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1 **Stability of U(VI) doped calcium silicate hydrate gel in repository-**  
2 **relevant brines studied by leaching experiments and spectroscopy**

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## 25 **Abstract**

26 The stability of calcium silicate hydrate (C-S-H) gel doped with uranium to form calcium uranium  
27 silicate hydrate (C-U-S-H) gel was investigated in 2.5 M NaCl, 2.5 M NaCl/0.02 M Na<sub>2</sub>SO<sub>4</sub>, 2.5 M  
28 NaCl/0.02 M NaHCO<sub>3</sub> or 0.02 M NaHCO<sub>3</sub> solutions relevant to the geological disposal of radioactive  
29 waste. The C-U-S-H gel samples were synthesized by direct U(VI) incorporation and characterized  
30 with time-resolved laser-induced luminescence spectroscopy (TRLFS), infrared (IR) spectroscopy,  
31 powder X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning  
32 calorimetry (DSC), and thermogravimetric analysis (TGA). Time-dependent pH changes as well as the  
33 Ca, Si and U release from C-U-S-H gels into the brines, determined by inductively coupled plasma  
34 mass spectrometry (ICP-MS), were monitored for three calcium-to-silicon (C/S) ratios (0.99, 1.55 and  
35 2.02) over 32 d. Subsequently, changes of the U(VI) speciation and C-S-H mineralogy caused by  
36 leaching were investigated with TRLFS, IR spectroscopy and XRD. Results indicated that  
37 composition and pH value of the leaching solution, the presence of portlandite as well as formation  
38 and solubility of calcite as secondary phase determine the U(VI) retention by C-S-H gel under high  
39 saline and alkaline conditions. At high ionic strengths, the Ca release from C-S-H and secondary  
40 phases like calcite is increased. Under hyperalkaline conditions only small amounts of U(VI) were  
41 released during leaching. A decrease of the pH due to the additional presence of carbonate was linked  
42 with an increased U(VI) release from C-S-H gel leading to the formation of aqueous calcium uranyl  
43 carbonate in the supernatant solution.

44

## 45 **1. Introduction**

46 The long-term isolation of high-level nuclear waste, such as spent fuels from nuclear power  
47 plants, in deep geological formations behind multiple protective barriers is recognized worldwide as  
48 preferred strategy to protect humans and environment. In this concept, as part of the geo-engineered  
49 barrier cementitious materials in the form of concrete or grout are foreseen to ensure mechanical  
50 stability and sealing of disposal tunnels. Moreover, cementitious materials are commonly used for the  
51 solidification of low and intermediate level radioactive waste. For a reliable long-term safety

52 assessment of a nuclear waste repository, it is necessary to identify materials and processes that  
53 contribute to the retention of radionuclides potentially released due to water intrusion into a disposal  
54 site. In addition, criteria that might lead to a mobilization of radionuclides have to be identified.

55 The immobilization potential of hardened cement paste (HCP) as well as of C-S-H, as main  
56 component of HCP, towards radionuclides such as Cm(III), Th(IV) or U(VI) has been shown in a  
57 number of literature studies, e.g. (Pointeau et al., 2004; Stumpf et al., 2004; Wieland et al., 1997).  
58 Among the components of spent nuclear fuel 95.5% of the mass is contributed by the uranium isotopes  
59 235, 236 and 238 (OECD, 2006). Their long half-lives and high chemo-toxicity render them important  
60 long-term pollutants.

61 Studies on U-containing HCP showed the presence of uranium in the oxidation state +VI mainly  
62 inside the C-S-H gel of HCP (Harfouche et al., 2006; Macé et al., 2013; Wersin et al., 2003; Zhao et  
63 al., 2000). The structure of C-S-H gel is similar to a defected 14 Å tobermorite structure, consisting of  
64 layered polyhedral CaO planes, silicate chains consisting of pairing and bridging Si tetrahedra called  
65 “dreierketten” and interlayers filled with water and Ca<sup>2+</sup> ions (Richardson, 2008). HCP and C-S-H  
66 characteristics, such as layer-to-layer distance, length of silicate chains, and co-presence of portlandite  
67 are defined by the molar C/S ratio of the cementitious material, which can exceed 1.7 in freshly  
68 hydrated Portland cement and fall below 0.6 in nearly decomposed HCP (Grangeon et al., 2013;  
69 Taylor, 1993; Thiery et al., 2013). The highest C/S ratio achieved by exclusively C-S-H in HCP is  
70 around 1.7 while further Ca is contributed in the form of portlandite (Ca(OH)<sub>2</sub>) (Yu et al., 1999).

71 Studies of C-U-S-H gel using TRLFS have identified 3 different U(VI) bonding environments: (i)  
72 a surface complex, (ii) interlayer incorporation, (iii) a Ca uranate-like surface precipitate (Tits et al.  
73 (2011; 2015)). An increase of the U(VI) retention by C-S-H gel with increasing C/S ratio was  
74 associated with a U(VI) uptake mechanism that involves Ca from the C-S-H interlayers. Androniuk et  
75 al. (2017) combined wet chemistry experiments and molecular dynamics computer simulations to  
76 identify the sorption behavior of gluconate and U(VI) on C-S-H gel. The authors identified several  
77 sorption sites for U(VI) on the C-S-H surface like mono and bidentate outer-sphere uranyl complexes  
78 bound to deprotonated oxygens of bridging Si tetrahedra. Due to a sorption of Ca<sup>2+</sup> ions on the same  
79 sorption sites, a competition between uranyl and Ca<sup>2+</sup> ions was suggested.

80 Gaona et al. (2012) developed a geochemical model for the interactions between U(VI) and C-S-  
81 H gel based on the results of extended X-ray absorption fine structure (EXAFS) spectroscopy  
82 (Harfouche et al., 2006) and TRLFS (Tits et al., 2011; Wieland et al., 2010). The authors confirmed  
83 that U(VI) is mainly located in the C-S-H interlayers similar to  $\text{Ca}^{2+}$  ions. In contrast, the release of  
84 U(VI) from HCP is controlled by dissolution and recrystallization of the C-U-S-H gel rather than by  
85 surface desorption processes (Tits et al., 2015). It is therefore important to identify factors that will  
86 affect the stability of C-U-S-H gel, such as pH, ionic strength and composition of the leaching  
87 solution, the formation of secondary phases and how these might incorporate U(VI), as well as the  
88 U(VI) species and their mobility in the leaching solution.

89 The majority of investigations on radionuclide retention by cementitious materials, however, have  
90 only been performed at low ionic strengths, e.g. (Gaona et al., 2012; Harfouche et al., 2006; Tits et al.,  
91 2011). Studies of cementitious materials in high ionic strength solutions include Hill et al. (2006),  
92 Kienzler et al. (2010; 2016) and Bube et al. (2014). Hill et al. (2006) studied the dissolution of  
93 radionuclide-free C-S-H gel (C/S 0.8–2.0) in 0.1 to 1 M NaCl solutions. The authors found an  
94 increasing amount of leached  $\text{Ca}^{2+}$  with increasing NaCl concentration which was attributed to an ion  
95 exchange mechanism between Na and Ca. Kienzler et al. (2010; 2016) and Bube et al. (2014) studied  
96 the corrosion of U(VI)-containing cement monoliths in saturated NaCl- or  $\text{MgCl}_2$ -rich brines.  
97 Comprehensive analyses of drill core fragments and bulk powder samples after long-term leaching  
98 showed the presence of a uranophane-like  $(\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O})$  phase while no becquerelite,  
99 meta-schoepite or di-uranate phases were detected. The U(VI) concentrations measured in leaching  
100 solutions were up to  $5 \times 10^{-7}$  M while a diffusive penetration of halite into the cement monolith surface  
101 up to 5 cm was observed.

102 Carbonate-containing high saline host rock pore waters, containing up to 4 M  $\text{Na}^+$ , 2.8 M  $\text{Cl}^-$ ,  
103 0.1 M  $\text{SO}_4^{2-}$ , and 0.06 M  $\text{HCO}_3^-$ , are reported for potential sites for nuclear waste repositories, e.g., for  
104 Cretaceous argillites in North Germany (Peryt et al., 2010; Wolfgramm et al., 2011), as well as for  
105 sedimentary bedrocks in Japan (Hama et al., 2007) and in Canada (Mazurek, 2004). However, to the  
106 best of the author's knowledge, systematic studies on the stability of cementitious phases and their

107 retention potential for U(VI) in complex repository-relevant brines have not been reported in the  
108 literature.

109 Such high ionic strengths pore waters could modify dissolution/recrystallization processes of C-S-  
110 H gel including the formation of secondary phases, which in turn could affect the stability of C-S-H  
111 gel as well as the U(VI) release or retention.

112 Thus, the objective of the present work was to evaluate the stability of C-U-S-H gel and its U(VI)  
113 retention capability in high ionic strengths pore waters. For this, C-U-S-H gel samples with three  
114 different C/S ratios (2.02, 1.55 and 0.99, representing a portlandite saturated C-S-H system as well as  
115 chemically degraded cement paste) were prepared and leached in solutions containing 2.5 M NaCl,  
116 0.02 M Na<sub>2</sub>SO<sub>4</sub> and/or 0.02 M NaHCO<sub>3</sub>. In addition, spectroscopic, microscopic and diffraction  
117 techniques were applied before and after leaching to obtain a mechanistic understanding of the  
118 underlying processes such as the evolution of the C-S-H gel and of U(VI) species on the solid phase as  
119 well as secondary phase formation and formation of U(VI) species in the leaching solution.

120

## 121 **2. Materials and experimental methods**

### 122 **2.1. Materials**

123 The synthesis of C-U-S-H gel and subsequent leaching experiments were performed in an inert  
124 gas glove box (N<sub>2</sub> atmosphere, O<sub>2</sub> < 2 ppm) using degassed deionized water (18 MΩ cm; mod. Milli-  
125 RO/Milli-Q-System, Millipore, Schwalbach, Germany). Prior to experiments, centrifuge tubes  
126 (polypropylene, Greiner bio-one, Kremsmünster, Austria) were immersed in 0.1 M HCl for 12 h and  
127 subsequently rinsed with deionized water to remove contaminants.

128 Solid UO<sub>3</sub> was prepared from uranyl peroxide (Chemapol Ltd, Czech Republic) after a method  
129 reported by Rosenheim and Daehr (1929). For C-S-H synthesis, KOH (ACS reagent, Roth, Karlsruhe,  
130 Germany), NaOH (p. a., Roth), fumed silica (AEROSIL 300, Evonik, Essen, Germany), and  
131 carbonate-free CaO (anhydrous, trace metals basis, Sigma-Aldrich, St. Louis, Missouri, USA) were  
132 used. Previously, NaOH and KOH surface carbonate was removed by washing the NaOH and KOH  
133 pellets several times with degassed deionized water in a Büchner funnel under inert gas atmosphere.

134 Total inorganic carbonate concentrations of prepared NaOH and KOH solutions were determined with  
135 a multi-N/C 2100 S (Analytik Jena, Jena, Germany) and were below 100  $\mu\text{M}$ . For drying, wet C-S-H  
136 samples were either frozen in liquid nitrogen, and dried at 1 mbar and  $-40\text{ }^\circ\text{C}$  for 1 d in a freeze-drying  
137 system (mod. ALPHA 1-4 LSCplus, Christ, Osterode am Harz, Germany) or exposed to a  $\text{CO}_2$ -free  $\text{N}_2$   
138 atmosphere over two weeks.

139

## 140 **2.2. Synthesis of C-U-S-H gel**

### 141 **2.2.1. Direct synthesis of C-U-S-H gel**

142 C-U-S-H gel samples (A–C) were prepared applying a direct incorporation method. For this, a  
143 U(VI)-containing artificial cement pore water (ACW; (Berner, 1992)) was prepared by adding an  
144 excess of solid  $\text{UO}_3$  to a solution of 0.18 M KOH and 0.114 M NaOH (pH 13.3) and stirring for a  
145 week. Subsequently, the ACW was separated from remaining solid  $\text{UO}_3$  by centrifugation ( $6800\times g$ ,  
146 mod. Avanti J-20 XP, Beckman Coulter, Krefeld, Germany) and analyzed for U(VI) by ICP-MS  
147 analysis (KED-mode, He gas, mod. NexION 350X/Elan 9000, PerkinElmer, Waltham, MA, USA)  
148 after adjusting the pH to 2 with concentrated  $\text{HNO}_3$ . The resulting ACW contained  $19.5\text{ }\mu\text{M}$  U. This  
149 U(VI)-containing ACW was added to a mixture of fumed silica and carbonate-free CaO. While the  
150 CaO to  $\text{SiO}_2$  ratio was varied depending on the targeted C/S ratio (1.0, 1.6, 2.0), the solid-to-liquid  
151 (S/L) ratio was fixed at  $24\text{ g L}^{-1}$ . Suspensions were shaken end-over-end with a rotator SB2 (Stuart,  
152 Staffordshire, UK) for 14 d, and then filtered through a Whatman ashless 541-grade filter ( $22\text{ }\mu\text{m}$  cut-  
153 off). The C-U-S-H gel samples were washed with deionized water and stored moist in sealed tubes for  
154 leaching experiments (cf. section 2.3) or dried for spectroscopy. For the determination of the elemental  
155 compositions, C-S-H samples were decomposed in hydrofluoric acid and then analyzed for Ca, Si, Na,  
156 K, and U by ICP-MS. An additional C-S-H gel (sample J) was synthesized at a S/L ratio of  $24\text{ g L}^{-1}$  in  
157 U(VI)-free ACW for SEM investigations that required a U(VI)-free C-S-H gel.

158

159

### 160 **2.2.2. Sorption of U(VI) onto C-S-H gel**

161 For a comparison of samples A–C with C-U-S-H gel synthesized by Tits et al. (2011), a further  
162 C-U-S-H gel (CSH<sub>Nitrate</sub>) with a target C/S ratio of 1.3 was prepared using the method proposed by  
163 these authors. For this, sample J was exposed to a UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solution which contained 19.5 μM  
164 U(VI) for 14 d (S/L ratio: 24 g L<sup>-1</sup>, pH after 14 d: 11.7). Subsequently, the C-U-S-H gel was similarly  
165 filtered off, washed with deionized water, and stored moist.

166

### 167 **2.3. Leaching experiments**

168 For batch leaching experiments, wet C-U-S-H gel samples (A–C), prepared by direct synthesis,  
169 were equilibrated in 2.5 M NaCl, 2.5 M NaCl/0.02 M Na<sub>2</sub>SO<sub>4</sub>, 2.5 M NaCl/0.02 M NaHCO<sub>3</sub> or 0.02 M  
170 NaHCO<sub>3</sub> at a S/L ratio of 10 g L<sup>-1</sup> by shaking the samples end-over-end with a rotator SB2 for up to  
171 32 d. Subsequently, the water contents of samples A–C were determined by TGA to determine the  
172 actual S/L ratios in each leaching experiment. After different time intervals, up to 768 h, samples were  
173 centrifuged at 6800×g. Each supernatant solution was analyzed for Ca, Si and U as well as for the pH  
174 value. Solid and liquid phases after leaching were characterized by spectroscopic and further analytical  
175 methods (cf. section 2.4.). All leaching experiments mentioned above were performed as triplicates.

176 Additionally, sample B was leached in 2.5 M NaCl/0.075 M NaHCO<sub>3</sub> for 768 h to visualize  
177 changes in the TRLFS spectrum of C-U-S-H gel after leaching in solutions with high concentrations of  
178 carbonate. To determine the influence of increasing carbonate concentrations on the pH evolution and  
179 U(VI) release from C-U-S-H gel, sample A was exposed to solutions containing 1, 2, 10, 20, 50, and  
180 75 mM NaHCO<sub>3</sub> for 768 h. Subsequently, the supernatants were separated by centrifugation and  
181 analyzed for the pH value and released U. To get detailed information about the Ca and Si release in  
182 dependence on NaCl concentrations, sample J was exposed to solutions containing 0, 0.5, 1.0, 1.5, 2.0,  
183 and 2.5 M NaCl at an actual S/L ratio of 1.5 g L<sup>-1</sup> for 7 d. Subsequently, the supernatants were  
184 analyzed for Ca and Si.

185



## 186 **2.4. Analytical techniques and calculation methods**

187 For TRLFS investigations, C-U-S-H gel samples were suspended in deionized water, transferred  
188 into Boro 5.1 (ASTM type 1 class B glass, 5 mm) tubes (Deutero, Kastellaun, Germany) and shock-  
189 frozen in liquid N<sub>2</sub>. The tubes were placed in a cryogenic cooling system (mod. TG-KKK, KGW-  
190 Isotherm, Karlsruhe, Germany) and further cooled with N<sub>2</sub> vapor to a constant temperature of  
191 (153 ± 2) K. The cooling of the samples was necessary to generate a detectable U(VI) luminescence  
192 signal by the suppression of dynamic quenching effects (Wang et al., 2005a). The laser set-up was  
193 optimized for high intensities and good signal-to-noise ratios of the spectra: front entrance of 500 μm,  
194 gate width of 2 ms and a delay time between 0.1 μs and 2 ms. To generate the excitation wavelength  
195 of 266 nm, a Nd:YAG laser (mod. Minilite, Continuum, Santa Clara, CA, USA) with an average pulse  
196 energy of 0.3 mJ was used. Emission wavelengths were detected between 14,947 cm<sup>-1</sup> (669 nm) and  
197 27,100 cm<sup>-1</sup> (369 nm) by accumulating 100 laser pulses with a spectrograph (mod. iHR 550, HORIBA  
198 Jobin Yvon, Unterhaching, Germany) and an ICCD camera (mod. ICCD-3000, HORIBA Jobin Yvon).  
199 Positions of luminescence bands were determined by calculating the minima of the second derivative.

200 Immediately after removing the C-U-S-H gel from the N<sub>2</sub> atmosphere, IR samples were prepared  
201 under ambient conditions by mixing approximately 1 mg of the dried samples with 300 mg dried KBr  
202 and subsequently pressing for 2 min at 1×10<sup>9</sup> Pa until clear pellets were obtained. IR samples were  
203 measured with a Vertex 70/v spectrometer (Bruker, Billerica, Massachusetts, USA) equipped with a  
204 D-LaTGS-detector (Lalanine doped triglycine sulfate), over a range of 400 to 4,000 cm<sup>-1</sup> in the  
205 transmittance mode, with a spectral resolution of 4 cm<sup>-1</sup>. Each spectrum was averaged over 64 scans.

206 Powder XRD data of C-U-S-H gel were collected with a MiniFlex 600 diffractometer (Rigaku,  
207 Tokyo, Japan) equipped with a Cu Kα X-ray source (40 keV/15 mA) and the D/teX Ultra 1D silicon  
208 strip detector. The diffractograms were recorded in the Bragg-Brentano  $\theta$ -2 $\theta$  geometry at a scanning  
209 speed of 0.6° per min. For sample preparation, the C-U-S-H gel was mounted as wet paste on a zero-  
210 background Si sample holder with a Kapton window under inert gas conditions. The subsequent  
211 Rietveld analysis of diffractograms was done with the program PDXL 2 (Rigaku) and the ICDD PDF-  
212 4+ 2016 database.

213 For TGA and DSC investigations, the various C-S-H gels (sample J (freeze-dried), samples A–C  
214 (wet pastes), sample C (dried under N<sub>2</sub> atmosphere)) were transferred in an Al<sub>2</sub>O<sub>3</sub> crucible and  
215 measured between 25 and 1000 °C at 20 K min<sup>-1</sup> in an Ar atmosphere with a STA 449 F5 Jupiter  
216 thermal analysis instrument (Netzsch, Selb, Germany).

217 SEM imaging with secondary electrons was performed using a S-4800 microscope (Hitachi,  
218 Tokyo, Japan) operated at an accelerating voltage of 10 kV. For sample preparation, the freeze-dried  
219 C-S-H gel was put onto an aluminum stub covered with a carbon tab.

220 The pH values of solutions were measured with a pH meter (inoLab pH 720, WTW, Weilheim,  
221 Germany) with a SenTix<sup>®</sup> Mic pH microelectrode (WTW) calibrated against standard pH buffers (pH:  
222 6.865, 9.180 and 12.454) (WTW). The pH values of solutions with high ionic strengths were corrected  
223 using a method reported by Altmaier et al. (2003; 2008).

224 The solubilities of calcite in 0–2.75 M NaCl solutions at pH 10, of portlandite in 0–3.2 M NaCl  
225 solutions and of a C-S-H gel (C/S 1.1) in 0–3.2 M NaCl solutions at a S/L ratio of 1.5 g L<sup>-1</sup> were  
226 calculated with the geochemical speciation code Geochemist's Workbench (GWB), Module React  
227 (vers. 11.0.6) (Bethke, 2008) using the Pitzer ion interaction model. The thermodynamic database was  
228 "THEREDA" (Thermodynamic Reference Database, <https://www.thereda.de>, Release No. 6). U(VI)  
229 speciation in the carbonate-containing supernatant solution was also calculated with GWB using the  
230 "PSI/Nagra Chemical Thermodynamic Database 12/07" (Thoenen et al., 2014). The parameter files  
231 used for solubility and speciation calculations are added as supplementary material.

232

### 233 **3. Results and discussion**

#### 234 **3.1. Characterization of C-U-S-H gel**

##### 235 **3.1.1. Elemental composition**

236 C-U-S-H gel samples A–C, synthesized by the direct incorporation method, possessed C/S ratios  
237 of 0.99, 1.55 and 2.02 (Table 1). From the Ca and Si amounts applied for C-S-H synthesis, ≤2.3%  
238 remained in the ACW after the reaction time of 14 d (Table S1). That means, the C/S ratios after  
239 syntheses are almost identical to the targeted C/S ratios. More than 96.5% of U, originally present in

240 the alkaline starting solution, was taken up by the C-S-H samples. U(VI) loadings were between  
 241  $1.34 \times 10^{-4}$  and  $2.29 \times 10^{-4}$  mol kg<sup>-1</sup> which correspond to 31.9 to 54.5 ppm U(VI). The distribution  
 242 ratios,  $R_d = \frac{c_0 - c_{eq}}{c_{eq}} \cdot \frac{V}{m}$  [L kg<sup>-1</sup>], increased from  $1.2 \times 10^3$  to  $1.2 \times 10^4$  L kg<sup>-1</sup> with increasing C/S ratio.

243 Compared to the distribution ratios reported by Tits et al. (2011) ( $1.0 \times 10^3$  to  $1.0 \times 10^6$  L kg<sup>-1</sup>),  
 244 Poiteau et al. (2004) ( $3 \times 10^4$  to  $1.5 \times 10^5$  L kg<sup>-1</sup>) as well as determined for CSH<sub>Nitrate</sub> ( $2.1 \times 10^3$  L kg<sup>-1</sup>),  
 245 the direct incorporation method provides comparable  $R_d$  values. While the sample CSH<sub>Nitrate</sub> possesses  
 246 a high U(VI) loading, its  $R_d$  value is similar to those of samples A–C. This is caused by a hydration  
 247 effect and discussed in the supplementary material (Text S2).

248

249 **Table 1**  
 250 Composition of C-U-S-H gel samples and distribution ratios ( $R_d$ ) for U uptake by C-S-H gel.

Sample	C/S ratio	Ca [mol-%]	Si [mol-%]	Na [mol-%]	K [mol-%]	U [ppm]	$R_d$ [L kg <sup>-1</sup> ]
C	2.02	63.3	31.4	2.2	3.1	54.5	11700
B	1.55	53.6	34.5	4.9	6.8	37.3	4820
A	0.99	37.9	38.3	9.4	14.4	31.9	1169
J	1.35	53.7	39.9	2.9	3.6	<0.01	–
CSH <sub>Nitrate</sub>	1.25	54.3	43.6	0.7	1.4	183	2130

251

### 252 **3.1.2. IR spectroscopic, powder XRD, TGA and DSC investigations**

253 Analyses of the samples A–C by IR (Fig. S2, Text S3), XRD (Fig. S3, Text S4), TGA and DSC  
 254 (Fig. S4, Text S5) were entirely consistent with the formation of a tobermorite-like C-S-H gel with the  
 255 co-existence of 18 mass-% portlandite for sample C (Text S1). Water contents of samples A–C were  
 256 between 77 and 88% as shown in Table S2, Fig. S1 and Text S1.

257

### 258 **3.1.3. TRLFS investigations**

259 The TRLFS spectra and luminescence properties of the C-U-S-H gel samples are compiled in Fig.  
 260 1 and Table S3, respectively. The first emission band in the TRLFS spectra of C-U-S-H is termed 0-0

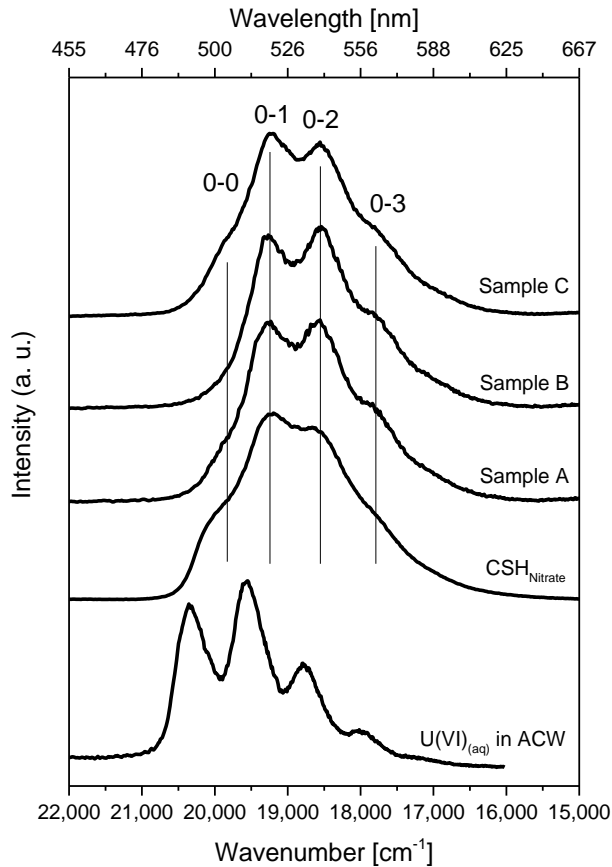
261 band and originates from the de-excitation of the  $5f_{\delta}$  und  $5f_{\phi}$  atomic orbital of U(VI) to the vibration  
262 ground state of the  $\sigma_u$  molecular orbital, mainly dominated by axial bound O (Su et al., 2014). Further  
263 de-excitations to vibration coupled states of  $\sigma_u$  are termed 0-1, 0-2 and so on.

264 A shift of emission bands towards lower energies (red-shift) was reported in the literature for an  
265 increase of electron density of the uranyl ligands (Liu and Beitz, 2006; Tits et al., 2011). This can be  
266 caused by a ligand change from e.g. water against hydroxide ions in ACW or a sorption of U(VI) on  
267 the C-S-H surface whereby hydroxide ligands are substituted against silicate. An incorporation of  
268 uranyl in the C-S-H interlayer should even further red-shift the emission bands due to the complete  
269 absence of hydroxide ligands and the exclusive presence of silicate ligands in the C-S-H interlayer.  
270 The electron density from relevant ligands increases in the following order:  $\text{H}_2\text{O} < \text{OH}^- < \text{SiO}_4^{4-}$ .

271 Observed luminescence emission bands of U(VI) dissolved in ACW (Fig. 1) are in good  
272 agreement with bands reported for the uranyl hydroxide complex,  $\text{UO}_2(\text{OH})_4^{2-}$ , occurring in ACW  
273 under comparable conditions (Tits et al., 2011) (Table S3). The 0-0 band of sample C is located at  
274  $19,992 \text{ cm}^{-1}$ , thus between the 0-0 bands of the U(VI)/C-S-H surface complex ( $20,150 \text{ cm}^{-1}$ ) and the  
275 U(VI)/C-S-H incorporated species ( $19,844 \text{ cm}^{-1}$ ), reported by Tits et al. (2011) for a C-U-S-H gel with  
276 a C/S ratio of 1.07. Compared to the further emission lines of samples A–C, the 0-0 band is weakly  
277 pronounced. Since the 0-0 band is located in higher proximity to the 0-0 band of U(VI) coordinated by  
278 hydroxide in ACW, it is concluded that the 0-0 band in samples A–C and  $\text{CSH}_{\text{Nitrate}}$  is mainly caused  
279 by a U(VI) species located on the C-S-H surface where  $\text{OH}^-$  and  $\text{SiO}_4^{4-}$  ligands are present.

280

281



282

283 **Fig. 1.** TRLFS spectra of samples C, B, A and CSH<sub>Nitrate</sub> (C/S: 2.02, 1.55, 0.99 and 1.25) before leaching as well as U(VI)<sub>(aq)</sub>  
 284 (19.5 μM) in ACW.  
 285

286 Note that the 0-0 band of the reference sample CSH<sub>Nitrate</sub>, synthesized according to the procedure  
 287 reported by Tits et al. (2011), is more distinct than in samples A–C. Due to the surface exposure of  
 288 sample J to uranyl nitrate during the synthesis of CSH<sub>Nitrate</sub>, U(VI) is probably first sorbed on the C-S-  
 289 H surface before it is incorporated in the C-S-H interlayer by recrystallization. This was also described  
 290 by Tits et al. (2011) who observed an ongoing incorporation of U(VI) in the C-S-H crystal structure  
 291 over a time period of 6 months after U(VI) surface sorption on C-S-H gel. Due to the shorter synthesis  
 292 time of 14 d compared to 6 months, CSH<sub>Nitrate</sub> probably possesses a higher amount of surface sorbed  
 293 U(VI) which is also higher compared to samples A–C where U(VI) is mainly located in the C-S-H  
 294 interlayers.

295 The positions of the 0-1 and 0-2 bands of samples A–C are distinct around 19,300 and  
 296 18,500 cm<sup>-1</sup>, respectively, and most probably belong to uranyl incorporated in the C-S-H interlayer.  
 297 Thus, during the 14 d of synthesis of the C-U-S-H gel the direct incorporation method ensures a fast

298 incorporation of U(VI) in the C-S-H gel whereas the U(VI) sorption procedure requires longer time  
299 periods (up to 6 months) to acquire a high ratio of U(VI) incorporated in the C-S-H interlayer. Thus,  
300 for the preparation of C-U-S-H gel, representative for cement encapsulated nuclear waste, within short  
301 times (14 d) the direct incorporation method is preferable.

302 Luminescence decay lifetime analyses of samples A–C show the presence of two U(VI) species,  
303 one with short lifetimes of 103–119  $\mu\text{s}$  and one with long lifetimes of 521–604  $\mu\text{s}$  (Table S3). These  
304 lifetimes are in the same range as the lifetimes determined for the U(VI)/C-S-H surface complex  
305 ( $(205\text{--}293) \pm 50 \mu\text{s}$ ) and the U(VI)/C-S-H incorporated species ( $(546\text{--}647) \pm 50 \mu\text{s}$ ) reported by Tits  
306 et al. (2011). However, it should be noted that the lifetime of U(VI) species in solid C-S-H gel is  
307 influenced by sample preparation, C/S ratio, moisture of the sample, and presence of quenchers. Thus,  
308 a species identification based on the lifetime is only reasonable to a limited extent (Chisholm-Brause  
309 et al., 2001; 2004).

310 From the TRFLS study it can be concluded that the U(VI) in samples A–C is predominantly  
311 incorporated into the interlayer structure of C-S-H gel and to a much smaller degree sorbed on the C-  
312 S-H gel surface.

313

### 314 **3.2. Leaching of C-U-S-H gel**

315 The results of batch leaching experiments, between 18 and 768 h exposure time, are shown for  
316 sample B (C/S 1.55) in terms of Ca, Si and U release into the supernatant solution (Fig. 2[a], Fig. S5,  
317 Fig. S6). The actual S/L ratios during leaching, that differed from the applied S/L ratio of  $10 \text{ g L}^{-1}$  due  
318 to the bulk water content of the wet gels, were determined with 1.2, 1.5 and  $2.3 \text{ g L}^{-1}$  for samples A, B  
319 and C, respectively (Table S2).

320 For all samples (A–C), final Ca, Si and U concentrations as well as pH values of the supernatant  
321 solutions after 768 h leaching are given in Table 2. Between 18 and 768 h leaching, the pH values  
322 varied with  $\pm 0.1$  around the values given in Table 2. For the calculation of the percentage dissolution  
323 of samples A–C, the Ca, Si and U concentrations for a hypothetical complete dissolution at actual S/L  
324 ratios are given in Table S4.

325

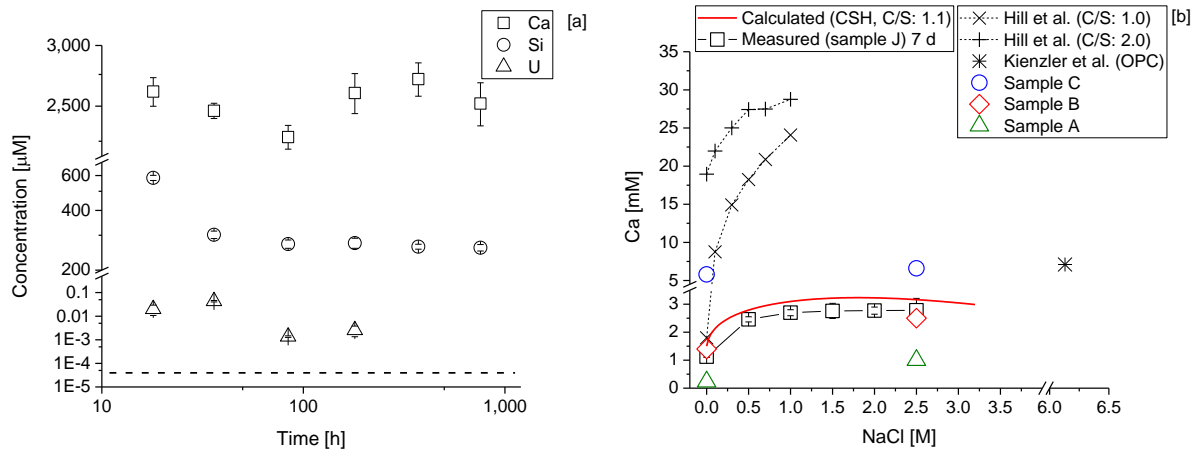
### 326 **3.2.1. Leaching in 2.5 M NaCl and 2.5 M NaCl/0.02 M Na<sub>2</sub>SO<sub>4</sub>**

327 The contact of samples A–C with a 2.5 M NaCl leaching solution leads to a Ca concentration in  
328 solution of about 1.0–6.6 mM (Fig. 2, Table 2). Consequently, the pH value of the leaching solution  
329 increased from 7 to 11.7–12.2.

330 Hill et al. (2006), who monitored the Ca release from radionuclide-free C-S-H gel into 0 to 1 M  
331 NaCl solutions over 1 month (Table S5 ([Ca]: 2–29 mM leached, C/S: 1.0–2.0, S/L: 10–77 g L<sup>-1</sup>),  
332 showed that the presence of 1 M NaCl increased the amount of Ca leached from C-S-H gel compared  
333 to pure water. The authors suggested an ion exchange mechanism between Na and Ca which increased  
334 the Ca release from C-S-H gel in the presence of 1 M NaCl. They also found a good agreement of the  
335 Ca release from portlandite and C-S-H gel with a high C/S ratio in 1 M NaCl.

336 Compared to this study, the results of the present study show a lower Ca mobilization into  
337 solution which is attributed to the lower S/L ratios (1.2 to 2.3 g L<sup>-1</sup>) and salting in/salting out effects  
338 that have an impact on the Ca solubility. To study the C-S-H gel solubility behavior at low S/L ratios,  
339 sample J (C/S 1.35) was exposed to salt solutions between 0 and 2.5 M NaCl at a S/L ratio of 1.5 g L<sup>-1</sup>  
340 over 7 d. Between 0 and 1.5 M NaCl, an increase of the Ca release from 1.1 mM towards 2.7 mM  
341 (Fig. 2[b]) was observed. At higher NaCl concentrations, the Ca release stagnated around 2.7 mM. The  
342 Si release of sample J reached a maximum of 0.95 mM between 0.5 and 1 M NaCl (Fig. S7). Leaching  
343 results of samples A–C in pure water were in good agreement with these observations and showed a  
344 lower release of Ca, especially for C-S-H gel with a low C/S ratio, compared to the leaching in 2.5 M  
345 NaCl (Fig. 2[b]). Additionally, the Ca release from a C-S-H gel with a C/S ratio of 1.1 was calculated  
346 at a S/L ratio of 1.5 g L<sup>-1</sup> for 0 to 3.2 M NaCl solutions (Fig. 2[b]). The calculations showed an  
347 increase of the Ca release from the C-S-H gel up to a maximum at 1.5 M NaCl and a slight decrease at  
348 higher NaCl concentrations. This is in good agreement with the leaching results of samples B and J.  
349 Therefore, in terms of Ca release from C-S-H gel the effect of a 2.5 M NaCl solution is comparable to  
350 a 1 M NaCl solution.

351



352

353 **Fig. 2.** Calcium, silicon and uranium concentration in the supernatant solution after leaching of sample B in 2.5 M NaCl as a  
 354 function of time (ICP-MS detection limit for U is  $4.2 \times 10^{-5} \mu\text{M}$  (dashed line)) [a]. Calculated solubility of a C-S-H  
 355 gel with a C/S ratio of 1.1 in NaCl solutions between 0 and 3.2 M at a S/L ratio of  $1.5 \text{ g L}^{-1}$  [b] (calculation cf.  
 356 section 2.4). Measured calcium release from sample J (S/L  $1.5 \text{ g L}^{-1}$ ) between 0 and 2.5 M NaCl and from samples C  
 357 (S/L  $2.3 \text{ g L}^{-1}$ ), B (S/L  $1.5 \text{ g L}^{-1}$ ) and A (S/L  $1.2 \text{ g L}^{-1}$ ) in water and 2.5 M NaCl in comparison to literature data of  
 358 Hill et al. (2006) (S/L  $50 \text{ g L}^{-1}$ ) and Kienzler et al. (2010) (OPC = ordinary Portland cement) [b].  
 359

360 The Si release of sample B into the 2.5 M NaCl solution amounts to 2.1% of total Si (0.26 mM)  
 361 after 768 h (Fig. 2[a]). Please note that due to the release of Ca and Si from the C-S-H gel, the final  
 362 C/S ratios of the C-S-H gel samples after leaching are decreased in dependency on the initial C/S  
 363 ratios and the composition of the leaching solutions (Table 2). To ease the recognition of the various  
 364 samples, however, we continue to use the C/S ratios before leaching in the following text. Generally,  
 365 an increased Ca and Si release from concrete at higher ionic strength is equivalent to a faster chemical  
 366 degradation of HCP in a nuclear waste repository.

367



368 **Table 2**  
 369 Calcium, silicon and uranium concentrations and pH values of supernatant solutions as well as C/S ratios determined after  
 370 768 h leaching of sample C (C/S 2.02, S/L 2.3 g L<sup>-1</sup>), sample B (C/S 1.55, S/L 1.5 g L<sup>-1</sup>) and sample A (C/S 0.99, S/L  
 371 1.2 g L<sup>-1</sup>). Values in brackets give the percentage dissolution of the ions present in the respective samples.

	Leaching solutions				
	Water	2.5 M NaCl	2.5 M NaCl/ 0.02 M Na <sub>2</sub> SO <sub>4</sub>	2.5 M NaCl/ 0.02 M NaHCO <sub>3</sub>	0.02 M NaHCO <sub>3</sub>
<b>Ca [mM]</b>					
Sample C	5.8 (13.0)	6.6 (14.8)	7.4 (16.6)	0.21 (0.5)	0.034 (0.1)
Sample B	1.4 (7.5)	2.5 (13.4)	2.4 (12.8)	0.16 (0.9)	0.062 (0.3)
Sample A	0.23 (2.4)	1.0 (10.3)	1.9 (19.6)	0.18 (1.9)	0.17 (1.8)
<b>Si [mM]</b>					
Sample C	0.029 (0.1)	0.11 (0.5)	0.068 (0.3)	3.8 (17.1)	5.3 (23.9)
Sample B	0.13 (1.1)	0.26 (2.1)	0.26 (2.1)	2.4 (19.8)	8.4 (69.4)
Sample A	0.48 (4.9)	0.64 (6.5)	0.48 (4.9)	2.6 (26.5)	8.6 (87.8)
<b>U [μM]</b>					
Sample C	7.8×10 <sup>-4</sup>	< 4.2×10 <sup>-5</sup>	< 4.2×10 <sup>-5</sup>	0.16 (4.6)	0.022 (0.6)
Sample B	8.7×10 <sup>-4</sup>	< 4.2×10 <sup>-5</sup>	< 4.2×10 <sup>-5</sup>	0.20 (12.5)	0.64 (40.0)
Sample A	1.1×10 <sup>-3</sup>	< 4.2×10 <sup>-5</sup>	< 4.2×10 <sup>-5</sup>	0.18(16.4)	0.24 (21.8)
<b>pH</b>					
Sample C	12.0	12.2	12.0	10.4	10.3
Sample B	11.7	11.9	11.7	10.1	9.6
Sample A	11.4	11.7	11.5	9.9	9.3
<b>C/S ratio after leaching</b>					
Sample C	1.75	1.57	1.69	–	–
Sample B	1.45	1.37	1.38	–	–
Sample A	1.01	0.96	0.84	–	–

372

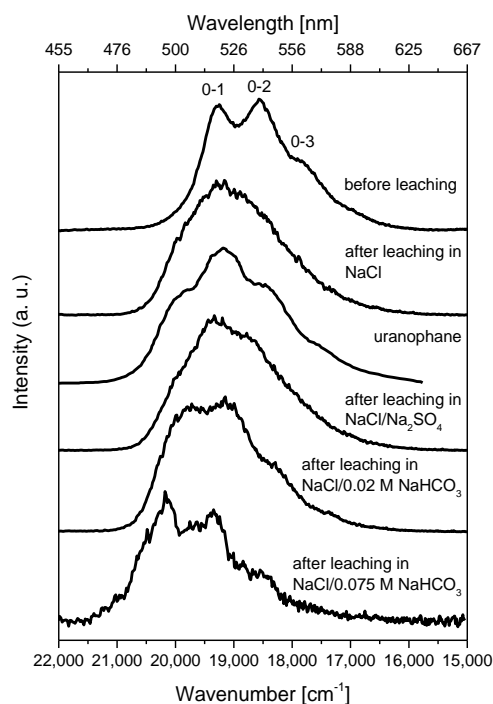
373 Only 2.7% ( $4.3 \times 10^{-2}$  μM) of the total U(VI) of sample B was released in the first 36 h of leaching  
 374 (Fig. 2[a]). After 186 h, the U(VI) concentration decreased below the ICP-MS detection limit of  
 375  $4.2 \times 10^{-5}$  μM, indicating a reincorporation of U(VI) into the C-S-H gel or into a secondary phase  
 376 formed.

377 Kienzler et al. (2016) investigated the U(VI) release from U(VI)-containing cementitious material  
378 prisms submerged in highly saline salt solutions (5.98 M NaCl, 0.02 M CaSO<sub>4</sub>, 0.02 M MgSO<sub>4</sub>) over  
379 32 years and observed an increase of uranium concentrations from  $2 \times 10^{-3} \mu\text{M}$  towards  $5 \times 10^{-1} \mu\text{M}$   
380 over that time period. Despite the differences in solution composition, mineral assemblages and S/L  
381 ratios, both experiments showed only small amounts of mobilized uranium due to the presence of  
382 saline solutions.

383 To clarify the U(VI) speciation for the leached solids in the present study, TRLFS was applied  
384 (Fig. 3). The spectrum of sample B leached in 2.5 M NaCl is broadened and shifted towards higher  
385 energies indicating the presence of a uranophane-like phase with a maximum around  $19,230 \text{ cm}^{-1}$  (Fig.  
386 3). The presence of a diuranate-type U(VI) mineral would shift the maximum of the spectrum towards  
387 lower energies around  $18,100 \text{ cm}^{-1}$  (Tits et al., 2011) and was therefore excluded.

388 These findings correspond well with the observations of Kienzler et al. (2010) who characterized  
389 concrete drill dust after leaching by XRD, TRLFS and EXAFS and reported the presence of a  
390 uranophane-like phase.

391



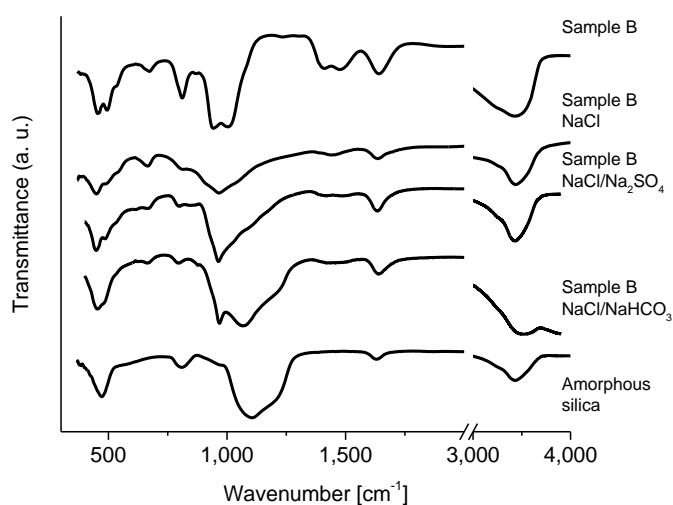
392

393 **Fig. 3.** TRLFS spectra of sample B (C/S 1.55) before and after 768 h of contact with different leaching solutions (2.5 M  
394 NaCl, 2.5 M NaCl/0.02 M Na<sub>2</sub>SO<sub>4</sub>, 2.5 M NaCl/0.02 M NaHCO<sub>3</sub>, 2.5 M NaCl/0.075 M NaHCO<sub>3</sub>) in comparison to  
395 the spectrum of uranophane (Kienzler et al., 2010).

396

397 The IR spectrum of sample B leached in 2.5 M NaCl shows a decrease of band resolution due to a  
398 reduction of the C/S ratio and crystallinity due to leaching (Fig. 4). The Si–OH vibration at  $960\text{ cm}^{-1}$   
399 was not shifted which indicates that the silanol (Si-OH) groups with bridging tetrahedra of the C-S-H  
400 structure remained intact after leaching in 2.5 M NaCl.

401



402

403 **Fig. 4.** IR spectra of sample B (C/S 1.55) before and after 768 h of contact with different leaching solutions (2.5 M NaCl,  
404 2.5 M NaCl/0.02 M Na<sub>2</sub>SO<sub>4</sub>, 2.5 M NaCl/0.02 M NaHCO<sub>3</sub>) in comparison to the spectrum of amorphous silica  
405 (AEROSIL 300).  
406

407 In summary, due to increased ionic strength (2.5 M NaCl) the Ca and Si release from C-S-H gel  
408 increased compared to pure water while the U(VI) environment partially changed from C-S-H towards  
409 a uranophane-like phase. Nonetheless, the structure of the C-S-H gel remained mostly stable and  
410 almost no U(VI) was released into the aqueous phase.

411 With regard to safety assessment of HCP barriers in deep geological waste disposals for actinides,  
412 after contact with about 2.5 M NaCl solutions, a uranophane-like phase becomes the mobility  
413 controlling phase for U(VI) on the HCP surface.

414 The Ca, Si and U release of sample B in 2.5 M NaCl/0.02 M Na<sub>2</sub>SO<sub>4</sub> after 768 h (Fig. S5) was  
415 similar to the Ca, Si and U release in 2.5 M NaCl (Table 2). Moreover, TRLFS and IR investigations  
416 of C-U-S-H gel leached in 2.5 M NaCl/0.02 M Na<sub>2</sub>SO<sub>4</sub> show no further changes compared to the  
417 leaching in 2.5 M NaCl (Fig. 3, Fig. 4). Only the Si release kinetic in the first 18 h of leaching is

418 decreased due to the additional presence of 0.02 M Na<sub>2</sub>SO<sub>4</sub> (Fig. 2[a], Fig. S5). This could be caused  
419 by the adsorption of sulfate on the C-S-H surface as reported by (Divet and Randriambololona, 1998).  
420 After 768 h of leaching, the Si concentrations in both leaching experiments matched. Conclusively,  
421 0.02 M Na<sub>2</sub>SO<sub>4</sub> does not have any negative effects on C-S-H stability or U(VI) retention by C-S-H gel.

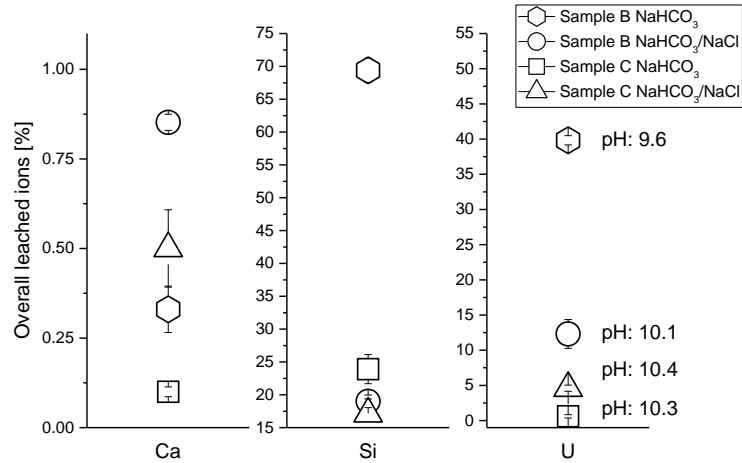
422

### 423 **3.2.2. Leaching in 2.5 M NaCl/0.02 M NaHCO<sub>3</sub> and 0.02 M NaHCO<sub>3</sub>**

424 The presence of carbonate increased the amount of leached Si for samples A–C to 17.1-26.5%  
425 (2.4–3.8 mM) in 2.5 M NaCl/0.02 M NaHCO<sub>3</sub> and to 23.9-87.8% (5.3–8.6 mM) in 0.02 M NaHCO<sub>3</sub>  
426 (Fig. S6, Table 2, Fig. 5). Thus, for all samples a partial destabilization of the silicate chains of the C-  
427 S-H structure leading to the formation of SiO<sub>2(am)</sub> can be assumed. This was confirmed by IR  
428 spectroscopy due to the appearance of a shoulder at 1,234 cm<sup>-1</sup> which is also present in the IR  
429 spectrum of SiO<sub>2(am)</sub> (Fig. 4). For sample C leached in carbonate-containing solutions, the SiO<sub>2(am)</sub>  
430 band was only weakly pronounced (Fig. S8), suggesting that a part of the NaHCO<sub>3</sub> preferentially  
431 reacted with portlandite, consequently, less SiO<sub>2(am)</sub> was formed. However, the IR spectrum of sample  
432 C leached in 2.5 M NaCl/0.02 M NaHCO<sub>3</sub> shows a distinct carbonate band around 1,400 cm<sup>-1</sup> (Fig.  
433 S8) that probably belongs to calcite (Sato and Matsuda, 1969) formed by reaction of portlandite and  
434 carbonate. In contrast, only a weak carbonate band around 1,400 cm<sup>-1</sup> is observed in the IR spectrum  
435 of sample B leached in 2.5 M NaCl/0.02 M NaHCO<sub>3</sub>, indicating a low amount of solid CaCO<sub>3</sub>. This  
436 implies that, compared to Ca(OH)<sub>2</sub>, the C-S-H gel reacts to a lesser extent with carbonate.

437 Compared to carbonate-free leaching experiments, the leaching of sample B in 2.5 M  
438 NaCl/0.02 M NaHCO<sub>3</sub> causes a lower Ca concentration (0.9%, 0.16 mM) as well as a lower pH (10.1)  
439 in the leaching solution (Table 2, Fig. 5). Under carbonate-free conditions, the pH in a concrete system  
440 is buffered by the dissolution of portlandite. In the presence of HCO<sub>3</sub><sup>-</sup>, the precipitation of CaCO<sub>3</sub>  
441 removes Ca<sup>2+</sup> and OH<sup>-</sup> from the solution, thus, lowering the pH and Ca concentrations compared to  
442 carbonate-free solutions. Final C/S ratios of leached samples were not determined since the Ca content  
443 of C-U-S-H gel after leaching is distributed between C-S-H and CaCO<sub>3</sub>.

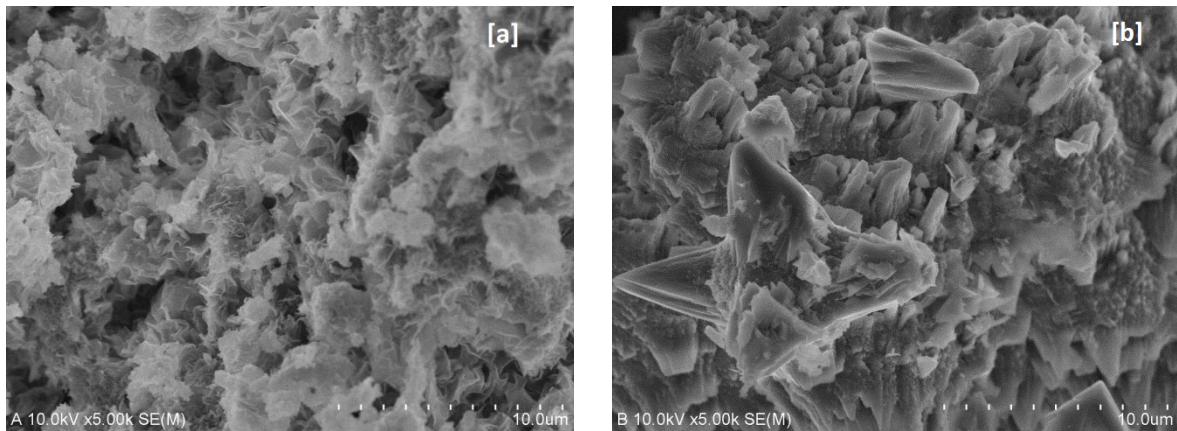
444



445

446 **Fig. 5.** Percentage amount of leached calcium, silicon and uranium with corresponding pH values after leaching of sample B  
 447 (C/S 1.55) and sample C (C/S 2.02) in 0.02 M NaHCO<sub>3</sub> or 2.5 M NaCl/0.02 M NaHCO<sub>3</sub> for 768 h.  
 448

449 Before leaching, the SEM image shows the typical C-S-H fiber structure (Ashraf and Olek, 2016)  
 450 (Fig. 6[a]). After leaching in 0.02 M NaHCO<sub>3</sub>, the overgrowth of the C-S-H surface of sample J with  
 451 euhedral calcite crystals (Ashraf and Olek, 2016) was observed (Fig. 6[b]).



452

453 **Fig. 6.** SEM images of sample J (C/S 1.35) before leaching [a] and after leaching in 0.02 M NaHCO<sub>3</sub> [b].  
 454

455 The U(VI) release of sample B due to leaching in 2.5 M NaCl/0.02 M NaHCO<sub>3</sub> is strongly  
 456 increased to 12.5% (0.2 μM, pH 10.1) of the overall U(VI) (circle in Fig. 5, Table 2). This effect is  
 457 even more distinct in the absence of 2.5 M NaCl where the 0.02 M NaHCO<sub>3</sub> leaching solution  
 458 mobilizes 40% of the U(VI) of sample B (hexagon in Fig. 5, Table 2). In contrast, sample C shows a  
 459 lower amount of released U(VI) of 4.6% (0.16 μM, pH 10.4) in 2.5 M NaCl/0.02 M NaHCO<sub>3</sub> and

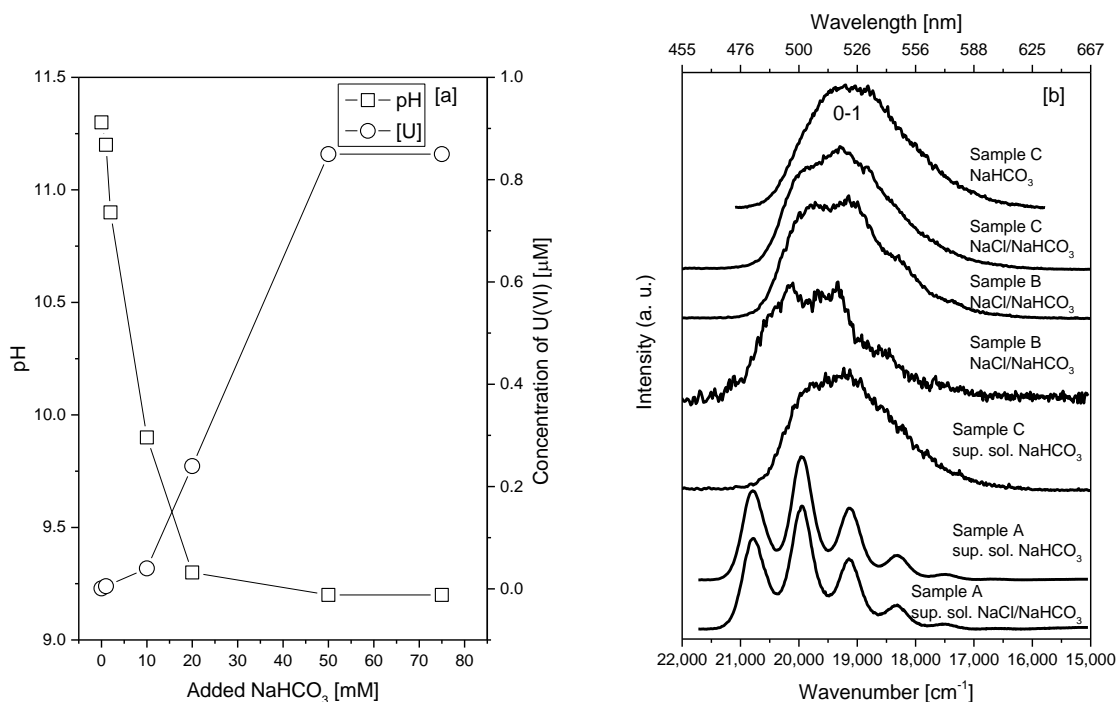
460 0.6% in 0.02 M NaHCO<sub>3</sub> (triangle/square in Fig. 5, Table 2). These results are a clear indication for an  
461 increased U(VI) mobility in the presence of carbonate and a reduction of the pH which influences the  
462 U(VI) speciation in the leaching solution.

463 Under hyperalkaline (pH > 12) conditions, U(VI) hydroxide complexes such as UO<sub>2</sub>(OH)<sub>4</sub><sup>2-</sup> or  
464 UO<sub>2</sub>(OH)<sub>3</sub><sup>-</sup> dominate U(VI) speciation and solubility (Torrents, 2014), whereas a lower pH (8 < pH <  
465 10.6) soluble uranyl carbonate complexes (e.g., UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup>) can occur in carbonate-containing  
466 aqueous systems (Wang et al., 2004). In the presence of 0.034-0.21 mM Ca, determined in solution in  
467 the current study, ternary calcium uranyl carbonate complexes, Ca<sub>2</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>(aq) and CaUO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>2-</sup>,  
468 would likely form (Bernhard et al., 2001). These ternary species impede the U(VI) sorption onto solids  
469 as shown, for instance, for ferrihydrite and quartz (Fox et al., 2006), clay (Joseph et al., 2013) and  
470 granite (Schmeide et al., 2014).

471 To investigate U(VI) speciation changes in the leaching solution from UO<sub>2</sub>(OH)<sub>4</sub><sup>2-</sup> or UO<sub>2</sub>(OH)<sub>3</sub><sup>-</sup>  
472 towards aqueous calcium uranyl tricarbonatate in dependence on pH and amount of NaHCO<sub>3</sub>, a leaching  
473 series of sample A in solutions containing up to 75 mM NaHCO<sub>3</sub> was performed (Fig. 7[a]). The  
474 leaching solutions of sample A show a non-linear decrease of the pH value coupled with increasing  
475 amounts of released U in dependence on the NaHCO<sub>3</sub> contents. TRLFS investigations confirmed the  
476 predominance of aqueous calcium uranyl tricarbonatate (Fig. 7[b]) for NaHCO<sub>3</sub> concentrations ≥  
477 75 mM which corresponds to pH 9.3. This complex possessed well-defined emission bands at 20,803,  
478 19,964, 19,157 and 18,348 cm<sup>-1</sup> and a lifetime of 750 μs (at 153 K) similar to the data reported by  
479 Wang et al. (2004) (20,812, 19,952, 19,131 and 18,315 cm<sup>-1</sup>; 1282 μs (at 6 K)) (Table S2). This  
480 complex was also observed in the presence of 2.5 M NaCl when the pH and carbonate content were  
481 similar (Fig. 7[b]).

482 Speciation calculations performed for the composition determined in the supernatant solution of  
483 sample B after leaching in 2.5 M NaCl/0.02 M NaHCO<sub>3</sub> ([Ca]: 0.159 mM, [Si]: 2.4 mM, [U]: 0.2 μM,  
484 [carbonate]: 14 mM, pH: 10.1), supported the formation of aqueous calcium uranyl tricarbonatate  
485 complexes.

486 At higher pH values, the high concentration of OH<sup>-</sup> suppresses the formation of calcium uranyl  
 487 tricarbonate, and spectra with low intensities and without any band resolution are detected (sample C  
 488 sup. sol. NaHCO<sub>3</sub>, Fig. 7[b]).  
 489

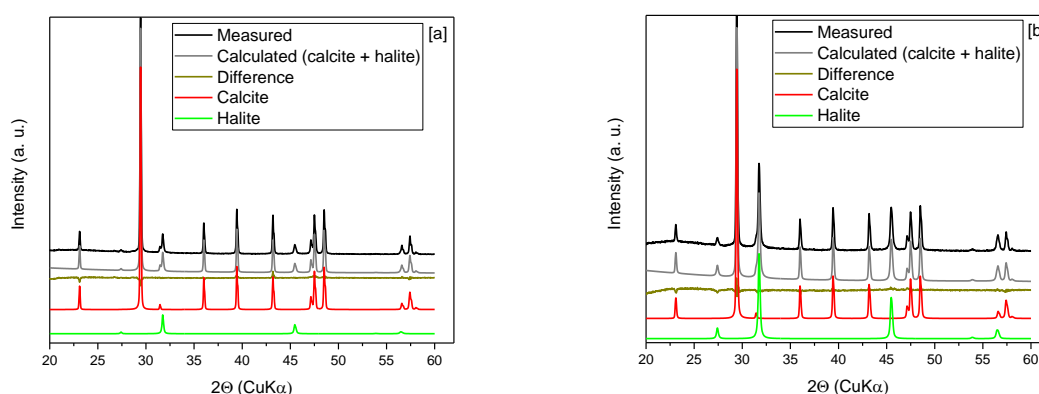


490  
 491 **Fig. 7.** Evolution of pH value and U concentration of the supernatant solution of sample A as function of added NaHCO<sub>3</sub>,  
 492 (768 h leaching, S/L 1.2 g L<sup>-1</sup>) [a]. TRLFS spectra of sample C leached in 0.02 M NaHCO<sub>3</sub>, sample C leached in  
 493 2.5 M NaCl/0.02 M NaHCO<sub>3</sub>, sample B leached in 2.5 M NaCl/0.02 M NaHCO<sub>3</sub>, sample B leached in 2.5 M  
 494 NaCl/0.075 M NaHCO<sub>3</sub>, supernatant solution of sample C leached in 0.02 M NaHCO<sub>3</sub>, supernatant solution of  
 495 sample A leached in 0.1 M NaHCO<sub>3</sub>, supernatant solution of sample A leached in 2.5 M NaCl/0.075 M NaHCO<sub>3</sub>,  
 496 (768 h leaching) [b].  
 497

498 Nonetheless, further factors such as formation of secondary CaCO<sub>3</sub> phases like calcite, vaterite  
 499 and aragonite and their solubility in dependence on ionic strength may also influence the U(VI)  
 500 mobility due to sorption of U(VI) on these CaCO<sub>3</sub> polymorphs. To investigate the influence of the  
 501 secondary phase formation, TRLFS spectra of leached samples A–C were recorded. The TRLFS  
 502 spectra of sample B leached in 2.5 M NaCl/0.02 M NaHCO<sub>3</sub> or 2.5 M NaCl/0.075 M NaHCO<sub>3</sub> (Fig.  
 503 7[b]) show a shift of the 0-1 band towards higher energies from 19,318 cm<sup>-1</sup> to 19,980 cm<sup>-1</sup> and  
 504 20,234 cm<sup>-1</sup>, respectively. These shifts towards higher energies can be explained by an increased  
 505 amount of U(VI) sorbed or incorporated in calcite formed as secondary phase as reported in the  
 506 literature (Elzinga et al., 2004; Geipel et al., 1997; Smith et al., 2015).

507 TRLFS investigations of a natural U(VI)-containing calcite showed 0-0 and 0-1 bands at 20,790  
508 and 20,000  $\text{cm}^{-1}$ , respectively (Wang et al., 2005b). Since the leached samples contain a mixture of  
509 U(VI) sorbed on calcite and U(VI) remaining in the C-S-H gel, the recorded spectra after leaching in  
510 carbonate-containing solutions are caused by an overlap of both U(VI) coordination environments.

511 Rietveld analyses of the XRD patterns of sample C and A leached in 2.5 M NaCl/0.02 M  
512  $\text{NaHCO}_3$  (Fig. 8) show, that C-U-S-H gel and portlandite are partly converted to  $\text{CaCO}_3$  whereby  
513 exclusively calcite was detected.



514  
515 **Fig. 8.** Powder XRD patterns of samples C (C/S 2.02) [a] and A (C/S 0.99) [b] after leaching in 2.5 M NaCl/0.02 M  
516  $\text{NaHCO}_3$ , (768 h leaching), calcite (database card number 01-083-4601), halite (database card number 00-005-0628),  
517 (Cu  $K\alpha$  X-ray source).  
518

519 XRD patterns of samples C and A leached in 0.02 M  $\text{NaHCO}_3$  but absence of NaCl (Fig. S9) also  
520 suggest that the samples are partly converted into secondary  $\text{CaCO}_3$  phases: A part of sample A is  
521 converted into 70% calcite and 30% metastable aragonite while sample C, that consists of C-U-S-H  
522 gel and portlandite, is partly converted into 80% calcite and 20% metastable vaterite (Table S6). A  
523 comparison with data from (Black et al., 2007), who investigated carbonation effects in  
524 mechanochemically prepared C-S-H gels with C/S ratios between 0.2 and 1.5 under ambient  
525 conditions, revealed the occurrence of predominantly vaterite for samples with C/S ratios  $\geq 0.67$  while  
526 in C-S-H samples with C/S ratios  $\leq 0.5$  mainly aragonite was detected. Although this trend is similar to  
527 that of the present study, the absence of calcite and the lower C/S boundary for the vaterite formation  
528 confirm differences between both studies. This can probably be attributed to different preparation  
529 methods and carbonation techniques of both studies. Further studies where similar cementitious  
530 systems were exposed to carbonate detected either the simultaneous presence of calcite, vaterite and

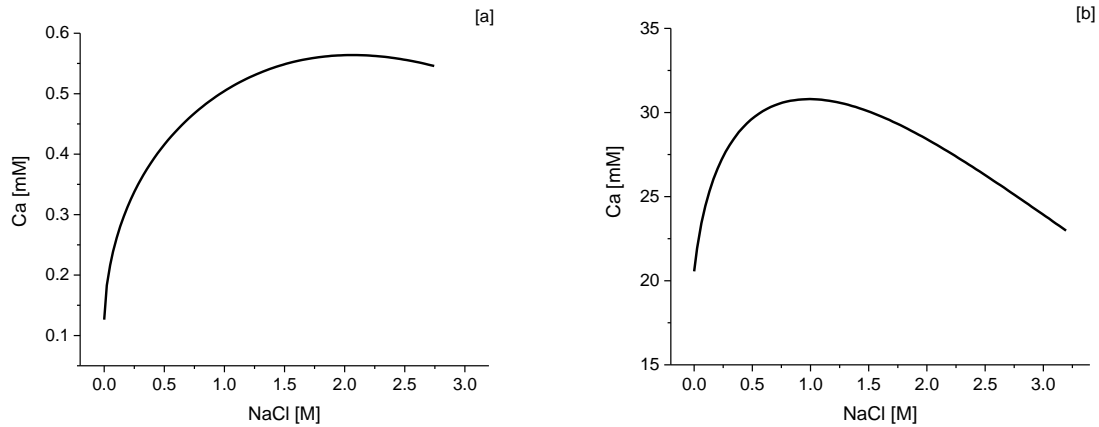


531 aragonite (Chang and Fang, 2015; Ibanez et al., 2007) or a reversed trend where aragonite was  
532 observed at higher and vaterite at lower C/S ratios (Auroy et al. (2018)). These findings suggest that  
533 the formation of the various  $\text{CaCO}_3$  modifications depends on the cement system and the carbonation  
534 method. The results of the present study also suggest that high amounts of NaCl suppress the  
535 formation of metastable  $\text{CaCO}_3$  modifications such as vaterite and aragonite. This is tentatively  
536 attributed to an increased recrystallization rate of these phases as suggested by Takita et al. (2007).

537 TRLFS investigations of sample C leached in exclusively 0.02 M  $\text{NaHCO}_3$  showed a broad  
538 spectrum without any band resolution that is less blue-shifted than the spectrum of sample B leached  
539 in 0.02 M  $\text{NaHCO}_3$  (Fig. 7[b]). Due to the higher amount of portlandite in sample C, combined with  
540 the higher solubility of portlandite compared to C-S-H gel, most of the carbonate is precipitated as  
541 calcite and vaterite (Fig. S9). Thus, the amount of carbonate in solution, which could contribute to a  
542 decomposition of the C-U-S-H structure, is reduced. Simultaneously, a higher pH value in solution  
543 after  $\text{CaCO}_3$  precipitation is maintained. Since portlandite does not contain U(VI) its dissolution does  
544 not contribute to a U(VI) mobilization. Calcite, however, acts as a U(VI) sink as implied by the  
545 TRLFS investigations (Fig. 7[b]). Compared to metastable  $\text{CaCO}_3$  phases like vaterite, better U(VI)  
546 retention properties were reported for calcite (Noubactep et al., 2006).

547 Compared to the leaching of sample C in 0.02 M  $\text{NaHCO}_3$  solution, the additional presence of  
548 2.5 M NaCl increased the amounts of released U(VI) and Ca from 0.6 to 4.6% and from 0.1 to 0.5%,  
549 respectively (square/triangle, Fig. 5), although the pH values were with 10.3 and 10.4 very similar.  
550 Solubility calculations (cf. section 2.4) showed that the calcite solubility increases with increasing  
551 NaCl concentrations between 0 and 2.5 M NaCl (Fig. 9[a]). Also the solubility of portlandite increases  
552 between 0 and 1 M NaCl, but decreases afterwards (Fig. 9[b]). If, in turn, less calcite precipitates,  
553 which also leads to somewhat higher  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  concentrations in the supernatant, less U(VI) can  
554 be immobilized on the calcite surface. Thus, the formation of aqueous calcium uranyl tricarbonate is  
555 favored against the formation of U(VI) hydroxide complexes at a pH around 10.4.

556



557

558 **Fig. 9.** Calculated solubilities of calcite in 0–2.75 M NaCl solutions at pH 10 [a] and of portlandite in 0–3.2 M NaCl  
 559 solutions [b]. Details of calculations are given in section 2.4.

560

561

## 562 4. Conclusions

563 The stability of C-U-S-H gel and its U(VI) retention capability in high ionic strengths pore waters  
 564 was studied. For this, C-U-S-H gel samples with three different C/S ratios (0.99, 1.55 and 2.02) were  
 565 synthesized applying a direct incorporation method which ensured an U(VI) incorporation  
 566 predominantly into the interlayer structure of C-S-H.

567 These C-U-S-H gel samples were leached in solutions containing 2.5 M NaCl, 0.02 M Na<sub>2</sub>SO<sub>4</sub>  
 568 and/or 0.02 M NaHCO<sub>3</sub>, thus, reflecting conditions expected for host rock pore waters of potential  
 569 nuclear waste repositories. The results showed that the composition of the leaching solution had a  
 570 direct influence on the alteration of the C-S-H structure and evolution of the pH value in these  
 571 systems.

572 Compared to pure water, the leaching in a 2.5 M NaCl solution increased the release of Ca from  
 573 C-S-H gel from 1.4 to 2.5 mM (initial C/S ratio: 1.55, S/L ratio: 1.5 g L<sup>-1</sup>). The effect of a 2.5 M NaCl  
 574 solution was comparable to a 1 M NaCl solution. Despite the release of Ca, IR investigations  
 575 suggested that the C-U-S-H structure remained stable, while U(VI) retention was largely unaffected  
 576 due to a formed uranophane-like phase detected by TRLFS. The additional presence of 0.02 M  
 577 Na<sub>2</sub>SO<sub>4</sub> did not show any effect on the stability of the C-U-S-H structure.

578 In the presence of carbonate (0.02 M), the U(VI) retention was coupled to the alteration stage of  
579 the C-S-H structure as well as to the pH evolution of the leaching solution. Carbonate preferentially  
580 reacted with portlandite to form calcite and vaterite while the C-U-S-H structure remained intact,  
581 which was confirmed by XRD and IR investigations. Furthermore, the absence of a distinct blue-shift  
582 of the U(VI) luminescence spectrum of the leached portlandite-rich sample confirmed the persistent  
583 presence of U(VI) in the C-U-S-H gel. In the case of C-U-S-H gel with a lower C/S ratio, representing  
584 altered concrete, carbonate removed Ca from solution which subsequently led to a further release of  
585 Ca from the C-U-S-H gel. Thus, the polyhedral CaO plane of the C-U-S-H structure was increasingly  
586 destabilized, as verified by the appearance of Si-O bands of amorphous silica in the IR spectrum. The  
587 thereby formed secondary CaCO<sub>3</sub> phases, detected by XRD after leaching, contributed to a certain  
588 extent to U(VI) retention, as shown by a blue-shift of the U(VI) luminescence spectrum of the leached  
589 solid. Nevertheless, the destabilization of the polyhedral CaO plane of the C-U-S-H structure led to an  
590 enhanced release of U(VI). Due to an overall lower pH value in the presence of carbonate, aqueous  
591 calcium uranyl tricarbonate was formed as confirmed by TRLFS.

592 The U(VI) release from the portlandite-rich C-U-S-H sample into carbonate-containing solutions  
593 was slightly higher in the presence than in the absence of NaCl. This was attributed to an increased  
594 calcite solubility at enhanced salinities, which led to higher Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> concentrations in solution,  
595 and thus, to formation of aqueous calcium uranyl tricarbonate.

596 In the context of a nuclear waste repository, the high immobilization potential of C-U-S-H gel for  
597 U(VI) appears to be unaffected by highly saline groundwaters. In the presence of carbonate, however,  
598 it is expected that the release of U(VI) from C-U-S-H gel will be greatly enhanced.

599

600

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608

## 609 **Appendix A. Supplementary material**

610 Supplementary data associated with this article can be found, in the online version, at

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