

Article

Investigations on the Interaction of EDTA with Calcium Silicate Hydrate and Its Impact on the U(VI) Sorption

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Abstract: The interaction of EDTA with calcium silicate hydrate (C-S-H) and its impact on the sorption of U(VI) by C-S-H in the presence of EDTA at varying concentrations has been investigated under N₂ and ambient atmosphere. The solid phase characterization was performed by FTIR, XRD and TGA measurements and the uranium concentration in solution has been determined by alpha-spectroscopy. At increased EDTA concentrations ([EDTA] > 0.1 M) calcium is complexed and extensively extracted from the solid resulting in a quantitative dissolution of the Ca(OH)₂ phase and deterioration of C-S-H. At lower EDTA concentrations ([EDTA] ≤ 0.01 M), EDTA is sorbed into the solid phase and the associated adsorption capacity ($q_{\max} = 0.67$ mol/kg) has been evaluated by fitting the corresponding data with the *Langmuir* isotherm model. The incorporation of EDTA in the C-S-H matrix was corroborated by FTIR, XRD and TGA measurements. Regarding the effect of EDTA on the U(VI) sorption by C-S-H, evaluation of the experimental data reveal a significant decrease of the K_d values in the presence of EDTA most probably due to the stabilization of U(VI) in the form of U(VI)-EDTA complexes in solution. Under ambient conditions a further decrease of the K_d values is observed because of the formation of U(VI)-carbonato complexes related to CO₂ dissolution and hydrolysis.



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Keywords: uranium; C-S-H; EDTA; sorption; K_d

1. Introduction

Prior storage in underground geological repositories low- and intermediate-level radioactive waste is commonly solidified in a cementitious matrix [1]. The main binding component of such cementitious matrices are calcium silicate hydrate (C-S-H) phases, which have a layered structure and consist of Ca–O sheets linked on each side to silicate chains [2]. Immobilization of radionuclides by the cementitious matrix occurs through adsorption of $UO_2(OH)_4^{2-}$ on the surface of the C-S-H components and incorporation of U(VI) into the C-S-H phase. Due to its high recrystallization rate, C-S-H can effectively incorporate lanthanide and actinide ions by substituting Ca ions in the interlayers and the Ca–O layer of the C-S-H phases [3].

Uranium is an important component of radioactive wastes and is expected under the redox conditions prevailing in the alkaline cementitious environment to exist predominantly in the hexavalent oxidation state (U(VI)) and in the form of the hydrolyzed uranyl species, $UO_2(OH)_4^{2-}$ [4]. The chemical behavior of uranium in nuclear waste repositories is of particular interest not only because of the amounts and the different isotopes uranium is present in the nuclear waste, but also because U(VI) could act as an analogue for other hexavalent actinides such as Pu(VI) [5]. There are several studies on the U(VI) interaction with C-S-H and include sorption as well as spectroscopic studies to better understand and describe the U(VI)-C-S-H system [4,6–12]. There are also investigations on ternary U(VI)-C-S-H organic ligand systems [13] indicating the significant impact of the organic ligand on the chemical behavior of U(VI) in such systems. However, there are no systematic studies on the effect of EDTA on the sorption of U(VI) on C-S-H.

EDTA (ethylene diamine tetraacetic acid) is a chelating agent that has been widely used as a decontamination agent in nuclear facilities and therefore is found at relatively increased levels in radioactive wastes. However, as hexadentate ligand EDTA forms very stable complexes with polyvalent metal ions (e.g., actinides and lanthanides) and thus strongly affects their stability in the aqueous phase and their leaching from cementitious matrices. Generally, investigations regarding the U(VI) sorption by cementitious matrices are of particular interest with respect to long-term performance assessment and safety of nuclear waste disposal facilities, because cement is a main part of the engineered barrier, which contains and isolates the radionuclides from the biosphere [14].

In this study, which aims reveal the impact of EDTA on the cementitious matrix and the U(VI) sorption, C-S-H was selected as the cementitious phase to study the U(VI) sorption in the presence of EDTA at varying concentrations. Firstly, the interaction of EDTA with C-S-H and its impact on the C-S-H stability was investigated by determining the calcium concentration in solution and performing XRD, TGA, and FTIR measurements of the related solid phases. The sorption studies were performed in aqueous solution containing uranium ($[U(VI)] = 5 \times 10^{-5}$ M) and EDTA at various concentrations (0, 0.0001, 0.001 and 0.01 M). Moreover, in order to study the effect of carbonate the experiments were performed under N_2 - and ambient atmosphere.

2. Experimental

2.1. Materials

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 NPL (National Physical Laboratory, Teddington, UK). EDTA solutions of different concentration (0.0001, 0.001, 0.01 and 0.1 M) have been prepared by dissolution of disodium EDTA dihydrate ($C_{10}H_{14}N_2O_8 \cdot 2Na \cdot 2H_2O$, Aldrich) in de-ionized water.

Solid calcium-silicate-hydrate (C-S-H) has been synthesized according to Maddalena et al. [15] at a C:S ratio of 1.27 and the solid product has been characterized by FTIR spectroscopy (FTIR, FTIR-ATP 8900, IR Prestige-2, Shimadzu, Europa GmbH, Duisburg, Germany) and X-Ray diffraction Shimadzu XRD-6000 Series). The preparation of C-S-H was carried out by mixing 12.02 g Ludox (50%, Aldrich) with 8.52 g CaO (Aldrich) in 35 mL de-ionized water under N_2 . The product was cast in cubes and left for one month under water-vapour saturated N_2 -atmosphere. Finally, the C-S-H cubes have kept overnight in dried-aceton to remove excess water and then dried under vacuum at 70 °C for 24 h.

2.2. Interaction of EDTA with C-S-H

The effect and sorption of EDTA on the C-S-H solid was investigated by contacting a certain amount of the solid (0.2 g) with 20 mL aqueous solution of EDTA (0, 0.0001, 0.001, 0.01 and 0.1 M). After 30 days contact time, the calcium concentration in solution was determined by flame-photometry (PFP7 flame photometer, Jenway, Staffordshire, UK) and after solid–liquid phase separation the solids have been analyzed by X-ray diffraction (XRD-6000 Series, Shimadzu, Europa GmbH, Duisburg, Germany), thermogravimetric analysis (TGA-50, Shimadzu, Europa GmbH, Duisburg, Germany) and FTIR (FTIR-ATR 8900, IR Prestige-21 Shimadzu, Europa GmbH, Duisburg, Germany).

2.3. The Effect of EDTA on the Sorption of U(VI) by C-S-H

Sorption studies were performed in batch type experiments using 0.2 g C-S-H in 20 mL aqueous solution of EDTA (0, 0.0001, 0.001 and 0.01 M), at a U(VI) concentration of 5×10^{-5} M and pH 11. The experiments were performed under ambient conditions and N_2 atmosphere to investigate the effect of carbonate on the sorption capacity of U(VI) in the studied system. After 30 days contact time, aliquots of the solution have been obtained, filtrated using membrane filters (pore size: 450 nm) and the uranium concentration in solution was determined by alpha-spectroscopy (Alpha Analyst Integrated Alpha Spectrometer, Canberra, Montigny-le-Bretonneux, France) after electrodeposition on

a stain-less steel planchet as described elsewhere [16]. Prior electrodeposition the sample-electrolyte mixture was traced with 50 mBq of the U-232 isotope to account for any uranium losses during electrodeposition. The activity concentration measurements were performed in triplicate and the mean value (m) is given in the related graphs and tables.

The partition coefficient, K_d (L/kg), is here defined as the ratio of the quantity of the radionuclide adsorbed per mass of dry C-S-H (C_{ads}) to the amount of the radionuclide remaining in solution (C_{aq}).

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

3. Results and Discussion

3.1. Impact of EDTA on the C-S-H Stability

Figure 1 presents the powder X-ray diffractograms of C-S-H in contact with 0.1 M EDTA solution and de-ionized water. The spectrum corresponding to the C-S-H sample in contact with de-ionized water is a characteristic C-S-H diffractogram, which has a disordered layered structure similar to tobermorite [17]. On the other hand, in the diffractogram of the sample in contact with 0.1 M EDTA the relative intensity of the characteristic C-S-H peaks decreases indicating the deterioration of the C-S-H phase. This can be attributed to the calcium ion complexation by EDTA [18] and following dissolution of the Ca(OH)_2 phase. The dissolution of the Ca(OH)_2 phase is extensive, and the remaining solid phase consists mainly of amorphous silica as indicated by the dominating broad peak at $2\theta = 30^\circ$ in the diffractogram corresponding to 0.1 M EDTA. EDTA is a strong chelating agent for polyvalent metal cations, including calcium cations (Ca^{2+}) [18]. Hence, in the presence of EDTA calcium cations are complexed and extracted from the solid phase affecting the stability of C-S-H.

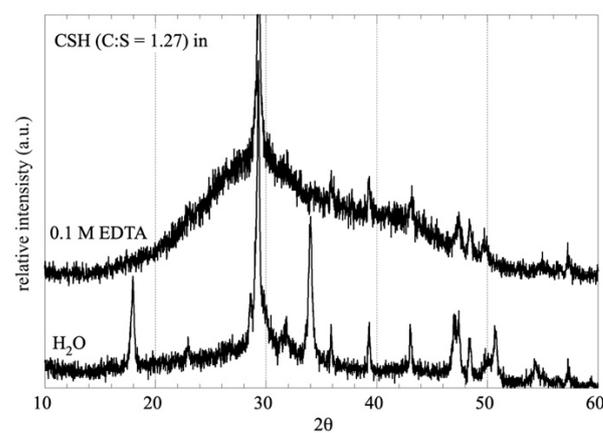


Figure 1. X-ray diffractograms of a C-S-H solid phase in contact with 0.1 M EDTA solution and de-ionized water.

Figure 2 shows the IR spectrum of a C-S-H solid phase, which was in contact with 0.1 M EDTA solution, and for comparison also the IR spectrum of a C-S-H sample which was in contact with de-ionized water. The broad peak at 3450 cm^{-1} is associated with the O-H stretching vibration, the band at 1636 cm^{-1} in the spectra of both samples corresponds to the bending vibration of the coordinated water, the strong peak at 1430 cm^{-1} is associated with the bending mode of the Ca-OH vibration and the peak at 964 cm^{-1} could be attributed to the antisymmetric stretching vibration of Si-O-Si and the stretching vibration of O-Si-O [19].

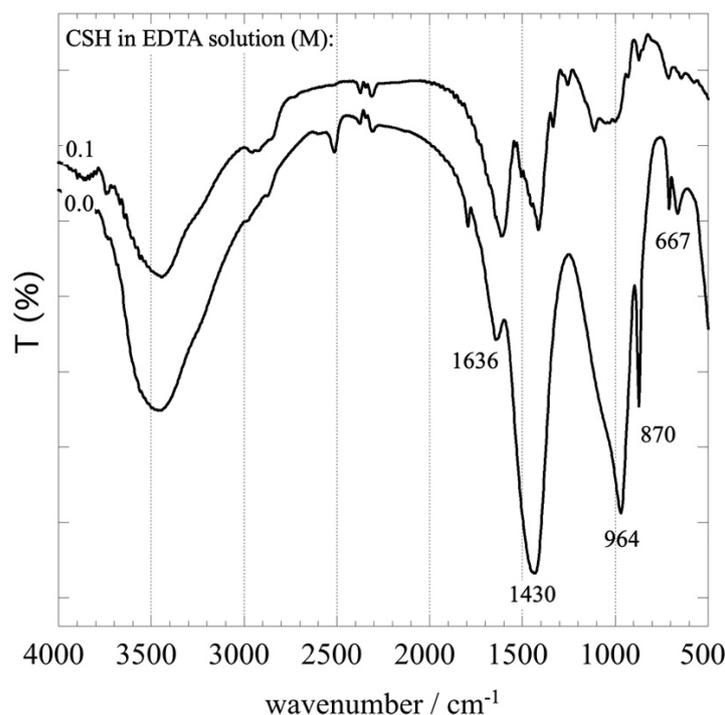


Figure 2. FTIR spectra of a C-S-H solid phase in contact with de-ionized water and 0.1 M EDTA solution.

According to the FTIR spectra in Figure 2, the strong peak at 1430 cm^{-1} , which is associated with bending mode of the Ca-OH vibration [19] almost disappears in the presence of 0.1 M EDTA indicating the extensive dissolution of the $\text{Ca}(\text{OH})_2$ phase. Following, the sorption experiments with C-S-H were performed in solutions with lower EDTA concentrations ($[\text{EDTA}] \leq 0.01\text{ M}$). At lower concentrations EDTA forms complexes basically with the adsorbed, counter calcium ions, which compensate the negative surface charge of the C-S-H surface. Moreover, EDTA is expected to be adsorbed by C-S-H through the interaction with calcium ions at its surface [20].

3.2. Sorption of EDTA by C-S-H

The sorption/incorporation of small organic molecules in the C-S-H phase has been described by previous studies [20,21]. In the present study, the sorption of EDTA by C-S-H was investigated by determining the calcium concentration in solution as a function of the initial EDTA concentration in solution. The calcium concentration is expected to be equal to the EDTA concentration in solution, because of the strong complexing affinity of EDTA towards polyvalent metal ions, including Ca^{2+} ($\log_{10} K_f = 12.57$) [18]. This strong complexing capacity assumes quantitative complexation of EDTA with Ca^{2+} and the predominance of the Ca(II)-EDTA complex in solution.

Figure 3 shows the concentration of Ca(II)/Ca(II)-EDTA as a function of the initial EDTA concentration. Generally, the EDTA (Ca(II)-EDTA) concentration in solution is lower than the initial one suggesting sorption/incorporation of EDTA through an interaction with calcium ions at the C-S-H surface [20]. The sorption is very pronounced at an initial concentration of 0.001 M EDTA under the given experimental conditions (e.g., 0.2 g C-S-H in 20 mL solution). Most probably, the surface complexation of EDTA is favored under the given conditions. At higher EDTA concentrations the equilibrium is expected to shift towards the formation of soluble Ca(II)-EDTA complexes. In order to prove the sorption of the EDTA/Ca(II)-EDTA by the C-S-H phase aliquots of the respective solid phases have been investigated by X-ray diffraction, FTIR spectroscopy and thermogravimetric (TGA) measurements.

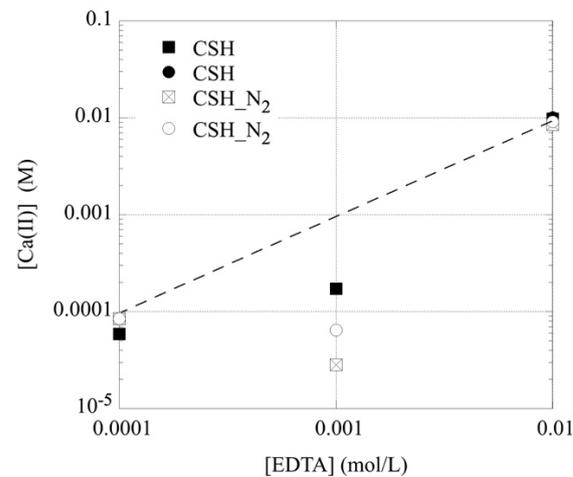


Figure 3. Calcium (Ca-EDTA) concentration in solution as a function of the initial EDTA concentration.

The X-ray diffractograms of C-S-H in contact with aqueous solutions of varying EDTA concentrations are shown in Figure 4b (magnification) [17]. The diffractograms (Figure 4a) do not indicate any significant changes of C-S-H after 30 days contact time with the studied EDTA solutions. However, the magnified diffractograms (Figure 4b) show that with increasing EDTA concentration in solution there is a gradual small shift of the peaks to higher 2θ values, which can be attributed to the incorporation of EDTA into the C-S-H phase [22,23].

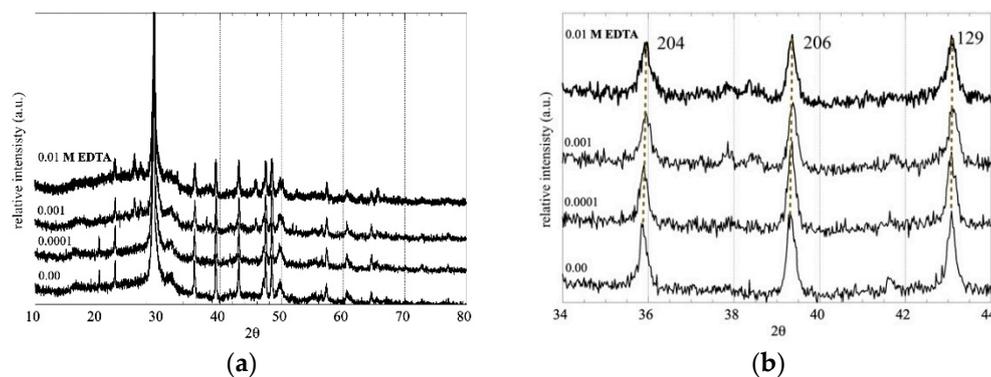


Figure 4. XRD diffractograms of C-S-H solid phases in contact with aqueous solution of varying EDTA concentration (a); magnification (b).

In addition, FTIR spectra of C-S-H solid phases, which were separated after contact with aqueous solutions of varying EDTA concentrations have been obtained and are shown in Figure 5. According to the spectra in Figure 5, the intensity of the IR band at 1070 cm^{-1} , which is attributed to EDTA [24], increases with increasing the EDTA concentration in solution. This indicates that “EDTA” is sorbed/incorporated into the C-S-H solid phase. The sorption/incorporation of complexing organic molecules and their calcium complexes is described also in other studies [20,21].

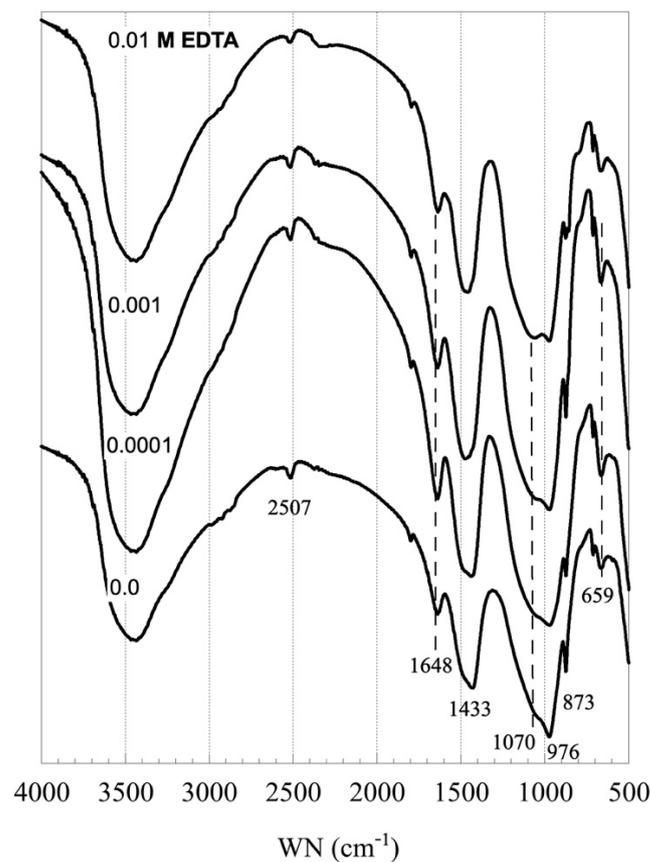


Figure 5. FTIR spectra of C-S-H solid phases, which were in contact with aqueous solution of varying EDTA concentration for 30 days.

Moreover, thermogravimetric curves of C-S-H samples in contact with aqueous solution of varying EDTA concentrations have been obtained and are shown in Figure 6. Up to 700 °C, the TGA curves are typical for C-S-H. Specifically, the first step of weight loss observed in the temperature range between 25 and 200 °C is associated with the evaporation of pore water and the dehydration of C-S-H. The second step, which occurs in the range between 350 and 485 °C is related to the dehydroxylation of the $\text{Ca}(\text{OH})_2$ phase. The relatively small step in the range between 600 and 700 °C corresponds to CO_2 loss of CaCO_3 formed because of the surface carbonation of the samples during sample preparation [25].

According to Figure 6, the samples in contact with 0.00 M EDTA and 0.0001 M EDTA present the highest water loss (~13%) due to adsorbed water evaporation and $\text{Ca}(\text{OH})_2$ de-hydroxylation. The corresponding water loss is about 7% and 10% for the samples in contact with 0.001 and 0.01 M EDTA, respectively. Taking into account that the sorption/incorporation of small organic molecules retards the effectiveness of the C-S-H hydration [20], it is evident that the significantly lower water loss due to adsorbed water evaporation and $\text{Ca}(\text{OH})_2$ de-hydroxylation of the samples in contact with 0.001 and 0.01 M EDTA is associated with the higher amount of EDTA adsorbed/incorporated into the C-S-H phase in the respective samples and complexation of calcium ions. On the other hand, the pure C-S-H sample shows very similar thermogravimetric behavior as the sample in contact with 0.0001 M EDTA solution, indicating that the negligible effect of EDTA on the C-S-H solid phase at the respective organic ligand concentration.

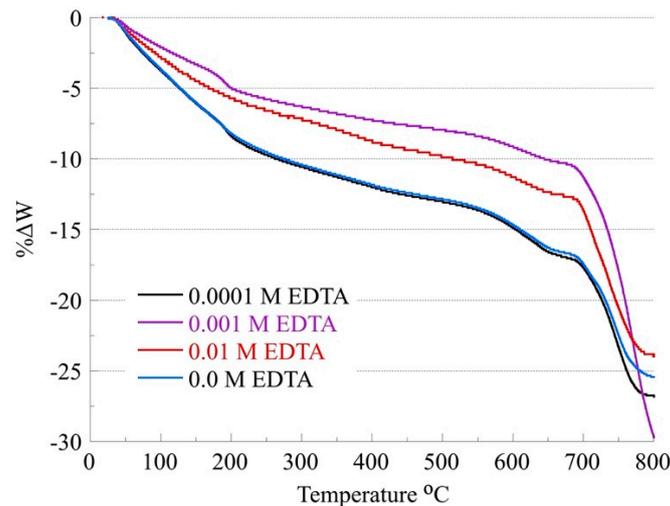


Figure 6. Thermograms of C-S-H solid phases, which were in contact with aqueous solution of varying EDTA concentration for 30 days.

The X-ray diffractograms, FTIR spectra and TGA thermograms of the C-S-H solid phases, which have been in contact for 30 days with aqueous EDTA solutions of varying concentration corroborate the sorption/incorporation of EDTA/Ca(II)-EDTA into C-S-H. In order to determine the sorption capacity, the sorption experiments have been performed using the C-S-H solid phase under N_2 - and ambient atmosphere. The experimental data have been fitted with the *Langmuir* isotherm and both experimental data and fitted lines are shown in Figure 7. The sorption capacity values of C-S-H for EDTA under N_2 - and ambient atmosphere are $q_{max} = 0.65$ and $q_{max} = 0.8$ moles EDTA/kg C-S-H solid phase, respectively, indicating the enormous sorption capacity of C-S-H for EDTA.

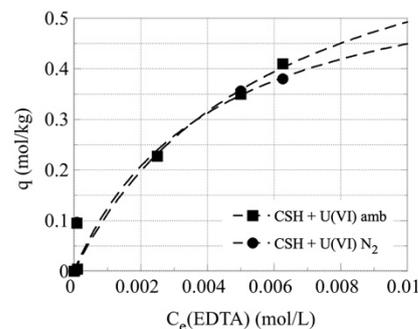


Figure 7. Sorption data and fitted *Langmuir* isotherms obtained for the “EDTA” sorption by C-S-H solids under ambient conditions and N_2 -atmosphere.

3.3. The Effect of EDTA on the Sorption of U(VI) by C-S-H

The interaction of U(VI) with C-S-H has been extensively studied and the studies have shown that at low U(VI) loading the immobilization of U(VI) by the cementitious material occurs not only through adsorption of $UO_2(OH)_4^{2-}$ on the surface of the C-S-H components but also by incorporation of U(VI) into the C-S-H phase [4,11,12]. However, there are no systematic studies dealing with the effect of EDTA on the sorption U(VI) by C-S-H.

To evaluate the effect of EDTA on the U(VI) sorption by C-S-H, 5×10^{-5} M U(VI) have been added to C-S-H suspensions in aqueous EDTA solutions of varying concentration, at pH 11, under ambient and N_2 atmosphere. After 30 days contact time the U(VI) has been determined and the corresponding K_d values have been determined according to Equation (1) and are graphically presented in Figure 8. According to the data in Figure 7, the K_d value ($\log_{10}K_d = 4.6 \pm 0.1$) obtained for the C-S-H in the absence of EDTA is close to K_d

values obtained for similar systems [12]. However, when EDTA is added in solution the K_d values ($\log_{10}K_d = 4.3 \pm 0.2$) decrease with increasing EDTA concentration in solution. This can be attributed to the stabilization of U(VI) in the aqueous phase basically through complex formation between EDTA and U(VI) [26].

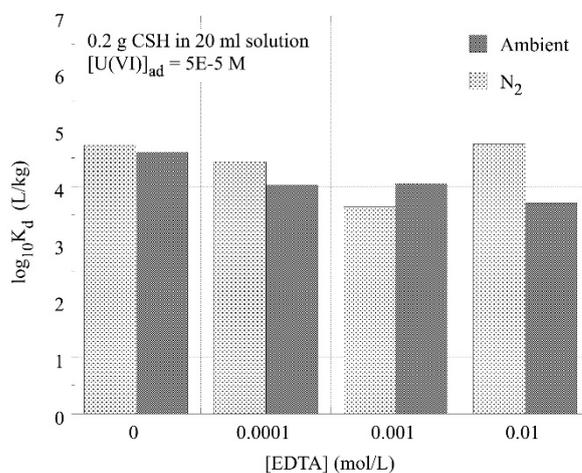


Figure 8. The $\log_{10}K_d$ values calculated for the U(VI) sorption by C-S-H under ambient and N_2 atmosphere.

Moreover, comparison of the K_d values obtained under ambient conditions and N_2 -atmosphere show that generally the K_d values corresponding to ambient conditions are generally lower ($\log_{10}K_d = 3.9 \pm 0.2$) assuming further stabilization of U(VI) in solution through the formation of U(VI) carbonate complexes which are formed because of the elevated carbonate concentration ($\log_{10}[CO_3^{2-}] = 0.35$) in solution under the given conditions [27].

4. Conclusions and Future Work

At an increased concentration ($[EDTA] > 0.01$ M), the interaction of EDTA with C-S-H results in degradation of the solid phase, because of the extensive dissolution of $Ca(OH)_2$.

At lower EDTA concentrations ($[EDTA] \leq 0.01$ M), the organic ligand is sorbed by the solid phase, most probably in the form of Ca(II)-EDTA complexes. Fitting of the corresponding experimental sorption data with the *Langmuir* isotherm model results in a maximum sorption capacity (q_{max}) value of 0.7 mol EDTA/kg C-S-H. The incorporation of EDTA in the C-S-H matrix is corroborated by FTIR spectroscopic and XRD measurements.

Addition of EDTA in the U(VI)-C-S-H system results in the decrease of the U(VI) sorption efficiency and the decline of the associated K_d values most probably due to the stabilization of U(VI) in the form of U(VI)-EDTA complexes in solution. Under ambient conditions and the presence of carbonate in solution the sorption efficiency and the corresponding K_d values decline further, because of the formation of U(VI)-carbonato complexes, which stabilize U(VI) in solution and compete sorption on C-S-H.

The results of the present study reveal that EDTA can affect the immobilization of U(VI) by forming stable complexes with U(VI) and altering the surface properties of C-S-H upon adsorption/incorporation into the cementitious phase.

Further studies under CO_2 atmosphere as well as the involvement of solid NMR studies and sophisticated spectroscopic methods (e.g., Raman, XPS, EXAFS) could give detailed information on the sorption process at the molecular level and improve our knowledge regarding the effect of EDTA on the U(VI) sorption by C-S-H.

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