WATER MOBILITY AND STRUCTURE IN NATURAL CLAY SYSTEMS

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From current and previous work by the present authors, experimental results showing the connectivity and the water mobility in natural clay systems are emphasized. Using various low-field Nuclear Magnetic Resonance techniques, a large range of time- and length scales, from nm to cm, can be explored. The amount of water in the interlayer space of smectites at different relative humidities can be detected and quantified. Simple criteria such as unimodal or multimodal relaxation time distributions give a simple and quick indication of connectivity between different porosity compartments. A new technique has allowed the orientation of water in the interlayer space of smectites to be determined; from 39 to 66% of the water molecules are noted as being 'oriented.'

1. Introduction

For various applications such as geologic storage of CO₂, nuclear-waste management, and shale-gas production, there is increasing interest in porous media in which clays represent a major fraction of the total solid content. Understanding the detail of transport properties is a challenge because the pore sizes extend down to the nanometer range. In spite of the very small pore sizes, the mobility of water can be significant and, at the same time, interactions can occur such as restriction of the rotational mobility of water molecules. Nuclear Magnetic Resonance (NMR) operated at low field (0.5 T) is used to assess the magnetization carried by the water molecules as they diffuse in the pore-network structure. The time- and length scales that can be explored using the different NMR techniques described here are unique and extend over a large range (Figure 1). From relaxation experiments, diffusive exchanges between different porosity compartments can be probed, starting at the millisecond time scale and from nm to μm length scales. From self-diffusion pulsed field gradient NMR techniques, time-scales are probed from milliseconds to seconds and the corresponding diffusion lengths (1–100 μm for water). Finally, using deuterium tracer techniques, macroscopic diffusion coefficients at cm scales can be obtained. For comparison, water mobility can also be studied in detail using neutron scattering techniques (e.g. QUENS) but the time frame is much shorter, of the order of 1 ns.
1.1. Probing mobility with NMR techniques

In low-field NMR experiments, the magnetization carried by water molecules is recorded. Essentially, the amount of magnetization gives the total number of hydrogen nuclei in the system after calibration, and the magnetization decay (often a distribution of exponential times) is driven by the nuclear interactions between the hydrogen nuclei and the solid surface when spin-bearing molecules are diffusing in the pore space. To interpret these decay times, a well-known model (Brownstein and Tarr, 1979) was established in biological cells: when water molecules diffuse inside a cell, they interact with the surface and the measured exponential decay time can be interpreted as a measure of the surface-to-volume ratio of the compartment in which molecules are confined. In porous media, this model can be reformulated very simply, as follows: the relaxation process is the result of interactions between the nuclear spins carried by molecules exploring the pore space by diffusion and the electronic spins at the solid surface. These interactions are only effective close to the surface in a layer thickness, $\varepsilon_S$, of the order of one or two times the molecular size (i.e., $<0.5$ nm for water) and are characterized by a decay time constant, $T_S$. Similarly, far from the surface, the intra- and intermolecular interactions between molecules are characterized by a much longer decay time constant, $T_B$. In a closed pore, let us define two regions: a bulk volume with a volume fraction, $f_b$, and a surface layer with a volume fraction, $f_s$ ($f_b + f_s = 1$). Due to molecular diffusion, exchange occurs between the surface and bulk volumes with a typical exchange time, $\tau_{ex}$. In the so-called fast-exchange regime ($\tau_{ex} \ll T$) or fast-diffusion regime, the measured relaxation rate, $1/T$, is an average of the bulk and surface relaxation rates weighted by the volume fraction:

$$\frac{1}{T} = \frac{f_s}{T_{2S}} + \frac{f_b}{T_{2B}} \approx \frac{S_p}{V_p} \frac{\varepsilon_S}{T_{2S}} + \frac{1}{T_{2B}}$$

Figure 1. Typical time- and length scales explored using the NMR techniques described here.
The transverse relaxation time, $T_2$, was used here, the most commonly used for this type of measurement. The equation above yields the well-known dependence on the surface-to-volume ratio ($S_p/V_p$) of a pore. The strength of interactions with the solid is usually expressed as the surface relaxivity, $\rho_2$, or relaxation velocity at the pore surface defined as $\rho_2 = \varepsilon_S/T_{2S}$. Using typical values of surface relaxivities between 1 and 10 $\mu$m/s, the relaxation time of water located in a sheet-like pore of thickness 1 nm, for example, $(V/S = 1 \text{ nm})$ will be in the range of 0.1 to 1 ms. Such relatively short values are easily accessible to most commercial NMR spectrometers and to some in situ logging instruments. When the magnetization decay can be captured, the total porosity can be measured reasonably accurately if appropriate laboratory protocols are used. In natural porous rocks (including shales), surface relaxivity is dominated by paramagnetic impurities (essentially Fe and Mg) but no direct dependence on the amount of impurities has been established.

In a pore-network system in which pores are connected through throats (or any restriction), molecules can diffuse from one pore to another during the magnetization decay time. Hence, the $V/S$ dependence of the relaxation time depends on the diffusion length when the latter is larger than the pore size, and the ratio $V/S$ will be averaged over a certain unknown distance (pore-coupling effect). In the extreme case of complete coupling, a single relaxation time can be observed even though a distribution of $V/S$ exists. Specific NMR techniques (Fleury and Soualem, 2009) exist to capture the exchange between pores when the diffusion length is of the same order of magnitude as the distance between the different pore compartments. In nano-porous systems, the mechanism above can be used to characterize the connectivity between two compartments having different $V/S$ ratios: if two relaxation times are measured, then the two compartments are poorly connected (by diffusion) at the timescale given by the lifetime of the magnetization; on the other hand, if a single relaxation time is observed, then these two compartments are well connected. An illustration of the mechanism above can be found in clay suspensions (Guichet et al., 2008): in general, these clay suspensions of various concentrations were characterized by a single relaxation time although many pore sizes $(V/S)$ exist. Multimodal $T_2$ distributions were only observed in the case of clay aggregation (or coagulation, Figure 2) that was induced experimentally either by increasing the salt concentration or by using divalent ions, allowing the determination of a textural diagram for the system studied. With a diffusion length much greater than the average distance between clay particles, this means that two weakly connected compartments exist when clay flocculation occurs.

To estimate a diffusion length, a macroscopic measurement of the diffusion coefficient is necessary and several techniques can be used. For nuclear-waste applications in compact systems, tritium through-diffusion techniques have been employed for the most part. NMR self-diffusion techniques can also be used in some cases, e.g. in clay suspensions and gels (Guichet et al., 2008 – dioctahedral smectites) the effective diffusion coefficient was reduced according to $D_e = D_0 \exp (-0.031 w)$ where $w$ is the clay weight fraction and $D_0$ is the molecular self-diffusion coefficient of water (m$^2$/s). In compact natural systems in which the lifetime of the magnetization is short (1 ms), self-diffusion NMR techniques are technically not feasible.
(except with very specific equipment) but, instead, a fast NMR deuterium tracer technique is used to measure macroscopic diffusion coefficients (Berne et al., 2009). From various experiments on caprock and shale samples using this technique, diffusion was observed to be driven at first order by porosity, $\Phi$, following a power-law relationship $D_c = D_0 \Phi^{-(m-1)}$ originating from resistivity models (Archie relationship) where $m$ is the cementation factor and varies roughly between

**Figure 2.** Examples of multimodal relaxation time in a floculated smectite suspension, indicating the existence of two weakly connected compartments. $T_2$ values of $\sim 1 \text{ ms}$ are attributed to water molecules relaxing within smectite aggregates, whereas $T_2$ values of $\sim 10 \text{ ms}$ are attributed to water molecules relaxing between smectite aggregates. The diffusion length is of the order of $10 \mu\text{m}$.

**Figure 3.** Pore-entry size distribution from mercury injection experiments for a reservoir shale sample. The limit of resolution is reached.
1.9 and 2.5. The primary factor governing diffusion is porosity while the variation of the empirical exponent, \( m \), expresses the influence of the texture. For example, for a shale of porosity 7\%, the diffusion coefficient will be reduced by a factor of 11 to 54 relative to \( D_0 \). For a caprock of porosity 15\%, the reduction factor is 5 to 17. Hence, the diffusion length \((6D_0t)^{1/2}\) is of the order of 1 \( \mu \)m for a typical diffusion time of 1 ms. An example is given below for a shale sample of porosity 7.1\% and permeability \( 2 \times 10^{-21} \text{ m}^2 \). The high-pressure mercury injection (Figure 3) indicates pore-entry sizes down to 4 nm, representing only half of the porosity measured by NMR. The deuterium diffusion data (Figure 4) represent the hydrogen concentration vs. time as deuterium is diffusing in and water is diffusing out of the sample which is a cylinder of diameter = 15 mm and length = 15 mm. After data fitting, a diffusion coefficient of \( 6.2 \times 10^{-11} \text{ m}^2/\text{s} \) was found yielding a diffusion length of 1.4 \( \mu \)m at 5 ms (the dominant relaxation time, not shown).

2. Water in the interlayer space of smectites

To study the behavior of water in clays in more detail, a study of the water content and the dynamics of water molecules was performed in the interlayer space of smectite powders equilibrated at different relative humidities varying from 11 to 97\% (Fleury et al., 2013). Under such conditions, water is present mainly in the interlayer space. From a porous media perspective, the interlayer space is a unique, sheet-like pore model of variable thickness ranging from \( \sim 0.3 \) to 1 nm in which the dynamics of water can be studied. From a clay-science perspective, the precise water quantity for different counter-ions could be measured directly and correlated with the spacing measured by Small Angle X-ray Scattering (SAXS, Figure 5). In particular, whatever the ions (Na, Ca, Mg or K), the interlayer water content is linearly related to the \( d_{001} \) basal spacing measured by SAXS. However, the relationship with relative humidity is more complex and depends on the type of ions in a non-straightforward way (Figure 5).

Focusing now on the particular case of high relative humidity (97\%), a single relaxation time decay is observed (Figure 6), although two different compartments are present in this case: the interlayer of width 1 nm (three water layers), and an external
volume outside the interlayer representing 20% of the total water content. This fraction was measured by freezing of the system down to –60°C (Fleury et al., 2013). A quick exchange between internal and external water must occur during the lifetime of the magnetization. Here, a two-dimensional (2D) map of the longitudinal and transverse relaxation times is presented instead of the more common one-dimensional distribution. Within the fast-exchange model expressed by equation 1, no additional information is given by the longitudinal relaxation time, $T_1$, and the $T_1/T_2$ ratio is usually fixed and has a value of $\sim 2$. The $T_1–T_2$ maps are useful in distinguishing protons with low

**Figure 5.** Measurement of the water content in the interlayer space of smectites for different counter-ions and relative humidities (left), and as a function of the interlayer distance, $d_{001}$ (right). For the latter, outliers not following the main regression are due to experimental difficulties during SAXS measurements. The mass of water $M_w$ (mg/g) is given by $36.91 \times d_{001} – 339.17$.

**Figure 6.** $T_1–T_2$ maps for a smectite powder equilibrated at 97% relative humidity with water (left) and with ethylene glycol (right). Lines represent three values of $T_1/T_2$ ratio (1, 1.5, and 8). This is the same smectite as in Figure 5 but with both Na and Ca in the interlayer space (natural state).
rotational mobility and characterized by high $T_1/T_2$ ratios. Such is the case for pseudo-solid protons belonging to hydroxyl groups clearly detected below 0.1 ms ($T_1/T_2 \approx 30$, Figure 6). When equilibrating the same powder with ethylene glycol (EG), the $T_2$ distribution clearly becomes bimodal: EG molecules inside the interlayer ($T_2 < 0.1$ ms) are restricted in their translational and rotational motions and behave as pseudo-solid protons ($T_1/T_2 \approx 8$, $T_2 < 0.1$ ms). The $V/S$ model (equation 1) does not apply for $T_2 < 0.1$ ms.

The smectite samples prepared with various counter-ions at various relative humidities described above also offered an opportunity to evaluate the water interactions with ions. From a NMR perspective, this can be quantified by the orientation of water molecules when confined in the interlayer space. For bulk water, molecular motions are such that the proton relaxation time is dominated by intermolecular interactions. Similarly, close enough to a solid surface containing paramagnetic impurities, relaxation is dominated by hetero-nuclear interactions (proton nuclear spin vs. electronic spin of free electrons). When water molecules are oriented, the relaxation mechanism is dominated by intra-molecular interactions when the molecular tumbling is reduced. This change of interaction mechanism is indicated by a Pake doublet in NMR spectra obtained at high field strength (Sanz et al., 2006), which can be used directly to deduce a water orientation. From detailed spectral analysis in synthetic clays, the orientation of water molecules is believed to persist up to microseconds (Trausch et al., 2008), a huge difference compared to free water re-orientating at the picosecond time scale. However, such analysis can only be performed if all layers are oriented with respect to the magnetic field and in the case of ‘clean’ systems containing a small amount of or no paramagnetic impurities. Without the need for clay-layer orientation, a new technique (Fleury and Canet, 2014) allows the observation and quantification of oriented water within the interlayer as a function of relative humidity and type of ions. Despite the random orientation of the clay layers within the powder, the resulting signal is different from water interacting with the solid and one can deduce the relative amount of these two-proton populations. The results are that the relative amount of oriented water ranges from 0.5 to 2.5 water molecules per ion for RH values between 11 and 75% and a ranking with the ionic potential could be established (Na > Mg > Ca > K). Relative to the total amount of water in the interlayer, ~50% of the molecules are oriented (39–66% depending on the ion).

3. Conclusion

The primary factor governing diffusion in compact systems is porosity, while the texture or the pore network details, as opposed to permeability, play a secondary role. Tracer measurements on a shale indicate macroscopic diffusion coefficients of the order $5 \times 10^{-11}$ m$^2$/s even though most pores are <10 nm. For small pores in the 1–100 nm range, unimodal or multimodal NMR relaxation-time distribution can provide simple criteria to characterize connectivity between different compartments in the pore-network system at a timescale corresponding to the lifetime of the magnetization and
for length scales of the order of 1 μm or larger. In the interlayer space of smectites, water is surprisingly highly mobile even when strongly confined and despite a strong affinity for the counter-ions. The orientation of water molecules can be observed using specific NMR sequences and between 39 and 66% of the water in the interlayer was found to be oriented. The typical timescale of this interaction is 1 μs.

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References