uncertainties.

### 3.4.2 Th(IV) uptake by C-S-H phases prepared using the “direct reaction” method

The results from the Th(IV) sorption kinetic tests and co-precipitation kinetic tests in ACW and in alkali-free solutions (pH = 10 - 12.5) with C-S-H phases prepared using the “direct reaction” method are shown in Figs. 3.14 - 3.19 (uncertainties corresponding to 95% confidence interval (1.96$\sigma$) from four replicates). The figures show all data except a few outliers which were rejected in advance based on the $R_{d,max}$ criteria (Tits et al. 2002). $R_{d,max}$ denotes the largest $R_d$ values which can be determined based on an acceptable counting statistics. The value of $R_{d,max}$ depends on the lowest $^{228}$Th activity, $A_{\text{min}}$, measurable in solution. The lowest measurable $^{228}$Th activity is further determined by the background activity and by the maximum in the allowed relative uncertainty on the activity measurements. This value is generally fixed at 10% (Tits et al. 2002). In the present study some $R_d$ values which were calculated based on the activity measurements, were found to be larger than $R_{d,max}$. These values were rejected.

The results from the sorption and co-precipitation studies with C-S-H phases prepared using the “direct reaction” method are comparable to those previously reported for the C-S-H phases prepared using the “solution reaction” method: 1) The $R_d$ values determined in all sorption and co-precipitation tests were very high ($R_d > 10^7$ L kg$^{-1}$) both in ACW (Figs. 3.14 – 3.17) and in the pH range 10 - 12.5 (Figs. 3.18 and 3.19); 2) Uptake was fast, and equilibrium was reached within one day; 3) $R_d$ values were constant within the uncertainty for the investigated time period (up to 120 days); 4) $R_d$ values were independent of the C:S ratios taking into account the uncertainties on the data; 5) $R_d$ values obtained from the co-precipitation experiments tended to be slightly higher than those determined in the sorption experiments (factor of about 2-5). Thus, it is inferred that strong Th(IV) uptake occurs on all C-S-H phases, and the influence of the C-S-H composition (C:S ratio) is negligibly small. Furthermore, Th(IV) binding to C-S-H phases seems to be slightly enhanced in the co-precipitation samples.
Fig. 3.12: Th(IV) sorption and co-precipitation kinetics on C-S-H phases prepared in ACW using the “solution reaction” method with target C:S ratios of 0.65, 0.9, 1.10 and 1.65. Experimental conditions were as follows: pH 13.3; S:L ratios: 1.25 - 1.56 g L\(^{-1}\) at C:S = 0.65, 1.23 - 1.57 g L\(^{-1}\) at C:S = 0.9, 0.98 - 1.58 g L\(^{-1}\) at C:S = 1.1, 0.73 - 1.12 g L\(^{-1}\) at C:S = 1.65; total Th(IV) concentration = 10\(^{-11}\) M.

Fig. 3.13: Th(IV) sorption and co-precipitation kinetics on C-S-H phases prepared using the “solution reaction” method with C:S ratio of 0.65, 0.9, and 1.1 (target values). Experimental conditions were as follows: pH varied between 10.5 (C:S = 0.65) and 12.0 (C:S = 1.1); S:L ratios: 0.86 - 1.1 g L\(^{-1}\) at C:S = 0.65, 0.73 - 0.92 g L\(^{-1}\) at C:S = 0.9, and 0.50 - 0.79 g L\(^{-1}\) at C:S = 1.1; total Th(IV) concentration = 10\(^{-11}\) M.
Fig. 3.14: Th(IV) sorption kinetics and desorption for a C-S-H phases with an actual C:S ratio of 1.07 in ACW (pH 13.3) synthesised following the “direct reaction” method.

Fig. 3.15: Th(IV) co-precipitation kinetics and desorption for a C-S-H phases with an actual C:S ratio of 1.07 in ACW (pH 13.3) synthesised following the “direct reaction” method.
Fig. 3.16: Effect of ageing on the Th(IV) sorption kinetics for three C-S-H phases with different actual C:S ratio in ACW (pH 13.3) synthesised following the “direct reaction” method.

Fig. 3.17: Th(IV) co-precipitation kinetics for two C-S-H phases with different actual C:S ratios in ACW (pH 13.3) synthesised following the “direct reaction” method.
Fig. 3.18: Th(IV) sorption kinetics for four C-S-H phases with different actual C:S ratios in the equilibrium solutions (pH ranges from 10 to 12.5) synthesised following the “direct reaction” method.

Fig. 3.19: Th(IV) co-precipitation kinetics for four C-S-H phases with different actual C:S ratios in the equilibrium solutions (pH ranges from 10 to 12.5) synthesised following the “direct reaction” method.
Desorption of Th(IV) from the C-S-H phase with C:S ratio = 1.07 was checked under ACW conditions (Figs. 3.14 and 3.15). The $R_d$ values obtained from desorption tests were found to be slightly higher than those determined in the sorption experiments, in those samples equilibrated for 1 day and 20 days, while they are similar in value within the expected uncertainty range in the samples equilibrated for longer time periods. Note that desorption experiments are difficult as the Th(IV) concentrations involved are extremely low. The slightly higher desorption $R_d$ values after 1 day and 20 days equilibration should therefore be interpreted with caution. Thus, the overall conclusion from these findings is that Th(IV) binding to C-S-H phases is a reversible process.

Ageing was found to be a parameter that could influence Th(IV) uptake by C-S-H phases. Fig. 3.16 shows that the $R_d$ values appear to be a factor of about 5 lower for a C-S-H phase with C:S ratio = 0.96 aged for 7 months than for the C-S-H phases with C:S ratios = 0.75 and 1.07 aged for two weeks. Nevertheless, it should be noted that this conclusion is based on a single data set, and on the assumption that the $R_d$ values of C-S-H phases aged for two weeks should be the same irrespective of the C:S ratios of the solids. The latter assumption holds if all data are taken into account. Nevertheless, a factor of 5 variation in the data was found to be common in all experiments due to strong uptake of Th(IV) by these phases. Thus, this observation implies that the lower $R_d$ value consistently observed for C-S-H phase with C:S = 0.96 could be within the variability of the data sets. However, on the assumption that the differences in $R_d$ values between fresh and aged C-S-H phases are significant, the data suggest a pronounced effect of the ageing of C-S-H phases on Th(IV) uptake. This finding could be explained by the slow transformation of initially amorphous C-S-H phases into (micro) crystalline tobermorite-like C-S-H phases formed with increasing ageing period, which have a lower specific surface area. To date, however, no independent and comprehensive data set exists that could support the above conclusions.

### 3.4.3 Summary and conclusions

The Th(IV) sorption data obtained for the two different types of C-S-H phases are very similar within the expected uncertainties, indicating that the method used for C-S-H synthesis has no significant influence on Th(IV) uptake. Nevertheless, some general observations that are true for both C-S-H phases can be outlined: 1) $R_d$ values are extremely high in all experiments, ranging in value from $10^5$ L kg$^{-1}$ to $10^7$ L kg$^{-1}$, with no measurable effect of the solution composition (e.g. pH). Note again that uncertainties on the experimental data are large, which does not allow small trends in the data to be discerned clearly. 2) No significant effect of the solid composition, in particular the C:S ratio, on the $R_d$ value is indicated neither in the experiments carried out in ACW (pH = 13.3) nor those carried out in the pH range 10 - 12.5. 3) Sorption and co-precipitation kinetics are very fast, i.e., maximum Th(IV) uptake was reached within 1 day. 4) Th(IV) uptake seems to be reversible. 5) Some of the data determined in ACW and in the pH range 10 - 12.5, suggest that the $R_d$ values determined in the co-precipitation tests are slightly higher ($10^6$ L kg$^{-1}$ to $10^7$ L kg$^{-1}$) than those obtained from the sorption experiments ($10^5$ L kg$^{-1}$ to $10^6$ L kg$^{-1}$). This would indicate that Th(IV) is partly incorporated into the C-S-H structure during formation of the C-S-H phases (co-precipitation). 6) Ageing of the C-S-H phases seems to exert a small effect on Th(IV)
uptake which is tentatively explained by the formation of micro-crystalline C-S-H phases with reduced specific surface areas.

The results obtained in the framework of this study can be compared with those from earlier in-house investigations (Wieland et al. 1998; Tits et al. 2000; Wieland et al. 2002; Wieland et al. 2004). The observed strong Th(IV) uptake by the C-S-H phases agrees with these earlier findings. In all cases \( R_d \) values for Th(IV) ranging in value from \( 10^5 \) L kg\(^{-1} \) to \( 10^7 \) L kg\(^{-1} \) were reported for cementitious systems in the absence of complexing agents. This corroborates our finding that Th(IV) binds strongly onto C-S-H phases irrespective of the method used for C-S-H synthesis as well as the solution or solid (C:S ratio) compositions. Since a large set of consistent data for Th(IV) uptake by C-S-H phases and hardened cement paste is already available it was decided to refrain from additional experimental work, in particular measurements of sorption isotherms.

The present study shows that Th(IV) (and presumably other fourvalent actinides) in a cementitious waste repository are strongly bound onto the C-S-H phases in the cement matrix. This conclusion holds for all C-S-H phases, irrespective of the C:S ratio. Therefore, the degradation of the cementitious materials, which takes place with progressing service life of the repository and results in increasing C:S ratios of the C-S-H phases, will not have a detrimental effect on the retention of fourvalent actinides in the cement-based near field of a repository. Only a complete degradation of the cementitious materials (i.e. complete dissolution of the C-S-H phases) might affect the retention of the fourvalent actinides, but even then it is to be expected that these types of radionuclides will strongly be taken up by other solids in the degraded near field, such as calcite.

### 3.5 U(VI) sorption and co-precipitation experiments

#### 3.5.1 U(VI) uptake by C-S-H phases prepared using the “solution reaction” method

The results of U(VI) sorption and co-precipitation kinetics experiments with C-S-H phase prepared using the “solution reaction” method are shown in Fig. 3.20 (pH = 13.3) and Fig. 3.21 (pH = 11.9). Note again that the actual C:S ratio of the C-S-H phase with target C:S ratio of 0.65 is either 0.73 (in low alkali media) or 0.74 (in ACW) because a significant portion of Si was dissolved in the equilibrium solution. The C-S-H phase with a target C:S ratio of 1.65 in ACW turned out to have an actual C:S ratio of 1.47 because a significant portion of Ca was dissolved in the equilibrium solution. For the other C-S-H phases, however, target and actual C:S ratios agree.

The \( R_d \) values for U(VI) uptake by C-S-H phases are lower in ACW of pH = 13.3 (\( R_d > 10^3 \) L kg\(^{-1} \)) than in the solution of pH = 11.9 (\( R_d > 10^5 \) L kg\(^{-1} \)). Reduction of U(VI) uptake with increasing pH is attributed to differences in U(VI) speciation in solution. At pH = 13.3 \( \text{UO}_2(\text{OH})_3^- \) and \( \text{UO}_2(\text{OH})_4^{2-} \) are the dominant hydrolysis species. At a pH ~ 12, however, \( \text{UO}_2(\text{OH})_3^- \) dominates. Thus, reduction in the \( R_d \) value by one order of a magnitude can tentatively be explained by the higher concentration of the
hydrolysis species (mass action). Nevertheless, the uptake process is more complex in C-S-H systems. It will be shown that U(VI) uptake also increases with increasing Ca concentration in solution. Note further that the Ca concentration increases with decreasing pH in the C-S-H systems.

Time dependence of the $R_d$ values is similar in ACW and at pH = 11.9 (Figs. 3.20 and 3.21). $R_d$ values reach a maximum after approximately 20 days equilibration in all experiments. Subsequently, $R_d$ values remained constant over the investigated time period (up to 120 days). An influence of the C:S ratio on the $R_d$ value could not be determined equivocally due to significant uncertainties on the kinetic data, which does not allow possibly small trends in the data to be discerned. The kinetic data further show that the $R_d$ values determined in the co-precipitation experiments tended to be higher than those obtained from the sorption experiments. Nevertheless, differences are small and hardly significant taking into account uncertainties on the data.

Sorption isotherms were determined for C-S-H phases synthesized in solutions at pH ~ 12 with target C:S ratios of 0.65 and 1.10 and in ACW (pH = 13.3) with target C:S ratios of 0.64 and 1.09 (Fig. 3.22). All isotherms were found to be non-linear, thus suggesting involvement of more than one uptake process. The sequence of processes (e.g. binding to different surface sites) seems to be dependent on the U(VI) concentration in the system.

The results from the isotherm measurements at pH = 11.9 and at pH = 13.3 further show a clear trend to higher $R_d$ values with increasing C:S ratios of the C-S-H phases. These observations suggest that U(VI) uptake by C-S-H phases depends on the Ca concentration in solution, i.e. U(VI) uptake increases with increasing Ca concentration in solution. Note that the equilibrium Ca concentration of a C-S-H phase with C:S ratio of about 0.7 is more than an order of a magnitude lower than the equilibrium Ca concentration of a C-S-H phase with C:S ratio of about 1.1 (Table 3.7). The finding that U(VI) uptake increases with increasing Ca concentration is in contrast to observations from previous studies on Sr(II) and Ra(II) uptake by C-S-H phases (Tits et al. 2006a and b).
Fig. 3.20: U(VI) sorption and co-precipitation kinetics on C-S-H phases with target C:S ratios of 0.65, 0.9, 1.1 and 1.65 in ACW (pH = 13.3; solution composition see Table 3.7) prepared with the “solution reaction” method. Experimental conditions: S:L ratios = 1.23 – 2.51 g L⁻¹ at C:S = 0.65, 1.21 – 2.44 g L⁻¹ at C:S = 0.9, 0.82 – 2.39 g L⁻¹ at C:S = 1.1, 1.12 – 1.89 at C:S = 1.65; total U(VI) concentration = 10⁻⁶ M.

Fig. 3.21: U(VI) sorption and co-precipitation kinetics using C-S-H phases with target C:S ratios of 0.65, 0.9, and 1.1 in solutions at pH ≈ 11.9; solution composition see Table 3.7) prepared using the “solution reaction” method. Experimental conditions: S:L ratios = 0.80 - 1.19 g L⁻¹ at C:S = 0.65, 0.71 – 1.08 g L⁻¹ at C:S = 0.9, 0.60 - 0.96 g L⁻¹ at C:S = 1.1; total U(VI) concentration = 10⁻⁶ M.
Fig. 3.22: U(VI) sorption isotherm on C-S-H phases with target C:S ratios of 0.65 and 1.10 in solutions at pH = 11.9 and in ACW prepared using the “solution reaction” method. a) The concentration of U(VI) sorbed versus the equilibrium U(VI) concentration. The solid lines represent fits on the basis of Langmuir isotherms. b) Ca and Si concentrations in solution.
3.5.2 U(VI) uptake by C-S-H phases prepared using the “direct reaction” method

The results of the sorption kinetic experiments for C-S-H phases prepared using the “direct reaction” method in ACW and in alkali-free solutions (pH 11.4 - 12.5) are shown in Figs. 3.23 and 3.24. The $R_d$ values determined for the different C-S-H phases ranged in value between $10^2$ L kg$^{-1}$ in ACW and $10^5$ L kg$^{-1}$ in alkali-free solution. U(VI) uptake was stronger in the pH range between 11.4 and 12.5 than in ACW (pH = 13.3). Time dependence of the $R_d$ values was similar in ACW and at pH ~ 12 (Figs. 3.23 and 3.24). $R_d$ values reached a maximum after ~ 20 days equilibration in most of the experiments. In ACW U(VI) was found to exhibit a significantly different behaviour depending on the C:S ratio. It should be noted that the results from sorption kinetics studies on C-S-H phases synthesised using the “solution reaction” method did not show an effect of the C:S ratio on the uptake kinetics. Therefore, it is inferred that this variation in kinetics behaviour is due to the high uncertainty on the data. Note that, generally, the sorption data on these C-S-H phases are consistent with those determined on the C-S-H phases synthesized using the “solution reaction” method.

The observations made in the co-precipitation experiments were similar to those in the sorption experiments (Figs. 3.25 and 3.26), i.e., high co-precipitation $R_d$ values reaching a maximum after ~ 20 days, no effect of the C:S ratio and stronger uptake in the pH range between 11.4 and 12.5 than in ACW (pH = 13.3). Note, however, that the $R_d$ values obtained from the co-precipitation experiments in ACW were significantly higher than those determined in the sorption experiments (compare Figs. 3.23 and 3.25). The difference in $R_d$ values was about one order of magnitude for the same C:S ratios. By contrast, no difference in the $R_d$ values deduced from the sorption and co-precipitation experiments was observed in alkali-free solution within the uncertainty on the data (compare Figs. 3.24 and 3.26). Note further that the observed difference in U(VI) uptake by co-precipitation with C-S-H phases or due to sorption was less evident in the previous experiments with the C-S-H phases prepared using the “solution reaction” method (Fig. 3.20), although a similar trend was anticipated. At present, the latter observation cannot be explained conclusively.

In the framework of this study four U(VI) sorption isotherms on C-S-H phases prepared using the “direct reaction” were determined (Fig. 3.27). Two isotherms were determined in ACW using C-S-H phases with C:S ratios = 0.75 and 1.07. Two additional isotherms were determined in alkali-free solutions (pH ~ 12) using a freshly prepared C-S-H phase and a C-S-H phase aged for more than 6 months with a C:S ratio of 1.07. The latter isotherms were determined to assess whether or not ageing has an effect on U(VI) uptake. Comparison of the isotherm data obtained in ACW and in alkali-free solution shows that U(VI) uptake by C-S-H phases was higher at pH ~ 12 than at pH = 13.3 in agreement with the kinetic data. These results are further consistent with those obtained on the C-S-H phases prepared using the “solution reaction” method (see previous section). In there, it was shown that U(VI) uptake by C-S-H phases depends on the Ca concentration in solution. Therefore, increasing uptake at decreasing pH suggests increasing Ca concentration, which was confirmed by the ionic compositions of the solutions (Fig. 3.27b). All isotherms were found to be slightly non-linear, thus suggesting involvement of more than one uptake process, such as binding to two
different sorption sites, which depends on the U(VI) concentration in the system. Non-linear sorption behaviour was more pronounced in ACW than in alkali-free solution (see e.g. Fig. 3.27a). Note that non-linear sorption isotherms were already observed for the C-S-H phases prepared using the “solution reaction” method (Fig. 3.22a). Thus, non-linear sorption of U(VI) seems to be a common phenomena irrespective of the procedure used for C-S-H synthesis. Another interesting finding concerns the U(VI) solubility in these systems. Although the maximum U(VI) concentration of about $10^{-6}$ M, for which U(VI) solutions were found to be stable (see sections 3.3.1 and 3.3.2), was exceeded in the isotherm experiments, the formation of a pure U(VI) bearing phase is not indicated from the isotherm data. In case of solid phase formation the U(VI) concentration in solution should be fixed at a constant concentration of about $10^{-6}$ M. Note further that the solution compositions did not change with increasing U(VI) uptake by the C-S-H phases (Fig. 3.27b) suggesting that no cation exchange process was involved in the uptake.

![Sorption kinetics of U(VI) on C-S-H phases with actual C:S ratios = 0.75, 1.07, 1.15 and 1.18 in ACW (pH = 13.3; solution composition see Table 3.6) prepared using the “direct reaction” method. Experimental conditions: S:L ratio = 5.0 g L$^{-1}$, total U(VI) concentration = $5.4 \cdot 10^{-7}$ M.](image-url)
Fig. 3.24: Sorption kinetics of U(VI) on C-S-H phases with actual C:S ratios = 0.75, 1.07, 1.29 and 1.6 in alkali-free solution (pH 11.4 - 12.5; solution composition see Table 3.6) prepared using the “direct reaction” method. Experimental conditions: S:L ratio = 5.0 g L\(^{-1}\); total U(VI) concentration = 5.4 \(\times\) 10\(^{-7}\) M.

Fig. 3.25: Co-precipitation kinetics of U(VI) on C-S-H phases with actual C:S ratios = 0.75 and 1.08 in ACW (pH = 13.3, solution composition see Table 3.6) prepared using the “direct reaction” method. Experimental conditions: S:L ratio = 5.0 g L\(^{-1}\); total U(VI) concentration = 5.4 \(\times\) 10\(^{-7}\) M.
Fig. 3.26: Co-precipitation kinetics of U(VI) on C-S-H phases with actual C:S ratios = 0.75, 1.07, 1.29 and 1.6 in alkali-free solution (pH 11.4 - 12.5, solution composition see Table 3.6) prepared using the “direct reaction” method. Experimental conditions: S:L ratio = 5.0 g L⁻¹; total U(VI) concentration = 5.4·10⁻⁷ M.
Fig. 3.27: U(VI) sorption isotherms on C-S-H phases with actual C:S ratios = 0.75 and 1.07 in ACW and in alkali-free solutions (pH = 11.4 - 12) prepared using the “direct reaction” method. a) U(VI) sorbed versus the equilibrium U(VI) concentration. Solid lines represent Langmuir fits. b) Ca and Si concentration in solution at equilibrium. Solid lines are added to guide the eye.

Fig. 3.27: U(VI) sorption isotherms on C-S-H phases with actual C:S ratios = 0.75 and 1.07 in ACW and in alkali-free solutions (pH = 11.4 - 12) prepared using the “direct reaction” method. a) U(VI) sorbed versus the equilibrium U(VI) concentration. Solid lines represent Langmuir fits. b) Ca and Si concentration in solution at equilibrium. Solid lines are added to guide the eye.
3.5.3 Discussion and conclusions

The C-S-H phases prepared using the two different procedures for C-S-H synthesis, i.e., the “solution reaction” and “direct reaction” method, showed similar sorption properties with regard to U(VI) uptake, in particular, 1) relatively fast kinetics (adsorption and co-precipitation), 2) $R_d$ values typically ranging between $10^3$ L kg$^{-1}$ and $10^4$ L kg$^{-1}$ in ACW (pH = 13.3) and $10^5$ L kg$^{-1}$ and $10^6$ L kg$^{-1}$ in alkali-free solution (pH = 10 - 12.5), 3) increasing sorption with increasing C:S ratio (isotherms), and 4) non-linear sorption isotherms. The only discrepancy concerns differences in the U(VI) uptake in the co-precipitation and sorption experiments carried out in ACW, which can presently not be explained.

The strong influence of pH on U(VI) uptake can be attributed to changes in the U(VI) speciation and/or in the Ca concentration. The trend towards a higher stability of the U(VI) sorbed species in alkali-free systems can be attributed to increasing competition with aqueous uranyl-hydroxy complexes in ACW (higher pH) resulting in lower sorption/co-precipitation. Nevertheless, this interpretation only holds under the assumption that these uranyl hydroxy species are not sorbing and that the free $\text{UO}_2^{2+}$ cation is the only sorbing species. Calculation of the U(VI) solution speciation under alkaline conditions, however, shows that this assumption is unrealistic as the calculated free $\text{UO}_2^{2+}$ concentration is extremely low under these conditions (<$10^{-25}$ M), and the main U(VI) species under alkaline conditions are $\text{UO}_2(\text{OH})_3^{-}$ and $\text{UO}_2(\text{OH})_4^{2-}$. Note, however, that the two effects can presently not be treated separately.

Increasing U(VI) uptake at increasing Ca concentration is suggested by the measurements carried out at the same pH with C-S-H phases with different C:S ratios (Fig. 3.27a). At decreasing pH, the Ca concentration in equilibrium with a C-S-H phase having a specific C:S ratio increases due to the common ion effect (Table 3.6). Increasing U(VI) uptake at increasing Ca concentration is in contrast to previous investigations of uptake processes on C-S-H phases, for example Sr binding to C-S-H phases (Tits et al. 2006a). The latter reaction could be modelled in terms of a competition between Ca and Sr binding to C-S-H phases (ion exchange mechanism). Thus, in contrast to Sr, U(VI) appears to be bound to C-S-H phases in a “precipitation” mechanism in which Ca and U(VI) are simultaneously bound to the solid phase. This could suggest the formation of a solid solution, in which U(VI) binding is controlled by the formation of species with variable composition incorporated in C-S-H phases. Identification of the solid solution involved, however, is not possible based upon the presently available batch sorption data. More information might be obtained with spectroscopic techniques such as X-ray absorption spectroscopy and time-resolved laser fluorescence spectroscopy.

Formation of solid solutions with different endmember stoichiometries is further suggested from the non-linear sorption behaviour of U(VI) in C-S-H systems as revealed from the sorption isotherm measurements (Figs. 3.22a and 3.27a). Interestingly, the formation of a pure U(VI) bearing solid phase is not indicated from the latter measurements. This finding is in contrast to the previous solubility tests with U(VI) solutions (concentration range $10^{-8}$ M - $10^{-3}$ M U(VI)) where it was observed that
U(VI) solutions are not stable in the C-S-H equilibrium solutions at concentrations above about 10^{-5} M in ACW and 10^{-6} M at pH = 12.5.

As mentioned earlier the sorption isotherms obtained with both the “solution reaction” and “direct reaction” method exhibit a non-linear sorption behaviour. Non-linearity of the sorption process seems to be more pronounced in the presence of alkalis than in alkali-free solution. Alkalis are present in the systems with C-S-H phases prepared using the “solution reaction” method, in which Na₂SiO₃·9H₂O is used as Si source in the synthesis and in those experiments carried out in ACW using the “direct reaction” method.

In the following, a simplified approach is applied to fit all the sorption isotherms with a 2 site Langmuir isotherm of the form (Stumm & Morgan 1996):

\[
\Gamma_{U(VI)} = \frac{\Gamma_1 K_1 [U(VI)]}{1 + K_1 [U(VI)]} + \frac{\Gamma_2 K_2 [U(VI)]}{1 + K_2 [U(VI)]} \quad \text{(mol kg⁻¹)}
\]  

(3.8)

\( \Gamma_{U(VI)} \): U(VI) surface concentration (mol kg⁻¹),
\( \Gamma_1, \Gamma_2 \): site densities of site 1 and 2, respectively (mol kg⁻¹),
\( K_1, K_2 \): Langmuir adsorption constant for U(VI) sorption on site 1 and 2, respectively (L mol⁻¹),
\( [U(VI)] \): aqueous U(VI) concentration at equilibrium (mol L⁻¹).

All sorption isotherms clearly show two linear ranges which can be attributed to two types of sorption sites denoted hereafter as strong and weak sorption sites. Note that none of the sorption isotherms shows a sorption maximum for the second type of sorption sites (weak sites), which does not allow the site density for this site to be determined based on the fitting procedure. For this reason \( \Gamma_2 \) was arbitrarily fixed at 0.6 mol U(VI) kg⁻¹ (1.2 eq kg⁻¹), which corresponds to the density of surface sites on C-S-H phases (see section 3.1.2; Tits et al. 2006a).

A stepwise approach was used for data analysis. First, the sorption data determined for the C-S-H phases prepared using the “solution reaction” method were fitted as non-linearity was more pronounced. This allowed the parameters for the first range of the sorption isotherm to be determined more precisely. In the second step the isotherm data determined for the C-S-H phases prepared using the “direct reaction” method were fitted (Fig. 3.27a). All fitting parameters are listed in Table 3.13.
Tab. 3.13: Parameters of the two site Langmuir-type sorption model.

<table>
<thead>
<tr>
<th>Exp. Cond.</th>
<th>Synthesis method</th>
<th>C:S</th>
<th>$K_1$ (L mol$^{-1}$)</th>
<th>$K_2$ (L mol$^{-1}$)</th>
<th>$\Gamma_1$ (mol kg$^{-1}$)</th>
<th>$\Gamma_2$ (mol kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low alkali Alkali-free / solution</td>
<td>0.65</td>
<td>(1.2±0.5)·10$^6$</td>
<td>(4.1±0.1)·10$^4$</td>
<td>(1.9±0.5)·10$^3$</td>
<td>0.6</td>
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</tr>
<tr>
<td>Alkali-free / direct</td>
<td>0.81</td>
<td>(3±2)·10$^8$</td>
<td>(2±1)·10$^5$</td>
<td>(1.1±0.5)·10$^3$</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>ACW solution</td>
<td>0.65</td>
<td>(3±2)·10$^6$</td>
<td>(1.0±0.5)·10$^3$</td>
<td>(1.3±0.5)·10$^3$</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>ACW direct</td>
<td>1.03</td>
<td>(1.2±0.6)·10$^8$</td>
<td>(2±1)·10$^3$</td>
<td>(1.5±0.6)·10$^3$</td>
<td>0.6</td>
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</tr>
<tr>
<td>ACW direct</td>
<td>0.75</td>
<td>(1.0±0.5)·10$^6$</td>
<td>(8±4)·10$^2$</td>
<td>1.5·10$^3$</td>
<td>0.6</td>
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</tr>
<tr>
<td>ACW direct</td>
<td>1.07</td>
<td>(3±2)·10$^6$</td>
<td>(3±2)·10$^3$</td>
<td>1.5·10$^3$</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

The site density of the first sorption site, $\Gamma_1$, is very similar for all sorption isotherms regardless whether they were determined in alkali-free solution or in the presence of alkalis. Note that $\Gamma_1$ has a large uncertainty due to the only weakly non-linear behaviour for most C-S-H phases. In all these cases, $\Gamma_1$ was fixed at 1.5 · 10$^{-3}$ mol kg$^{-1}$, which is the mean value of the best fit for $\Gamma_1$ obtained from the isotherm data of the C-S-H phases prepared using the “solution reaction” method. The site density of the first sorption site is very low (< 1%) compared to the number of surface sites on the C-S-H particles (0.6 mol kg$^{-1}$). This indicates that only very few “strong“ sorption sites exist.

The parameters $K_1$ and $K_2$ can be interpreted in terms of the stability of U(VI) sorbed species. The values listed in Table 3.13 suggest that the U(VI) sorbed species are more stable in alkali-free solutions than in ACW, which is consistent with the of higher $R_d$ values determined under these conditions. Furthermore, the stability of the sorbed species tends to slightly increase with increasing C:S ratio.
3.6 EXAFS investigations

3.6.1 Influence of C-S-H preparation on EXAFS data

The uranium L_{III}-edge EXAFS spectra for all C-S-H samples are displayed in Figs. 3.28 and 3.29 along with the corresponding RSFs. The results from the data analysis are listed in Tables 3.14 and 3.15. Note that the loadings were as follows: \( \sim 0.014 \) mol kg\(^{-1}\) in the samples prepared using the “direct reaction” method and \( \sim 0.005 \) mol kg\(^{-1}\) in the samples prepared using the “solution reaction” method. Note further that all U(VI) doped C-S-H materials were prepared in ACW, i.e., in the presence of alkalis. For these systems the above U(VI) loadings correspond to the experimental conditions where the second type of U(VI) sorption complex is formed (compare Figs. 3.22a and 3.27a).

The U(VI) doped C-S-H phases compared in Fig. 3.28 have similar C:S ratios, and thus, differ solely by the method used for the preparation, i.e., using either the “solution reaction” or the “direct reaction” method. Fig. 3.28 reveals negligible differences in the EXAFS data at low C:S ratios (target C:S ratios = 0.65 and 0.75). Minor differences, however, appear in the EXAFS spectra of the two sorption samples with target C:S ratios = 1.1 and 1.29, and the co-precipitation samples. These preliminary conclusions will further be substantiated in the following discussion of the EXAFS data. Thus, it appears that C-S-H phases with similar structural environments for U(VI) sorption and incorporation were generated using the two procedures of C-S-H synthesis. As a consequence, a stepwise approach was employed to more detailed interpretation of the EXAFS data. First, the samples prepared using the “direct reaction” method were fitted because the spectra had a lower signal-to-noise ratio due to the higher U(VI) loadings. This resulted in a better quality of the EXAFS data. Thereafter, the fit approach was applied to analyse the EXAFS data of the samples prepared using the “solution reaction” method.

3.6.2 EXAFS data of the sorption samples

Fig. 3.30 shows that all spectra of the sorption samples were dominated by low frequency oscillations arising from the backscattering of axial oxygen atoms (O\(_{ax}\)), which accounts for the main peak observed at \( \sim 1.5 \) Å in the RSFs. The average U-O\(_{ax}\) distance was determined to be 1.81(2) Å (range 1.79-1.86 Å) (Tables 3.14 and 3.15), which corresponds to values previously reported for U(VI) sorbed on natural minerals (Dent et al. 1992; Chisholm-Brause et al. 1994; Allen et al. 1995; Reich et al. 1996; Allen et al. 1996; Hudson et al. 1996; Reich et al. 1998; Sylvester et al. 2000b; Hennig et al. 2002) and U(VI) bound in cementitious systems (Sylvester et al. 2000a; Zhao et al. 2000; Macé et al. 2013). In agreement with the latter studies it is concluded that the linear [O=U=O]\(^{2+}\) structure was preserved upon sorption onto C-S-H or incorporation in the C-S-H structure. It is to be noted that the U-O\(_{ax}\) distance of the UO\(_{2}^{2+}\) species sorbed on C-S-H seems to be slightly shorter than in the co-precipitation samples, i.e., \( R = 1.79-1.82 \) Å and \( R = 1.82-1.86 \) Å, respectively (Tables 3.14 and 3.15). Nevertheless, it is believed that the difference is hardly significant with a view to the uncertainty of the interatomic distance \( R (\pm 0.02 \) Å).
The best fit to the data of all sorption samples was obtained with a structural model consisting of three oxygen coordination shells. The axial oxygen atoms represented the first coordination shell. Thus, EXAFS data analysis reveals a split equatorial shell for the UO$_2^{2+}$ species sorbed on C-S-H. At a bond distance of about 2.24(2) Å (range 2.23 - 2.26 Å) the uranium atom was surrounded by a coordination sphere consisting of 3 - 5 equatorial oxygen atoms (O$_{eq1}$). The third shell of oxygen atoms (O$_{eq2}$) at a bond distance of about 2.41(2) Å (range 2.36 - 2.45 Å) had a low coordination number (N = 0.5 – 1.5).

Fig. 3.28: $k^3$-weighted experimental EXAFS data (left) and their corresponding RSFs (right) to compare between “solution reaction” samples (solid line) and “direct reaction” samples (dashed line) samples; k range was taken between 2.4 and 11 Å$^{-1}$ for all Fourier transforms (FT).
Tab. 3.14: Structural parameters for the U(VI)/C-S-H systems using the “direct reaction” procedure for C-S-H synthesis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>R(Å)</th>
<th>$\sigma^2$(Å²)</th>
<th>$\Delta E_0$(eV)</th>
<th>Res (%)</th>
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</thead>
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<td></td>
<td></td>
</tr>
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<td>1.82</td>
<td>0.003</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$_{eq1}$</td>
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<td>0.003</td>
<td>0.4</td>
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<tr>
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<td>O$_{eq2}$</td>
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<td>0.003</td>
<td>0.4</td>
<td>8.6</td>
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<tr>
<td></td>
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<td>3.07</td>
<td>0.007</td>
<td>0.4</td>
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</tr>
<tr>
<td></td>
<td>Si$_l$</td>
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<td>3.75</td>
<td>0.007</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
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<td>3.81</td>
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</tr>
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* N is the number of atoms (estimated error: ±20%), R is the distance between central atom and neighbors (Å) (Estimated error: ±0.02 Å), $\sigma$ is the Debye-Waller factor (Å), $\Delta E_0$ is the energy shift (eV). Res (%) corresponds to the residual factor (relative residual in percent) and represents the deviation between experimental data and fit ($y_{exp}$ = experimental data points, $y_{fit}$ = fitted data points):

$$%\text{Res} = \frac{\sum_{i=1}^{N} |y_{exp}(i) - y_{theo}(i)|}{\sum_{i=1}^{N} |y_{exp}(i)|} \times 100$$
Tab. 3.15: Structural parameters for the U(VI)/C-S-H systems using the “solution reaction” method for C-S-H synthesis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>R(Å)</th>
<th>$\sigma^2$(Å$^2$)</th>
<th>$\Delta E_0$(eV)</th>
<th>Res (%)</th>
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<td>4.05</td>
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<td>4.14</td>
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</table>

For N, R, $\sigma$, $\Delta E_0$ and Res% see footnote in Table 3.14.
Fig. 3.29: $k^3$-weighted EXAFS spectra and their corresponding RSFs of experimental (solid) and fitted (dashed line) U L$_{III}$ EXAFS. RSF peak positions are not corrected for phase shift. a) EXAFS spectra and b) RSFs of the samples prepared using the “solution reaction” method for C-S-H synthesis. c) EXAFS spectra and d) RSFs of the samples prepared using the “direct reaction” method for C-S-H synthesis.
The Continuous Cauchy Wavelet Transform (CCWT) modulus displayed in Fig. 3.30 indicates that the backscattering contributions from O$_{eq2}$ and Si neighbours at short distance are superimposed, giving rise to a small peak at 2.2 Å in the RSF (Figs. 3.29a and 3.29b). From the experimental data it further emerges that the total coordination number of the equatorial oxygen shells ranged in value between 4.1 and 6.4. Assuming an error of ~0.5 to 1 atoms, the above range is consistent with results from previous studies where coordination numbers ranging in value between 4.7 and 6.2 have been reported (Dent et al. 1992; Chisholm-Brause et al. 1994; Allen et al. 1995; Reich et al. 1996; Allen et al. 1996; Hudson et al. 1996; Reich et al. 1998; Sylvester et al. 2000b; Hennig et al. 2002). These studies further revealed that a split equatorial shell is indicative of a direct bonding of UO$_2^{2+}$ onto mineral surfaces. Therefore, as a bond split of the equatorial shell is observed in the U(VI)/C-S-H systems, inner-sphere coordination of UO$_2^{2+}$ (adsorption or formation of a solid solution) is assumed to be the predominant mode of interaction.

The bond distances and coordination numbers of the equatorial oxygen atoms can be compared with those previously reported for cementitious systems (Table 3.16). The U-O$_{eq1}$ and U-O$_{eq2}$ distances reported in Sylvester et al. (2000b) range in value between 2.23 and 2.30 Å and 2.39 and 2.53 Å, respectively, which agrees with the corresponding distances determined in this study. On the assumption that UO$_2^{2+}$ interacts with Si tetrahedra of the C-S-H structure, the structural parameters obtained for U(VI) taken up by C-S-H can be compared with those reported earlier for UO$_2^{2+}$ sorbed on silica (Reich et al. 1998; Sylvester et al. 2000b) (Table 3.16). The U-O$_{eq1}$ distances in the C-S-H samples (R = 2.23 - 2.26 Å) are slightly shorter than those reported for UO$_2^{2+}$ sorbed on silica (R = 2.26 - 2.29 Å). However, the coordination number tends to be larger in the C-S-H systems (N = 3.3 - 5.0 compared to 1.7 - 3.5). The U-O$_{eq2}$ bond length is shorter for UO$_2^{2+}$ bound to C-S-H (R = 2.36 - 2.45 Å) than in the U(VI)/silica system (R = 2.46 - 2.52 Å). The trend towards shorter equatorial oxygen distances suggests a stronger bonding of UO$_2^{2+}$ by C-S-H compared to silica.

The coordination numbers deduced for the equatorial oxygen shell can be further assessed using the bond-valence approach (Pauling 1929). Bond-valence calculations can be applied to estimate the valence balance at the central uranium atom. In this approach the sum of bond valence for all bonds to a given atom should equal the atom’s formal valence ($\sum v_{ij} = V_i$) (Pauling 1929). For each pair of atoms (central-first neighbour), the individual bond valence, $v_{ij}$ is related to the bond length $R_{ij}$ as follows (Brown & Altermatt 1985):

$$v_{ij} = \exp(- (R_{ij} - R_0)/b)$$

whereby $ij$ refers to the U(VI) central atom and neighbouring oxygen atoms. $R_0$ is the tabulated bond-valence parameter of the U(VI)-O pair and $b$ is a constant equal to 0.37. Bond-valence parameters for solids were developed by Brown & Altermatt (1985) and Brese & O’Keefe (1991). Using the reported U(VI)-O bond-valence parameter ($R_{UO}^{VI-O} = 2.075$ Å; Brese & O’Keefe 1991) and the experimental U(VI)-O$_{ax}$, U(VI)-O$_{eq1}$, and U(VI)-O$_{eq2}$ distances from this study, i.e., 1.80 Å, 2.24 Å, and 2.40 Å, the bond strengths of the U(VI)-O$_{ax}$, U(VI)-O$_{eq1}$, and U(VI)-O$_{eq2}$ bonds were estimated to be about 2.1 v.u., 0.64 v.u., and 0.42 v.u., respectively. Saturation of the bond valence for the axial oxygen atoms indicates that no other chemical bonds in the C-S-H structure are formed. Note that absence of any interaction of axial oxygen atoms with the mineral
structure has previously been observed on crystalline uranyl compounds (Farges et al. 1992). Based on the bond-valence approach, the coordination number of the equatorial oxygen atoms (O_{eq1}, O_{eq2}) required for satisfying the bond valence at the uranium atom is estimated to be about 4, which corresponds to the lower limit of the experimentally determined coordination number (O_{eq1}: N = 3 - 5; O_{eq2}: N ~ 1).

Fig. 3.30: Wavelet analysis for a U-L_{III} edge EXAFS spectrum of a U(VI)/C-S-H sample prepared using the “direct reaction” method for C-S-H synthesis (CSH0.75-30d_ads) showing the 2D CCWT modulus of the EXAFS signal (center), k^3-weighted EXAFS spectrum (below) and FTs (left).
Tab. 3.16: Structural parameters of uranyl orthosilicate, uranophane and $\text{UO}_2^{2+}$ sorbed on concrete and silica gel.

<table>
<thead>
<tr>
<th>Reference</th>
<th>No. of samples</th>
<th>Shell</th>
<th>$N$</th>
<th>R(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{UO}_2^{2+}$/treated concrete$^1$</td>
<td>7</td>
<td>$\text{O}_{\text{ax}}$</td>
<td>2.0</td>
<td>1.81-1.83</td>
</tr>
<tr>
<td></td>
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<td>2.5-4.6</td>
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<tr>
<td></td>
<td></td>
<td>$\text{O}_{\text{eq2}}$</td>
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<td>2.39-2.53</td>
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<tr>
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<td></td>
<td></td>
<td>$\text{U}$</td>
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<td>Uranyl orthosilicate$^3$</td>
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<td></td>
<td></td>
<td>$\text{Ca}$</td>
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<td>4.07</td>
</tr>
<tr>
<td>$\text{UO}_2^{2+}$ sorbed on silica$^6$</td>
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<td>$\text{O}_{\text{ax}}$</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Si}$</td>
<td>0.5</td>
<td>2.72</td>
</tr>
</tbody>
</table>

$^a$ Measurement of one sample
$^1$ Sylvester et al. (2000a)
$^2$ Reich et al. (1996)
$^3$ Demartin et al. (1992)
$^4$ Thompson et al. (1997)
$^5$ Ginderow (1988)
$^6$ Reich et al. (1998)
3.6.3 EXAFS data of the co-precipitation samples

For the co-precipitation samples a split equatorial oxygen shell was only found in the sample prepared using the “direct reaction” method for C-S-H synthesis (CSH1.29-30d_cop). A different structural model, however, had to be used to fit the experimental data of the corresponding “solution reaction” samples (CSH0.65-30d_cop, CSH1.1-30d_cop). In these samples only one equatorial oxygen shell was observed instead of a split equatorial oxygen shell. Note that a uniform equatorial shell is characteristic of the uranyl aquo ion (U-Oeq = 2.42±0.01 Å). The resulting structural parameters suggest that 5 oxygen atoms (N = 4.8 and 5.4) surrounded the uranium atom at short distance (2.25(2) Å). The absence of a split equatorial oxygen shell was previously reported for uranyl silicate (Reich et al. 1998) and outer-sphere coordination of UO$_2^{2+}$ on clay minerals (Chisholm-Brause et al. 1994; Sylvester et al. 2000b). In contrast to the formation of the uranyl silicate-like chemical environment in the U(VI)/C-S-H systems, outer-sphere coordination seems to be very unlikely in view of the short distances determined for the equatorial oxygen shell. The following parameters were reported for the equatorial oxygen shell in uranyl silicate: R = 2.38 Å, N = 5.4 (Reich et al. 1996). Thus, a uniform equatorial oxygen shell at short distance, which is determined for the co-precipitation samples prepared using the “solution reaction” method, suggests strong interaction of UO$_2^{2+}$ with the C-S-H structure, and furthermore, a coordination environment similar to that in uranyl silicate. Nevertheless, the formation of a pure U(VI) solid phase can be excluded because backscattering contributions from neighbouring uranium atoms were not observed in the EXAFS spectra of these samples.

By contrast, a split equatorial shell and U-U backscattering contribution resulted from the fitting in case of the co-precipitation sample, which was prepared using the “direct reaction” method for C-S-H synthesis (CSH1.29-30d_cop). Note that the U(VI) loading was higher by about a factor of three in this sample compared to the U(VI) loadings of the “solution reaction” samples. Further, it was observed that portlandite is an important impurity (~ 5 wt%) in the C-S-H materials with target C:S ratios = 1.29 due to incomplete reaction under the given chemical conditions (pH = 13.3) (Tits et al. 2006a). Thus, we can speculate that the formation of a U(VI) solid phase was facilitated by the high U(VI) concentration in the system and heterogeneity of the reacting solid system.

3.6.4 Structural model for U(VI) sorption onto C-S-H

The above discussion implies that crystalline model structures that account for the different binding modes between U(VI) and the neighbouring atoms can be applied to allow a more detailed interpretation of the U(VI)/C-S-H EXAFS data. In this study, soddyite, (UO$_2$)$_2$(SiO$_4$)$·$2H$_2$O, and uranophane, (Ca(UO$_2$)$_2$(SiO$_3$OH)$_2$$·$5H$_2$O), are regarded as suitable reference compounds. Two uranophane structures $\alpha$ and $\beta$, which differ only slightly in their crystallographic parameters, were characterized in the studies of Viswanathan & Harneit (1986) and Ginderow (1988). The structure of soddyite was described in Demartin et al. (1992). In uranophane, the uranium atoms display a pentagonal bipyramidal coordination. The uranyl units form a continuous edge-sharing chain. The units of one chain are connected in a bidentate fashion (edge-sharing) to SiO$_4$ tetrahedra. The latter are bound via monodentate coordination (corner-sharing) to the uranyl units of the adjacent chains, thus linking uranyl chains in a
fashion to form sheets. The uranophane structure consists of parallel uranyl silicate sheets with Ca atoms located in the interlayer. The structure of soddyite has the same basic features, consisting of edge-sharing uranyl units forming chains that are crosslinked by SiO$_4$ tetrahedra. In contrast to uranophane, however, soddyite does not display a sheet structure with Ca ions compensating the negative charge in the interlayer. In both structures, uranophane and soddyite, one Si atom appears at short distance (3.14 Å and 3.16 Å) and 2 and 3 Si atoms, respectively, at long distances (3.72 and 3.81 Å). This corresponds to edge-sharing (bidentate) and corner-sharing (monodentate) coordination of Si to the central uranium atom. Furthermore, in both structures, bidentate coordination of Si occurs via equatorial oxygen atoms at longer distance to the uranium atom (uranophane: 2.45 Å; soddyite: 2.41 and 2.42 Å), whereas monodentate coordination is associated with the equatorial oxygen atoms at shorter distance (uranophane: 2.24 and 2.30 Å, soddyite: 2.31 Å). Interestingly, the characteristic bond lengths and coordination numbers for bidentate and monodentate connections have been observed in the U(VI)/C-S-H sorption samples (Tables 3.14 and 3.15). At maximum one silicon atom (N = 0.5±0.4) appears at short distance (~3.08(2) Å), which may be bound via the equatorial oxygen atoms at longer distance (R = 2.36 - 2.45 Å) to UO$_2$$^{2+}$. Furthermore, a total of 2 to 3 Si atoms are located at a distance of about 3.75(5) Å, which may be bound via the equatorial oxygen atoms at shorter distance (R = 2.23 - 2.26 Å) to UO$_2$$^{2+}$.

The EXAFS data further indicate that, in the U(VI) doped C-S-H sorption samples, about 2 to 3 Ca atoms are located at the distance of 3.83(5) Å. The presence of neighbouring Ca atoms further supports the idea of an uranophane-like coordination environment of U(VI) in C-S-H phases. Note, however, that the U–Ca distance in uranophane is significantly longer (R = 4.07 Å; Ginderow 1988). RSFs of the EXAFS spectra recorded for the “solution reaction” samples imply an additional backscattering contribution by Ca atoms located at a distance of about 4.2(1) Å, which was not observed in the samples prepared using the “direct reaction” method. A tentative explanation can be given if it is considered that U(VI) loading was higher in the latter sample by about a factor of three. Increasing structural disorder in the C-S-H systems with increasing loading may result in destructive interference of the spectral components from more distant neighbouring atoms. This could be the reason why Ca atoms at longer distance were not detected. It should further be noted that backscattering contributions at a distance of about 4.2 Å could, in principle, indicate the presence of an uranium atom. Nevertheless, evidence for U-U backscattering pairs was only found in one co-precipitation sample, which was prepared using the “direct reaction” method for C-S-H synthesis (R~4.3(2) Å, N~1).
Fig. 3.31: Schematic presentation of the structural model for U(VI) binding by C-S-H proposed in consistency with the EXAFS parameters.
4. Summary

C-S-H phases are an important mineral component of hardened cement paste. These types of minerals may control the release of many radionuclides from the cementitious near field of a repository for radioactive waste because of their long-term stability and their high immobilization potential for many cations. This report describes the results of a study on the immobilization of Th(IV) and U(VI) by C-S-H phases under alkaline conditions carried out as a collaboration between the Central Research Institute of the Electric Power Industry (CRIEPI), Japan, and the Paul Scherrer Institute (PSI), Switzerland. The aim of this work was to investigate the retention of Th(IV) and U(VI) by C-S-H phases under conditions relevant to a repository for radioactive waste, to assess the effect of C-S-H synthesis methods on the sorption behaviour of these two cations and to distinguish sorption and co-precipitation processes on C-S-H phases. The study consisted of three parts: i) a preliminary investigation of the stability (presence of precipitates or colloidal material) of Th(IV) and U(VI) solutions under alkaline conditions; ii) a batch sorption study of the sorption and co-precipitation of Th(IV) and U(VI) by C-S-H phases using 2 different procedures for the synthesis of C-S-H phases (“direct reaction” and “solution reaction” method); iii) a complementary X-ray absorption spectroscopy study of the retention of U(VI) by C-S-H phases.

Th(IV) solutions in alkaline conditions were found to be stable up to concentrations of $10^{-8}$ M. This limiting concentration corresponds to the solubility limit of ThO$_2$(s) under alkaline conditions. Solutions with higher total Th(IV) concentrations were found to contain Th(IV) colloids. The stability of alkaline U(VI) solutions was found to depend on the Ca concentration in solution; i.e., the solubility of U(VI) increases with decreasing Ca concentration indicating that U(VI) is more soluble in alkaline solutions with low Ca concentrations. It is further shown that the stability limits of all the alkaline U(VI) solutions can be explained by assuming the formation of CaUO$_4$(s) (log$_{10}$ $K_{s,0}=23.1$) as proposed earlier by Moroni & Glasser (1995).

Th(IV) sorption and co-precipitation data obtained on the two different types of C-S-H phases, synthesized following the “direct reaction” method and the “solution reaction” method, were very similar, indicating that the method used for C-S-H synthesis had no significant influence on Th(IV) uptake. $R_d$ values were very high for both types of CSH phases, ranging in value from $10^5$ to $10^7$ L kg$^{-1}$, with no measurable effect neither of the solid or solution compositions nor the chemical process (sorption versus co-precipitation) involved. The above findings clearly show that Th(IV) sorbs very strongly on C-S-H phases, irrespective of the C:S ratio of these phases.

The C-S-H phases prepared using the “solution reaction” method and the “direct reaction” method, showed similar retention properties with regard to U(VI) uptake; i.e., i) fast kinetics (sorption and co-precipitation), ii) a significant effect of pH with $R_d$ values typically ranging from $10^3$ to $10^4$ L kg$^{-1}$ in ACW (pH 13.3) and $10^4$ to $10^5$ L kg$^{-1}$ at lower pH (pH 10.5 to 12.5), and iii) a slight effect of the aqueous Ca concentration. U(VI) sorption and co-precipitation isotherms were found to be non-linear and tentatively interpreted in terms of a two site Langmuir-type sorption model. Nevertheless, it is believed that the formation of a solid solution in which Ca and U(VI)
are simultaneously bound in the solid phase is likely to control U(VI) uptake by C-S-H phases.

The EXAFS measurements performed on U(VI)-doped C-S-H phases, which were prepared using both methods for C-S-H synthesis, revealed structural parameters similar to those reported for uranophane; i.e., a linear uranyl structure with a split equatorial oxygen shell, neighbouring Si atoms at short and long distances, as well as neighbouring Ca atoms. This structural model was found in all sorption samples regardless of the synthesis procedure used. The coordination environment of U(VI) co-precipitated with C-S-H phases using the “solution reaction” method consisted of 5 oxygen atoms at short distances in a uniform equatorial shell. By contrast, the structural environment of U(VI) co-precipitated with C-S-H phases using the “direct reaction” method is characterized by a split equatorial oxygen shell in a similar way as the U(VI)-doped C-S-H phases.

Thus, the local coordination environment of U(VI) in the C-S-H structure generated during co-precipitation processes seems to be influenced by the reaction conditions, e.g. the U(VI) concentration and whether the reactants are solid or liquid. Nevertheless, the factors influencing U(VI) coordination in these systems are presently unknown.

In general, the results from the EXAFS studies support indications from the batch sorption investigations that the uptake of U(VI) by C-S-H phases may be controlled by the formation of solid solutions.

Regarding the storage of radioactive waste, this study allows the following conclusions to be drawn:

1) Th(IV):
   - This actinide strongly sorbs on C-S-H phases which are the main component of hardened cement paste;
   - The strong sorption is reversible and independent of pH in the pH range where cementitious materials are stable (10.5 < pH < 13.3);
   - No influence of the degradation of cement on the sorption is to be expected.

2) U(VI):
   - The sorption of this hexavalent actinide increases with decreasing pH in the pH range where cementitious materials are stable (10.5 < pH < 13.3);
   - The sorption is influenced by the Ca concentration;
   - The sorption is likely controlled by solid solution formation; the coordination environment of U(VI) in these solid solutions can be determined with the help of spectroscopic methods such as EXAFS and TRLFS.
   - The degradation of cement in an evolving nuclear waste repository gives rise to a lower pH and an increase in the C:S ratio of the C-S-H phases, thus resulting in an increase in the U(VI) uptake by degraded cement.
5. Acknowledgment

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