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The effect of EDTA on the desorption of uranium from calcium silicate hydrate matrices

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Abstract

The desorption of uranium from a U(VI)-contaminated C-S-H matrix has been investigated as a function of the EDTA concentration in solution under N_2- and ambient atmosphere. The K_d values evaluated from the experimental data indicate that U(VI) is retarded in the solid phase due to sorption of EDTA through interaction with U(VI) at the C-S–H surface. On the other hand, under ambient conditions the formation of stable U(VI)-carbonato species results in higher U(VI) concentration in solutions compared to corresponding systems under N_2-atmosphere.

Keywords C-S-H · Uranium · EDTA · Desorption · K_d

Introduction

Before final storage in underground repositories low- and intermediate-level radioactive waste is usually solidified in cementitious matrices [1]. The main binding component of a cementitious matrix is calcium silicate hydrate (C-S-H). C-S-H has a layered structure, which consists of Ca–O sheets linked on each side to silicate chains [2]. The immobilization of uranium by the C-S-H matrix occurs via sorption of U(VI) species (e.g. $UO_2(OH)_3^-$, $UO_2(OH)_4^{2-}$)) on the solid surface and incorporation of the radionuclide in the C-S-H phase. The effective incorporation of lanthanide and actinide ions by substituting Ca ions in the interlayers and the Ca–O layer of the C-S-H phase is ascribed to its high recrystallization rate [3].

Uranium is used as primary fuel nuclear power reactors and therefore is an important component of nuclear waste. Under the redox conditions prevailing in the alkaline cementitious environment, uranium is expected to exist predominantly in its hexavalent oxidation state (U(VI)) and predominantly in the form of the tri- or tetra-hydroxo uranyl complex ($UO_2(OH)_3^-$, $UO_2(OH)_4^{2-}$) [4, 5]. According to the Eh–pH diagram calculated using the *Geochemist's Workbench* ® [5], the tri-hydroxo uranyl complex ($UO_2(OH)_3^-$) is the predominant species in the pH range between 8 and 12, whereas the tetra-hydroxo uranyl complex ($UO_2(OH)_4^{2-}$) dominates for pH > 12. The geochemical behavior of uranium in the near field of the nuclear waste repositories is of particular interest, because of the amounts the element and its isotopes are present in the spent fuel, as well as because the U(VI) chemistry is expected to be similar to other hexavalent actinides (e.g. Pu(VI)) [6]. The interaction of U(VI) with C-S-H has been subject of several studies, which investigated its sorption by the cementitious phase and applied sophisticated spectroscopies to better understand and describe the interaction between U(VI) and C-S-H [4, 7–13]. Investigations have been carried out also on ternary U(VI)-C-S-H organic ligand systems [14], including EDTA [15]. These studies indicate the strong impact of the organic ligand on the sorption of U(VI) by C-S-H. Nevertheless, there are no systematic studies on the effect of EDTA on the desorption of U(VI) from C-S-H matrices, which have been previously contaminated with uranium during preparation.

EDTA (ethylene diamine tetraacetic acid) is a chelating agent that is found at increased levels in the environment and in radioactive wastes because it has been used as a decontamination agent in nuclear facilities and other industrial processes [16]. EDTA is a hexadentate ligand that forms very stable complexes with polyvalent metal ions, including U(VI) and therefore governs their stability in the aqueous solutions [17] and affects their leaching from cementitious and other mineral matrices [18, 19]. Generally, investigations on the (de)sorption of uranium by C-S-H matrices are

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fundamental regarding the safety and performance assessment of radioactive waste disposal facilities. This is because cementitious matrices are the main components of the engineered barrier, which encapsulate and isolate uranium and other (radio)toxic elements from the biosphere [1, 7–11].

In this study, the impact of EDTA on the desorption of U(VI) from a cementitious C-S-H matrix has been investigated by contacting a U(VI)-contaminated C-S-H phase with EDTA solutions of varying concentrations. The experiments were performed under N_2- and ambient atmosphere to study the effect of carbonate on the uranium desorption. In addition, the related solid phases have been characterized by XRD and FTIR measurements.

Experimental

In all experiments, analytical grade reagents and de-ionized water were used. The ^{232}U-tracer solution, which was added for the uranium quantification, was obtained from National Physical Laboratory (NPL, Teddington, UK). The EDTA solutions of varying concentrations (0.0001, 0.001, 0.01 and 0.1 M) have been prepared by dissolution of disodium EDTA dihydrate ($C_{10}H_{14}N_2O_8$ 2Na·2H_2O, Sigma-Aldrich, Darmstadt, Germany) in de-ionized water. The U(VI) stock solution was prepared by dissolution of $UO_2(NO_3)_2·6H_2O$ (Merck) in de-ionized water.

Solid phase preparation and characterisation

Solid calcium-silicate-hydrate (C-S-H) has been synthesized according to Maddalena et al. [20] at a C:S ratio of 1.27 and a U(VI)/Ca(II) ratio of 1/10000. The solid product has been characterized by FTIR spectroscopy (FTIR-ATP 8900, IR Prestige-2, Shimadzu,) and X-Ray diffraction (Shimadzu XRD-6000 Series). The preparation of C-S-H was carried out by mixing 12.02 g Ludox (50%, Sigma-Aldrich, Darmstadt, Germany) with 8.52 g CaO (Sigma-Aldrich, Darmstadt, Germany) in 35 mL aqueous solution containing U(VI), under N_2. The product was cast in cubes and left for one month under water-vapour saturated N_2-atmosphere. Following, the C-S-H cubes have kept overnight in dried-aceton to remove excess water and finally dried under vacuum at 70 °C for 24 h.

Desorption studies

The desorption investigations were performed in batch type experiments using 0.2 g C-S-H/U in 20 mL aqueous solution of EDTA (0, 0.0001, 0.001 and 0.01 M), at a U(VI)/Ca(II) ratio of 1/10000 and pH 11. The experiments were performed under ambient conditions (e.g. 23 ± 2 °C, 0.03% CO_2) and N_2 atmosphere to investigate the effect of carbonate on the desorption of U(VI) from the studied system. After 30 days contact time, aliquots of the solution have been taken, filtrated by means of membrane filters (pore size: 450 nm) and the uranium concentration in solution was analysed by alpha-spectroscopy (Alpha Analyst Integrated Alpha Spectrometer, Canberra) after electrodeposition on stain-less steel discs as described elsewhere [21]. Prior electro-deposition the solution was traced with U-232 (50 mBq) to evaluate the uranium yield.

The partition coefficient, K_d (L/kg), is here defined as the ratio of the amount (in moles) of the radionuclide sorbed per mass of dry C-S-H (C_{ads} in mol/kg) to the equilibrium concentration of the radionuclide in solution (C_{aq} in mol/L). Because of the relative low amount of uranium added in the system used we can assume that the surface binding sites are in great excess with respect to the radionuclide concentration in solution. Therefore, we expect a linear relation between sorbed and non-sorbed species.

$$K_d = C_{ads}/C_{aq}(L/kg) \tag{1}$$

Results and discussion

Solid phase characterisation

The FTIR spectra of the C-S-H solid precipitated in the absence (C-S-H) and in the presence of U(VI) are shown in Fig. 1. In both spectra, the broad peak at 3450 cm^{-1} is ascribed to the O–H streching vibration, whereas the band at 1636 cm^{-1} corresponds to the bending vibration of the coordinated water. In addition, the strong peak at 1430 cm^{-1} is related to the bending mode of the Ca-OH vibration and the peak at 964 cm^{-1} could be associated with the antisymmetric

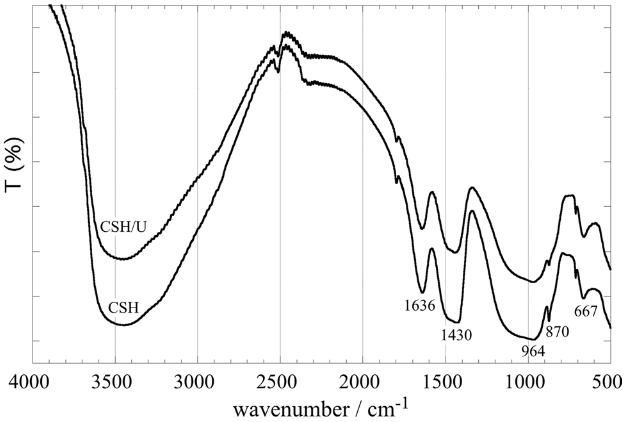

Fig. 1 FTIR spectra of C-S-H solids precipitated in the absence (CSH) and presence of hexavalent uranium (CSH/U)

stretching vibration of Si–O–Si and the stretching vibration of O–Si–O [22].

The spectra in Fig. 1 almost identical indicating that two solids formed under different conditions are similar. This was expected because the amount of U(VI) added to the precursor solution was relatively low with a U(VI)/Ca(II) ratio equal to 1:10,000. In addition, the x-ray diffractograms of the two solids have been obtained and compared.

The diffractograms of the two C-S-H solids are shown in Fig. 2. and are characteristic C-S-H diffractograms with a disordered layered structure similar to tobermorite [22]. However, a careful observation of the peak position in the 2θ range between 35 and 50 degrees, reveals a small shift of the peaks to higher 2θ values in the diffractogram of the U(VI)-contaminated C-S-H sample. This is an indication that U(VI) has been incorporated in the C-S-H phase forming a solid solution [23].

Effet of EDTA on the U(VI) desorption from C-S-H

In a previous study we investigated the effect of EDTA on the sorption of U(VI) by a similar C-S-H solid [15]. In the previous study the uranium was added in the EDTA solution and then contacted with the C-S-H phase, while in this study the U(VI) was co-precipitated with the C-S-H during the cementitious solid preparation from the precursor materials. This is of particular interest because the distribution coefficients obtained from the two different approaches may indicate on similarities and differences regarding the sorption/desorption process.

Figure 3 summarizes partition coefficient values as a function of the EDTA concentration in solution under N_2- and ambient atmosphere. Surprisingly, in the systems under N_2-atmosphere the K_d values increase with increasing EDTA concentration in solution and are generally higher ($4.9 < [\log_{10}K_d] < 5.8$) than the corresponding K_d value ($\log_{10}K_d = 4.9$) determined in the EDTA-free suspension. This is in contradiction with the results obtained from sorption experiments, which revealed the opposite effect due to stabilization of U(VI) in solution in the form of U(VI)-EDTA complexes [15]. The increased K_d values, which are associated higher U(VI) amounts adsorbed by the C-S-H phase could be ascribed to enhanced sorption of EDTA through an interaction with calcium and uranium ions present at the C-S-H surface and the formation of ternary surface complexes [24].

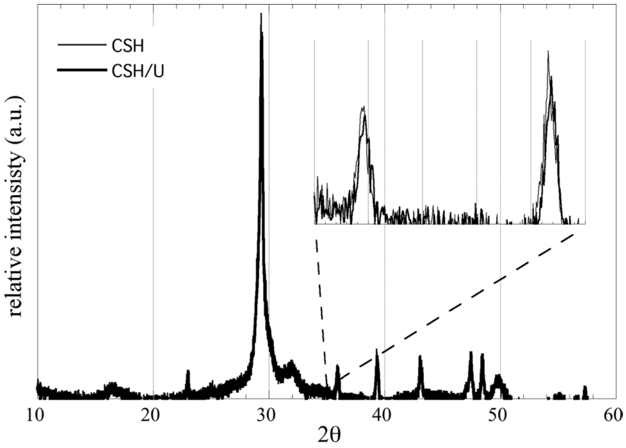

Fig. 2 X-ray diffractograms of C-S-H solids formed in the absence (CSH) and presence of hexavalent uranium (CSH/U)

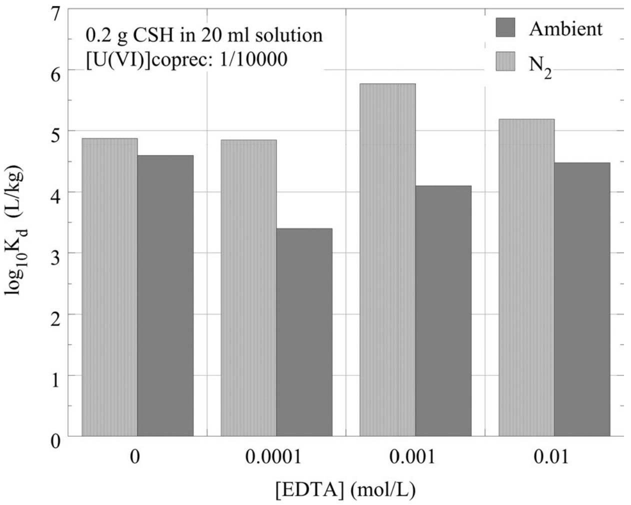

Fig. 3 Partition coefficient values as a function of the EDTA concentration in solution under N_2- and ambient atmosphere

It is notable that the highest K_d value ($\log_{10}K_d = 5.8$) and lowest U(VI) desorption from the C-S-H phase is observed at an initial concentration of 0.001 M EDTA under the existing experimental conditions (e.g., 0.2 g C-S-H in 20 mL solution). A similar effect was observed in a previous study, where increased EDTA sorption by the C-S-H phase was observed under similar experimental conditions [15]. In the latter case the retardation of EDTA was ascribed to the sorption of EDTA through an interaction with calcium ions at the C-S-H surface [24]. Similarly, EDTA could be sorbed in the C-S-H phase via interaction with the U(VI) cations present in the solid phase. This interaction retards U(VI) in the solid phase resulting in lower U(VI) levels in solution compared to EDTA-free solutions.

On the contrary, under ambient atmosphere the K_d values ($3.4 < [\log_{10}K_d] < 4.5$) obtained are generally lower than the K_d value determined in the EDTA-free suspension and significantly lower than the corresponding K_d values obtained under N_2-atmosphere. This indicates that under ambient conditions the equilibrium is shifted towards the U(VI) species in solution. Under ambient atmospheric conditions and at pH 11, CO_2 is extensively dissolved in the aqueous phase and exists predominantly in the form of the carbonate anion (CO_3^{2-}) [15, 25]. U(VI) forms with carbonate anions very stable complexes (e.g. $UO_2(CO_3)_3^{4-}$, $\log\beta = 19.5$) [25], which compete the U(VI) sorption by C-S-H, resulting in lower K_d values. Similar behavior was observed also in the case of experiments related to the U(VI) sorption by C-S-H in the presence of varying EDTA concentrations and the higher U(VI) levels had been ascribed to the formation of U(VI)-carbonato species [15, 25], which compete the sorption by C-S-H and stabilize U(VI) in solution as described by Eq. 2.

$$CSH - UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons CSH + UO_2\left(CO_3\right)_3^{4-} \qquad (2)$$

Conclusions

U(VI) in a C-S-H phase is stabilized in the presence of EDTA due to sorption of the organic molecule through interaction with U(VI) at the C-S-H surface. The effect is more pronounced when the experiments are performed under N_2-atmosphere.

Under ambient conditions the formation of stable U(VI)-carbonato species results in higher U(VI) concentrations in solutions compared to corresponding systems under N_2-atmosphere.

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