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1 Molecular Dynamics Simulation of the Interaction of Uranium (VI)  
2 with the C-S-H Phase of Cement in the Presence of Gluconate

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15

## 1 **Abstract**

2       Due to their high durability and immobilization properties, cementitious materials  
3 have found a considerable application in the design and construction of radioactive  
4 waste repositories in the last decades. During cement paste production, organic  
5 additives are introduced to modify various properties of cement. The presence of such  
6 organic complexants may negatively affect the immobilizing properties of cement with  
7 respect to radionuclides. For better understanding and prediction of the effects of  
8 interactions between organic molecules and cementitious materials with radionuclides,  
9 we have developed several representative models consisting of three principal  
10 components: (i) calcium silicate hydrate (C-S-H) phase - the main binding phase of  
11 cement; (ii) gluconate, a simple well-described molecule, as a representative of organic  
12 additives; (iii) U(VI), as one of the most studied radionuclides of the actinide series. The  
13 C-S-H phase with low Ca/Si ratio (~0.83) typical for “low-pH” and degraded cement  
14 pastes has been selected for this modelling study. Structural, and energetic aspects of  
15 the sorption processes of uranyl, gluconate, and their mutual correlations on the surface  
16 of cement were quantitatively modeled by classical molecular dynamics (MD) and  
17 potential of mean force (PMF) calculations. The ternary surface complex formation  
18 between uranyl hydroxides and Ca<sup>2+</sup> cations at the C-S-H aqueous interfaces is shown  
19 to have an important role in the overall sorption process. In the presence of gluconate,  
20 U(VI) sorption on C-S-H is facilitated by weakening the Ca<sup>2+</sup> binding with the surface.  
21 Additionally, Na<sup>+</sup> is proven to be an important competitor for certain surface sorption  
22 sites and can potentially affect the equilibrium properties of the interface.

23 **Key words** C-S-H, cement, uranyl, gluconate, sorption, molecular dynamics simulation

## 1 **1. Introduction**

2 Cementitious materials are widely used in the design and construction of  
3 geological radioactive waste repositories, in particular in the Callovo-Oxfordian  
4 argillaceous rock formation in the East of the Parisian basin in France (e.g., Grambow,  
5 2016; Kořátková et al., 2017). They are the principal construction material for the waste  
6 storage galleries and access shafts of the underground repositories, but can also serve  
7 as part of the packaging for some intermediate level waste or as the sealing material for  
8 storage cells.

9 Calcium silicate hydrate (C-S-H) is the main binding phase of cements and controls  
10 their mechanical and chemical durability. C-S-H phases are formed as a result of  
11 hydration of alite ( $\text{Ca}_3\text{SiO}_5$ ) and industrial belite ( $\text{Ca}_2\text{SiO}_4$ ), the two silicates that are the  
12 essential constituents of cement clinker (Taylor, 1997; Richardson, 2010). Because of its  
13 critical role, C-S-H was selected as the cement model in this work. However, an  
14 accurate nano-scale description of C-S-H phases is very challenging and the interest in  
15 understanding their atomistic structure and the nature of structural disorders continues  
16 to be strong. A significant amount of research has been devoted recently to clarify these  
17 issues using various experimental and theoretical approaches, and there is now a  
18 general consensus that the C-S-H phases have structural similarity with such minerals  
19 as tobermorite and jennite (Cong and Kirkpatrick, 1996; Yu et al., 1999; Pellenq et al.,  
20 2009; Richardson et al., 2010; Grangeon et al., 2016, 2017; Kumar et al., 2017). It is  
21 also established that Ca/Si ratio is a single most important characteristic of the C-S-H  
22 phase which significantly affects such chemical and physical properties of cement as pH

1 of the pore water, the surface charge, and equilibrium ion concentrations (Chen et al.,  
2 2004; Lothenbach and Nonat, 2015).

3 The atomistic models of C-S-H used in this study to simulate the interaction of  
4 actinides with cement in the context of radioactive waste repository environment were  
5 constructed on the basis of experimental observations and earlier computer simulations.  
6 They provide a compromise between the necessity to realistically represent the true  
7 compositional and structural complexity of the C-S-H phase and still maintain relative  
8 simplicity, which should facilitate better quantitative investigation of the specific  
9 molecular mechanisms of interaction among different chemical species near the surface  
10 (Androniuk et al., 2017).

11 The sorption behavior of actinides on C-S-H phases has already been studied  
12 recently, and a strong effect of the Ca/Si ratio has been found (Pointeau et al., 2004;  
13 Harfouche et al., 2006; Tits et al., 2011; Gaona et al., 2012; Macé et al., 2013; Häußler  
14 et al., 2018; Tits and Wieland, 2018). Even though in ordinary Portland cement we can  
15 observe predominantly C-S-H phases with Ca/Si ratios higher than 1.5, lower ratios are  
16 typical for “low-pH” cements with added fly ash and silica fume, and in degraded cement  
17 pastes because of the decalcification (Glasser et al., 2008). As the first step, C-S-H  
18 phases with low Ca/Si ratio ( $\sim 0.83$ ) have been selected for this modelling study.

19 During cement paste production, various kinds of organic additives are typically  
20 used to enhance mechanical properties of the final cement material, and the presence of  
21 these potentially reactive and mobile chemicals may cause additional safety concerns  
22 (Keith-Roach, 2008). Consequently, the molecular mechanisms of their interaction with

1 all components of the waste storage system should be systematically studied,  
2 quantitatively described, and understood in detail. Several recent studies shed light  
3 upon the behavior of organics in cementitious materials (Nalet and Nonat, 2016;  
4 Chaudhari et al., 2017; Orozco et al., 2017) and their effect on the mobility of  
5 radionuclides in cement (Pointeau et al., 2006, 2008; García et al., 2018). However, to  
6 our knowledge, the molecular mechanisms controlling the behavior of the ternary  
7 systems (C-S-H/radionuclide/organic) have not yet been investigated. In the present  
8 work, we are addressing this gap by atomistic computer simulations of a model ternary  
9 system. Gluconate ( $C_6H_{12}O_7$ ) ion, a relatively simple hydroxy acid that is chemically  
10 stable in alkaline solutions, is used here as a proxy model for organic additives, while  
11 U(VI), one of the most important and well-studied actinide elements, is used as a model  
12 radionuclide.

13 The structural defects in the C-S-H surface silicate chains can serve as potential  
14 sorption sites for the interfacial species. The variations in structure and surface charge  
15 distribution of the C-S-H surface models create different opportunities for the cations to  
16 bind. However, not all of the binding sites are equivalent, some of them offer more  
17 favorable local steric environments and/or lower energies for stronger binding. This is  
18 where the computational molecular modelling becomes very helpful by providing a  
19 detailed quantitative atomic scale picture of the site-specific interactions on the interface.  
20 A combinational analysis of the local structures, density profiles and surface maps for  
21 target atoms gives an insight of what are the preferential sorption sites on the C-S-H  
22 surface (Androniuk et al., 2017).

1 A number of studies (Viallis-Terrisse et al., 2001; Hill et al., 2006; Sugiyama, 2008;  
2 Labbez et al., 2011; Bach et al., 2013; Henocq, 2017; Dufresne et al., 2018) have  
3 demonstrated that the presence of alkali on the interface of C-S-H can significantly  
4 change its equilibrium solution and surface physical and chemical properties: they can  
5 affect the surface zeta potential, compete for the sorption sites. Taking this into account  
6 consideration, Na<sup>+</sup> is introduced to the simulated systems as a counter ion of gluconate.  
7 The free energies of adsorption for the ions of interest (Ca<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, gluconate, Na<sup>+</sup>) at  
8 different surface sites of calcium silicate hydrates are calculated, analyzed, and  
9 discussed in this paper.

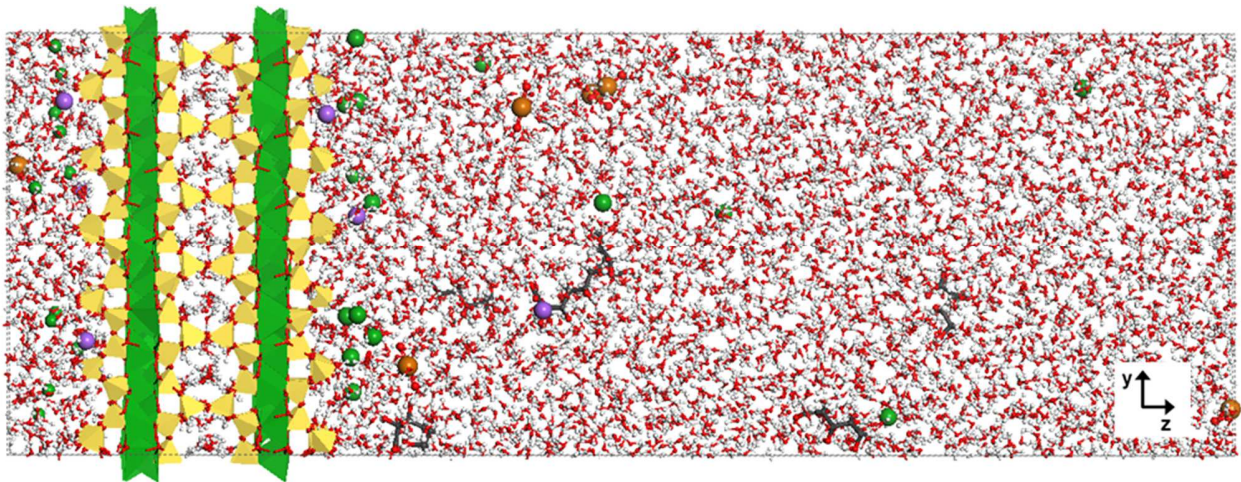
10

## 11 **2. Methods**

12 The atomistic model of the C-S-H surface for our simulations was constructed  
13 based on the crystal structure of tobermorite, that was proven to be the closest to the  
14 real cement hydrate (e.g., Grangeon et al., 2016, 2017; Kumar et al., 2017; Kunhi  
15 Mohamed et al., 2018). First, the tobermorite crystallographic unit cell  
16 (Ca<sub>5</sub>Si<sub>6</sub>O<sub>16</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O; Hamid, 1981; Merlino et al., 2001) has been multiplied along the  
17 *a* and *b* directions (6 × 6 × 1) to create the crystal supercell of the dimensions  
18 40.2 × 44.4 × 25.5 Å<sup>3</sup>. This supercell was then cleaved in the middle of interlayer along  
19 the (0 0 1) crystallographic plane to create a basic model of the C-S-H surface. Next, the  
20 top layers of the cleaved crystal were modified by randomly removing the bridging Si  
21 tetrahedra in accordance with available experimental NMR and IR data (Cong and  
22 Kirkpatrick, 1996; et al., 1999; Beaudoin et al., 2009; Roosz et al., 2018), and  
23 introducing additional Ca<sup>2+</sup> cations into the interlayer (Fig. 1). The protonation state of

1 surface silanol groups was assigned based on the theoretical considerations (Churakov  
2 et al., 2014), and adjusted to correspond the range of pH ~ 10-11 typical of C-S-H with a  
3 low Ca/Si ratio. More specifically, all silanol groups of bridging Si and one of the pairing  
4 Si (replacing the introduced defect) were deprotonated. The deprotonated oxygens of  
5 the surface were assigned a partial charge of  $q_{\text{onb}} = -1.3|e|$ , higher than the protonated  
6 ones in the standard ClayFF model (see Kirkpatrick et al., 2005a, 2005b, and the  
7 discussion below). The structural defects were not introduced for the silicate chains  
8 inside the bulk tobermorite substrate, since only the surface interactions are the principal  
9 focus of the present work.

10



11

12 **Figure 1.** A snapshot of the entire simulation supercell. The color scheme is as follows:

13 Si – yellow; Ca – green; O – red; H – white; Na – violet; U – dark-orange; and

14 C – dark-grey.

15



1        The interfacial aqueous solution contained 6 ions of  $\text{Na}^+$ ,  $\text{UO}_2(\text{OH})^{3-}$ , and gluconate  
2 each, with  $\sim 4500$   $\text{H}_2\text{O}$  molecules, that approximately corresponds to 0.07 M ion  
3 concentrations. These relatively high concentrations had to be used in the simulations  
4 for better statistical sampling of the model systems, but they should not affect overall  
5 results. Three dimensional periodic boundary conditions (Allen and Tildesley, 2017)  
6 were applied to the constructed model interfaces, and the thickness of the solution layer  
7 between the two C-S-H surfaces was large enough ( $\approx 70$  Å) to ensure that the  
8 interactions at one surface would not affect the other, and result in bulk-like solution  
9 behavior in the middle of the model simulation box (Fig. 1).

10        The interatomic interaction parameters for C-S-H,  $\text{H}_2\text{O}$ , and  $\text{Ca}^{2+}$  ions were taken  
11 from the ClayFF parameterization (Cygan et al., 2004), and its later modifications for  
12 cement systems (Kirkpatrick et al., 2005b; Kalinichev et al., 2007; Mishra et al., 2017).  
13 Polarizability of actinides, such as U(VI), can generally be considered as an important  
14 factor contributing to overall interatomic interactions (Clavaguera-Sarrio et al., 2003;  
15 Newcomb, 2018; Duvail et. al., 2019). However, in our simulations U(VI) is only present  
16 in the form of a uranyl cation,  $\text{UO}_2^{2+}$ , and non-polarizable force field parameterization for  
17 such species has long been already proven to be a good compromise providing  
18 accurate simulation results validated by experimental data (Guilbaud and Wipff, 1996;  
19 Greathouse et al., 2002; Kerisit and Liu, 2014). The interaction parameters for uranyl  
20 ions used in this work (Guilbaud and Wipff, 1996) are also consistent with ClayFF  
21 (Teich-McGoldrick et al., 2014).

22        Based on the recent comparison of several clay-organic force field combinations  
23 (Szczerba and Kalinichev, 2016), the general AMBER force field GAFF (Wang et al.,

1 2004) was used to describe the interatomic interactions involving gluconate ions.  
2 Standard Lorentz-Berthelot mixing rules (Allen and Tildesley, 2017) were applied to  
3 calculate short-range Lennard-Jones interactions between the unlike atoms (with a cut-  
4 off distance of 14 Å). Long-range electrostatic forces were evaluated by means of the  
5 Ewald summation method. All molecular dynamics (MD) simulations were performed  
6 using LAMMPS software package (Plimpton, 1995). The Newtonian equations of atomic  
7 motions were numerically integrated with a timestep of 1 fs, and the model systems  
8 were initially equilibrated for 3 ns in the isobaric–isothermal statistical ensemble (*NPT*),  
9 then for 2 ns in the canonical ensemble (*NVT*). Temperature and pressure were  
10 constrained using the Nose-Hoover thermostat and barostat (Allen and Tildesley, 2017)  
11 at ambient conditions ( $T = 300$  K,  $P = 0.1$  MPa). Model equilibration was carefully  
12 monitored by assessing the temperature, pressure, kinetic and potential energy of the  
13 system, and dimensions of the simulation box, in order to confirm that these parameters  
14 reach their equilibrium steady state values on average (Braun et al., 2019).

15 To probe the structure of bulk aqueous solutions for comparison with the interfacial  
16 solutions, several preliminary MD simulation runs were performed for the systems  
17 containing pairs of ions ( $\text{UO}_2(\text{OH})_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Ca}(\text{OH})^+$ ,  $\text{Na}^+$ , and gluconate) placed in a  
18 cubic  $40 \times 40 \times 40$  Å<sup>3</sup> simulation box filled with  $\text{H}_2\text{O}$  molecules at a density  
19 corresponding to ambient conditions. When necessary, aqueous  $\text{OH}^-$  and  $\text{Na}^+$  ions were  
20 added to maintain the total electrostatic neutrality of the models.

21 In the first series of unconstrained MD simulations, the most probable sorption  
22 sites on the C-S-H surfaces were determined based of the calculation of time-averaged  
23 atomic density profiles in the direction perpendicular to the surface, and atomic density

1 distributions parallel to the surface in the layer of solution nearest to it. The local atomic  
2 density is calculated through the evaluation of the average number of atoms of a certain  
3 type ( $\bar{N}_A$ ) found at a distance  $z$  (i.e, within the range of distances from  $z$  to  $z+\Delta z$ ) parallel  
4 to the surface:

$$5 \quad \text{Density}_A = \frac{\bar{N}_A (\Delta z)}{V_{cell}}$$

6 where  $V_{cell}$  is the total volume of the simulation cell,  $\Delta z = 0.1 \text{ \AA}$ . The two-dimensional  
7 distributions in the  $xy$  plane within a layer of solution parallel to the surface at a certain  
8 distance  $z$  are defined by the probability of finding an atom of type A at a position  $(x,y)$   
9 above the surface within a range of distances from  $z$  to  $(z+\Delta z)$ :

$$10 \quad \text{Surface density}_A(x,y) = \bar{N}_A(\Delta x \Delta y)$$

11 where  $\Delta z = 2 \text{ to } 5 \text{ \AA}$ ,  $\Delta x = \Delta y = 0.2 \text{ \AA}$ .

12 The change of free energy is the driving force of any process, such as surface  
13 sorption. In this case, the difference in free energy between different states of the  
14 system (surface-sorbed ion vs the same ion in bulk aqueous solution) along a reaction  
15 coordinate can quantitatively characterize the strength of the adsorption sites of interest.  
16 Free energy is related to the probability distribution of the thermodynamic states along  
17 the reaction coordinate, and statistical analysis of an MD simulation trajectory allows one  
18 to quantitatively evaluate free energy evolution in the system using the so-called  
19 "umbrella sampling" algorithm or potential of mean force (PMF) calculation (Allen and  
20 Tildesley, 2017).

1 A complete calculation requires a number of separate independent simulations to  
2 cover the entire range of the reaction coordinate. In each of these "sampling windows"  
3 the distance between the reacting species is restrained at a required value using a  
4 harmonic force to allow the system to sample all possible configurations around that  
5 particular value of the reaction coordinate. The histograms of such simulation series are  
6 carefully monitored to ensure adequate and relatively uniform sampling along the  
7 reaction coordinate and sufficient overlaps of the sampling windows with each other.  
8 This ensures proper recovery of the unbiased PMF curve from the simulated ensemble  
9 of the biased histograms using the weighted histogram analysis method (WHAM). A  
10 detailed description of the umbrella sampling and WHAM algorithms used here can be  
11 found in literature (Kästner, 2011; Grossfield, 2014).

12 Here we additionally used the recently developed approach of site-specific PMF  
13 calculations (Loganathan and Kalinichev, 2017) where an additional weak  $xy$  constraints  
14 were applied as a "soft cylindrical wall" of a small diameter in order to keep the atom  
15 above a defined sorption site on the surface and not to allow its significant drift in the  
16 directions parallel to the surface. In this way, quantitative description of the adsorption  
17 free energy profiles was obtained for  $\text{UO}_2^{2+}$ ,  $\text{UO}_2(\text{OH})_3^-$ ,  $\text{Ca}^{2+}$ , and  $\text{Na}^+$  ions as functions  
18 of their distance between each other in bulk aqueous solutions, and from the C-S-H  
19 surface at the aqueous interfaces with solutions of various compositions (with and  
20 without gluconate present in the system). For each PMF curve obtained, approximately  
21 90 constrained MD simulations (sampling windows) were run in the  $NVT$  ensemble ( $T =$   
22 300 K) for 1 ns. Monte Carlo bootstrapping approach implemented in WHAM algorithm  
23 has been used to evaluate the statistical uncertainties (Grossfield, 2014; Grossfield et

1 al., 2018). The calculated average value of 0.02 kcal/mol is taken as an estimate of  
2 uncertainty for all PMF curves presented in this work.

3

### 4 **3. Results and Discussion**

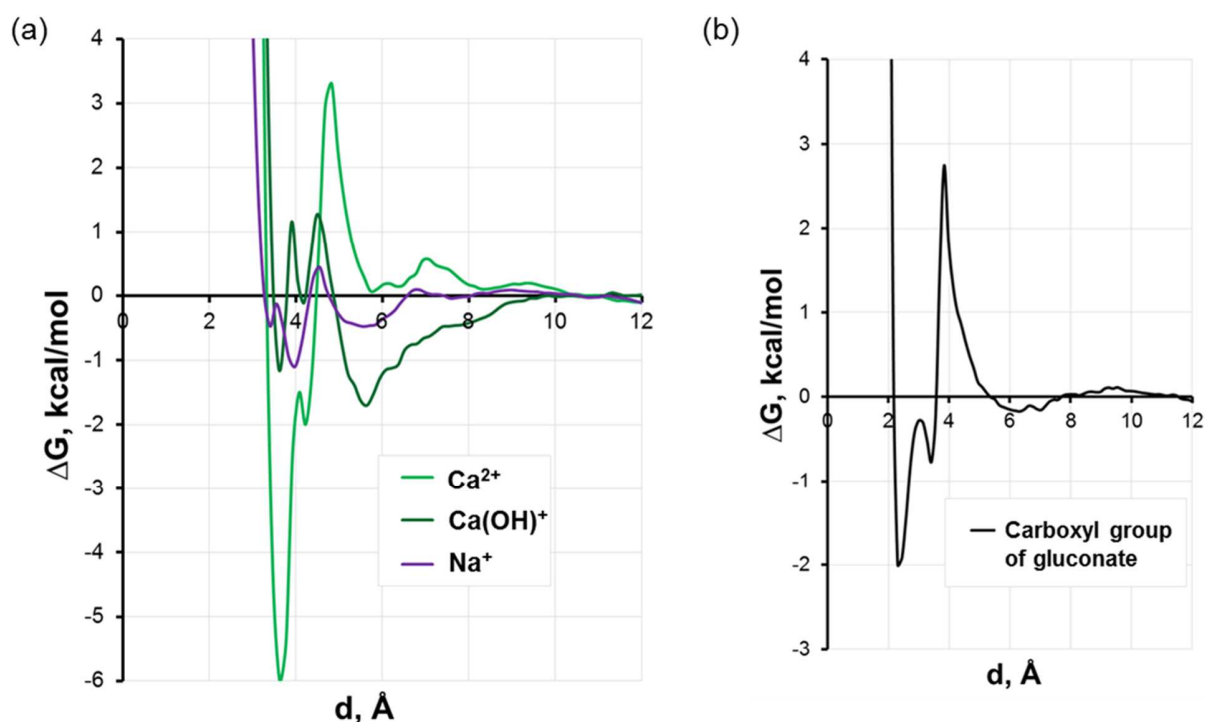
#### 5 **3.1. Complexation of $\text{UO}_2^{2+}$ in aqueous solutions**

6 Uranium (VI) exists in aqueous solutions in the form of uranyl cation,  $\text{UO}_2^{2+}$ , and in  
7 alkaline solutions it forms hydroxocomplexes of different stoichiometry with a general  
8 formula  $(\text{UO}_2)_m(\text{OH})_n^{2m-n}$  (Choppin and Mathur, 1991; Krestou and Panias, 2004; García-  
9 Hernández et al., 2006; Moll et al., 2014; Drobot et al., 2016). Hydroxyl ions in the  
10 coordination sphere of  $\text{UO}_2^{2+}$  are negatively charged, and different properties are  
11 expected for the hydrolysed species compared to the aqua complexes in solutions at  
12 lower pH. To better understand the sorption behaviour of  $\text{UO}_2(\text{OH})_3^-$  on C-S-H surfaces,  
13 a series of PMF calculations were performed for the selected pairs of ions in bulk  
14 aqueous solutions (Fig. 2).

15 Formation of calcium uranate carbonate complexes is known for carbonated  
16 systems (Dong et al., 2005; Fox et al., 2006; Stewart et al., 2010; Smith et al., 2015;  
17 Richter et al., 2016; Saleh et al., 2018), but in the absence of  $\text{CO}_2$  a formation of  
18 hydroxo complexes can be suggested where cations are bound with a hydroxyl “bridge”.  
19 The stabilisation by  $\text{Ca}^{2+}$  in alkaline solutions has been already proven for a number of  
20 actinides (Altmaier et al., 2008; Rabung et al., 2008; Fellhauer et al., 2010, 2016) and  
21 thus is also expected for U(VI). From the PMF profiles in Fig. 2(a) it can be clearly seen  
22 that there is a strong interaction between aqueous  $\text{UO}_2(\text{OH})_3^-$  and  $\text{Ca}^{2+}$  ions: a stable

1 complex is formed with the energy barrier about 10 kcal/mol. Two main energy minima  
2 found at interionic distances of  $\sim 4.1$  and  $\sim 3.6$  Å correspond to the formation of one and  
3 two OH<sup>-</sup> bridges, respectively.

4



5

6 **Figure 2.** The potential of mean force as a function of distance between  $\text{UO}_2(\text{OH})_3^-$  and  
7 cations (a) or carboxyl group of gluconate (b) in aqueous solution.

8

9 A fraction of calcium in alkaline solution can be present as  $\text{Ca}(\text{OH})^+$ , and a free  
10 energy profile for this pair has also been calculated. The energy minima are found at the  
11 same distance as for  $\text{Ca}^{2+}$  cation but the formed complexes have much lower stability:  
12 the energy barriers are about 2.2 kcal/mol at  $\sim 3.6$  Å and 1.7 kcal/mol at 5.5 Å.

1 Additionally,  $\text{Na}^+$  has been studied as a potentially competitive cation that is introduced  
2 into the system as a counterion of gluconate, and it is one of the major cations present in  
3 the real cement pore water. Sodium only weakly interacts with uranyl hydroxide in water  
4 showing only two shallow minima at distances of  $\sim 3.3$  and  $\sim 4.0$  Å. As it can be seen, the  
5 double free energy minimum is found for all the ions studied. The complexation of U(VI)  
6 with  $\text{Ca}(\text{OH})^+$  and  $\text{Na}^+$  can be considered weak, and these interactions should not  
7 interfere significantly with its uptake by C-S-H.

8 Uranyl can form complexes with more than one gluconate anion under alkaline  
9 conditions (Birjkumar et al., 2011; Colàs et al., 2013). The cation will mostly coordinate  
10 with deprotonated carboxyl groups of organic ion, but at highly alkaline solutions  
11 ( $\text{pH} > 13.9$ ) the gluconate hydroxyl groups can be deprotonated and can also participate  
12 in U(VI) complexation. The plot in Fig. 2(b) shows the free energy of binding a gluconate  
13 carboxyl group to the  $\text{UO}_2(\text{OH})_3^-$  ion. Even though both ions are negatively charged,  
14 complexation is possible due to the presence of an exchangeable water molecule in the  
15 solvation shell of  $\text{UO}_2(\text{OH})_3^-$ . The calculation results show that the energy required to  
16 replace this water molecule by gluconate is  $\sim 5$  kcal/mol. The distinct energy minima  
17 found at  $\sim 2.5$  Å  $\sim 3.4$  Å corresponding to the direct binding of U(VI) to the oxygens of the  
18 carboxyl group. The difference in the distance between the two of them can be  
19 explained by the different binding configuration of the organic molecule. In addition, it  
20 was observed that these complexes are stabilised by formation of hydrogen bonds  
21 between the oxygen of aqueous  $\text{OH}^-$  ion and one or two hydrogens of the closest  
22 gluconate alcohol functional groups.

1 To summarize, the combination of the results for U(VI) in solution with the available  
2 literature data allows us to suggest that complex formation between uranyl hydroxides  
3 and  $\text{Ca}^{2+}$  cations present at aqueous C-S-H interfaces should play a significant role in  
4 the sorption process. Meanwhile, complexation with other interfacial ions is minor, but  
5 cannot be excluded completely.

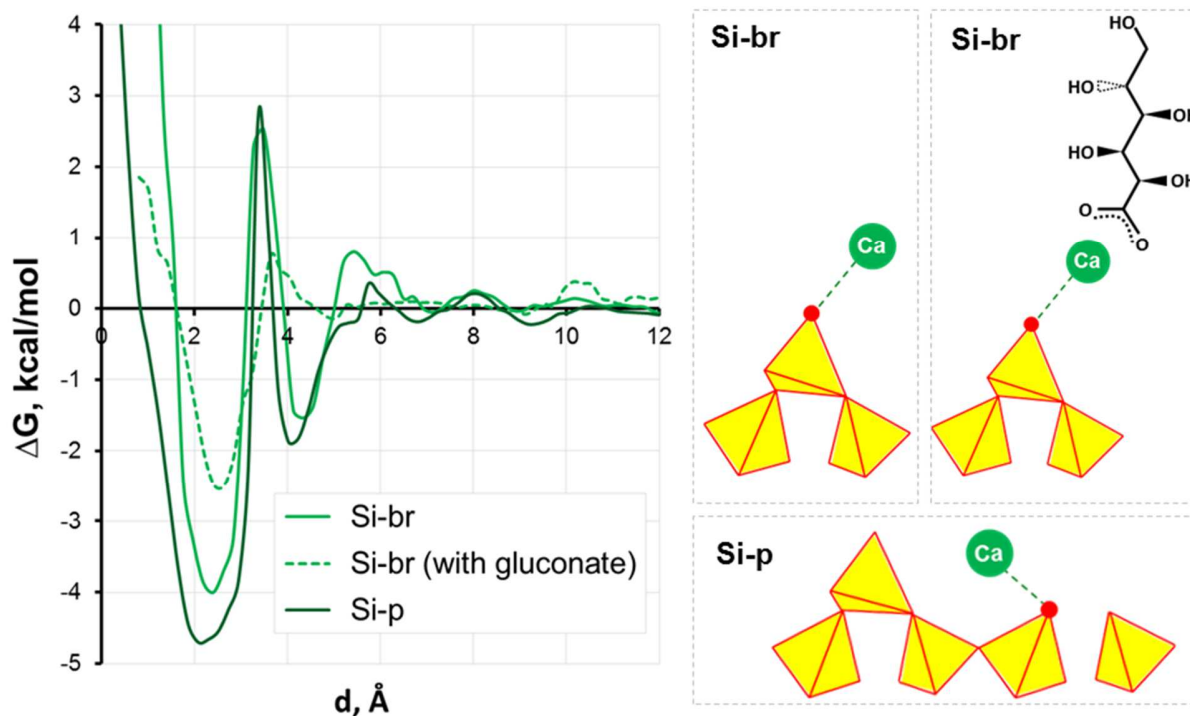
### 6 **3.2. Complexation of $\text{Ca}^{2+}$ and Ca-gluconate at the C-S-H interface**

7 The deprotonated silanol groups can be considered the most reactive groups of the  
8 C-S-H surface due to their high negative charge. Two typical sorption sites for  $\text{Ca}^{2+}$  on  
9 the C-S-H surface were selected for the PMF calculations in order to obtain quantitative  
10 information on the site-specific adsorption free energy: the deprotonated silanol group of  
11 the bridging silicon tetrahedron, and the deprotonated silanol group of the pairing silicon  
12 tetrahedron (the schematic representations of the sites are shown in Fig. 3).

13 The adsorption free energy profiles calculated for  $\text{Ca}^{2+}$  cations above two selected  
14 binding sites in Fig. 3 with and without gluconate demonstrate that in the absence of  
15 organics the energy of adsorption is nearly the same for both sorption sites sampled.  
16 The first energy minimum (at  $d \approx 2.5 \text{ \AA}$ ) corresponds to the inner-sphere coordination to  
17 the deprotonated surface oxygen, while the second pronounced minimum (at  $d \approx 4.2 \text{ \AA}$ )  
18 – to the outer-sphere coordination. The energy barrier between the inner- and outer-  
19 sphere complexes is 7.5 kcal/mol for the bridging Si site and 6.5 kcal/mol for the pairing  
20 Si site. This means that the complexation of  $\text{Ca}^{2+}$  with C-S-H surface is strong and a  
21 relatively high energy is required to replace the bound cation by another ion or molecule  
22 on the site.



1



2

3 **Figure 3.** Adsorption free energy profiles as functions of the distance between  $\text{Ca}^{2+}$  ion  
4 and the deprotonated silanol groups on the C-S-H surface. The schematic  
5 representation of the two distinct sorption sites (Si-br – bridging Si  
6 tetrahedron; Si-p – pairing Si tetrahedron) is shown on the right.

7

8 It is important to note that  $\text{Ca}^{2+}$  cations are not located strictly above the selected  
9 sorption sites, so the position of the first minimum does not represent the binding  
10 distance, but shows only how close the cation is to the surface on average; the z-  
11 coordinate of the deprotonated oxygen is taken as a reference of zero distance.

1 In our study, we consider that the cement system was equilibrated with organics  
2 prior to contact with U(VI). The C-S-H phases with low Ca/Si ratio would typically have a  
3 high number of bridging sites, therefore, these sites were selected to study the sorption  
4 of a  $\text{Ca}^{2+}$  gluconate complex in the PMF calculation, where constraints were applied only  
5 to the  $\text{Ca}^{2+}$  ion. At high pH, the formation of very stable multinuclear Ca-gluconate  
6 complexes is expected (Pallagi et al., 2014). Nevertheless, the concentrations of  
7 gluconate used here are far too low to observe such complexation. In the absence of  
8 ligand excess, cation complexation with deprotonated carboxyl group is the most  
9 probable interaction that is mostly driven by electrostatic forces.

10 The free energy of adsorption (dashed green line in Fig. 3) is noticeably different  
11 for  $\text{Ca}^{2+}$  when a carboxyl group of the gluconate contributes to the first coordination  
12 sphere of the cation. The first minimum at  $d \approx 2.5 \text{ \AA}$  is due to the same inner-sphere  
13 complexation as for the organic-free system, but the energy necessary to replace  
14 surface oxygen by a water molecule is lower by half in the presence of gluconate,  
15  $\sim 2.5 \text{ kcal/mol}$ . Also, the second energy minimum corresponding to the outer-sphere  
16 complexation disappears. Accordingly, the binding of  $\text{Ca}^{2+}$  to the C-S-H surface  
17 becomes much weaker and potentially may result in a higher probability of substitution  
18 for a competing solution cation (e.g.,  $\text{Na}^+$  or  $\text{UO}_2^{2+}$ ).

### 19 **3.3. Complexation of $\text{UO}_2^{2+}$ , $\text{UO}_2(\text{OH})_3^-$ , and $\text{Na}^+$ on the C-S-H surface**

20 The MD simulations of  $\text{UO}_2^{2+}$  cations without ligands at the C-S-H surface have  
21 been performed here in order to understand the effects of aqueous hydroxyl ions and  
22 dissolved organics on the surface adsorption.  $\text{UO}_2^{2+}$  cations are bound to the same

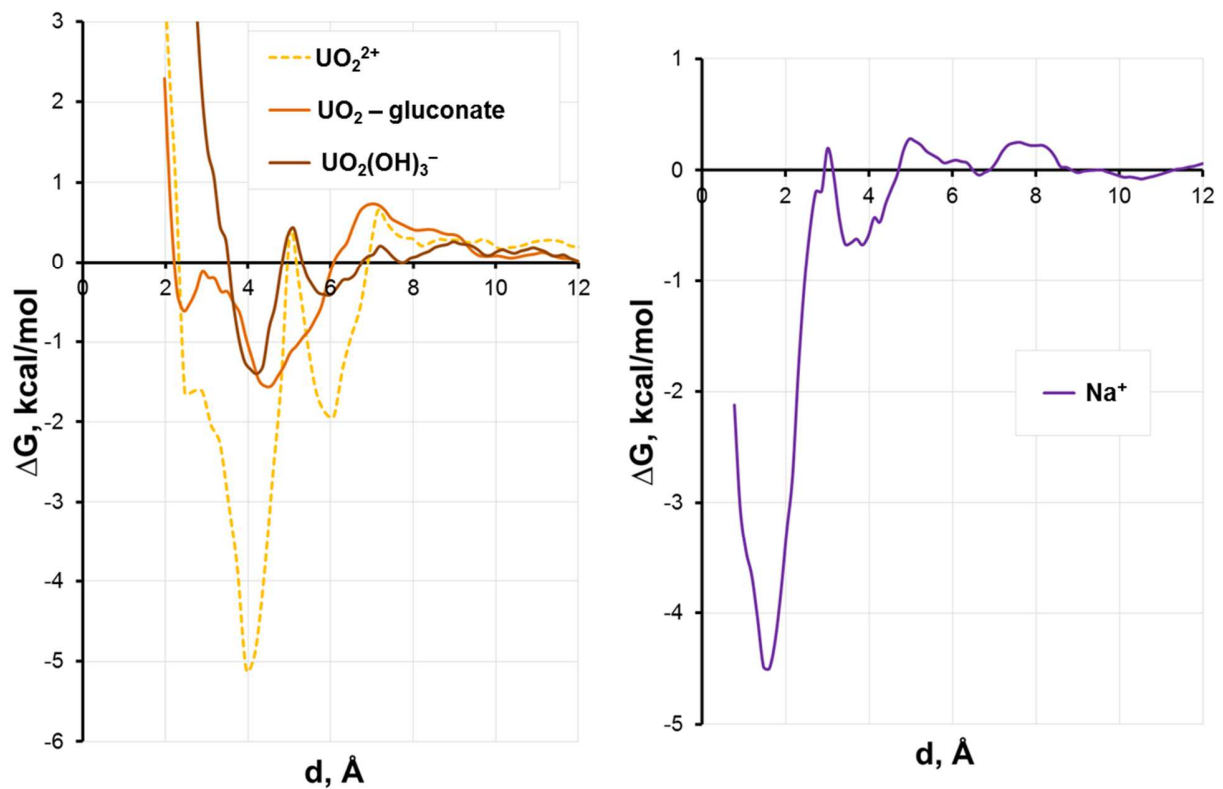
1 surface sites as  $\text{Ca}^{2+}$  cations and a competition between them can be expected as it  
2 was previously discussed (Androniuk et al., 2017). A preferential  $\text{UO}_2^{2+}$  sorption on the  
3 deprotonated sites is observed. The adsorption free energy profile of the uranyl cation  
4 as a function of distance from the Si-bridging site is presented in Fig. 4 (dashed line).  
5 There are two main energy minima at  $\sim 4.0$  and  $\sim 6.0$  Å from the surface which  
6 correspond to the formation of the inner- and outer-sphere surface complexes,  
7 respectively. Compared to  $\text{Ca}^{2+}$ ,  $\text{UO}_2^{2+}$  binds farther from the surface and the energy  
8 barrier for the transition between two surface complexes is about 5.5 kcal/mol, which is  
9 2 kcal/mol lower.  $\text{UO}_2^{2+}$  will preferably bind with the deprotonated oxygen as an inner-  
10 sphere complex on the Ca-free sites or on the sites where  $\text{Ca}^{2+}$  is sorbed as an outer-  
11 sphere complex, since the energy necessary to substitute the directly bound  $\text{Ca}^{2+}$  cation  
12 is relatively high.

13 The PMF oscillations seen in Fig. 4 can be associated with the local structural  
14 properties of the interface for the selected cation and sorption site: the influence of other  
15 neighboring ions, the high negative charge of the surface, and the  $\text{H}_2\text{O}$  surface  
16 rearrangements through hydrogen bonding, etc.

17 The general trends of  $\text{UO}_2(\text{OH})_3^-$  sorption behaviour have been first analysed from  
18 the unconstrained MD simulations. The atomic density profiles (Fig. 5(a)) show that the  
19 closest peak for U(VI) is found at a distance of  $\sim 4\text{-}5$  Å from the position of the top-most  
20 surface silanol groups. The direct binding has not been observed during the  
21 unconstrained simulations. However, the complexation of  $\text{UO}_2(\text{OH})_3^-$  with  $\text{Ca}^{2+}$  cations  
22 has been distinctly identified in the surface density maps (as illustrated in Fig. 5(b)). As  
23 expected, the PMF curve (Fig. 4) reveals that the sorption of  $\text{UO}_2(\text{OH})_3^-$  complex is much

1 weaker but two distinct minima can be seen at the same distance from the Si-bridging  
2 site as for the bare  $\text{UO}_2^{2+}$  ion with the energy barriers of about  $\sim 1.8$  and  $\sim 0.3$  kcal/mol,  
3 respectively.

4



5

6 **Figure 4.** Adsorption free energy profiles of uranyl (left) and  $\text{Na}^+$  (right) as functions of  
7 their distance from the Si-bridging sorption site on C-S-H surface.

8

9 The adsorption free energy of  $\text{UO}_2^{2+}$  cation coordinated with gluconate has been  
10 calculated next (solid yellow line in Fig. 4). The free energy of adsorption of the  
11  $\text{UO}_2^{2+}$ /gluconate complex is comparable to the one of the hydrolysed ion. However, a

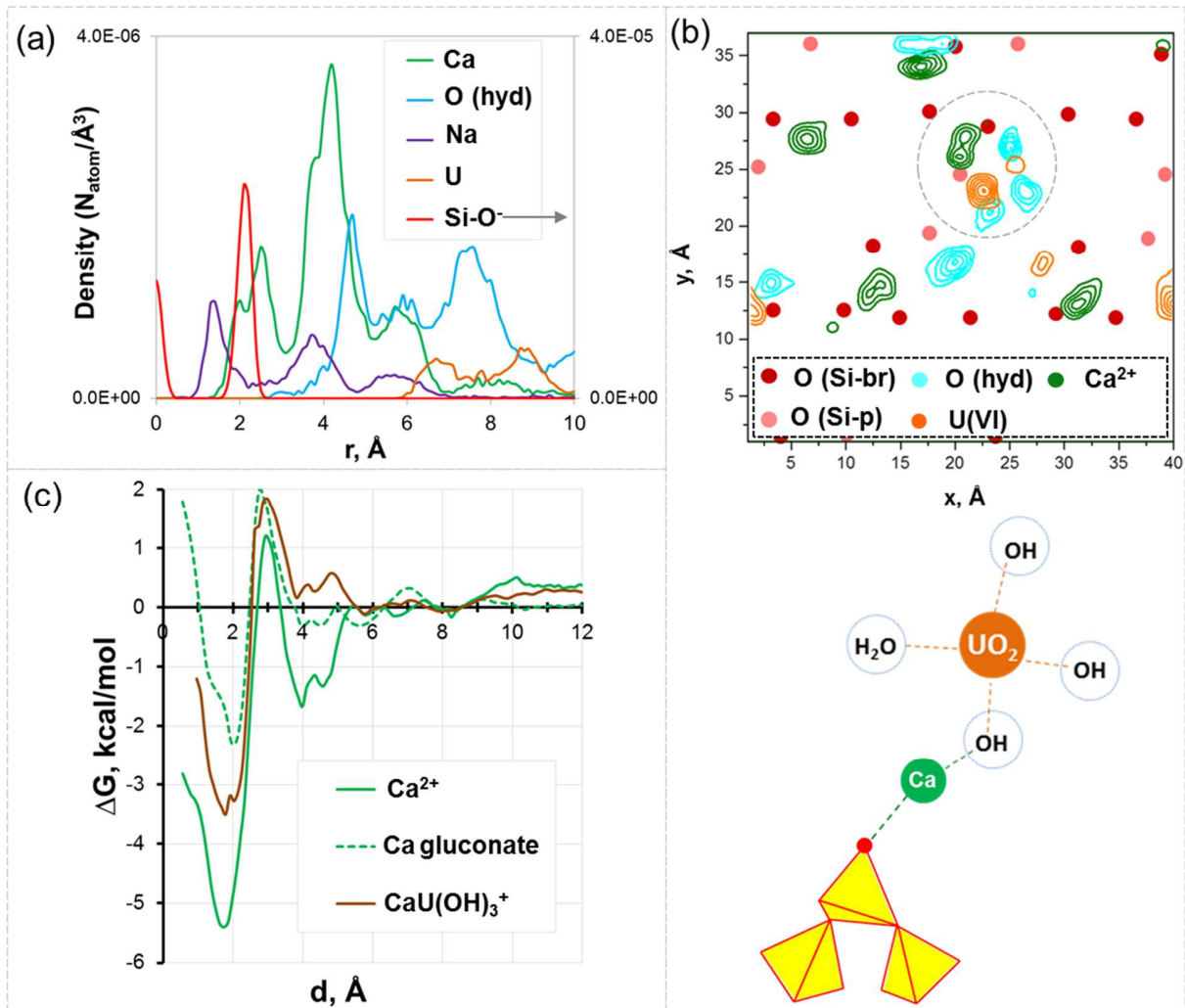
1 distinct difference in the binding energies can be observed: there is no clear separation  
2 between outer- and inner-sphere complexation with a broad shallow energy minimum  
3 found at distances  $d > 4 \text{ \AA}$ . It can be concluded that the presence of gluconate has a  
4 much more important effect on the  $\text{UO}_2^{2+}$  surface sorption, compared to  $\text{Ca}^{2+}$ , and there  
5 is more than a threefold decrease of the free energy minimum while pulling the position  
6 of the minimum further away from the surface ( $d \approx 4.5 \text{ \AA}$ ).

7 In combination with the results from the PMF calculations in bulk solution  
8 ( $\text{UO}_2(\text{OH})_3^-/\text{Ca}^{2+}$ ), it would therefore be presumed that the  $\text{UO}_2(\text{OH})_3^-$  complex will  
9 preferably form a stable association with  $\text{Ca}^{2+}$  cations bound to the surface. Similar  
10 behaviour has been observed for uranyl complexation on Ca bentonite at high pH  
11 conditions (Philipp et al., 2019), where inner-sphere adsorption was found despite an  
12 anionic character of predominant aqueous species, and 4-fold coordination of U(VI)  
13 surface complexes has been proven experimentally suggesting the possible mediating  
14 contribution of  $\text{Ca}^{2+}$  cations.

15 Finally, the adsorption free energy of the identified  $\text{CaUO}_2(\text{OH})_3^+$  complex  
16 (Fig. 5(b)) has also been analyzed. In our model, the C-S-H surface does not have  
17 homogeneous distribution of sorption sites of the same type, so the free energy profile  
18 for an individual case will also slightly depend on the neighboring sites and sorbed  
19 cations. Thus, the PMF curves for  $\text{Ca}^{2+}$  and Ca gluconate have been analyzed for the  
20 same sorption site to provide a better reference for comparison. The main energy  
21 minima that correspond to inner-sphere complexation with the deprotonated silanol  
22 group can be found at about  $\sim 2 \text{ \AA}$  (see Fig. 5 (c)). It can be clearly seen that the sorption  
23 of  $\text{CaUO}_2(\text{OH})_3^+$  is still weaker than for  $\text{Ca}^{2+}$ , but stronger than for Ca gluconate. Thus, it

1 can be assumed that  $\text{CaUO}_2(\text{OH})_3^+$  will become an important competitor for the sorption  
2 sites in the presence of gluconate at the interface.

3



4

5 **Figure 5.** Atomic density profiles of solution species near the C-S-H surface (a), atomic  
6 density contour maps of time-averaged surface distributions of selected  
7 atoms at  $d \approx 4-7$  Å from the surface with the schematic representation of the  
8 surface ternary complex (b), and adsorption free energy profile of Ca  
9 complexes as functions of their distance from the Si-bridging sorption site (c).

1

2        It has previously been reported that U(VI) sorption is the strongest on C-S-H with  
3 lower Ca/Si ratios in the absence of alkali (Tits et al., 2011). Our present work is  
4 consistent with these results. We find that there are two main mechanisms controlling  
5 the U(VI) sorption on the C-S-H surface: the binding to unoccupied deprotonated  
6 silanols and the formation of ternary surface complex with  $\text{Ca}^{2+}$  cations. It has to be  
7 mentioned that minor fraction ( $< 5\%$ ) of other possible species ( $\text{UO}_2(\text{OH})_2^0$ ,  $\text{Ca}(\text{OH})^+$ ,  
8  $\text{UO}_2(\text{OH})^+$ ,  $\text{UO}_2^{2+}$ , etc) will also contribute to surface sorption, even though they were not  
9 analysed in detail in this work. For C-S-H with higher Ca/Si ratio and at higher pH, U(VI)  
10 will mostly be found as a  $\text{UO}_2(\text{OH})_4^{2-}$  complex and a larger fraction of Ca will be present  
11 as  $\text{Ca}(\text{OH})^+$ . Therefore, it can be assumed that the direct binding to the surface oxygens  
12 would be less probable, and the sorption through the formation of ternary complexes will  
13 be reduced due to the less favourable binding with  $\text{Ca}(\text{OH})^+$  compared to  $\text{Ca}^{2+}$ , as it was  
14 discussed above. Several recent spectroscopic works (Tits et al., 2011; Macé et al.,  
15 2013; Tits et al., 2015) have shown that three distinguishable types of U(VI) species can  
16 be identified in the cementitious systems: (i) surface complexed; (ii) incorporated; (iii)  
17 precipitated. The suggested incorporated U(VI) species should not be affected by the  
18 presence of organics in the pore solution, so they were not considered in this study.

19        Additionally, we have analyzed the sorption of  $\text{Na}^+$  cations on the Si-bridging site. It  
20 has been previously confirmed that the nature of interaction between alkali and C-S-H is  
21 electrostatic, and  $\text{Na}^+$  will preferably sorb on the external surfaces of C-S-H particles  
22 (Bach et al., 2013; Henocq, 2017). In our simulations, it was observed that  $\text{Na}^+$  cations  
23 are strongly attracted by the surface and most of them are found surface-bound for the

1 entire time of the equilibrium MD simulation run.  $\text{Na}^+$  has an ionic radius similar to  $\text{Ca}^{2+}$ ,  
2 but its solvation shell is weaker due to the lower charge and lower hydration energy.  
3 Thus, much less energy is required to replace a water molecule in its first coordination  
4 sphere by a negatively charged surface oxygen. It can be seen from the adsorption free  
5 energy profile (Fig.4) that there is almost no energy barrier to overcome for  $\text{Na}^+$  to sorb  
6 on the Si-bridging surface site. Also, the sorption behaviour of  $\text{Na}^+$  is very similar to that  
7 of the  $\text{Ca}^{2+}$ /gluconate complex while the energy gain is almost twice as large  
8 ( $\sim -4.5$  kcal/mol for the former vs  $\sim -2.5$  for the latter). It can be concluded that  $\text{Na}^+$   
9 cations in solution can be very important competitors for the surface sorption sites, they  
10 are able to replace  $\text{Ca}^{2+}$  and  $\text{Ca}^{2+}$ /gluconate complex on the C-S-H surface and affect  
11 the  $\text{UO}_2(\text{OH})_3^-$  adsorption. However, the peak position of  $\text{Na}^+$  density at the distance of  
12  $\sim 1\text{-}2$  Å from the Si-pairing silanols shows that  $\text{Na}^+$  is able to sorb on the sites that are  
13 less attractive for  $\text{Ca}^{2+}$ , most probably due to the difference in their charges (Fig. 5(a)).  
14 Thus, the noticeable effect of  $\text{Na}^+$  on the sorption properties of C-S-H will be more  
15 pronounced at higher concentrations when the free sorption sites would be saturated.

16

#### 17 **4. Conclusions**

18 The most probable mechanisms of molecular interactions in the ternary system  
19 C-S-H / U(VI) / gluconate have been quantitatively analyzed and described using  
20 classical and constrained molecular dynamics simulations. It is shown that complex  
21 formation between uranyl hydroxides and  $\text{Ca}^{2+}$  cations at the C-S-H aqueous interfaces  
22 has an important role in the overall sorption process. The existence of stable surface



1 ternary complexes of  $\text{UO}_2(\text{OH})_3^-$  and  $\text{Ca}^{2+}$  were first identified using unconstrained MD  
2 simulations, then their adsorption free energies characterizing specific surface sites  
3 were quantitatively evaluated by the PMF calculations. Additionally, it was observed that  
4  $\text{UO}_2(\text{OH})_3^-$  complex can bind directly to the unoccupied deprotonated surface silanols  
5 increasing its total adsorption on C-S-H surfaces with low Ca/Si ratios, which agrees well  
6 with available data in the literature.

7         The effect of gluconate ions on the U(VI) uptake by the C-S-H surfaces has been  
8 found to be indirect. We have shown that gluconate forms stable complexes with  $\text{Ca}^{2+}$ ,  
9 decreasing the strength of its binding to the surface sorption sites. As a result, it would  
10 be easier for Ca-uranyl complexes to substitute  $\text{Ca}^{2+}$ , thus potentially increasing the  
11 uptake of U(VI) by the C-S-H phases. Finally,  $\text{Na}^+$  is proven to be an important  
12 competitor for certain surface sorption sites and can potentially affect the equilibrium  
13 properties of the interface. However, C-S-H surfaces provide numerous other sorption  
14 sites for  $\text{Na}^+$  ions, and the effect of the competitive alkali presence would be noticeable  
15 once these available sorption sites are occupied.

16         The suggested mechanisms of U(VI) sorption on the C-S-H surface with low Ca/Si  
17 ratios can be studied for other actinides that were proven to be stabilized by  $\text{Ca}^{2+}$  in  
18 alkaline solutions. C-S-H phases with low Ca/Si ratio are the model for low pH cement  
19 and degraded cements. Therefore, it is crucial to atomistically model cement at other  
20 degradation stages for the most comprehensive description of the molecular  
21 mechanisms involved in U(VI) uptake by cementitious materials. Further studies will  
22 gauge the effect of gluconate on U(VI) sorption on C-S-H phases with higher Ca/Si ratio.

1

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