EVALUATION OF PORE STRUCTURE IN COMPACTED SATURATED BENTONITE USING NMR RELAXOMETRY

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INTRODUCTION

The permeability and diffusivity of a compacted bentonite, which is a candidate buffer material in various Japanese geological disposal systems, have been examined to assess its barrier performance and provide input for tailoring engineering barriers to specific geological environments. Despite considerable accumulation of experimental data in the past, the relationship of pore structures (both the interlayer pores of the clay and the intralayer pores resulting from particle aggregation) to aqueous pathways in compacted saturated bentonite is not yet fully understood. In order to clarify some of the factors involved, we have applied NMR relaxometry (relaxation distribution analysis of 1H NMR) to saturated compacted bentonite.

NMR RELAXOMETRY AND EXPERIMENTAL PROCEDURE

The proton longitudinal relaxation time, T₁, measured by NMR of fluids in porous media, is strongly influenced by fluid-solid interaction. One interesting application of such relaxation measurements is the determination of the surface-volume ratio of pores,

\[ \frac{1}{T_1} = \rho_s \left( \frac{S}{V} \right)_{\text{pore}} \]  

where \( \rho_s \) is the surface relativity, \( S \) and \( V \) are the surface area and volume of the pore. In saturated clays, \( (S/V)_{\text{pore}} \) corresponds to the surface-volume ratio of pores filled with water. A possible source of surface relaxation is the presence of magnetic impurities along the pore wall, in this particular application paramagnetic ions like Mn²⁺ and Fe³⁺ in clay.

Measurements were performed using an NMR spectrometer (Maran Ultra, Resonance Instrument, UK) at 23.4 MHz. A saturation recovery sequence with 256 recovery values from 0.1 to 52 ms was used. The decay of nuclear magnetization obtained from these measurements was analyzed numerically using an inverse Laplace transformation (Provencher, 1982) to derive the T₁ distribution.

MATERIAL

The bentonite material examined is Kunigel VI, which is a Na-bentonite provided by Kunimine Industries Co., Ltd. Kunigel VI contains 47 wt% montmorillonite, 37 wt% chalcedony, 4 wt% plagioclase, 3 wt% analcime, 2 wt% calcite 2 wt% dolomite, 0.6 wt% quartz, and 0.6 wt% pyrite (total 96.2 wt%). Due to its high surface area and content of magnetic impurities, the relaxation time measured is expected to be due to the montmorillonite component. Do you think it is worth adding this sentence? Compacted bentonite samples with dry densities, \( \rho_s \), of 1.33 and 1.80 Mg/m³ were prepared. After compaction, saturation of the samples with distilled water was carried out at fixed volume over a period of 2 months. Montmorillonite soks and gels were also prepared by adding distilled water to Kunipia F, which is a purified bentonite containing over 98 wt% montmorillonite, to estimate the surface relativity of the clay component of the Kunigel.
RESULTS
First, we estimated $\rho_1$ of montmorillonite through $T_1$ measurements of dispersed montmorillonite sols and gels. A single $T_1$ value was observed for these uncompactedNot all have high water content – e.g. 6.7% sample illustrated below systems. The $(S/V)_{\text{pore}}$ in these systems is determined by the specific surface area, $S_0$, of montmorillonite and the solid/liquid ratio by weight [(clay)/(water)], $C$; that is, $(S/V)_{\text{pore}} = S_0 C \rho_w$, where $\rho_w$ is density of bulk water. $S_0$ was measured as 700 m$^2$/g by the EGME (ethylene-glycol-monoethyl-ether) method (Kozaki et al., 1999). A simple linear regression analysis of $C$ against $1/T_1$ for 13 samples with $C < 0.5$ resulted in $\rho_1 = 0.212$ nm/ns (standard fitting error 0.47%)I think it is valuable to add this information.

Results of relaxation distribution analysis for saturated $\rho_1 = 1.33$ and 1.80 Mg/m$^3$ samples and Kunipia F with water content 6.7 wt% are shown in Fig. 1. The relaxation distribution of the Kunigel samples indicate two peaks within the relaxation time ranges of 0.1-1.0 ms (range $A$) and 1.0-10 ms (range $B$), which are clearly dependent on $\rho_1$. The peak position in range $A$ is 0.546 ms for the Kunipia F powder sample, interpreted as surface monolayer water. The peak positions in range $B$ are 1.7 and 3.7 ms for $\rho_1 = 1.33$ and 1.80 Mg/m$^3$, respectively. For the assignment of these peaks, results of X-ray diffraction (XRD) for compacted Na-montmorillonite saturated with water are used (Kozaki et al., 1998). A 3-water molecule interlayer hydrate of Na-montmorillonite with a basal spacing of 1.8 nm was observed for $\rho_1 = 1.3$ Mg/m$^3$, and a 2-molecule hydrate with a basal spacing of 1.5 nm for $\rho_1 = 1.8$ Mg/m$^3$. The basal spacing is easily convertible into interlayer space dimensions by subtracting the thickness of montmorillonite layers (about 1 nm), and thus these results can be directly related to the relaxation times determined in this study. If an extended planar pore water distribution between montmorillonite layers is assumed, $(S/V)_{\text{pore}}$, I think it is better to use $S/V$ here as this has been used in all discussion up to this point calculated from the relaxation time is equal to $[1/(hydrate layer thickness)]$. On this basis, the relaxation times calculated by equation (1) using XRD dimensions of the 2- and 3-layer hydrate are 2.6 and 4.1 ms, respectively. These results are slightly larger than the maximum peak positions in range $B$ in this study. This could be due to effects of interlayer cations or surface diffusivity of water, but we can clearly assign relaxation time in range $B$ to interlayer water in compacted bentonite.

We are also trying to extend the NMR relaxometry method to compacted bentonite with changes of key parameters influencing diffusivity and permeability - such as sand content and composition of water. Some perspectives on the associated relaxometry approach will be given.

References: