

Complete Restriction of ³⁶Cl⁻ Diffusion by Celestite Precipitation in Densely Compacted Illite

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ABSTRACT: Industrial companies and public waste management agencies envision clay-rich materials as efficient barriers for large-scale confinement of nuclear waste and subsurface CO_2 . In clays, small pores hinder water flow and make diffusion the dominant solute-transport mechanism. Most clay mineral structures exhibit a negative charge that is balanced by an electrical double layer at the mineral water interface. This clay mineral property delays cation migration through adsorption processes, decreases the accessible porosity and diffusion fluxes for anions compared to those of water and cations, and gives rise to semipermeable membrane properties. Here we present experimental data that demonstrate for the first time that anions can be completely excluded from the smallest pores within a compacted illitic clay material, an observation that has important implications for the ability to accurately predict the containment



capacity of clay-based barriers. In a series of multitracer diffusion experiments, celestite $(SrSO_4)$ precipitation reduced the porosity of compacted illite to the point where the water tracer diffusion flux decreased by half, while the chloride diffusion flux decreased to zero. This result demonstrates that anions can be completely excluded from the smallest pores within a compacted clay material.

INTRODUCTION

How do the properties of water and ions confined in clay nanopores differ from those of bulk liquid water? Answers to this question have profound implications in performance predictions for waste storage facilities, CO2 geological sequestration sites, and other large-scale confinement applications for which clay materials are used or envisioned as effective engineered or natural barriers.¹⁻⁴ For these applications, the main clay minerals in targeted indurated clayey rocks are smectite, illite, and mixed layer illite/smectite.5-7 These minerals exhibit a small particle size and a large aspect ratio because of their layered structure (each phyllosilicate layer, TOT layer, is ~1 nm thick and up to 2 μ m wide; clay mineral particles consist of 1-20 stacked TOT layers) and are among the natural minerals with the largest specific surface areas (~750 and ~100 m² g⁻¹ for smectite and illite, respectively). Because of this large specific surface area, clayey media have small median pore sizes (on the order of $10^0 - 10^2$ nm), very low hydraulic conductivities ($\sim 10^6$ times lower than that of sandstone), and macroscopic properties that are strongly influenced by physical and chemical processes taking place at clay mineral surfaces.⁸ In particular, molecular diffusion is the main mass transfer mechanism in clayey media under most conditions. In addition, TOT layers bear a negative structural charge that is compensated by cation accumulation and anion depletion near their surfaces in a region known as the electrical double layer (EDL). This property gives clay materials their semipermeable membrane properties: ion transport in the clay material is hindered by electrostatic repulsion of anions from the EDL porosity, while water is freely admitted to the membrane.

To date, diffusion experiments performed on clay materials at a very high clay dry density (up to 1.9 kg dm⁻³, where the average pore width is <1 nm) have shown in every case the presence of anion (Cl⁻) diffusive flux.⁹ This observation suggests that the minimal pore size for total anion exclusion from the pores cannot be reached by mechanical compaction alone and that anion diffusion can never be completely blocked, regardless of the pore throat size (model 1 in Figure 1). An

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Figure 1. Conceptual models of the diffusion connectivity in compacted illite before and after celestite precipitation. In model 1, anion exclusion in pore throats is only partial and ${}^{36}Cl^{-}$ can diffuse in the porosity regardless of pore size. After celestite precipitates in the largest pores, the diffusion pathway is reduced but not completely disrupted because pore throats are not completely blocked for ${}^{36}Cl^{-}$ diffusion. In model 2, before celestite precipitation, anions are excluded completely from the smallest pore throats (red), thus reducing the number of ${}^{36}Cl^{-}$ diffusion pathways. After celestite precipitation in the larger pores, the pore network connectivity is completely disrupted for ${}^{36}Cl^{-}$ but still open to HTO diffusion. Model 1 predicts nonideal membrane properties after celestite precipitation, while model 2 predicts that ideal membrane properties can be realized.

alternative interpretation of this result is that Cl⁻ has no access to the smallest pores or pore throats, but that connectivity between large pores remains, whatever the material's compaction¹⁰ (model 2 in Figure 1). Consequently, it remains unclear on the basis of the diffusion experiments conducted to date whether anions, as opposed to water, can be excluded completely from the smallest pores of a clay material. Modeling studies at the molecular level may help solve this problem, but the two available molecular dynamics studies dedicated to this problem disagree in their conclusions.^{11,12} Therefore, we need an alternative experimental evaluation of the different hypotheses. Here we present results obtained by performing multitracer diffusion experiments in compacted illite, a clay material in which only interparticle pore throats ensure pore network connectivity. That connectivity was altered in the course of the experiment by inducing precipitation of celestite (SrSO₄) in the sample, and resulting changes in water and anion diffusive fluxes were monitored before and during celestite precipitation. These changes were interpreted in connection with the changes of the compacted illite sample microstructure, which was determined after the celestite precipitation using a focused ion beam coupled to scanning electron microscopy.

MATERIALS AND METHODS

The clay material used in this study was Illite du Puy, a natural clay extracted from the Puy-en-Vellay (Massif Central, France) Upper Eocene clay formation. The natural material contains up to 30% carbonates and quartz, with a clay fraction composed primarily of illite (80-100%).¹³ The clay material was first equilibrated with 1 M NaCl buffered to pH 3.5 by formic acid/ formate (for calcite removal) and, then, washed by adding a 1 M NaCl solution, centrifuging the clay dispersion, and removing the supernatant (three times). Excess salts were then removed by dialysis. The mineralogical composition was determined by X-ray diffraction (XRD) (Siemens D5000, equipped with a graphite monochromator and cobalt $K\alpha$ 1 radiation). XRD patterns were obtained on random crushed powders in the 4–84° 2 θ CoK α interval with a counting time of 10 s per step of 0.04. The XRD pattern agreed with the presence of 2/1 type clay minerals (80–90%), K-feldspar (5– 12%), and micas (1–5%).

The background electrolyte used to saturate the pores of the compacted material was a 0.5 M NaCl solution made using reagent-grade Merck NaCl. Celestite (SrSO₄) was selected as the mineral responsible for the porosity reduction because of its simple chemical formula, its relatively low solubility at 25 °C, and its fast precipitation kinetics.¹⁴ To precipitate celestite at the Sr²⁺ and SO₄²⁻ diffusion front, 0.5 M SrCl₂ and 0.5 M NaSO₄ solutions (made using reagent-grade Merck SrCl₂·6H₂O and Na₂SO₄) were used.

Conservative radiotracers were used to follow the evolution of the material's diffusion properties during porosity reduction. A cocktail of tritiated water, HTO (2000 Bq mL⁻¹), and ³⁶Cl⁻ (2000 Bq mL⁻¹) was added to the SrCl₂ solution. The HTO stock solution was a 1.11×10^{10} Bq L⁻¹ solution provided by



Figure 2. Results of the diffusion experiment. Schematic of the measurement setup (top) and normalized HTO (squares) and ${}^{36}Cl^{-}$ (circles) through-diffusion fluxes (left) and cumulative activity (right) prior to (reference sample) and during porosity reduction by celestite precipitation (samples 1 and 2) in an illite sample (bottom). The ${}^{36}Cl^{-}$ flux decreases to zero at approximately day 80, demonstrating selective disruption of pore network connectivity for ${}^{36}Cl^{-}$, while HTO is not disrupted. This indicates that ${}^{36}Cl^{-}$ is totally excluded from the pore throats.

Tritium Laboratory Karlsruhe (TLK). The ${}^{36}\text{Cl}^-$ stock solution was ordered from Eckert & Ziegler as a carrier-free isotope standard with an activity of 73 kBq mL⁻¹. HTO and ${}^{36}\text{Cl}^$ activities were measured by liquid scintillation counting (LSC) with a PerkinElmer Tricarb 3110 TR instrument for 1 h. The LSC samples were prepared by mixing 0.5 mL of the cation solution or 1 mL of the anion solution with 10 mL of UltimaGold XR cocktail.

Two samples were prepared by compacting 8.6 g of illite in a half-open PEEK diffusion cell to a dry bulk density of 1700 kg m⁻³ corresponding to a total porosity ϕ of ~0.40. The illite pellets were 24.7 mm in diameter and 10 mm in thickness. The compacted material was water-saturated and equilibrated with a 0.5 M NaCl solution for 4 days. Once the pore space was fully water-saturated, pore reduction experiments were started. The SrCl₂ and Na₂SO₄ solutions were pumped through the endpieces, closing the diffusion cell at a rate of 50 μ L min⁻¹ to homogenize the salt and tracer concentrations in the filters and in the reservoirs. There was no bulk volumetric flow (i.e., water flow) through the clay sample. Only molecular diffusion took place. The SrCl₂ solution reservoir volume was 500 mL, and it contained the tracer cocktail. Its large volume ensured a constant boundary condition. The Na₂SO₄ solution reservoir volume was 15 mL. This reservoir was renewed on a regular basis to keep the low-concentration boundary conditions as constant as possible (with virtually zero tracer concentration). The SrCl₂ solution reservoir was sampled every time the Na₂SO₄ solution reservoir was renewed. The diffusion properties of a reference sample were obtained using the

same procedure, but with a 0.5 M NaCl solution in both reservoirs.

HTO and $^{36}\mathrm{Cl^{-}}$ diffusive fluxes (in Bq m⁻² s⁻¹) were calculated on the basis of the accumulated activity in the NaSO₄ solution reservoir divided by the diffusion surface area and sampling time intervals. The fluxes were normalized to the tracer concentration in the SrCl₂ solution reservoir for a better direct comparison (normalized flux in Bq m⁻² s⁻¹/(Bq m⁻³) = m s⁻¹).

One of the experiments was stopped after diffusion for 80 days, to determine the microstructure of one sample after celestite precipitation. The sample was impregnated with a methyl methacrylate (MMA) resin to preserve its texture in a waterlike saturation state without losing the illite confinement and modifying the pore space geometry during the manipulation of the samples (see experimental methods of ref 15). The sample was then characterized by dual beam focused ion beam—scanning electron microscopy—nanotomography (FIB-SEM-nt).

RESULTS AND DISCUSSION

HTO and ${}^{36}\text{Cl}^-$ diffusion breakthrough curves (Figure 2) in the absence of celestite precipitation show lower diffusion fluxes for ${}^{36}\text{Cl}^-$ than for HTO after renormalization to their respective self-diffusion coefficient in water. This behavior has been reported multiple times for diffusion in charged clay materials and is related to the semipermeable membrane properties of those materials and partial anion exclusion.^{9,16} HTO and Cl⁻ diffusivities in the reference illite sample were estimated by



Figure 3. SEM microstructure characterization. (A) Backscattered electron (BSE) SEM image of celestite grains (white) precipitated in the pore space of compacted illite (dark gray). The white box represents the location of the FIB-nt acquisition. (B) FIB-nt two-dimensional energy and angle selective (EsB) BSE cross section image (milled surface) with a resolution pixel size of 5 nm, showing the precipitation of the celestite (white) in the illite interaggregate porosity. The inset is a BSE SEM image showing the volume milled by the FIB.

numerical modeling taking into account the effect of the filters on the diffusion gradients: $De(HTO) \sim 1.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$; $De(^{36}Cl^{-}) \sim 0.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. These values are similar to values reported for illite under similar compaction and ionic strength conditions.⁹

Celestite precipitation in the pore space of the compacted illite had a marked effect on the HTO diffusion flux, decreasing it by a factor of 2. It had an even more marked effect on the $^{36}Cl^-$ diffusion flux, decreasing it by a factor of 4. By day 70, a further drop in the HTO diffusivity was evident, while the $^{36}Cl^-$ flux decreased to zero.

Because ³⁶Cl⁻ diffusion was more strongly by precipitation affected than HTO diffusion, we can conclude that the celestite must have precipitated in the pore fraction where most of the ³⁶Cl⁻ diffusion occurs. FIB-SEM-nt observations show unambiguously that celestite precipitation occurs preferentially in the largest pores (Figure 3). These largest pores are where most or all of the anion diffusion is expected to take place, because anions are repelled from the negatively charged surfaces of illite. Consequently, by blocking a large part of the ³⁶Cl⁻ diffusion pathway in this pore fraction, celestite precipitation first decreases the ³⁶Cl⁻ diffusion flux more than it does the HTO diffusion flux and then completely blocks the ³⁶Cl⁻ diffusion flux once clogging of the larger pores due to precipitation of celestite is complete. HTO continued to diffuse through the illite over the course of the entire experiment. Thus, we conclude that the portion of the porosity that was not completely clogged by celestite precipitation (open to HTO diffusion, closed to ³⁶Cl⁻ diffusion) has ideal semipermeable membrane properties. Note that it would suffice that a thin semipermeable barrier forms in the clay pellet for the system to exhibit ideal membrane properties. From the diffusion results alone, it is not possible to know if the ideal semipermeable properties were due to the modification of illite surfaces by celestite precipitation (the surface charge of celestite is also negative under our experimental conditions¹⁷) or to the restriction of the pore connectivity in densely packed illite particle aggregates after celestite precipitation, with these aggregates exhibiting ideal semipermeable properties. Three hypotheses can be formed. (1) Only pores with illite surfaces modified by celestite precipitation were connected. (2) Only pores with illite surfaces not modified by celestite precipitation were connected. (3) Both types of pores ensured the connectivity of the pore network. Celestite did not precipitate in large aggregates of illite particles (Figure 3), and these aggregates, and thus their pores, are interconnected as

evidenced by connectivity analyses in reconstructed threedimensional volumes. From this observation, we can conclude that the pores in these aggregates, whose illite surfaces were not modified by celestite precipitation, were responsible, at least partially, for the observed complete disruption of the ³⁶Cl⁻ diffusion pathway. Consequently, model 2 in Figure 1 is the correct model. Based on the experimental results alone, we cannot quantify unambiguously the fraction of the initial pore space that was available for HTO diffusion and unavailable for anions, and we cannot estimate the threshold pore size that leads to total anion exclusion. Still, our results can be put in perspective with molecular dynamics simulation results,¹² according to which a pore width corresponding to two layers of water (~6 Å) between two negatively charged clay mineral surfaces should not be accessible to anions. This study provides the first experimental evidence of such clay (infra)nanopores having this ideal membrane property.

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Author Contributions

T.S., F.C., A.C., C.T., and T.K. conceived and designed the diffusion experiments. A.C. and T.K. performed the diffusion experiments. S.G. and I.E. performed the FIB-SEM characterization. C.T., F.C., T.S, C.I.S., and I.C.B. analyzed the data. A.C., T.S., S.G., and T.K. contributed materials and analysis tools. C.T., A.C., I.C.B., and C.I.S. cowrote the paper.

Notes

The authors declare no competing financial interest.

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