

# Time-resolved porosity changes at cement-clay interfaces derived from neutron imaging

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## Abstract

Interfaces between cement and clay are common in engineered barrier systems for the underground disposal of radioactive waste. The geochemical contrast between clay and cement leads to alterations of both materials following dissolution and precipitation reactions. Porosity is a key parameter for, and a key outcome of, such reactive transport. Here we report on the evolution of porosity within small samples made from ordinary portland cement and Na montmorillonite. Water contents, a proxy for porosity in saturated samples, were derived from neutron imaging. Specific calibration procedures were developed to account for multiple scattering effects. An increase in cement porosity was observed propagating  $\sim 2$  mm away from the interface within 600 days, and a considerable decrease in clay porosity within  $\sim 2$  mm. Our experiments provide unique information on the dynamics of the processes up to nearly two years. The data set provides valuable input to better constrain reactive transport models.

*Keywords:* neutron imaging, cement-clay interaction, radioactive waste (E), porosity, water content, reactive transport, image analysis (B), interfacial transition zone (B), transport properties (C), cement paste (D), portland cement (D), waste management (E)

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## 1. Introduction

Cement and clay are two key components of the barrier systems of radioactive waste repositories. In the multi-barrier design of such repositories, intended to mechanically reinforce open galleries and to enclose waste canisters, large amounts of cementitious material will be used in direct contact with the clay formations or with clays of the engineered barrier systems (EBS). One of the factors affecting the EBS performance is the long-term development of the contact zone between cement and clay. Differences in chemical compositions between these two materials cause diffusive mass flux across their interface, possibly followed by mineral dissolution and precipitation reactions which will alter the composition and structure of both materials.

Several laboratory and field experiments [e.g., 1–11] as well as evidences from natural analogues [e.g., 12] provide information on possible alterations at the material interfaces. For instance, the cement-clay interaction (CI) field experiment in the Mont Terri rock laboratory was initialized to investigate interactions between Opalinus Clay and various types of concretes and cements [2–4]. Alterations within clay or cement matrix were investigated with various techniques. The presence of aggregate grains within the concrete made the application of these techniques difficult, but it was possible to delineate various reaction zones based on SEM/EDX element mapping and XRD measurements. Porosity values derived from impregnation with a traced resin followed by autoradiography were reported by Jenni et al. [2]. They reported a reduction in porosity in the first  $\sim 1$  mm of cement compared to the cement porosity further away, which they related to carbonation. Porosities in both cement regions were, however, larger than expected based on the used water to cement ratio.

Autoradiography and petrophysical measurements of Gaboreau et al. [7] on cement-clay interface samples from the Tournemire underground research laboratory (France) after 15 years of interaction showed a clogging of the porosity in the claystone, likely due to precipitation of secondary phases (e.g., C-S-H), and a porosity increase in the cement. They observed heterogeneous zones of

31 the porosity evolution on both sides of the interface, with extents on the order  
32 of centimeters (3.5 cm in the cement and 1.5-2 cm in the claystone). In another  
33 study at the same location, Techer et al. [8] confirmed a limited spatial extent  
34 of the interactions in the clay-rich rock, with the alteration extending over a few  
35 centimeters. In an experiment, also at the Tournemire site, Lalan et al. [10, 11]  
36 contacted ordinary portlandite heated to 70°C for one year with the argillite.  
37 They found a decrease of porosity on both sides of the interface.

38 Cruz Alonso et al. [5] and Fernández et al. [6] reported on the interaction  
39 of concrete with bentonite in the FEBEX experiment at the Grimsel Test Site.  
40 After 13 years of interaction, pronounced changes were observed within the  
41 first centimeter of a concrete plug in contact with bentonite. The complete  
42 disappearance of portlandite in this first centimeter was noted along with a  
43 massive ettringite formation, with the sulfate very likely originating from the  
44 bentonite. A limited impact on the bulk mineralogy was found on the clay  
45 side, with only small changes (some dissolution of primary minerals and some  
46 precipitation of secondary minerals) in the first few millimeters, but a somewhat  
47 more extended redistribution of exchangeable cations.

48 Various numerical studies were performed to predict mineral alteration path-  
49 ways when cementitious material interacts with clay. In a study on the inter-  
50 action of cement with different clay host rocks, Kosakowski and Berner [13]  
51 estimated for instance the extents of alteration zones for different transport  
52 scenarios in a set of long-term predictive calculations. After ~2000 years, the  
53 alterations were limited to a comparably narrow zone around the interface (< 5  
54 cm), with the porosity tending to zero in the clay, which stopped a further  
55 development in the diffusive transport scenario. In another numerical study,  
56 Traber and Mäder [14] obtained an altered zone at an Opalinus Clay-concrete  
57 interface with an extent of less than 20 cm. The uncertainties of numerical  
58 studies are rather large, among other things because kinetic reaction rates and  
59 the feedback of mineral alterations on the further diffusive transport are largely  
60 unknown [15, 16].

61 Even though clogging might eventually be favorable to delay the migration

62 of radionuclides to the surrounding clay formation, it may have a negative effect  
63 on the re-saturation of the clay formation after closure of a repository, reducing  
64 its chemical and mechanical buffer capacity as well as the overall functionality  
65 of the repository. It could also impact the release of gases at a later stage. De-  
66 veloping methodologies to provide experimental data on these alterations and  
67 their coupled feedback on the repository’s transport processes at different time  
68 scales is an essential task in order to refine the current assumptions used in pre-  
69 dictive transport simulations and to increase the reliability of these predictions.  
70 Porosity is a central input parameter in reactive transport models, but also a  
71 central outcome. Accordingly, knowing its evolution with time is particularly  
72 important.

73 Within the scope of the present study, a laboratory experiment has been  
74 designed and performed to investigate the above mentioned alterations under  
75 well controlled conditions, in a non-destructive way, and over a time period  
76 of months to several years. The experimental cell design makes it possible  
77 to benefit from a broad range of non-destructive analyses. Here we present  
78 the results from the first three years of monitoring of water contents at an  
79 ordinary portland cement (OPC) - Na-montmorillonite interface as obtained  
80 from neutron imaging.

## 81 **2. Materials and methods**

### 82 *2.1. Sample preparation*

83 The samples of hardened OPC paste, with 5 mm diameter and about 5  
84 mm length, were drilled out of a 14 years old CEM I 52.5 N HTS plug, which  
85 was prepared in 2001 [17–20], then stored in a sealed container and, before  
86 sample preparation, brought into contact with the artificial cement pore wa-  
87 ter, as described by Tits et al. [19]. For the clay samples, a conditioned Na-  
88 montmorillonite powder [21] was used. The powder was pre-saturated within a  
89 desiccator that contained humid air, then compacted to the final 5 mm diameter

90 and 5 mm length in a compaction cell. Details on the origin of the material are  
91 given in Shafizadeh et al. [22], including the chemical compositions.

92 The cement and clay plugs were then brought into direct contact in the  
93 diffusion cell designed to host the samples and at the same time to allow in-situ  
94 experimental techniques to be applied (Fig. 1). In detail, the samples were first  
95 introduced into the inert PTFE holders which was then inserted in the aluminum  
96 cell. The PEEK porous filters were added to both sides. The two PEEK end  
97 caps (screwed to the aluminum body) kept the samples, the PTFE and the  
98 filters in place while providing a connection to an external fluid reservoir. Cell  
99 type II was designed after the first measurement campaign with cell type I. The  
100 improved cell design led to a better signal to noise ratio and caused less artifacts  
101 in neutron radiographs, owing to the thinner aluminum part and the elimination  
102 of interfering joints. The cell geometry was also changed to a cylindrical shape  
103 for future tomography measurements. Also, the new cell has a smaller outer  
104 dimension compared to type I and thus allows for having an open beam section  
105 within the image, which lowers the uncertainty in data evaluation.

106 Table 1 summarizes the cement-clay interface samples prepared for this study  
107 as well as the properties of both cement and clay materials, prior to their contact.  
108 Samples were kept in the diffusion cell while the left and right ends were in  
109 contact with the corresponding pore water solutions. A peristaltic pump was  
110 used to continuously circulate the solution between sample and reservoir. The  
111 samples were kept in a glove box environment to avoid CO<sub>2</sub> contaminations and  
112 carbonation of the cement. The corresponding pore water compositions for the  
113 OPC and the Na-montmorillonite are reported in Table 2.

114 For the neutron radiography measurements, the cells were disconnected from  
115 the pump and the solution reservoir, and openings were closed with dead end  
116 screws to ensure the cell tightness.

## 117 *2.2. Neutron imaging measurements*

118 The high interaction probability of neutrons with hydrogenous compounds  
119 makes neutron imaging a powerful non-destructive technique to study water dis-

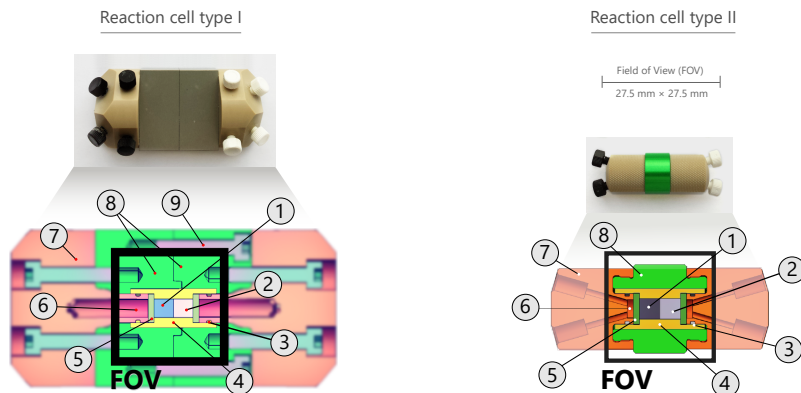


Figure 1: The two designs of the reaction cells used in this study. The components of both reaction cells are (1) Cement sample, (2) clay sample, (3) O-rings, (4) PTFE sample holder, (5) PEEK frits, (6) solution reservoirs within PEEK caps, (7) PEEK caps, (8) aluminum holder and (9) screws. The black square shows the field of view (FOV, 27.5 mm x 27.5 mm) for the neutron images. Outer cell dimensions (without screws): 83 mm x 40 mm x 25 mm (type I), 53 mm x 22 mm  $\varnothing$  (type II)

120 tribution inside porous materials [24]. At present, it allows measurements with  
 121 a spatial resolution down to  $\sim 10 \mu\text{m}$  and a temporal resolution of minutes to  
 122 hours [24–32]. Neutron radiography measurements of the cement-clay interface  
 123 samples were performed at the ICON beamline (Imaging with Cold Neutrons)  
 124 at the Paul Scherrer Institut (PSI) [33]. Technical specifications of the measure-  
 125 ments have been given earlier in Shafizadeh et al. [22]. The prepared interface  
 126 samples were radiographed at different times in order to obtain the evolution of  
 127 water content profiles across the interface.

128 The neutron beam is collimated from the Swiss spallation neutron source  
 129 (SINQ, PSI) through vacuum flight tubes towards the sample (collimation ratio  
 130 343 m/m). Once it reaches the sample, it can be transmitted through the sample  
 131 or interact with it, which results in attenuation. This attenuation happens when  
 132 neutrons are absorbed or scattered by the nuclei of the atoms. The transmitted  
 133 neutrons hit a Gd-based scintillator (with 20  $\mu\text{m}$  thickness) with a total field of

Table 1: Overview on the properties of the interface samples used in this study.

Cell No.	Clay			Cement			Interface contact date
	Dry bulk density	Porosity <sup>a</sup>	Length	Dry bulk density	Porosity	Length	
(-)	(g cm <sup>-3</sup> )	(m <sup>3</sup> m <sup>-3</sup> )	(mm)	(g cm <sup>-3</sup> )	(m <sup>3</sup> m <sup>-3</sup> )	(mm)	
C1	1.67	0.39	5.5	0.77	0.63	4.5	14.03.2013
C5	1.44	0.49	5.1	0.77	0.63	4.9	25.09.2013

<sup>a</sup> From dry bulk density with grain density of 2.76 g cm<sup>-3</sup> (C1) and 2.8 g cm<sup>-3</sup> (C5)

Common parameters:

Sample diameter is 5 mm

Cement initial pore water pH is 13.3 [19] and clay initial pore water pH is 8.7

134 view of 27 × 27 mm<sup>2</sup>. The scintillator converts the neutron signals into visible  
 135 light photons. The photons are then guided via a mirror and a lens system  
 136 to the cooled CCD camera (with 2048 × 2048 pixels), where they are digitally  
 137 recorded and displayed as a 16-bit gray value image. The exposure time of  
 138 90 s was needed to obtain a sufficiently high signal to noise ratio to allow a  
 139 quantitative analysis of the image data. It is also important in order to reach  
 140 the highest possible resolution which is reported to be 27 μm × 27 μm [33].  
 141 In own independent test measurements with the Siemens star periods around  
 142 50 μm could be resolved. The obtained gray value images were corrected (flat  
 143 field, dark noise, dose, geometry, [22] and Appendix C) and then processed to  
 144 obtain water content profiles across the interface sample.

The physical relation between the incident neutron beam  $I_0$  and transmitted neutrons  $I_T$  is described by the Beer-Lambert law,

$$\frac{I_T}{I_0} = e^{-\sum_{i=1}^n \mu_i d_i} \quad (1)$$

145 where  $\mu_i$  is the attenuation coefficient of each individual material present in the

Table 2: Aqueous total concentrations,  $\text{OH}^-$  concentrations, pH, and ionic strength (IS) of pore waters in OPC and montmorillonite, calculated by GEMS [23].

	OPC (mol L <sup>-1</sup> )	Initial gradient	Montmorillonite (mol L <sup>-1</sup> )
Na	0.11	↔	0.30
K	0.21	→	–
Ca	0.023	→	$1.0 \times 10^{-6}$
Mg	$1.0 \times 10^{-6}$	←	–
C <sup>IV</sup>	$1.1 \times 10^{-4}$	→	–
Cl	$1.7 \times 10^{-5}$	←	0.30
S <sup>VI</sup>	–	←	0.019
OH <sup>-</sup>	0.306	→	$5.1 \times 10^{-6}$
pH	13.3	→	8.7
IS	0.3		0.3



146 sample and  $d_i$  the distance that a beam travels through that material. The  
 147 attenuation coefficient  $\mu$  of a material is a measure of how strong neutrons  
 148 interact with the matter. The high attenuation coefficient of hydrogen atoms  
 149 (present mainly in water), relative to other elements in our samples, makes  
 150 neutron attenuation most sensitive to the amount of pore water in the cement-  
 151 clay interface samples.

Ideally, the thickness of an individual material (e.g.,  $d_w$  of water) in a sample  
 composed of several different materials can be calculated from Eq. 1 with known  
 $\mu_i$  and thicknesses  $d_{i \neq w}$  of all other materials. The contribution of all other  
 materials can be obtained from the image  $I_{T, dry}/I_{0, dry}$  of the dry sample, leading  
 to:

$$d_w = -\frac{1}{\mu_w} \left( \ln \left[ \frac{I_T}{I_0} / \frac{I_{T, dry}}{I_{0, dry}} \right] \right). \quad (2)$$

152 The water content  $\theta$  is then given as  $\theta = d_w/d_T$ , where  $d_T$  is the total thickness  
 153 of the sample. In reality, however, obtaining an image of the dry sample may  
 154 not be feasible, and the attenuation of neutrons through water is not fully linear,  
 155 making calibration not so simple. The details of our calibration procedure are  
 156 given in the next subsection.

### 157 *2.3. Calibration procedure*

158 As our samples had to remain saturated throughout the whole experiment,  
 159 the reference image of the dry sample was synthesized from separate image parts  
 160 with a dried cement and a dried clay [22]. This introduces additional uncertainty  
 161 especially with respect to single pixel values, but the following calibration can  
 162 compensate for a possible average bias. To derive the 2D water content field  
 163 in a radiograph, first the cylindrical geometry (variable  $d_T$ ) had to be taken  
 164 into account according to  $d_T(y) = 2\sqrt{2yr - y^2}$ , where  $r$  is the radius of the  
 165 sample and  $y$  the lateral position in the radiograph with the sample extending  
 166 from  $y = 0$  to  $y = 2r$  (Fig. 2). Then, the water attenuation coefficient ( $\mu_w$ ) is  
 167 needed. This 2D matrix can be obtained in principle from the theoretical values  
 168 for hydrogen and oxygen at the beam energy peak of the ICON instrument;

169 or, by performing a calibration measurement with pure water. Both of these  
 170 methods provide a single value for  $\mu_w$  but result in water contents that are not  
 171 matching with true water contents of our samples (measured for the cement and  
 172 calculated from the bulk density for the clay). Therefore, the contribution of  
 173 multiple scattering on the recorded radiographs as well as other image artefacts  
 174 need to be corrected for in a more detailed manner.

From calibration measurements with pure water (Fig. A.1a,b in the ap-  
 pendix), we observed that the effective attenuation coefficient  $\mu_w$  decreased with  
 increasing sample thickness, which coincides here with increasing distance from  
 the lateral boundaries of the sample (Fig. A.1c) due to multiple scattering [34].  
 Whereas using a single value for  $\mu_w$  will cause both under- and over-estimation  
 of water contents (Fig. A.1d, the green and red lines) in some regions of the  
 sample, a linear relation

$$\mu_{w,\text{eff}} = \mu_0 + \beta d_w \quad (3)$$

(Fig. A.1c, the blue line) will provide correct water contents in the sample  
 (Fig. A.1d, the dashed line). Using such a linear relation in Eq. 2 allows then  
 estimating the water content from  $\mu_0$  and  $\beta$  according to

$$\theta = \frac{d_w}{d_T} = -\frac{1}{d_T} \left[ \left( \frac{\mu_0}{2\beta} \right) + \sqrt{\left( \frac{\mu_0}{2\beta} \right)^2 + \frac{1}{\beta} \ln \left[ \frac{T_{\text{dry}}}{T} \right]} \right] \quad (4)$$

175 It is clear that the empirical linear relation for  $\mu_w$  will be only approximately  
 176 correct for cylindrical samples, even if they have homogeneous water contents  
 177 within their circular cross section, because effects of multiple scattering depend  
 178 not only on the local amount (thickness) of water but also on the distance  
 179 between sample and detector [34], which is a function of  $y$  for cylindrical samples.  
 180 Nevertheless, this approximate correction works well for samples of our size  
 181 having radially homogeneous water content, as was demonstrated for the pure  
 182 water sample. Accordingly, we expect it to lead to good results also for our  
 183 clay-cement samples, where no (or no large) radial gradients in water content  
 184 are expected.

In Shafizadeh et al. [22], it was suggested to use two internal parts of the

sample, denoted as 1 and 2, with known water contents  $\theta_1$  and  $\theta_2$  (e.g., one in clay and one in cement) to derive the two required calibration parameters  $\mu_0$  and  $\beta$  in Eq. 4. By substituting known  $\theta_1$  and  $\theta_2$ ,  $d_{T_1}$  and  $d_{T_2}$  from sample geometry, and  $A_1$  and  $A_2$  from the neutron radiographs where  $A_i = \ln \left[ \frac{T_{dry}}{T_i} \right]$ , Eq. 4 can be solved for  $\mu_0$  and  $\beta$ ,

$$\begin{aligned}\mu_0 &= \frac{A_2 \cdot \theta_1^2 \cdot d_{T_1}^2 - A_1 \cdot \theta_2^2 \cdot d_{T_2}^2}{d_{T_1} \cdot d_{T_2} \cdot \theta_1 \cdot \theta_2 (d_{T_1} \cdot \theta_1 - d_{T_2} \cdot \theta_2)} \\ \beta &= \frac{-A_2 \cdot \theta_1 d_{T_1} + A_1 \cdot \theta_2 d_{T_2}}{d_{T_1} \cdot d_{T_2} \cdot \theta_1 \cdot \theta_1 (d_{T_1} \cdot \theta_1 - d_{T_2} \cdot \theta_2)}.\end{aligned}\tag{5}$$

185 It was expected that these parameters, obtained from internal standards, can  
186 then be used with Eq. 4 to obtain the water content ( $\theta$ ) values across the whole  
187 sample domain.

188 This approach worked for one given sample, regardless of the detailed position-  
189 tioning (extent, lateral location) of the calibration regions within the unaltered  
190 clay or cement. However, this was not the case for most of the other samples.  
191 In these cases Eq. 5 could not be solved for  $\mu_0$  and  $\beta$ , which shows that a single  
192 calibration valid for both cement and clay did not exist. Therefore,  $\mu_0$  and  $\beta$   
193 parameters were separately calibrated for cement and clay.

For this purpose, a line in a region of the sample domain far from the inter-  
face and with the least alterations was chosen for each material. To improve  
the statistics, instead of just two-points [22], multiple points were selected (e.g.,  
averaged over  $10 \times 10$  pixels) along the calibration line. The transmissivities  
 $A = \ln \left[ \frac{T_{dry}}{T} \right]$  in these calibration regions represent projections of the circular  
cross sections, obtained for different water thicknesses  $d_w$ . Effective water  
attenuation coefficients  $\mu_{w,\text{eff}}(d_w)$  were then calculated using:

$$\mu_{w,\text{eff}}(d_w) = \frac{1}{\theta d_T} \ln \left[ \frac{T_{dry}}{T} \right]\tag{6}$$

194 for each calibration region. In this way, one obtains  $\mu_{w,\text{eff}}(d_w)$ , i.e., the effective  
195 scattering coefficients as a function of the total water thickness in each calibra-  
196 tion region (Fig. 2). Finally, the  $\mu_0$  and  $\beta$  valid for the clay or cement sample  
197 domain were estimated by fitting the scattered data linearly. The upper and

198 lower parts of the sample domain with the smallest sample thickness were ex-  
199 cluded from the calibration fit, as they showed generally much larger scatter.  
200 That is, only the inner part of the sample, shown by the red rectangle in Fig. 2,  
201 was used for the fit.

202 As a further problem, it turned out that even though the images were cor-  
203 rected for the variable average neutron intensity (dose), a calibration was only  
204 valid for measurements taken around the calibration time, but not for images  
205 taken at another time. This is probably related to variations in the beam in-  
206 tensity histograms for images taken at different times or days. Such variations,  
207 which were documented (Appendix B), may lead to differences in multiple scat-  
208 tering effects, which then preclude the application of a unique calibration ac-  
209 cording to our procedure. As a consequence, calibration had to be done for  
210 each image. The obtained  $\mu_0$  and  $\beta$  served then as the calibration paramet-  
211 ers in Eq. 4 for each measurement time. These parameters account for all the  
212 variables affecting the gray values of the image.

213 The calibration procedure allowed finally deriving the 2D water content field  
214 from the water transmission image. The 2D water content field was then aver-  
215 aged in  $y$  direction, perpendicular to the cylinder axis, in order to present the  
216 results as 1D profiles along the  $x$  direction across the material interface. Our  
217 samples were always connected to fluid reservoirs on each side, except during  
218 the neutron imaging experiments, where the samples were disconnected from  
219 the reservoirs but sealed. We thus expect them to be saturated, such that the  
220 volumetric water contents represent porosity.

### 221 **3. Results and Discussion**

222 Fig. 3 shows the time series of the obtained volumetric water content profiles  
223 across the interfaces of two samples (Table 1). As it can be seen from the  
224 general trend of the time-series profiles, the porosity (equal to volumetric water  
225 content) on the cement side of the interface tended to increase with increasing  
226 reaction time, accompanied by a porosity reduction on the clay side of the

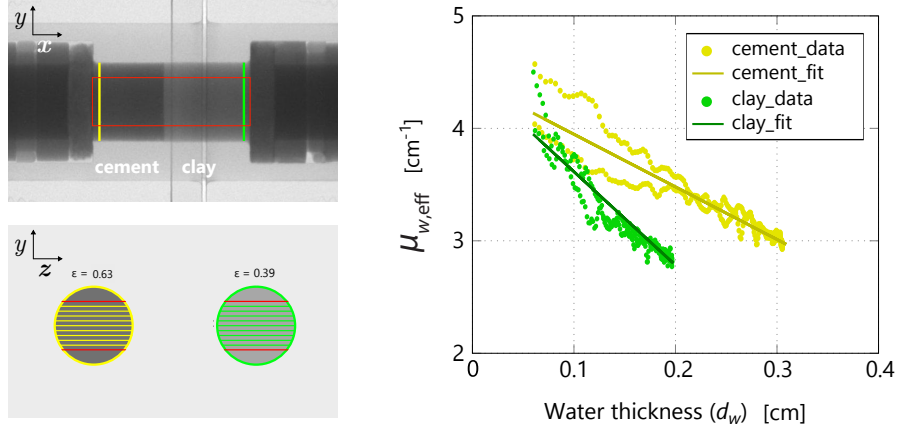


Figure 2: Internal calibration procedure:  $\mu_{w,\text{eff}}$  values were derived from transmission values  $A$  according to Eq. 6 using the known water content (cement: measured; clay: from bulk dry density) and the total sample thickness along the parallel lines shown in the bottom left figure. A linear fit provided  $\mu_0$  (intercept) and  $\beta$  (slope) for Equation 4, which was used to derive the water content image.

227 interface. Fig. 4 shows a closer view of the interface for the same samples  
 228 at select reaction times. Cement and clay zones near the interface changed  
 229 differently over time, very likely due to dissolution and precipitation reactions.  
 230 The results are discussed more in detail in the following.

### 231 3.1. Amount and extent of porosity changes

232 The porosity in the cement near the interface increased by  $\sim 0.05 \text{ m}^3 \text{ m}^{-3}$  at  
 233 most, whereas in the clay near the interface it was reduced by up to  $\sim 0.12 \text{ m}^3$   
 234  $\text{m}^{-3}$  (sample C1) and  $\sim 0.14 \text{ m}^3 \text{ m}^{-3}$  (sample C5). Although there is a trend  
 235 in reduction of clay porosity, a residual porosity clearly larger than zero was  
 236 preserved at the given spatial resolution of about 30–50  $\mu\text{m}$ . The extent of the  
 237 zone where porosity was altered is on the order of 2 mm on each side of the  
 238 interface in sample C1 within 20 months (599 d) of interaction time, and  $\sim 1$  mm

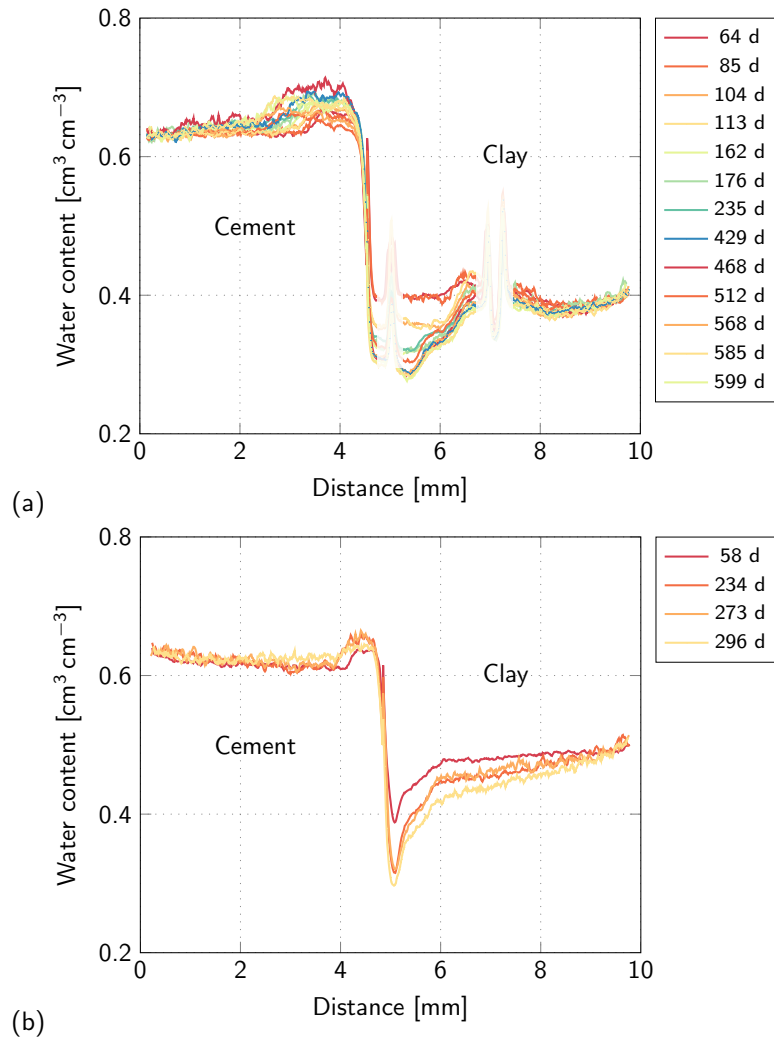


Figure 3: Evolution of profiles of water content with reaction time (in days) across two interface samples (top: sample C1, bottom: sample C5). The regions blanked out for sample C1 in the top figure are artefacts originating from the joints of the aluminum holder of cell type I; no such artefacts were present anymore with cell type II used for sample C5 in the bottom figure.

239 in sample C5 within 10 months (296 d) of interaction time.

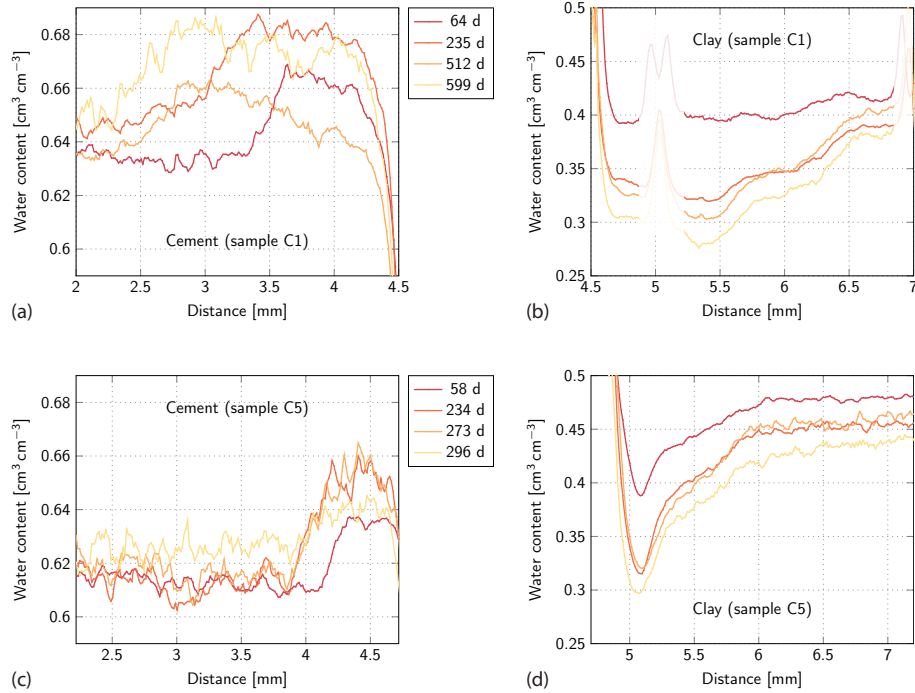


Figure 4: Details of the evolution of the water content profiles across sample C1 (top row) and sample C5 (bottom row) for the cement parts next to the interface (left plots), and for the clay parts next to the interface (right plots).

240 The two examples represent the typical behavior as observed in most sam-  
 241 ples, but in one sample no clear porosity changes were detected, and in another  
 242 sample porosity changes occurred mostly on one side only. It may be that dif-  
 243 ferent reactions did not occur at different locations in these samples, but in  
 244 a mixing zone where both precipitation and dissolution happened. Reactive  
 245 transport simulations have shown that the extent and location of mineral trans-  
 246 formations are very sensitive to various parameters, which may vary locally  
 247 (microstructural heterogeneities) or from sample to sample in our case. Also,  
 248 the different patterns could be related to technical limitations of radiographs  
 249 which flatten and average a possibly heterogeneous 3D structure into a 2D one.  
 250 This becomes especially crucial when the contact surface of the cement plug is

251 not perfectly flat, e.g., not at an angle of  $90^\circ$  with respect to the cylinder axis.  
252 Depending on the rotational position of the sample during the radiograph, a  
253 non-perpendicular interface may not be detected and lead to a mixing of clay  
254 and cement properties in the image. A tomography would be required to reveal  
255 the 3D interior of such a sample, but tomography measurements could not be  
256 obtained within the limited amount of beam time.

### 257 *3.2. Propagation of porosity front in cement and clay*

The water content profiles not only reveal information about the amount and the extent of porosity changes, but also about their temporal evolution. Fig. 5 presents the propagation of the porosity fronts in cement and clay. The location of the front is defined as midpoint of the steep increase or decrease in porosity, and the error bars illustrate the approximate width of this front. The front position on the cement side increased steadily with time up to the last observation date after about 600 d. The relation between the position of the porosity front and the reaction time can be approximately described by:

$$x \approx \sqrt{D_a \cdot t} \quad (7)$$

258 where  $x$  is the distance between the front and the interface,  $D_a$  is an apparent  
259 diffusion coefficient, and  $t$  is the reaction time since interface contact. The ap-  
260 parent diffusion coefficient  $D_a$  characterizes the approximate transient behavior  
261 of the porosity front, but it cannot be related to a retardation coefficient, as  
262 in the case of transport of a linearly sorbing tracer. Cement-clay interactions  
263 involve strongly non-linear, time-dependent reactions, so using a constant  $D_a$   
264 for the porosity front evolution on the cement side during the  $\sim 600$  d (solid  
265 blue line in Fig. 5a) is certainly a strong oversimplification. Detailed reactive  
266 transport simulations could give more comprehensive insight into the transient  
267 behavior. In any case, if transport parameters ( $\varepsilon$ ,  $D_p$ ) on both sides of the inter-  
268 face had varied strongly with time, a change in  $D_a$  with time should have been  
269 observed. Looking at the front propagation within the cement more in detail,  
270 it appears that there are two major steps during the 600 d of this experiment



271 (Fig. 5a - dashed blue line). The porosity front advanced during the first 200 d,  
 272 then remained at about 1.5 mm for the next 200 d, before it advanced to 2 mm  
 273 and slowed down again. Verifying the validity of this type of behavior needs for  
 274 instance reactive transport modeling.

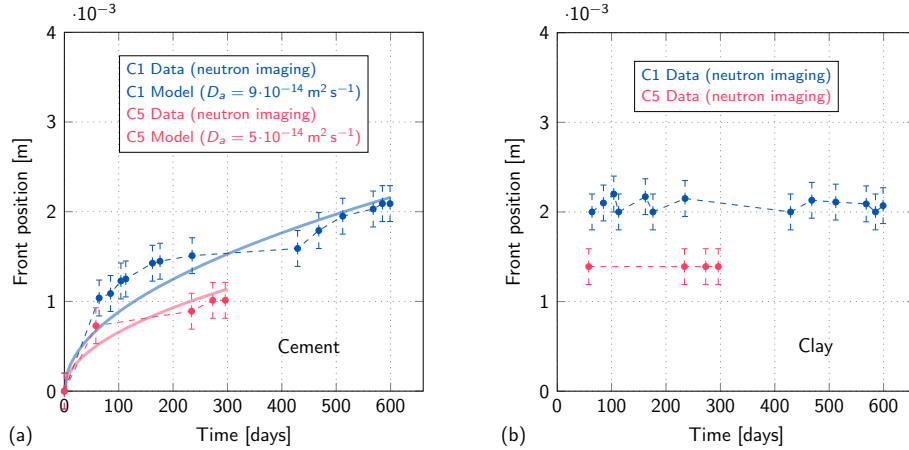


Figure 5: Advancement of the porosity front away from the interface as a function of time in samples C1 and C5. (a) Front position in cement, (b) front position in clay, both estimated as distance of midpoint of steep porosity change to the interface. The model curves in (a) are a strong oversimplification (see text for discussion).

275 For the clay side (Fig. 5b), the situation is different. The front of reduced  
 276 porosity in the clay did not advance with the same rate as the front of increased  
 277 porosity in the cement. The position of the front in the clay appears to be more  
 278 or less stagnant during the observations. Already at the first measurement after  
 279 two months (64 d), the front was located about 2 mm from the interface. It  
 280 seems a zone with perturbed porosity had been early created as a result of the  
 281 interface contact, but this zone did then not further expand significantly with  
 282 increasing reaction time up to about 600 d, even though reactions within this  
 283 zone (e.g., porosity reduction) further proceeded.

284 The porosity front on the cement side moved somewhat slower in sample C5  
 285 as compared to sample C1, and the distance of the porosity front on the clay  
 286 side is also somewhat smaller in sample C5 compared to sample C1. Sample

287 C5 had a lower initial montmorillonite density (and corresponding higher initial  
288 montmorillonite porosity), but it is unclear how this could be related to this  
289 lower propagation rate. As stated, small differences in local or sample-specific  
290 parameters may be responsible for observed quantitative differences between  
291 different samples. Reactive transport simulations can help to investigate such  
292 subtle sensitivities. In turn, the present data can be very helpful in discriminat-  
293 ing between different parameterizations of reactive transport models, especially  
294 with respect to the implementation of feedback between porosity and diffusion.

### 295 *3.3. Porosity changes as a function of reaction time*

296 The temporal evolution of porosity values at three different locations within  
297 the cement and the clay, respectively, was also derived from the neutron imaging  
298 data (Fig. 6). The porosity tended to alter more in areas close to the interface  
299 compared to the areas far away from it for both cement and clay. The amount  
300 of net porosity change is higher for the clay side compared to the cement side.

301 The porosity trends in sample C1 seem to be more or less monotonical in  
302 both, cement (increasing) and clay (decreasing), up to about day 450. Then, the  
303 trend appears to be inverted on both sides, with a porosity decrease in cement  
304 and a porosity increase in clay, up to about day 512. It remains unclear whether  
305 these temporary inversions of the trends are real or represent a measurement  
306 artefact (e.g., calibration problem). However, the inversions are strongest on the  
307 cement side close to the interface, and weaker further away from the interface  
308 and on the clay side, which may indicate that they are indeed related to local  
309 transport and reaction processes. If real, such changes of trends suggest that  
310 different reactions start to dominate at different times. While dissolution and  
311 precipitation reactions may occur in parallel, our observation in terms of the  
312 porosity, i.e., the sum parameter, just indicate that on the cement side, disso-  
313 lution mostly — with the exception around day 500 — outweighs precipitation  
314 during the experiment, whereas on the clay side, precipitation mostly outweighs  
315 dissolution.

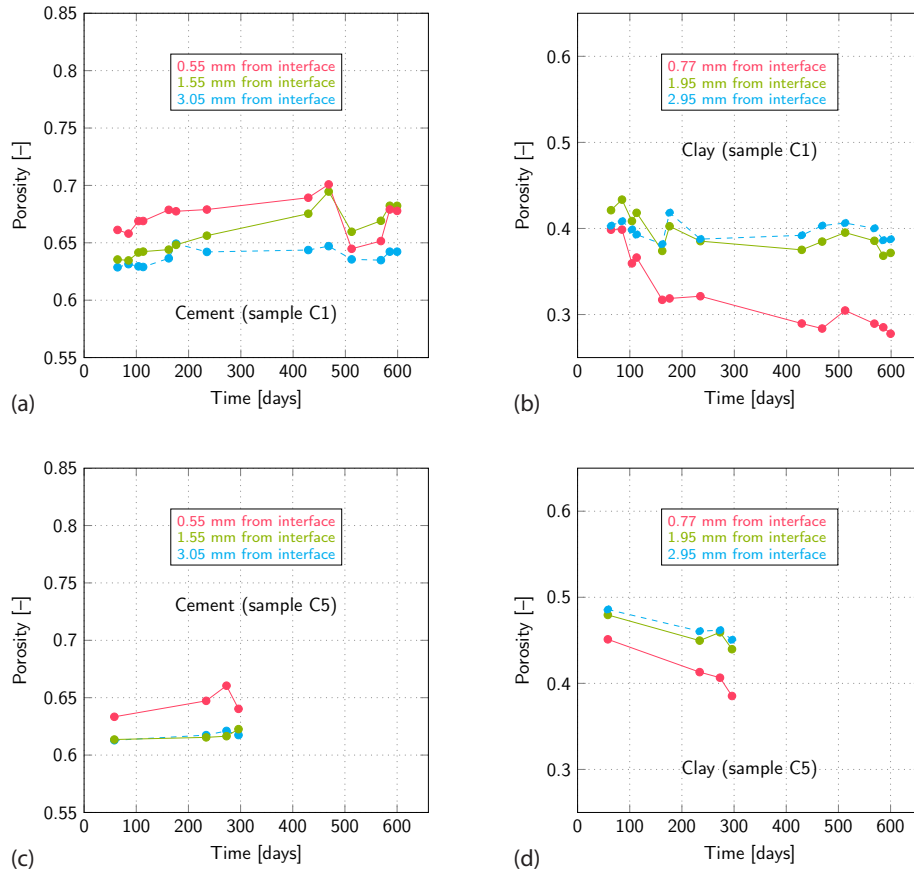


Figure 6: Porosity changes as a function of reaction time at different positions in cement (left plots) and clay (right plots) for samples C1 (top row) and C5 (bottom row).

316 *3.4. Significance of derived porosity data*

317 As mentioned above in subsection 3.1, not all our experimental results are  
 318 identical and there is some variability in the observations between different  
 319 samples, with some samples exhibiting less reactions. The reasons are unknown,  
 320 but the differences may be related to small parameter variations between the  
 321 different samples. Anyway, the data shown here represent typical observations.

322 The materials chosen, especially in the case of the clay, are simplified analogs  
 323 compared to those foreseen in natural or engineered barriers or used in field ex-  
 324 periments, as for instance in the CI experiment in the Mont Terri rock laboratory

325 [2]. This allowed us to focus on the most important interaction processes at the  
326 interface and also to provide simpler, better constrained initial conditions for  
327 numerical codes. The duration of the reaction between the selected cement and  
328 clay materials and the size of the samples (comparably small) were also different  
329 from other works on this topic. Although based on small samples, our method  
330 presented here has the advantage that it can provide the time and space depen-  
331 dence of porosity changes, in contrast to all methods that require a destructive  
332 sampling. Furthermore, it is possible to create and investigate many different  
333 samples with reasonable effort.

334 We are not aware of other studies that provide the porosity evolution at  
335 cement-clay interfaces as a function of time and space. In any case, the trends  
336 observed during the present study are qualitatively in agreement with obser-  
337 vations from other in situ and laboratory experiments. For example, there is  
338 a similarity between the findings from this study and the works of Read et al.  
339 [1], Gaboreau et al. [7], and Bartier et al. [9]. Fig. 7 shows how the porosity  
340 determined from petrophysical measurements varied as a function of distance  
341 from a cement-argillite contact in the Tournemire URL after 15 years of in-  
342 teraction [7]. From their measurements, these authors reported “a clogging of  
343 the porosity in the clay-rock while the porosity increases in the cement”. The  
344 porosity evolution was shown to extend to about a centimeter on both sides  
345 of the interface, but “heterogeneously distributed in space as a function of the  
346 fissure network and interface geometries”.

347 The observed changes in porosity are most likely related to mineral alter-  
348 ations. The porosity increase on the cement side is probably linked to the  
349 dissolution of portlandite [5], whereas the nature of the precipitating phase on  
350 the clay side is yet unclear at present. Besides precipitation and dissolution  
351 reactions, the interaction with cement also triggers modifications of the ex-  
352 changer population of a clay [e.g., 35, 36], with Na being replaced by K and  
353 Ca. Such modifications, which typically propagate more quickly as compared  
354 to the front(s) of dissolution or precipitation reactions, can affect the interlayer  
355 distances and thus the local distribution of water between different pore en-

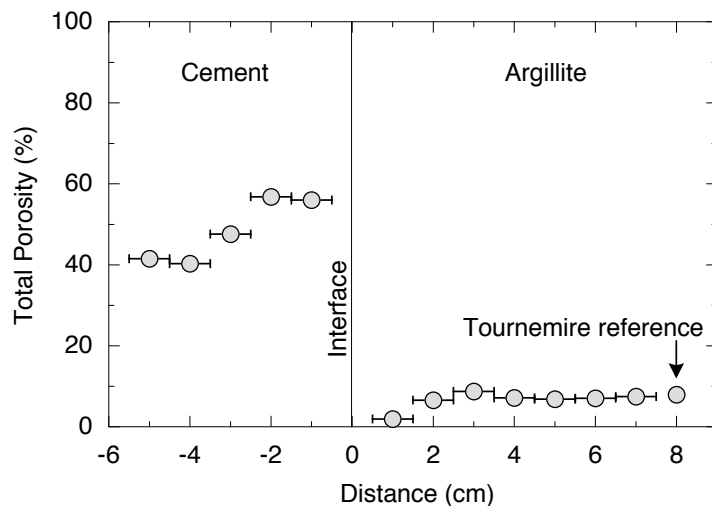


Figure 7: Total connected porosity at a cement-clay interface after 15 months of interaction (modified from [7]).

356 vironments (e.g., interlayer, interparticle). But for our confined samples, this  
 357 redistribution of the pore water is expected to have no or only a weak effect on  
 358 the total porosity.

#### 359 4. Conclusions and outlook

360 In this paper we presented time-series results of water content profiles across  
 361 several evolving cement-clay interfaces. The water contents, which served as  
 362 proxy for porosity, were evaluated from neutron radiographs with a new method-  
 363 ology. The present work showed the need to obtain a separate calibration mea-  
 364 surement for the neutron images for each material at every measurement time,  
 365 especially for investigations spanning long periods of time. Such a need for inter-  
 366 nal standard imposes some limits to the applicability of the method to evolving  
 367 samples. First, a suited internal calibration region has to be available for each  
 368 material. Second, mineral changes within each material should remain compa-  
 369 rably small; otherwise, the calibration may no longer be adequate. We used the  
 370 unaltered cement or clay material, far away from the interface, as internal cali-

371 bration region, and furthermore applied an approximate correction for multiple  
372 scattering effects.

373 The finally observed porosity trends appear reasonable both qualitatively  
374 and quantitatively. To cross check the validity of our observations, a D<sub>2</sub>O dif-  
375 fusion experiment was subsequently planned and performed on several interface  
376 samples. This is the topic of a forthcoming publication, but, without going  
377 into details, we expect that the derived porosity changes can be confirmed by  
378 the D<sub>2</sub>O exchange experiment. Also, a new scattering correction method was  
379 developed very recently, which will be applied in future experiments to improve  
380 the estimation accuracy [37, 38]. Neutron imaging, which can be combined with  
381 complimentary X-ray tomography in the future, offers thus unique possibilities  
382 to non-destructively determine porosity changes as a function of time in reacting  
383 cement or rock samples.

384 The time-series results revealed a clear evolution of water content or porosity  
385 close to the interface. An increase in the porosity on the cement side of the  
386 interface accompanied by a reduction of porosity on the clay side was observed.  
387 These trends are broadly in agreement with observations from in-situ studies.  
388 The porosity increase on the cement side is very likely related to portlandite  
389 dissolution [5]. The nature of the precipitating phase(s) on the clay side has  
390 still to be studied. The likely modification in the exchanger population of the  
391 clay (from Na to K, Ca, [e.g., 35, 36]) is expected to have only a minor effect  
392 on the total porosity in our confined samples.

393 The ultimate goal of this work was to provide quantitative porosity data  
394 at reacting cement-clay interfaces as a function of time, in order to serve the  
395 further development of reactive transport models, especially with respect to  
396 the feedback between porosity and diffusion. Porosity is at the same time a  
397 key parameter for, and a key outcome of, reactive transport. The obtained  
398 porosity data set, together with forthcoming chemical analyses of the reacted  
399 zones, can be examined using reactive transport codes. The comparably simple  
400 initial mineralogical composition of our system certainly facilitates the further  
401 interpretation and modeling of the observations. Based on the comparison of

402 experimental data and modeling results, one may have to adapt existing or  
403 introduce new model parameters and feedback mechanisms, all with the aim  
404 to eventually better simulate the evolution of cement-clay interfaces in waste  
405 repositories. The small-scale experimental observations obtained in this study  
406 may thus serve as benchmark data that assist in increasing the confidence in  
407 predictions of the long-term stability of cement and clay interfaces.

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578 **Appendix A**

579       The transmission values of a cylindrical cell fully filled with water are de-  
580 creasing with increasing water thickness (Fig. A.1a,b). Scattering effects lead  
581 to decrease of the effective attenuation coefficient  $\mu_w$  with increasing sample  
582 thickness (Fig. A.1c,d). This suggests using a linear calibration function for the  
583 attenuation coefficient of water in order to derive correct water contents. Such  
584 a calibration procedure was used in the present work.

585

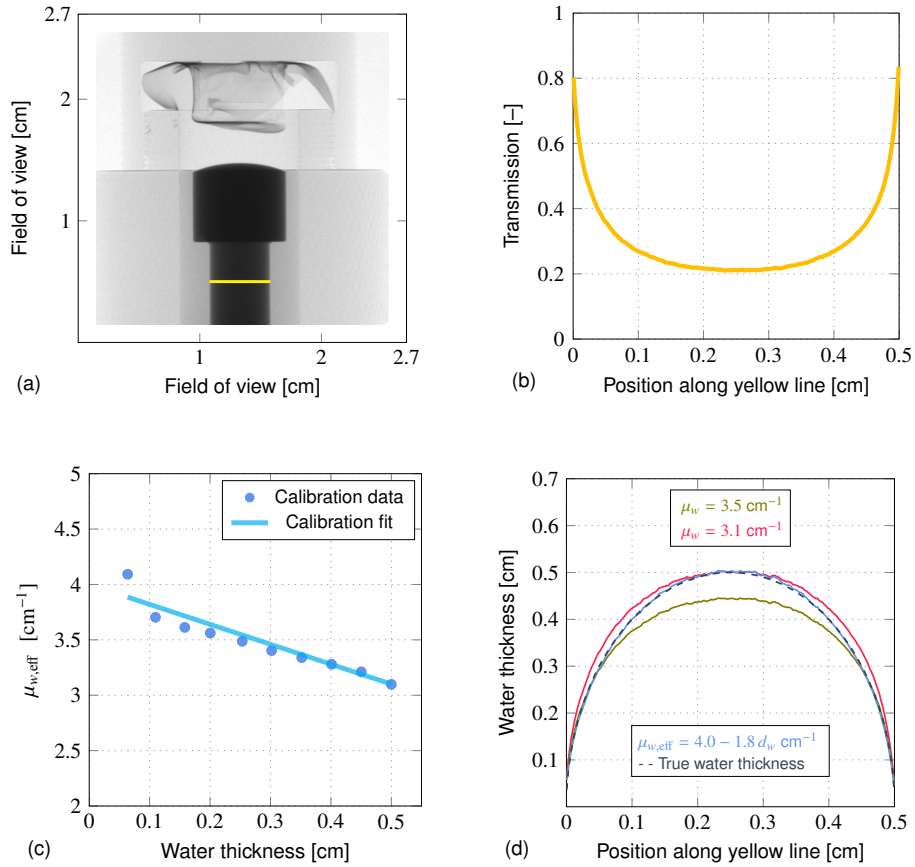


Figure A.1: Transmission values and attenuation coefficients obtained for the cylindrical sample cell (cell type II) filled with water. (a) Transmission image, with the yellow line indicating the evaluated cross section of the radial cell. (b) Transmission values along the yellow line. (c) Water attenuation coefficients as a function of true water thicknesses along the yellow line. (d) Comparison of true water thickness (dashed line) along the yellow line, and water thickness calculated by using constant attenuation coefficients  $\mu_w$  of 3.5 and 3.1  $\text{cm}^{-1}$ , or the  $\mu_{w,\text{eff}}$  that varies linearly with water thickness according to the calibration fit in (c).

586 **Appendix B**

587 Fig. B.1 shows histograms of several open beam intensities recorded over  
588 a period of 3 years. The values of 16-bit images range between 0 and 65,535  
589 ( $2^{16} - 1$ ), but our open beam images had a smaller range with values between 0  
590 and 10,500. The intensities were binned in intervals of 100. The histogram plots  
591 show clearly that not only the recorded mean intensity of the beam varies with  
592 time, but also the intensity distribution. It is likely that several parameters of  
593 the beamline setup, including the incident neutron beam intensity, varied over  
594 the 3 year observation time. The variations can affect the amount of neutrons  
595 scattered from the sample. The lowest gray values in the histograms indicate a  
596 probability of the presence of clearly lower energy neutrons in the poly-energetic  
597 beam. Low energy neutrons have a higher scattering probability when passing  
598 through the sample. Accordingly, any shifts or distortions in the energy spec-  
599 trum will affect the mean attenuation coefficient of the water in the sample, as  
600 well as the probability of multiple scattering. The partly variable shape of the  
601 histograms thus demonstrates that a simple dose window correction procedure is  
602 not able to fully account for intensity variations. The most important influence  
603 of such variations is their fingerprint on the energy dependent values of the water  
604 attenuation coefficient. This highlights the necessity of an experiment-specific  
605 time-dependent calibration procedure.



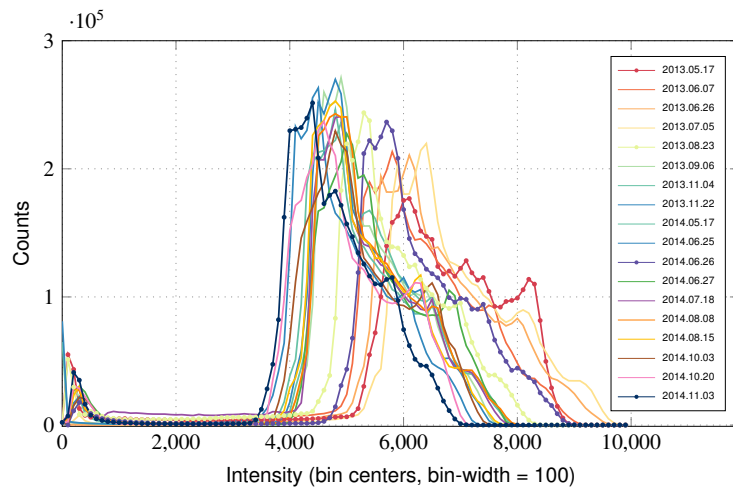


Figure B.1: Histograms of the open beam intensities over a period of 3 years as an indication of setup imposed deviations (beam energy, detector efficiency and camera system variations). The histograms present the frequencies of binned gray values. For our setup intensities of the gray values were between 0 and 10,500 (generally between 0 and 65,535 for a 16-bit image). The intensities were binned in intervals of 100, an arbitrary bin-width. The figure shows the counts in each interval for each open beam image.

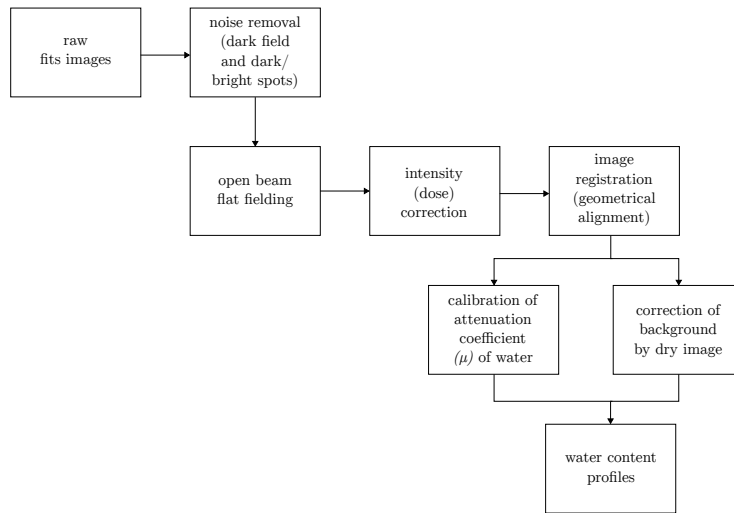


Figure C.1: Image processing sequence applied on the raw data to obtain the water content in the interface samples.