

Supporting Information

CO₂ Adsorption to Sub-Single Hydration Layer Montmorillonite Clay Studied by Excess Sorption and Neutron Diffraction

Gernot Rother^{*1}, Eugene S. Ilton², Dirk Wallacher³, Thomas Hauß³, Herbert T. Schaefer²,
Odetta Qafoku², Kevin M. Rosso², Andrew R. Felmy², Elizabeth G. Krukowski⁴, Andrew
G. Stack¹, Nico Grimm³, and Robert J. Bodnar⁴

¹Geochemistry and Interfacial Science Group, Chemical Sciences Division, Oak Ridge
National Laboratory, Oak Ridge, TN 37831-6110, USA

²Pacific Northwest National Laboratory, P. O. Box 999, MS K8-98, Richland, WA
99352, USA

³Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner Platz 1,
D-14109 Berlin, Germany

⁴Fluids Research Laboratory, Virginia Tech, Blacksburg, VA 24061, USA

*Email address: rotherg@ornl.gov

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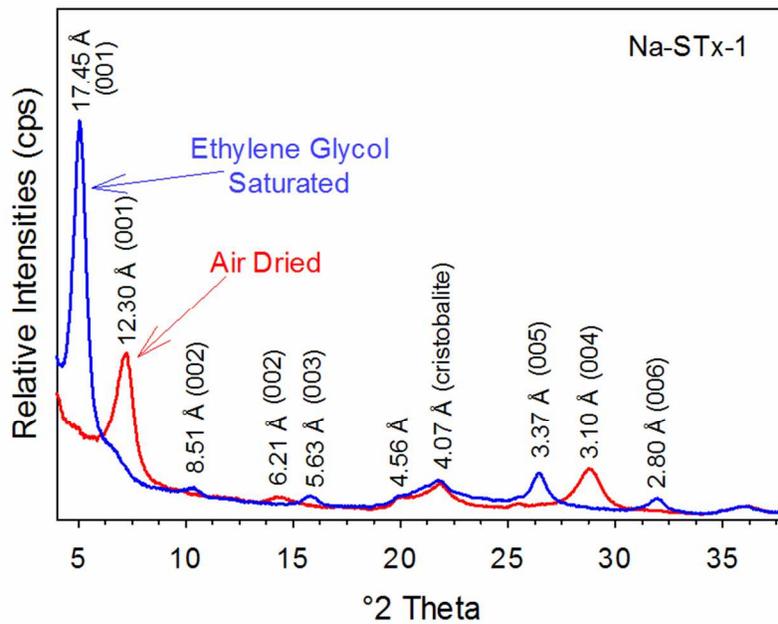
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Characterization of the Na montmorillonite clay

X-ray Diffraction

The XRD pattern confirms that Na montmorillonite with a fraction of cristobalite was synthesized.



Nitrogen BET Surface area

The nitrogen BET surface area was determined using a Quantachrome Autosorb apparatus. Before the measurement, the clay sample was degassed under applied vacuum at 150°C. Two consecutive measurements yielded a specific surface area of $S_{BET} = 30 \pm 1 \text{ m}^2/\text{g}$. This number is much lower than the $690 \text{ m}^2/\text{g}$ calculated for the interlayer surface area based on the

crystallographic data for 1W Na- MM. We conclude that nitrogen molecules do not enter the under the conditions of the BET measurement collapsed interlayer spaces. Instead, the BET surface area is entirely comprised by the outer grain boundaries. The outer grain boundaries thus comprise ca. 4% of the total clay surface area, which means that the clay particles are ca. 20 clay unit cells thick.

Experimental Details

Sorption and neutron diffraction measurements utilized the same high pressure setup.

The pressure was measured with a Keller Preciseline transducer (Series PAA 33X) with a range of 0-300 bar and calibrated accuracy of better than 0.01% FS. CO₂ with 99.999% purity was purchased from Linde, Germany. Bulk CO₂ densities have been calculated for the experimental P , T conditions using the NIST REFPROP 9 software package. The fluid was compressed by means of a piston pressurizer (HIP, Model 87-6-5), all high pressure tubing was 1/16 inch stainless steel capillary.

Excess sorption and pore density

The excess sorption is defined as the excess amount of fluid stored in the interfacial fluid layer:

$$n_e = \int_0^{\infty} (\rho(z) - \rho_b) dz$$

In this equation, $\rho(z)$ is the local fluid density at distance z from the interface, and ρ_b is the bulk fluid density. The exact form of the inhomogeneous interfacial fluid density profile is usually unknown, and cannot be obtained from excess sorption measurements alone. Instead, the net effect of fluid sorption is quantified with reference to the hypothetical state of zero sorption. For

sorption processes in narrow pores, the reference state is complete pore filling with fluid of bulk density.

In gravimetric excess sorption measurements, the weight of the sample in sorption equilibrium is measured. The data are corrected for the fluid-density dependent buoyancy of the sample and the buoyancy of the affected parts of the measurement apparatus (sample bucket, balance rods). The obtained excess sorption in units of mass of excess fluid per mass of adsorbent can be normalized to surface area and pore volume. The pore fluid density is calculated as the sum of the bulk fluid density and pore volume normalized excess density:

$$\rho_p = \rho_b + \rho_e$$

The excess sorption measurements were performed utilizing a Rubotherm magnetic suspension balance. Temperature was measured with a Pt-100 temperature sensor placed directly underneath the sample. The Pt-100 signal was used as input for a PID controller connected to a band heater wrapped around the measurement pressure cell. Temperature stability at the sample was within ± 20 mK. The suspension balance has a resolution of ± 0.01 mg and reproducibility of ± 0.02 mg. The data for pressure, temperature and sample weight were continuously recorded. Sorption equilibrium was assumed after all three parameters remained constant for at least 30 min. In the excess sorption measurements, the clay sample is placed inside the measurement cup, immersed in the fluid present in the pressure vessel. Therefore, the sample buoyancy depends on the density of the fluid and needs to be corrected for. The clay mass density used for this sample buoyancy correction is 2.33 g/cm^3 , the density for 1W Na- MM. The density of cristobalite is very similar to the density of 1 W Na- MM, i.e. $2.27 - 2.33 \text{ g/cm}^3$. Before experiments, the entire

pressure system and sample were briefly evacuated to remove the air initially present. Typical equilibration times per sorption isotherm data point were on the order of 0.5 - 1 hr.

Neutron Diffraction

Neutron scattering experiments were performed at the BER II research reactor neutron scattering facility at Helmholtz Zentrum Berlin. The Membrane Diffractometer, V1, was utilized in its standard two-circle configuration. A vertical focussing pyrolytic graphite monochromator was utilized to select cold neutrons with wavelength $\lambda = 5.23 \text{ \AA}$ and a narrow wavelength band ($\Delta\lambda / \lambda = 0.01$). The neutron beam was collimated by two slit systems before passing through the sample. Scattered neutrons were detected by an ^3He area detector with 128 x 128 square pixels of 1.5 mm edge length at a sample to detector distance of 102.52 cm. The pressure cell used in the diffraction experiments was of cylindrical shape with 4 mm inner diameter and made of high purity aluminium. A setup consisting of a LakeShore 340 temperature controller with electrical band heaters and a Pt100 temperature sensor at the sample was used to control sample temperature in the range of 25-100°C with temperature stability of ± 20 mK. The covered range of momentum transfers was $0.2 - 0.7 \text{ \AA}^{-1}$, typical measurement times were about 2 hours per scattering curve. The data were corrected for empty cell and background scattering using the data reduction software ALPHA, provided by HZB.