Water Migration and Swelling in Engineered Barrier Materials for Radioactive Waste Disposal

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> **Abstract** — Deep, underground repositories are needed to isolate radioactive waste from the biosphere. Because bentonite is an integral component of many multibarrier repository systems, information on the hydraulic behavior of bentonite is crucial for modeling the long-term viability of such systems. In this paper the hydraulic behavior of bentonite samples was analyzed as a function of aggregate size, and samples were subjected to hydrothermal treatments involving contact with NaCl, KCl, and deionized water. Neutron and X-ray imaging were used to quantify water sorption into packed bentonite samples and bentonite swelling into the water column. The distance between the original clay-water interface and the wetting front was determined as a function of time. Average water uptake exhibited a square-root-of-time dependence in freshly prepared samples, but more variable rates were observed for samples previously in contact with water. The radiography was supported by small-angle neutron scattering analysis and ultra-small-angle neutron scattering analysis of aggregate size distributions and by inelastic neutron scattering to understand the physicochemical environment of the sorbed water. Results showed that hydrothermal treatment with KCl had the greatest effect of increased water transport in the bentonite, possibly as a result of the interaction of  $K^+$  with smectite layers in the clay.

> **Keywords** — *Water uptake into bentonite, engineered clay barriers for nuclear fuel disposal, bentonite swelling, interfacial energy of water in porous bentonite, neutron radiography.*

**Note** — Some figures may be in color only in the electronic version.

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### I. INTRODUCTION

The U.S. Department of Energy (DOE) is evaluating various strategies for creating deep geologic repositories for the permanent disposition of spent nuclear fuel. Various geologic media and engineered repositories have been

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proposed for long-term fuel/waste storage; however, the current plan is to use multiple structures to create barriers to radionuclide transport.<sup>1,2</sup> The development of engineered barrier system design concepts and evaluation of potential radionuclide interactions with natural barriers or other engineered interfaces are, therefore, inherently important for predicting the long-term (i.e., tens of thousands of years) safety and performance of geologic repositories.<sup>3–5</sup>

In waste repositories both natural and engineered barriers are needed to limit the flow and movement of water and/or adsorb released radionuclides. Media selection for barriers includes the use of materials with very low permeabilities. However, the complete elimination of water movement through even low-permeability materials is not viewed as practical.<sup>6,7</sup> Rather, what is needed is a complete understanding of the mineralogical behavior and pore structures of barrier materials under various saturation conditions and the transport characteristics of water through potential engineered barrier materials. This will allow predictive modeling of radionuclide release.

Current understanding of barrier behavior and water migration is dependent on simulation modeling using codes such as TOUGH2 (Refs. 8 and 9) and PFLOTRAN (Ref. 10). These codes have been used to simulate the progress of hydration phenomena through various media.<sup>11</sup> There are, however, limitations to these simulations arising from a lack of understanding of the microphysics of water transport through the barrier materials under different conditions.<sup>12</sup> Thus, the goal of this project was to measure changes in barrier properties, such as porosity and permeability, with variations in the physical and chemical environment during permeation.

In the work described herein, the interactions of water with bentonite barrier materials were examined using several experimental methods. Neutron and X-ray imaging were used to measure rates of water movement through bentonite by capillary flow and diffusion. These were coupled with ultrasmall-angle neutron scattering (USANS) and small-angle neutron scattering (SANS) measurements to qualitatively and quantitatively evaluate the multiscale pore structure of the media before and after water transport.<sup>13</sup> Inelastic neutron scattering (INS) was also used to probe chemical and phase changes in sorbed fluids through the analysis of the vibrational spectra of trapped water molecules,<sup>14</sup> and quasi-elastic neutron scattering (QENS) provided the sorption energies of these same water molecules trapped in pores.<sup>15</sup> The samples analyzed included bentonites that were exposed to simulated wetting-drying-rewetting cycles to ascertain if changes in mineral hydration were temporary or permanent. Factors such as granule size and previous hydrothermal treatment were included in the analysis to determine their effects on

the sorption. Results from these experiments were used to probe the phenomena that govern groundwater association with clay minerals, which may affect transport processes and thus the ability of engineered bentonite barriers to safely contain spent fuel/waste over geologic timescales.

## II. EXPERIMENTAL

### **II.A. Sample Preparation**

Bentonite for these experiments was obtained from Colony, Wyoming. Bentonite from this location has undergone extensive mineralogical characterization and is composed by weight of 72% of the clay montmorillonite.<sup>5</sup> This material has previously been used in hydrothermal experiments to provide data for geochemical/mineralogical transport models simulated using the TOUGH2 computer code.<sup>8</sup>

Samples of the bentonite were prepared for two sets of experiments. The purpose of the first was to test the effect of granule or aggregate size prior to water exposure on fluid flow. Samples for this experiment were prepared by drysieving the samples to four sizes (>425  $\mu$ m, 90  $\mu$ m to 425  $\mu$ m, 45  $\mu$ m to 90  $\mu$ m, and <45  $\mu$ m). Details are given in the Appendix and in Table A.I. The purpose of the second set of experiments was to test the effects of hydrothermal treatment on water infiltration. Hydrothermal treatment has been shown in previous studies to alter the structure and chemistry of clay minerals.<sup>5</sup> Hence, this experiment was conducted to determine whether clay alteration affected water uptake.

Preparation of these samples began with the as-received material, and hydrothermal alterations included contact with deionized water as well as saturated NaCl and KCl solutions at 473 K under hydrostatic pressure  $(16 \times 10^5 \text{ Pa})$  for 13 days. This temperature was selected as being representative of repository conditions.<sup>5</sup> Samples 1, 2, and 3 were hydrothermally treated, and samples 4 through 7 were controls with no pretreatment. The samples were further divided into three fractions, with A and B analyzed by radiography and, later, by INS and QENS, and fraction C used for USANS analysis before and after imbibition.

Prior to the infiltration experiments, both the hydrothermally treated and corresponding control samples were vacuum dried to determine water content, with the results shown in Table I. Aggregate-sized samples that were not dried prior to uptake had an estimated moisture content by weight of about 4%. For the infiltration experiments, samples were packed into aluminum tubes (10.5-mm inside diameter, 12.5-mm outside diameter, and 20-cm length) at bulk densities of 1.7 to 1.9 g·cm<sup>-3</sup> for the aggregate-sized samples and 1.3 to 1.5 g·cm<sup>-3</sup> for the hydrothermally

Hydrothermal Treatment	Bentonite, ±1 g	Fluid, ±0.05 mL	Temperature, ±1 K	Duration, ±0.1 days	Mass Loss (%)
3.97 <i>M</i> NaCl 2.68 <i>M</i> KCl Deionized water Untreated	20 20 20 62	120 120 120	473 473 473 Not applicable	13 13 13	0.32 0.21 0.36 4.2

TABLE I

Hydrothermal Treatments and Water Content Prior to Uptake Experiments Measured by Mass Loss During Vacuum Drying

treated samples. Descriptions of the hydrothermally treated samples are given in the Appendix and in Table A.II.

## **II.B.** Radiography

Neutron imaging is an ideal technique for understanding the transport of fluids through porous or fractured media because it can be used to quantitatively monitor movement of hydrogen-rich fluids through porous materials to determine of the rate and pattern of infiltration in real time.<sup>16–19</sup> This is possible because the large neutron cross section of hydrogen readily attenuates (or blocks) neutrons through incoherent scattering, allowing dynamic imaging of fluid transport. The advantage of this approach for geological materials is that the neutrons penetrate deeply into the sample, thus providing information from the bulk of the material.<sup>20</sup> For instance, analysis of the spontaneous imbibition of water into finegrained granite matrices using dynamic neutron radiography<sup>21</sup> has shown that significant transport can occur and be observed in a material with a porosity as low as 0.6% and a permeability of only  $10^{-9}$  to  $10^{-4}$  µm<sup>2</sup> (Ref. 22).

In neutron radiography, transmission of neutrons not attenuated by the sample is proportional to the atom density (concentration) and thickness (path length) according to the Beer-Lambert  $law^{23}$ :

$$T = \frac{I}{I_0} = e^{-N\sigma t_s},\tag{1}$$

where

- I = measured intensity
- $I_0$  = incident intensity
- T = transmission
- N = atom density
- $\sigma$  = total neutron cross section
- $t_s$  = thickness of the sample.

Neutron imaging was carried out on the aggregate-sized samples at imaging beam line CG-1D at Oak Ridge National

Laboratory's (ORNL's) High Flux Isotope Reactor (HFIR). In addition, neutron and X-ray imaging were carried out simultaneously at the BT-2 neutron imaging facility at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) (Ref. 24). Details of the instrumental configurations are provided in the Appendix. In these experiments, 1 cm<sup>3</sup> of deionized water was introduced remotely by a syringe into the headspace of an aluminum tube containing the bentonite while simultaneously monitoring the radiographic images. Radiographic images were continuously collected every 30 s as the water infiltrated the bentonite and the clay began to swell. This was continued until the system appeared to reach a steady state, which was assumed to occur when the images showed negligible change and generally required a run time of 1 to 2 h.

After the first infiltration experiments, the hydrothermally treated samples were dried in an oven to a constant mass and then rewet in a repeat uptake experiment. These repeat experiments have been designated "second  $H_2O$  infiltration" in Table II.

Image analysis was carried out using either Image-J (Ref. 25) or Jupyter notebooks written in Python following published procedures.<sup>26</sup> The first image with water in the field of view (FOV), but before water contacted the bentonite, was selected as a normalization reference and served as an open beam standard for subsequent infiltration radiographs. Following normalization of each image to this starting image, a region of interest (ROI) was selected highlighting the region of infiltration or swelling. The pixel intensity was summed across this ROI along the length of the sample (the z-direction or vertical distance). The variance in the cumulative average from each end of the sample was then calculated to determine the point along the z-axis at which the most rapid change in signal intensity occurred. This point has been shown to indicate the leading edge of water infiltration in earlier studies<sup>27</sup>

The calculated maxima in cumulative variance as a function of time were analyzed using a nonlinear leastsquares fit to determine the power law expressed by the data. Previous experiments have indicated that imbibition

Sample Identifier	Infiltration Exponents	Sorption Rate, $R^2$ (mm·min <sup>-0.5</sup> )	Swelling Rate, $R^2$ (mm·min <sup>-0.5</sup> )
Packed grains 90 to 425 um	0.46	0 691 (0 94)	N/A <sup>a</sup>
Packed grains 90 to 425 µm	0.50	0.753 (0.95)	N/A
Packed grains, 90 to 425 µm	0.53	0.879 (0.96)	N/A
Packed grains, 50 to 425 µm	0.47	0.776 (0.93)	N/A
Packed grains, 45 to 90 µm	0.44	0.776(0.93)	0.440(0.01)
Packed grains, $45$ to $50 \mu m$	0.42	0.708(0.94) 0.631(0.94)	0.449 (0.91) N/A
Paakad grains, <45 µm	0.42	0.031(0.94) 0.770(0.96)	0.248(0.02)
Packed grains, <45 µm	0.42	0.775(0.90)	0.348(0.92) 0.389(0.94)
Packed grains, $>425 \ \mu m$	0.43	0.703(0.83)	0.589(0.94)
NoCl treatment	0.50	0.092 (0.93)	0.008 (0.90)
Neutrong	0.001	0.406 (0.00)	0.406 (0.65)
Neutrons V rous	0.091	0.406 (0.99)	1.24(0.08)
A-lays	0.49	0.441 (0.93)	1.24 (0.98)
Naci treatment	0.20	0.552 (0.08)	1 66 (0.00)
Neutrons	0.30	0.552 (0.98)	1.66(0.90)
X-rays	0.68	0.471 (0.98)	0.36 (0.88)
KCI treatment	0.15		
Neutrons	0.15	2.11 (0.96)	0.036 (0.84)
X-rays	0.48	3.71 (0.992)	0.919 (0.99)
KCI treatment	0.50		
Neutrons	0.50	2.21 (0.998)	1.29 (0.71)
X-rays	0.21	0.183 (0.92)	0.248 (0.98)
$H_2O$ treatment			
Neutrons	0.44	2.17 (0.997)	0.613 (0.91)
X-rays	0.56	0.394 (0.84)	0.634 (0.86)
H <sub>2</sub> O treatment			
Neutrons	0.41	0.365 (0.993)	0.423 (0.93)
X-rays	0.33	0.366 (0.991)	1.14 (0.97)
Control			
Neutrons	0.63	0.407 (0.99)	0.621 (0.99)
X-rays	0.44	0.433 (0.92)	1.29 (0.88)
Control			
Neutrons	0.53	0.685 (0.94)	1.07 (0.88)
X-rays	0.51	0.39 (0.95)	0.384 (0.69)
Control			
Neutrons	0.031	0.119 (0.96)	0.433 (0.80)
X-rays	0.39	0.404 (0.99)	0.480 (0.46)
Control			
Neutrons	0.35	0.314 (0.98)	0.473 (0.93)
X-rays	0.28	0.375 (0.99)	1.39 (0.93)
Control			
Neutrons	0.31	0.229 (0.79)	0.316 (0.94)
X-rays	0.25	0.348 (0.96)	1.96
Control			
Neutrons	0.40	0.314 (0.98)	0.368
X-rays	0.43	0.365 (0.98)	0.425
NaCl, second H <sub>2</sub> O infiltration	0.30	0.572 (0.98)	0.503
NaCl, second	0.63	0.543	0.382
H <sub>2</sub> O infiltration			
KCl, second H <sub>2</sub> O infiltration	0.43	4.76	0.834
KCl, second H <sub>2</sub> O infiltration	0.55	5.15	0.051
$H_2O$ , second $H_2O$ infiltration	0.25	0.318	0.482

TABLE II Uptake and Swelling Results for Bentonite Samples\*

(Continued)

Sample Identifier	Infiltration Exponents	Sorption Rate, $R^2$ (mm·min <sup>-0.5</sup> )	Swelling Rate, $R^2$ (mm·min <sup>-0.5</sup> )
H <sub>2</sub> O, second H <sub>2</sub> O infiltration	0.58	1.264	0.851
Control, second	0.47	0.404	0.389
$H_2O$ infiltration			
Control, second	0.62	0.167	0.240
H <sub>2</sub> O infiltration			
Control, second	0.90	0.44	0.063
H <sub>2</sub> O infiltration			
Control, second	0.63	0.269	0.946
$H_2O$ infiltration			
Control, second	0.66	0.188	0.232
$H_2O$ infiltration			
Control, second	0.42	0.754	0.748
$H_2O$ infiltration			

TABLE II (Continued)

\*Sample description, exponent of a nonlinear least-squares fit, fits of sorption of water uptake into the clay, and penetration rate of the clay into the water column. The data were obtained at two different institutions: The single data points were taken at CG-1D at ORNL; two data points—for neutron and X-ray radiographs—were taken at BT-2 (NIST). <sup>a</sup>N/A indicates that these data are unavailable because of the sample placement.

into geological specimens exhibits a square root dependence on time, which can be modeled as a capillary uptake phenomenon following the Washburn-Lucas equation  $as^{28,29}$ 

$$h = \sqrt{\left(\frac{\sigma r \cos\theta}{2\eta}\right)t} \tag{2}$$

and

$$h = S\sqrt{t} , \qquad (3)$$

where

h = height of the wetting front

 $\eta$  = fluid viscosity

- r = radius of the capillary
- $\sigma$  = surface tension of the fluid
- t = time after the first contact with the water
- $\theta$  = contact angle between the two materials
- $S = \text{constant referred to as the sorptivity.}^{16-18}$

The results from radiography are given in Table II.

## **II.C.** Inelastic and Quasi-Elastic Neutron Scattering

Another neutron scattering approach with important implications for understanding transport through barrier materials is INS, which uses neutrons to measure vibrational spectra. The spectra obtained via INS can document the changes in mineralogy,<sup>5</sup> cation absorption, interlayer interactions,<sup>14</sup> and hydrogen bonding between the clay and adsorbed water.<sup>30</sup> Such studies allow observation of the hydration and dehydration of minerals and the effect of ion exchange on water transport through the bentonite matrix.

Quasi-elastic neutron scattering is the limiting lowenergy case of INS, with energy transfers being small compared to the energy of the incident neutrons. QENS measures translational motions, which cause a broadening of the incident neutron energy spectrum. This allows dynamic processes, such as diffusion, to be probed. QENS experiments can be contrasted to inelastic scattering measurements, which result in well-separated lines that are distinct from the incident line, arising from interactions with discrete phonons or vibrations. The broadened QENS line can be fit with a superposition of Lorentzian functions. The full-width halfmaximum (FWHM) of these Lorentzian contributions to the line shape can be used to provide the transport rate as well as the activation energy for diffusion if plotted against the reciprocal of temperature.<sup>31</sup>

Powders from selected bentonite samples were examined using INS and QENS at the VISION vibrational

Sample Identifier – Hydrothermal Preparation	Humidity Pretreatment <sup>a</sup>	TGA Before, ±0.2 mg	TGA After, ±0.1 mg	Difference, ±0.2 mg (%)
1A - NaCl 2A - KCl 3A - H2O 4A - none 1A - NaCl 2A - KCl 3A -H2O 5A - none 1A - NaCl 2A - KCl 3A - H2O 5A - none 1B - NaCl 2B - KCl 3B - H2O 5B - none	Desiccator Desiccator Desiccator Desiccator Saturated air <sup>b</sup> Saturated air <sup>b</sup> Saturated air <sup>b</sup> Saturated air <sup>c</sup> Saturated air <sup>c</sup> Saturated air <sup>c</sup> Saturated air <sup>c</sup> Saturated air <sup>c</sup> Saturated air <sup>c</sup> Saturated air <sup>c</sup> K <sub>2</sub> CO <sub>3</sub> RH = 43% K <sub>2</sub> CO <sub>3</sub> RH = 43% K <sub>2</sub> CO <sub>3</sub> RH = 43%	58.7 $34.0$ $49.1$ $60.0$ $56.3$ $49.2$ $60.3$ $90.9$ $55.6$ $48.3$ $51.1$ $66.4$ $38.5$ $48.6$ $62.3$ $47.0$	57.2 33.6 47.8 58.2 51.3 47.9 53.1 85.9 53.2 47.4 49.0 55.0 34.4 44.9 50.4 38 5	$\begin{array}{c} 1.5 (3) \\ 0.4 (1) \\ 1.3 (3) \\ 1.8 (3) \\ 5.0 (9) \\ 1.3 (3) \\ 7.2 (12) \\ 5.0 (6) \\ 2.6 (4) \\ 0.9 (2) \\ 2.1 (4) \\ 11.4 (17) \\ 4.1 (11) \\ 3.7 (8) \\ 11.9 (19) \\ 8.5 (18) \end{array}$

TABLE III Experimental Matrix for INS

<sup>a</sup>Exposure is for 2 weeks unless noted otherwise.

<sup>b</sup>Overnight exposure.

<sup>c</sup>6-month exposure.

spectrometer (BL-16B) at the Spallation Neutron Source (SNS) at ORNL (e.g., Ref. 14). Details on the BL-16B instrument are provided in the Appendix. The samples examined included each of the three hydrothermally treated clays and one untreated control. Prior to analysis, bentonite samples were equilibrated at predetermined relative humidities at room temperature in sealed vessels following hydrothermal treatment. The samples were equilibrated over several weeks with saturated solutions of either  $K_2CO_3$  [relative humidity (RH) = 43%] or water (ambient RH, about 80%) or by storing them in a desiccator (RH <1%), all at 294 K. Because of limited instrument availability, detailed INS data were collected for only two of the samples, 1B and 2B, that were hydrothermally treated in NaCl and KCl solutions, respectively. The water content was measured for all of the samples by thermal gravimetric analysis (TGA) using a Setaram<sup>a</sup> thermal gravimetric analyzer/differential thermal analyzer. The Setaram thermal gravimetric analyzer/differential thermal analyzer was calibrated by heating Li<sub>2</sub>SO<sub>4</sub> through its phase transition at 851 K (Refs. 32 and 33). The experimental matrix and TGA data are given in Table III.

### II.D. Small-Angle Neutron Scattering

Small-angle neutron scattering and USANS provide data on the structure of materials at the 0.5- to 200-nm and 100- to  $10^4$ -nm scales, respectively. Neutrons can penetrate geological materials and scatter from mineral or pore interfaces, as long as there is a difference in scattering length density (SLD) across an interface. In porous materials, the intensity of scattered neutrons can be interpreted as arising from a distribution of pores across the length scale, allowing macroscopic properties, such as water infiltration, to be related to the nanostructure of a material.<sup>34</sup>

Each of the bentonite samples allotted for USANS, the C samples, was sectioned before and after water contact and sealed with wax to maintain its dry or wet status. Both dry and wet samples were pressure impregnated with epoxy prior to preparation of sample mounts for USANS following our standard protocols.<sup>35,36</sup> The NG-B 30m SANS (Ref. 37) and BT5 USANS (Ref. 38) instruments at the NCNR were used to collect porosity measurements on the bentonite samples. Details on the setup of these instruments are given in the Appendix, and the USANS results are presented in Table IV.

<sup>&</sup>lt;sup>a</sup> Certain trade names and company products are mentioned in the text or identified in an illustration in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the NIST nor does it imply that the products are necessarily the best available for the purpose.

Sample Name Hydrothermal – Treatment/ Uptake <sup>a</sup>	Void Fraction	Median Pore Diameter (Å)	Mean Pore Diameter (Å)
NaCl – dry (CD1)	$0.154 \pm 0.014$	12216	1513
NaCl – wet (CH1)	$0.093 \pm 0.010$	27942	2104
KCl – dry (CD2)	$0.140 \pm 0.017$	15647	1480
KCl – wet (CH2)	$0.155 \pm 0.017$	17746	1081
DI – dry (CD3)	$0.105 \pm 0.011$	15573	812
DI – wet (CH3)	$0.108 \pm 0.011$	24471	1284
Control – dry (CD5)	$0.078 \pm 0.013$	41319	9570
Control – wet (CH5)	$0.071 \pm 0.010$	35674	7996
Control – dry (CD6)	$0.100 \pm 0.015$	32647	3901
Control – wet (CH6)	$0.098 \pm 0.012$	23560	3171
Control – dry (CD7) <sup>b</sup>	$0.056 \pm 0.010$	31732	4532

TABLE IV

Pore Volume from SANS/USANS\*

\*Sample description, and void fraction and median and mean pore diameter from fitting the data as described in the text. <sup>a</sup>Data are not available for CH7.

<sup>b</sup>"D" samples are before water uptake. "H" samples are after water uptake.

## **III. RESULTS**

## **III.A. Radiography**

Neutron radiographs from the infiltration experiments were analyzed to provide rates of uptake into the bentonite samples. An example of coupled X-ray and neutron images is provided in Fig. 1. This shows the water meniscus at the top, the water layer on top of the clay, penetration of water into the clay, and expulsion of an air bubble from the clay into the water layer. Decreases in intensity (darker color) arose from increases in water content or from infiltration into the bentonite. Increases in intensity corresponded to displacement of water, arising from swelling of the bentonite into the water column above the sample. X-ray imaging data were interpreted similarly, but the changes in intensity



Fig. 1. (a) X-ray image and (b) neutron image of water infiltration, bentonite swelling, and air expulsion from the bentonite sample taken 50 min into the experiment (sample dimension: 12.7-cm diameter). The X-ray and neutron detectors were located 90 deg to each other. The sample, 6A, had no hydrothermal pretreatment. Sorption rates were measured from the interface downward into the bulk of the sample. Swelling rates were measured from the interface upward into the water column.



Fig. 2. Profile of radiographs after normalization for simultaneous neutron and X-ray imaging for sample 6A. Data were taken every 0.5 min after contact of water with the bentonite, starting the infiltration experiment. The sample had no hydrothermal pretreatment.

showed opposite trends, with increased intensity arising from water infiltration and decreased intensity (darker color) from clay swelling. Radiographic data showing a juxtaposition of neutron and X-ray profiles for the same sample 6A are shown in Fig. 2. Unlike other types of geological materials, such as shales<sup>39</sup> and sandstones,<sup>27</sup> bentonite swells significantly upon contact with water. Thus, the radiographs were analyzed in two separate sections: one above the initial bentonite-water interface, or the region into which swelling occurred, and one below the initial bentonite-water interface for water infiltration.

The "Infiltration Exponents" column in Table II presents the slopes of the best logarithmic fits of the uptake data. Because these are close to 0.5, they indicate that the infiltration can be reasonably expressed as a square root function of time, that is, as a diffusional process. The slopes of the sorption plots are presented in Table II along with the regression  $R^2$  values. Clay swelling is also expected to exhibit square-root-of-time behavior,<sup>12</sup> so these data were also fitted to a square-root-of-time function, and slopes for these plots are also given in Table II along with their  $R^2$  values. The swelling showed much greater variability, especially in samples that had been repeatedly exposed to drying-rewetting cycles. Very low  $R^2$  values indicated that the sorption or swelling was nonlinear, often arising from trapped air bubbling through and disrupting the clay interface during the experiment. Figures 3a, 3b, and 3c show infiltration, sorption, and swelling profiles for sample 5A. The infiltration exponents and sorption slopes were analyzed for mean, standard deviation, and outliers for the complete set of samples. The accumulated results are presented in Figs. 4a, 4b, and 4c.

### III.B. Inelastic and Quasi-Elastic Neutron Scattering

Additional studies of the interactions of clays with water were carried out by measuring water vibrational modes via INS coupled with TGA. Vibrational bands of  $H_2O$  in contact with the bentonite were observed at frequencies from 5 to 600 meV (40 to 4800 cm<sup>-1</sup>). The intensities of these bands were proportional to the amount of water absorbed into the sample, as determined by TGA. The librational mode of  $H_2O$  is a rocking feature that contributes a broad peak in the vibrational spectrum below 1000 cm<sup>-1</sup>, which can be used to probe the physics of confined water.<sup>40</sup> Figure 5 shows librational spectra from 5 K to 295 K of  $H_2$  O collected from two bentonite samples, 1B and 2B, which had undergone prior hydrothermal treatments with NaCl and KCl, respectively. A clear transition indicated by



Fig. 3. Computed (a) infiltration, (b) sorption, and (c) swelling profiles for sample 5A. The sample, 5A, had no hydrothermal pretreatment and was one of the controls for the hydrothermal experiments. It underwent the same drying procedure as the hydrothermal samples but was not pretreated in the pressurized reactor.

softening of the librational edge was observed in both samples between 250 K and 300 K, indicating a change in water structure. The transition in the NaCl-contacted sample was complete at 290 K while that of the KCl-contacted sample occurred at a slightly higher temperature (295 K), indicating a slight increase in binding energy in the latter

due to the potassium-ion substitutions in the bentonite structure.

The suggestion that water was more strongly bound to the bentonite structure in the KCl-treated sample than in the NaCl-treated sample was supported by analysis of the line widths of the QENS peaks. As can be seen in Figs. 6a and 6b,



Fig. 4. Measured infiltration by radiography, showing (a) nonlinear least-squares fit to the time profile of the water front through the sample, (b) the sorption rate, and (c) the swelling rate. These results include analyses of uptake data from neutron and X-ray radiographs for all of the samples. Each box shows the median (middle line), mean (x), first quartile (bottom of box), and third quartile (top of box), and the whiskers show the spread of data excluding outliers.

the QENS measurements of FWHM are provided for samples 1B (NaCl-treated) and 2B (KCl-treated), respectively. The log of the Lorentzian line width is plotted as a function of reciprocal temperature. In this case the slope of the plot represents the binding energy of water in each sample, which can be related to the activation energy for diffusion. The binding energy of the NaCl-contacted sample  $(5.7 \text{ kJ} \cdot \text{mol}^{-1})$  was significantly lower than that of the KCl-contacted sample  $(8.4 \text{ kJ} \cdot \text{mol}^{-1})$ .

### **III.C. Ultra-Small-Angle Neutron Scattering**

The porosity of the dry and hydrated bentonite samples was analyzed using USANS (Ref. 41). Porosity was calculated by assuming a two-phase system with scattering from pore-clay interfaces providing the greatest contribution to the observed intensity.<sup>42</sup> This assumption is based on the fact that the SLD difference is significantly greater between the clay matrix and empty pore space than between any pair of mineral phases in the sample. The SLD of the clay was calculated to be  $3.67 \times 10^{-10}$  cm<sup>-2</sup>, a typical value reported

for montmorillonite.<sup>43</sup> The SANS scattering patterns exhibited azimuthal symmetry, revealing that the samples were isotropic. Thus, the scattering intensity measurements were azimuthally integrated at all scattering vectors ( $Q = 2\pi\theta/\lambda$  at small angles  $\theta$ , where  $\lambda$  is the neutron wavelength). The slitsmeared USANS intensity data were de-smeared to put the USANS measurements on the same scale as the data from the pinhole SANS instrument. This was done using the iterative method proposed by Lake and discussed in greater detail in the Appendix.<sup>44</sup> The SANS and USANS patterns were then combined to yield a single scattering curve in the range of  $3 \times 10^{-5} \text{ Å}^{-1}$  to 0.2 Å<sup>-1</sup>.

Calculated results for the mean pore size, median pore size, and overall void fraction, derived from the SANS and USANS analyses by assuming that the pores were spherical in shape, are given in Table IV. Examples of pore size distribution are given in Fig. 7 for samples exposed to NaCl (CD1) and KCl (CD2) along with the corresponding controls (CD5 and CH5) showing the effect of hydrothermal treatment and rewetting on pore size distribution. As the pore size distributions were all



Fig. 5. Inelastic neutron scattering from bentonite samples from 0 to 150 meV, showing librational spectra for water absorbed in the sample matrix. These spectra, taken at temperatures from 5 K to 295 K, show evidence of a phase transition between 250 K and 290 K for sample 1B - NaCl treatment (upper traces) and softening of the librational edge between 290 K and 295 K for sample 2B - KCl treatment (lower traces). Data taken prior to melting show structure in the acoustic region, below 50 meV, that disappears after softening. The colors of the 5 K/250 K/290 K/295 K lines are black/red/purple/blue, respectively, with the 290 K trace indicated by the arrows.



Fig. 6. Arrhenius plots of the wide Lorentzian component of the QENS peak for (a) sample 1B (NaCl treatment) and (b) sample 2B (KCl treatment). The slope of the graph gives the activation energy for diffusion of pore-bound water divided by the gas constant.

multimodal, the total void volume results were the easiest to compare. In all samples, both the mean and median pore sizes were much greater than the peak in the volumetric distribution, i.e., the size with the greatest number of pores, which is less than 10 nm for all samples. As we have noted elsewhere, these small pores dominate the total surface area of the pore space.<sup>34</sup>

Overall, comparison of the data in Fig. 7a and Table IV shows that hydrothermal treatment with NaCl (blue) or KCl (red) appears to have increased the void fraction by about 50%. The volumetric pore size distribution, however, was shifted to a smaller pore size as measured by either the mean or median diameter. The deionized water-treated samples also indicated a shift in pore size distribution; however, there was only a slight change in void fraction with respect to the untreated samples.

## IV. DISCUSSION

The studies described here covered a wide range of initial conditions, pretreatments, and experimental conditions. In this section, the effects of these treatments are discussed separately, followed by a principal component statistical analysis to develop an understanding of the interplay of phenomena affecting water infiltration into bentonite barrier material.

#### IV.A. Hydraulic Conductivity and Aggregate Size

Hydraulic conductivity is a measure of how readily water moves through the medium being considered, bentonite clay in this instance. It depends on the hydraulic gradient, the saturation level, and the



Fig. 7. Pore size distributions for bentonite: (a) directly after hydrothermal treatment (before infiltration) with NaCl (blue), KCl (red), and the control (gray); (b) KCl-treated samples before (blue) and after (red) infiltration, with the control (gray) after infiltration; and (c), NaCl-treated samples before (blue) and after (red) infiltration, with the control (gray) after infiltration.

permeability of the clay. Because hydraulic conductivity depends on grain diameter,<sup>12</sup> an experiment was undertaken to investigate the conductivity of various bentonite samples as a function of grain size. As noted above, this was done by pressing the samples into an aluminum tube and measuring the uptake rate using neutron imaging.

As shown in Fig. 4b, the distribution in uptake for these samples was very narrow. Even mechanically disturbing the sample by introduction before imbibition of an artificial defect had little effect on the rate of water sorption into the sample. These results suggest that the bentonite was sufficiently deformed as it was pressed into the aluminum tube to eliminate the effect of particle size or artificial fracture. Matrix swelling during infiltration, as expected with smectite clay minerals, would also be expected to reduce the effects of grain size.

In order to investigate this result further, we examined the difference in uptake between the pressed samples and the hydrothermal controls (Fig. 4). The hydrothermal controls

show significantly greater variability in their infiltration exponent, sorption and swelling rates than the pressed samples. Although the absolute values are similar, the hydrothermal controls generally show greater and more variable rates of clay swelling and smaller infiltration exponents and sorption rates than the pressed samples. There also appears to be a relationship between void fraction and uptake rate. The USANS data for the controls (CD5, CH5, CD6, and CH6, Table IV) suggest they have lower void fractions than the other hydrothermally treated samples, and these samples also show relatively slow uptake rates  $(0.37 \pm 0.13 \text{ mm.min}^{-0.5})$ relative to the pressed samples  $(0.76 \pm 0.1 \text{ mm.min}^{-0.5})$ . Notably, the less-compacted control samples (5 and 6) also had a large variation in pore size distribution, in which the void fraction and the median diameter both varied by about one-third and the mean by a factor of 2.6. Thus, it appears that the mechanical compression of the aggregate samples, rather than clay swelling, was the main cause of consistency in the uptake data of the pressed samples. These results qualitatively agree with those from other clay compaction studies (e.g., Ref. 45).

## IV.B. Hydrothermal Treatment, Pore Size Distribution, and Binding Energies

Several studies have investigated the effects of hydrothermal treatment on clay mineral alteration.<sup>5,46–53</sup> In these investigations, application of temperatures up to 573 K and pressures up to 160 bar were able to achieve changes in clay mineral morphology and cation content as well as decomposition to produce  $SiO_2(aq)$ .

In our experiments, hydrothermal treatment generally reduced both the sorption rate and the infiltration exponent-the best logarithmic fit to the uptake data-and increased the variability of the swelling behavior. These effects are apparent in the increased uncertainty in the data presented in Fig. 4c and in the lower  $R^2$  values for the swelling rates presented in Table II. Hydrothermal treatment may also have reduced the cohesion of the clay sample, particularly at the clay-water interface, which had little geometric constraint on swelling or other deformation. The hydrothermally treated samples exposed to KCl are a notable exception. These can be explained by the higher void fraction and higher binding energy of the water in the clay matrix as observed by INS and QENS for the KCl-treated samples, as discussed below.

As noted above, vibrational spectroscopy (INS and QENS) data were collected on partially hydrated samples (equilibrated with saturated K<sub>2</sub>CO<sub>3</sub> for 2 weeks). The INS results showed that water retained in the pores of the KCltreated sample exhibited a phase transition at a higher temperature than that in the matrix of an NaCl-treated sample. This was in agreement with the binding energies for H<sub>2</sub>O in the sample pore volume obtained from the QENS data. In addition, the SANS/USANS results showed that the NaCl-treated samples had larger mean pore diameters than the KCl samples and a significantly smaller void fraction (Fig. 7a). The void fraction of the KCl was little affected by hydration, whereas significant swelling of the clay matrix and closing of small pores was observed in the NaCl-treated and watertreated samples, as shown in Figs. 7b and 7c, respectively. Thus, the higher binding energy in the KClexposed samples correlates with the presence of the fluid in smaller pores.

Previous studies have linked bentonite hydrothermal treatment with potassium ions to smectite-to-illite conversion, the former having a much greater tendency to swell on contact with water.<sup>5</sup> The higher intrapore binding energies for water molecules and the smaller pore size distributions observed in the  $K^+$  treated samples are consistent with this interpretation.

#### **IV.C.** Infiltration and Rewetting

Hydrothermal pretreatment also affected the response of the bentonite pore structure to water infiltration. As can be seen in Fig. 7b, the pore size distribution in the KCltreated clay appears to sharpen after infiltration, although the void fraction is nearly identical for both samples. This suggests that the KCl-treated sample has more of its porosity in smaller pores, as indicated by its small median pore size compared with the NaCl-treated sample. Rehydration of KCl-treated samples lowered the mean pore size and increased the median pore size. For the NaCl-treated samples, rehydration increased the mean and median pore sizes but reduced the void fraction (Fig. 7c). Many of the smaller pores were eliminated. The sample hydrothermally treated with water showed a similar change in the mean and median pore size values to that observed in the NaCl-treated sample, but without the change in void fraction. The pore size distributions of the untreated samples (the controls) were flattened in comparison to the hydrothermally treated samples, both before and after rewet, and showed larger and more variable mean and median pore sizes than the others, as shown in Fig. 7a. Both the mean and median of their pore size distributions dropped after water infiltration, although not to the range observed in the hydrothermally treated samples. These results suggest that bentonite that is exposed to elevated temperatures and pressures will sustain changes in porosity that will continue through a rewetting cycle, and the response to rewetting will depend on prior environmental exposure.

### **IV.D.** Principal Component Analysis

A principal component analysis was done to determine if correlations existed between the infiltration results (infiltration exponent, sorption rate, and swelling rate) and sample pretreatment. Results generated from the complete set of samples are presented in Fig. 8. The inputs to the principal component analysis were taken from results presented in Table II. The factors describing the infiltration coefficient are negatively correlated to those for swelling rate, suggesting that the samples that exhibited the most rapid uptake of water also had the least swelling into the water column. This could be attributed to these samples having a larger void fraction to accommodate the water ingress or to swelling reducing porosity and, thereby, permeability. The sorption rate, however, appears to vary with the type of hydrothermal treatment, with outliers attributed to the KCl pretreatment and one of the NaCl samples, in which a dramatic increase was observed. Again, this could be attributed to changes in void fraction, as the KCl samples and one of the NaCl samples had



Fig. 8. Principal component analysis of sorption data with respect to grain size (packed or aggregate samples) and hydrothermal treatment ( $H_2O$ , NaCl, KCl, or none). The arrows show the projection of the three vectors of normalized input data (infiltration exponent, sorption rate, and swelling rate) on the first and second principal components.

the largest initial void fractions according to the USANS results shown in Table IV.

# IV.E. Application to Development of Models for Engineered Barrier Performance

The need for realistic models of engineered barrier performance is cited in several studies, including those involving radionuclide transport<sup>54</sup> and hydrogeology in waste repositories.<sup>10</sup> In order to accurately predict the fate of the repository and its contents, the evolution of the clay buffer as part of the engineered barrier needs to be modeled as a coupled thermal-hydrological-mechanical-chemical process as a function of time at elevated temperatures and pressures. Although the data measured in these experiments are not expected to be wholly representative of engineered barrier behavior under subsurface conditions, they do indicate that changing hydrogeologic conditions will affect barrier permeability, chemistry, and fluid migration.

For instance, water penetration into bentonite will be affected by microstructure, the concentration and type of exchangeable cations, and by the mineralogy.<sup>55</sup> Given the variability in the uptake rates for the less-compacted clays and the larger variability after the first wetting, our results indicate that changes in microstructure affect the sorption of water into the bentonite. The imbibition

data in Table II show that the sorption rates for the potassium-ion hydrothermally treated systems were much higher than for the sodium ion systems, and both were higher than the controls. Thus, it is possible that the exchange of bivalent for univalent cations during hydrothermal treatment affected water uptake. Additionally, the results from the hydrothermal treatment of the initial bentonite with potassium ions are suggestive of clay mineral alteration and the formation of illite resulting in changes to the hydrologic behavior of the clay. The principal component analysis suggests potential correlations between the infiltration results (infiltration exponent, sorption rate, and swelling rate).

Detailed data can be used to develop phenomenological models of mineral hydration, dehydration, cation substitution, and alteration, the hydrogeology of clay minerals and interfacial interactions in aqueous systems that affect radionuclide chemistry and transport over evolving thermal conditions and geologic timescales, and allow us to predict the subsurface behavior of engineered repository barriers.<sup>56</sup> As these models are further developed with input from subsequent experimental studies and incorporated into repository scale flow and transport models, repository designers and safety analysts will gain a better understanding of how their material and design configuration choices impact repository performance.

## **V. CONCLUSIONS**

This project incorporated results from several different instruments to better understand transport and water phase behavior in pores in bentonite to provide a multiscale understanding of permeation as a function of pretreatments and changes in ambient conditions. Understanding these changes is an important factor in designing engineered barriers and predicting their performance in nuclear waste repositories.

Experiments were conducted using several neutron and X-ray methods to probe the interfacial interactions of a bentonite engineered barrier material with water. In general, sorption behavior followed the expected diffusion model with close to a square-root-of-time dependence within freshly pressed samples of bentonite clay. Hydrothermal pretreatments applied before the infiltration experiments greatly increased the variability in the infiltration and sorption results, likely as a result of changes in the hydration of the mineral samples before infiltration began. In the case of the potassium ions, the increased variability likely was also due to alteration of the clay mineralogy. These findings are consistent with spectroscopic results from INS and QENS for samples that underwent hydrothermal treatments with NaCl and KCl, which showed changes in the chemical environment of bound water within the clay matrices. They are also consistent with SANS/USANS results that showed changes in multiscale pore distribution upon infiltration as being dependent on the nature of hydrothermal pretreatment.

Sequential sample drying and rewetting cycles were also observed to change the morphology of the samples and increased the variability in infiltration rate. Drying and rewetting at ambient temperature and pressure affect clay packing, increasing the variability in water sorption and generally increasing the overall infiltration rate. However, sequential drying and rewetting did not change the association between the hydrothermal treatments and the infiltration parameters. Thus, these ambient-condition cycles were not enough to change the mineralogy of the clay minerals.

Ultimately, what we hope to achieve with these data is to inform sensitivity analyses such as a Geologic Disposal Safety Assessment.<sup>57</sup> Thermomechanical models of barrier behavior are used to describe radionuclide transport and capture within a bentonite matrix under conditions that will change over time. Thus, these models of fluid flow need to include uncertainties associated with the chemistry, mineralogy, nanoporosity, and microstructure of the engineered barriers and how these also evolve over time.

## APPENDIX

### **EXPERIMENTAL DETAILS**

### **A.I SAMPLE PREPARATION**

Bentonite was pulverized and then dry-sieved into four aggregate-sized fractions (>425 µm, 90 µm to 425  $\mu$ m, 45  $\mu$ m to 90  $\mu$ m, and <45  $\mu$ m). Two samples were prepared from each size aggregate by being pressed into an aluminum (Alloy 6061) tube for imaging. The samples were not dried before being pressed into the tubes. For each granule size range, the samples, which averaged about 4.5 g in mass, were compressed to a height of about 2.5 cm using an Enerpac<sup>a</sup> hydraulic press. The density achieved for these samples was approximately 1840 kg.m<sup>-3</sup>, determined by the mass and volume of the packed sample. Four samples, one from each size aggregate, were compressed with a defect introduced into the packing to simulate a fracture. The defect was formed by first partially compressing the powder to about 3.8 cm in height, inserting a clean spatula 2 cm into the sample, and then continuing to compress to a sample height of 2.5 cm  $\pm$  0.1 cm. Table A.I gives details on the composition of each sample.

### **A.II HYDROTHERMAL FRACTIONS**

Powdered bentonite was divided into four fractions, and three of these fractions were subjected to hydrothermal treatment, with the untreated fraction serving as the control (Table A.II). Each hydrothermal fraction was saturated with an aqueous fluid (i.e., deionized water, 3.97 M NaCl, or 2.68 M KCl). These slurries were then separately sealed in 300-mL bolted-closure vessels with SiO<sub>2</sub>-glass liners and heated to 473 K under hydrostatic pressure ( $16 \times 10^5$  Pa) for 13 days, with the temperature being mid-range in the range of conditions presented by Cheshire et al.<sup>5</sup> Following the hydrothermal treatment, the clay materials were washed to remove residual salts and dried overnight at 378 K.

The water content of each sample was determined before the infiltration experiments as follows. Treated and dried fractions 1, 2, and 3 and untreated fraction 4 were weighed, rinsed with deionized water, and then dried under vacuum for a further 138 h at 378 K. The samples were then removed from the oven to equilibrate with ambient air for 1 h (294 K) to reproduce the initial condition of the infiltration experiments. After equilibration, the fractions were reweighed, and the percentage of mass loss, i.e., the

Sample	Grain Size (µm)	Height, ±0.05 cm	Mass, ±0.01 g	Bulk Density, $\pm 0.1 \text{ g/cm}^3$	Artificial Defect
1_GS 2_GS 3_GS 4_GS 5_GS 6_GS 7_GS 8_GS 9_GS	90 to 425 90 to 425 90 to 425 45 to 90 45 to 90 <45 <45 <45 >425 >425	4.1 2.5 2.4 2.6 2.5 2.4 2.6 2.4 2.6 2.4 2.4	7.56 4.57 4.52 4.53 4.53 4.53 4.58 4.58 4.58 4.57 4.57	$ \begin{array}{r} 1.8(4) \\ 1.8(2) \\ 1.8(7) \\ 1.7(4) \\ 1.8(0) \\ 1.9(0) \\ 1.7(5) \\ 1.9(0) \\ 1.9(0) \\ 1.9(0) \end{array} $	Yes Yes Yes Yes

 TABLE A.I

 Experimental Parameters for Variable Grain Size Tests\*

\*Sieved grain size and variables describing the sample as packed into an aluminum tube for analysis.

difference in sample mass before and after oven drying, was calculated, as shown in Table A.II. Fractions 1, 2, and 3, which had been subjected to hydrothermal treatment, showed little mass loss because a significant amount of moisture evaporated during the intermediate vacuum drying step. The untreated bentonite, retaining its original moisture, as it had not experienced the post-hydrothermal drying step, showed a significant mass loss. Table A.II also includes the mass of sample packed into the aluminum tube, its height, and its bulk density.

## A.III DETAILS OF INSTRUMENTS USED IN THIS STUDY

Neutron radiography was done using the CG-1D instrument at ORNL's HFIR, and simultaneous neutron and X-ray radiography were carried out at NIST on the BT-2 instrument. At the CG-1D instrument, a micro-channel plate detector with a  $2.8 \times 2.8$ -cm FOV and a spatial resolution of about 55 µm was employed. Images were acquired at 2-min intervals using dynamic neutron radiography. At BT-2 (NIST), both X-ray and neutron radiographs were collected simultaneously on the Neutron and X-Ray Tomography (NeXT) system, every 0.5 min, at spatial resolutions of 25 and 15 µm, respectively.

Inelastic neutron scattering and QENS used the BL-16B instrument (ORNL-SNS). This instrument detects inelastically scattered neutrons over a broad range of energy transfer (-2 to 1000 meV) and functions similarly to a Raman spectrometer.

Sample preparation for USANS followed our standard protocols. Samples were evacuated under vacuum and then impregnated with epoxy under applied pressure. The samples were then cut, mounted on 1-mm-thick quartz slides with more epoxy, and polished to a 150-µm thickness. Oil was used as a lubricant instead of water to maintain the porosity during processing. This method of mounting geological samples has been found to minimize multiple scattering from different interfaces, as well as scattering contributions from the slide and glue.

The NG-B 30m SANS and BT5 USANS instruments at the NCNR were used to collect porosity measurements on the bentonite samples.58 On the NG-B 30m SANS instrument, spectra were obtained at three sample-todetector distances (1-, 4-, and 13-m lengths) to increase the observed angular range or Q-range. The source radius was 60 mm, and an 11-mm-diameter cadmium sample mask was used for each sample-to-detector distance. The trap radii were 24.5 mm at 1 and 4 m, and 14.3 mm at 13 m. The wavelengths of the neutrons were 6 Å at 1 and 4 m, and 8.4 Å at 13 m, the lens setup, with a wavelength spread or  $\Delta\lambda/\lambda = 14\%$ . The resultant scattering vector ranged from 0.001 to 0.2 Å<sup>-1</sup>, which corresponds to sizes from approximately 2.5 to 500 nm. Data were corrected for empty-beam scattering, background counts and detector uniformity, sample transmission, and scattering volume and were reduced to absolute scale (differential cross section per unit of volume) by normalization to the intensity of the direct beam.

On the BT5 USANS instrument, a pair of triple-bounce channel-cut perfect silicon (220) crystals was used for the monochromator and analyzer. A 12.5-mm-diameter cadmium sample mask was used for both the SANS and USANS measurements so that identical volumes were measured. The wavelength was 2.38 Å with a wavelength spread of  $\Delta\lambda\lambda = 5.9\%$ . The resultant scattering vector ranged from  $3 \times 10^{-5}$  Å<sup>-1</sup> to  $2 \times 10^{-3}$  Å<sup>-1</sup>, which corresponded to sizes from approximately 250 to  $1.6 \times 10^4$  nm (Ref. 59). Scattering intensity was corrected for constant background and the

Sample	Hydrothermal Treatment	Mass, ±0.0001 g	Height, ±0.05 cm	Bulk Density, $\pm 0.1 \text{ g/cm}^3$
1A	NaCl	3.9260	2.6	1.5
1B	NaCl	3.9256	2.6	1.5
1C	NaCl	3.9249	2.6	1.5
2A	KCl	3.9262	2.6	1.5
2B	KCl	3.9257	2.7	1.4
2C	KCl	3.9248	3.7	1.4
3A	Deionized water	3.9246	2.6	1.5
3B	Deionized water	3.9247	2.4	1.5
3C	Deionized water	3.9253	2.6	1.5
5A	None	3.9284	2.6	1.5
5B	None	3.9245	2.6	1.5
5C	None	3.9303	2.6	1.5
6A	None	3.6256	2.5	1.4
6B	None	3.6244	2.5	1.4
6C	None	3.6242	2.5	1.4
7A	None	3.3240	2.5	1.3
7B	None	3.3254	2.5	1.3
7C	None	3.3250	2.3	1.4

TABLE A.II Hydrothermally Treated Samples at 473 K\*

\*Hydrothermal treatment and variables describing the sample as packed into an aluminum tube for analysis.

empty beam. The data were then converted to absolute scale by correcting for the measured attenuation of the direct beam through the sample. As USANS is a one-dimensional measurement, the data were de-smeared for comparison with SANS data using the USANS data reduction software provided by the NCNR (Refs. 38 and 60). publish or reproduce the published form of this manuscript, or allow others to do so, for U.S. government purposes. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/ downloads/doe-public-access-plan).

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### References

- C. F. JOVÉ COLÓN et al., "Evaluation of Used Fuel Disposition in Clay-Bearing Rock," SAND2014-18303R, Sandia National Laboratories (2014).
- D. A. CHESNUT, "Demands Placed on Waste Package Performance Testing and Modelling by Some General Results of Reliability Analysis," *Nucl. Technol.*, 104, 2, 182 (1993); https://doi.org/10.13182/NT93-A34882.
- E. HARDIN et al., "Investigations of Dual-Purpose Canister Direct Disposal Feasibility (FY14)," FCRD-UFD-2014-000069, Rev. 1, p. 250, Sandia National Laboratories (2014).
- 4. P. E. MARINER et al., "Granite Disposal of US High-Level Radioactive Waste," SAND2011-6203, Sandia National Laboratories (2011).

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- M. C. CHESHIRE et al., "Bentonite Evolution at Elevated Pressures and Temperatures: An Experimental Study for Generic Nuclear Repository Designs," *Am. Min.*, 99, 8–9, 1662 (2014); https://doi.org/10.2138/am.2014.4673.
- O. BUZZI et al., "Hydromechanical Behaviour of Rock-Bentonite Interfaces Under Compression," *Rock Mech. Rock Eng.*, **41**, *2*, 343 (2008); https://doi.org/10. 1007/s00603-006-0099-2.
- M. V. VILLAR et al., "Physical Evolution of a Bentonite Buffer During 18 Years of Heating and Hydration," *Eng. Geol.*, 264, 105408 (2020); https://doi.org/10.1016/j. enggeo.2019.105408.
- K. PRUESS, O. OLDENBURG, and G. MORIDIS, "TOUGH2 User's Guide, Version 2," LBNL-43134, Lawrence Berkeley National Laboratory (2012).
- 9. E. HARDIN et al., "Investigations of Dual-Purpose Canister Direct Disposal Feasibility," SAND2014-19563C, Sandia National Laboratories (2014).
- J. M. FREDERICK et al., "Development of a Waste Form Process Model in PFLOTRAN," SAND2016-12456C, Sandia National Laboratories (2016).
- A. B. KERSTING et al., "Migration of Plutonium in Ground Water at the Nevada Test Site," *Nature*, **397**, 56 (1999); https://doi.org/10.1038/16231.
- P. GÉRARD-MARCHANT et al., "Estimating the Hydraulic Conductivity of Slowly Permeable and Swelling Materials from Single-Ring Experiments," *Water Resour. Res.*, 33, 6, 1375 (1997); https://doi.org/10.1029/ 97WR00616.
- E. PERFECT et al., "Neutron Imaging of Hydrogen-Rich Fluids in Geomaterials and Engineered Porous Media: A Review," *Earth-Science Rev.*, **129**, 120 (2014); https://doi. org/10.1016/j.earscirev.2013.11.012.
- R. T. CYGAN et al., "Inelastic Neutron Scattering and Molecular Simulation of the Dynamics of Inter Layer Water in Smectite Clay Minerals," *J. Phys. Chem. C*, **119**, *50*, 28005 (2015); https://doi.org/10.1021/acs.jpcc.5b08838.
- J. D. NICKELS et al., "Structure and Hydration of Highly-Branched, Monodisperse Phytoglycogen Nanoparticles," *Biomacromolecules*, 17, 3, 735 (2016); https://doi.org/10.1021/acs.biomac.5b01393.
- C.-L. CHENG et al., "Rapid Imbibition of Water in Fractures Within Unsaturated Sedimentary Rock," *Adv. Water Resour.*, 77, 82 (2015); https://doi.org/10.1016/j. advwatres.2015.01.010.
- R. HASSANEIN et al., "Investigation of Water Imbibition in Porous Stone by Thermal Neutron Radiography," *J. Phys. D*, **39**, *19*, 4284 (2006); https://doi.org/10.1088/ 0022-3727/39/19/023.
- M. KANG et al., "Diffusivity and Sorptivity of Berea Sandstone Determined Using Neutron Radiography,"

Vadose Zone J., **12**, 3 (2013); https://doi.org/10.2136/ vzj2012.0135.

- R. S. MIDDLETON et al., "Shale Gas and Non-Aqueous Fracturing Fluids: Opportunities and Challenges for Supercritical CO<sub>2</sub>," LA-UR-14-29299, Los Alamos National Laboratory. R. S. MIDDLETON et al., "Shale Gas and Non-Aqueous Fracturing Fluids: Opportunities and Challenges for Supercritical CO<sub>2</sub>," *Appl. Energy*, **147**, 500 (2005).
- K. GONG et al., "In Situ Quasi-Elastic Neutron Scattering Study on the Water Dynamics and Reaction Mechanisms in Alkali-Activated Slags," *Phys. Chem. Chemical Phys.*, 21, 20, 10277 (2019); https://doi.org/10.1039/C9CP00889F.
- A. CHO, M. MATSUBAYASHI, and S. HASEGAWA, "Visualization of Water Permeation into Granite by Neutron Radiography," *Nuclear Instrum. Meth. Phys. Res. A*, 605, 1–2, 197 (2009); https://doi.org/10.1016/j.nima.2009.01.153.
- INTERA ENVIRONMENTAL CONSULTANTS, "Porosity, Permeability, and Their Relationship in Granite, Basalt, and Tuff," ONWI-458, Battelle Office of Nuclear Waste Isolation (1983).
- D. F. SWINEHART, "The Beer-Lambert Law," J. Chem. Educ., 29, 7, 333 (1962); https://doi.org/10.1021/ed039p333.
- 24. J. M. LaMANNA et al., "Neutron and X-Ray Tomography (NeXT) System for Simultaneous, Dual Modality Tomography," *Rev. Sci. Instrum.*, 88, 11, 113702 (2017); https://doi.org/10.1063/1.4989642.
- J. SCHINDELIN et al., "Fiji: An Open-Source Platform for Biological-Image Analysis," *Nature Methods*, 9, 7, 676 (2012); https://doi.org/10.1038/nmeth.2019.
- 26. V. H. DISTEFANO et al., "Spontaneous Imbibition of Water and Determination of Effective Contact Angles in the Eagle Ford Shale Formation Using Neutron Imaging," *J. Earth Sci.*, 28, 5, 874 (2017).
- M. KANG et al., "Multiple Pixel-Scale Soil Water Retention Curves Quantified by Neutron Radiography," *Adv. Water Resour.*, 65, 1 (2014); https://doi.org/10.1016/j. advwatres.2013.12.004.
- R. LUCAS, "Ueber das Zeitgesetz des Kapillaren Aufstiegs von Flussigkeiten," *Kolloid Z*, 23, *1*, 15 (1918); https://doi. org/10.1007/BF01461107.
- E. W. WASHBURN, "The Dynamics of Capillary Flow," *Phys. Rev.*, **17**, *3*, 273 (1921); https://doi.org/10.1103/ PhysRev.17.273.
- N. W. OCKWIG et al., "Nanoconfined Water in Magnesium-Rich 2:1 Phyllosilicates," J. Am. Chem. Soc., 131, 23, 8155 (2009); https://doi.org/10.1021/ja900812m.
- E. MAMONTOV et al., "Simple Analytical Model for Fitting QENS Data from Liquids," *Phys. B*, 566, 50 (2019); https://doi.org/10.1016/j.physb.2019.01.051.
- 32. H. K. CAMMENGA et al., "The Temperature Calibration of Scanning Calorimeters. Part 2. Calibration Substances,"

*Thermochim. Acta*, **219**, 333 (1993); https://doi.org/10. 1016/0040-6031(93)80510-H.

- G. W. H. HÖHNE et al., "The Temperature Calibration of Scanning Calorimeters," *Thermochim. Acta*, 160, 1, 1 (1990); https://doi.org/10.1016/0040-6031(90)80235-Q.
- 34. L. M. ANOVITZ and D. R. COLE, "Characterization and Analysis of Porosity and Pore Structures," *Rev. Mineral. Geochem.*, 80, 1, 61 (2015); https://doi.org/10.2138/rmg. 2015.80.04.
- 35. L. M. ANOVITZ et al., "A New Approach to Quantification of Metamorphism Using Ultra-Small and Small Angle Neutron Scattering," *Geochim. Cosmochim. Acta*, **73**, *24*, 7303 (2009); https://doi.org/10.1016/j.gca. 2009.07.040.
- 36. L. M. ANOVITZ et al., "Analysis of Multiscale Porosity at the Coso Geothermal Field," *Proc. 38th Workshop Geothermal Reservoir Engineering*, Stanford, California, February 11–13, 2013, SGP-TR-198, Stanford University (2013).
- V. H. DiSTEFANO, "Storage of Organic Matter and Transport of Fluids in the Eagle Ford Shale," PhD Thesis, University of Tennessee, Knoxville (Aug. 2018).
- S. R. KLINE, "Reduction and Analysis of SANS and USANS Data Using IGOR Pro," J. Appl. Cryst., 39, 6, 895 (2006); https://doi.org/10.1107/S0021889806035059.
- V. H. DISTEFANO et al., "Solvent-Pore Interactions in the Eagle Ford Shale Formation,"*Fuel*, 238, 298 (2018); https://doi.org/10.1016/j.fuel.2018.10.010.
- R. KHATIB et al., "Molecular Dynamics Simulations of SFG Librational Modes. Spectra of Water at the Water-Air Interface," J. Phys. Chem. C, 120, 33, 18665 (2016); https://doi.org/10.1021/acs.jpcc.6b06371.
- J. ILAVSKY and P. JEMIAN, "Irena: Tool Suite for Modeling and Analysis of Small-Angle Scattering," *J. Appl. Crystall.*, 42, 2, 347 (2009).
- A. P. RADLIŃSKI, "Small-Angle Neutron Scattering and Rock Microstructure," *Rev. Mineral. Geochem.*, 63, 1, 363 (2006); https://doi.org/10.2138/rmg.2006.63.14.
- S.-M. CHOI, 2 "SANS Experimental Methods," presented at NCNR Summer School 2000; http://www.ncnr.nist.gov/ programs/sans/tutorials (current as of Mar. 14, 2020).
- J. LAKE, "An Iterative Method of Slit-Correcting Small Angle X-Ray Data," *Acta Crystallogr.*, 23, 2, 191 (1967); https://doi.org/10.1107/S0365110X67002440.
- 45. L. XIAODONG, R. PRIKRYL, and R. PUSCH, "THMC-Testing of Three Expandable Clays of Potential Use in HLW Repositories," *Appl. Clay Sci.*, **52**, *4*, 419 (2011); https://doi.org/10.1016/j.clay.2011.03.021.
- 46. C. W. DAVIS et al., "Physicochemical and Geotechnical Alterations to MX-80 Bentonite at the Waste Canister Interface in an Engineered Barrier System,"

*Geosciences*, 7, 3, 69 (2017); https://doi.org/10.3390/ geosciences7030069.

- 47. W. M. YE. et al., "Thermochemical Effects on the Smectite Alteration of GMZ Bentonite for Deep Geological Repository," *Environ. Earth Sci.*, **75**, *10*, 906 (2016); https://doi.org/10.1007/s12665-016-5716-0.
- M. H. MOHAMMED et al., "Interaction of Clay and Concrete Relevant to the Deep Disposal of High-Level Radioactive Waste," *Appl. Clay Sci.*, **118**, 178 (2015); https://doi.org/10.1016/j.clay.2015.08.008.
- R. FERNANDEZ, A. I. RUIZ, and J. CUEVAS, "The Role of Smectite Composition on the Hyperalkaline Alteration of Bentonite," *Appl. Clay Sci.*, **95**, 83 (2014); https://doi. org/10.1016/j.clay.2014.03.015.
- J. KASBOHM, R. PUSCH, and L. NGUYEN-THANH, "Lab-Scale Performance of Selected Expandable Clays Under HLW Repository Conditions," *Environ. Earth Sci.*, 69, 8, 2569 (2013); https://doi.org/10.1007/s12665-012-2085-1.
- T. DUDEK, J. CUADROS, and S. FIORE, "Interstratified Kaolinite-Smectite: Nature of the Layers and Mechanism of Smectite Kaolinization," *Am. Mineral.*, 70, 2, 323 (2006).
- P. WERSIN, L. H. JOHNSON, and I. G. McKINLEY, "Performance of the Bentonite Barrier at Temperatures Beyond 100°C: A Critical Review," *Phys. Chem. Earth.*, **32**, 8–14, 780 (2007); https://doi.org/10.1016/j.pce.2006. 02.051.
- A. MEUNIER et al., "Heterogeneous Reactions of Dioctahedral Smectites in Illite-Smectite and Koalinite-Smectite Mixed-Layers: Applications to Clay Materials for Engineered Barriers," *Appl. Geochem.*, 7, Suppl. 1, 143 (1992); https://doi.org/10.1016/S0883-2927(09)80070-X.
- 54. J. L. JERDEN, K. FREY, and W. EBERT, "A Multiphase Interfacial Model for the Dissolution of Spent Nuclear Fuel," *J. Nucl. Mater.*, 462, 135 (2015); https://doi.org/10. 1016/j.jnucmat.2015.03.036.
- S. KAUFHOLD, R. DOHRMANN, and M. KLINKENBERG, "Water-Uptake Capacity of Bentonites," *Clays Clay Minerals*, 58, 1, 37 (2010); https://doi.org/10.1346/CCMN.2010. 0580103.
- 56. ASTM C1174-20, "Standard Guide for Evaluation of Long-Term Behavior of Materials Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste," ASTM International, West Conshohocken, Pennsylvania (Mar. 2020); https://doi.org/ 10.1520/C1174-20.
- 57. E. R. STEIN, L. P. SWILER, and S. D. SEVOUGIAN, "Methods of Sensitivity Analysis in Geologic Disposal Safety Assessment (GDSA) Framework," SAND2019-1783C, Sandia National Laboratories (2019).

- 58. C. J. GLINKA et al., "The 30 M Small-Angle Neutron Scattering Instruments at the National Institute of Standards and Technology," *J. Appl. Cryst.*, **31**, *3*, 430 (1998); https://doi.org/10.1107/S0021889897017020.
- L. M. ANOVITZ et al., "Diagenetic Changes in Macroto Nano-Scale Porosity in the St. Peter Sandstone: An (Ultra) Small Angle Neutron Scattering and

Backscattered Electron Imagine Analysis," *Geochim. Acta*, **102**, 280; https://doi.org/10.1016/j.gca.2012.07. 035.

60. J. G. BARKER et al., "Design and Performance of a Thermal-Neutron Double-Crystal Diffractometer for USANS at NIST," J. Appl. Cryst., 38, 6, 1004 (2005); https://doi.org/10.1107/S0021889805032103.