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Hydration of bentonite in natural waters: Application of "confined volume" wet-cell X-ray diffractometry

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Abstract

The hydration behavior of compacted bentonites (Na- and Ca-montmorillonite varieties) in natural ground and sea water is studied using in situ wet-cell X-ray diffraction monitoring techniques. This approach allows us to determine the mechanism and rate of solution uptake in a confined volume, flow-through reactor and serves as an experimental analogue for predicting the performance of repository clay sealants. The pressed bentonite powders (densities of 0.94–1.14 g/cm^3) show continuous and strongly partitioned water uptake into montmorillonite interlayers, onto clay particle surfaces and within open pore spaces. During the hydration of compacted Na-bentonite in both ground and sea water, roughly equal quantities of both interlayer and non-interlayer water enter the material. In contrast, the Ca-bentonite was dominated by the intake of more loosely bound, surface and pore water, which amounted to roughly three times more than that incorporated into interlayer sites. Our experiments demonstrate how a confined reaction volume and the strength of the ionic solution both inhibit the interlayer expansion process. Based on the weakly compacted Na-bentonite analogue, a 1 m thick clay sealant is predicted to saturate within 7 years when infiltrated by typical continental ground water, and within 3 years in the case of a sea water breach. As significant volumes of solution are incorporated as loosely bound, non-interlayer water, quantification of the mechanism and rate of water storage is a necessary requirement for improved modeling of elemental transport in a hydrating bentonite medium.

Keywords: Bentonite; Backfill; Montmorillonite; Hydration; Natural water; Waste repository; Confined volume; Wet-cell XRD

1. Introduction

One of the most important technical properties of bentonite (montmorillonite-rich) clay is its ability to swell and self-seal when hydrated by the inflow of natural waters (Bradly et al., 1937; Norrish, 1954). As a result, this fine-grained material is considered as suitable backfill in the disposal of waste because it significantly restricts movement of aqueous fluids and thus helps retain toxic elements over significant periods of time (Karnland et al., 2000; Hermanns-Stengele and Plötze, 2000; Pusch, 2001). The hydration process not only influences permeability and fluid migration, but also affects chemical transport, pore pressure, material strength and diagenetic mineral reactions both within the backfill and the adjacent wall rock of underground repositories (Montes et al., 2003, 2004; Melkior et al., 2004; Warr et al., 2004).

During swelling, constituent montmorillonite clays hydrate and expand by sorption of water molecules around exchangeable cations that are attracted to the weakly charged interlayers of the sheeted tetrahedral–octahedral–tetrahedral structure (Farmer and Russell, 1971). The water layers order themselves in a structured arrangement, mirroring the charge sites of the tetrahedral sheets, and build up a number of discrete levels each between 2.3 and 2.8 Å in thickness (Karaborni et al., 1996). During this type of intracrystalline swelling up to 4 discrete water layers can form as a function of water activity (varying humidity), layer charge characteristics, type of interlayer cation and the ionic concentration of infiltrating solution (Jasmund

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and Lagaly, 1993; Chorom and Rengasamy, 1995). The amount of water incorporated into interlayers has been successfully quantified on the basis of water vapor adsorption–desorption isotherms (Bérend et al., 1995; Cases et al., 1997). In well dispersed Na-bentonite solutions of low ionic concentration the proportion of intercrystalline pore space dramatically increases as osmotic pressure transforms interlayers into free surfaces separating tactoid particles (Jasmund and Lagaly, 1993; Lagaly et al., 1997; Cases et al., 1997). For bentonite powders, the quantity of additional water uptake on particle surfaces has been calculated on the basis of the Brunauer–Emmet–Teller (BET) method (Cuadros, 1997; Bérend et al., 1995) and the size distribution of pore spaces assessed by Hg-injection techniques (Olson, 1985).

A common approach to studying the distinct hydration states of the montmorillonite swelling clays is to vary the conditions of relative humidity and to monitor interlayer expansion by X-ray diffraction (XRD) techniques (Mooney et al., 1952; Collins et al., 1992; Kühnel and van der Gaast, 1993; Chipera et al., 1997; Ferrage et al., 2005) or via bulk volume measurements (Likos, 2004). A number of investigations also addressed the nature of swelling in static aqueous and electrolyte solutions using experimental systems where particles expanded freely (Norrish, 1954; Norrish and Quirk, 1954; Laird et al., 1995; Shang et al., 1995; Wilson et al., 2004). More recently, the total bulk expansion of montmorillonite particles in solutions of varying salt concentration was quantified microscopically by in situ laser scanning microscopy (Suzuki et al., 2005), and the contributions of interlayer expansion and osmotically-driven swelling directly observed.

Despite the wealth of knowledge on the hydration behavior of bentonite clay, less work has been conducted to determine the mechanism and rate of hydration during the infiltration of natural waters into pressed bentonite powders within a confined reaction volume. In this study we address this topic by using a new type of flow-through reactor (wet-cells) mounted on an X-ray diffractometer to investigate the partitioning of solution between different water storage sites as the material becomes saturated. These experiments were designed as potential analogues for the infiltration of continental ground water or sea water into the backfill section of a waste disposal site, and provide time-dependent results on the mechanism and sites of hydration in relation to the total influx of water into compacted bentonite.

2. Materials and methods

The characteristics of two fine-grained industrial bentonite powders "IBECO-SEAL-80" (Na-activated) and "TIXOTON-TE" (Ca-activated) used for the flow-through wet-cell hydration experiments are summarized in Table 1. Both materials are considered to be representative of industrially available bentonites that may be employed in repository sites (Hofmann et al., 2004), with relatively high cation exchange capacities (71–82 meq/100 g) and low layer charge properties (0.29–0.33 eq/$(Si, Al)_4O_{10}$). The bentonites contain more than 80% montmorillonite and minor amounts of mica, calcite, feldspar and quartz. Prior to experimentation the samples were dried at 60 °C for 24 h and then re-equilibrated with laboratory conditions at 25 °C and 33–35% relative humidity. Although the bentonites are described as Na- or Ca-activated, their composition and hydration behavior indicates that minor amounts of other interlayer cations (Na, Ca, or Mg) may still be present (Hofmann, 2003; Pusch, 2001).

Two natural solutions were selected as representing typical continental ground and sea water. The ground water was collected from a source area of dominantly crystalline rocks in the Neckar valley, near Heidelberg (Germany), and the sea water was sampled from the Atlantic coastline of Cornwall (SW England). Both solutions were filtrated (<0.45 μm) and stored in a cool place until experiments started. The cation compositions of these waters are presented in Table 2.

The wet-cell device is a small flow-through reaction cell made of a Teflon compound that can be mounted onto the X-ray diffractometer. It allows in situ measurements of crystalline reactions during the infiltration of a solution into a fine-grained powder (Warr and Hofmann, 2003). The sample chamber of the cell is disc shaped (Fig. 1), with a diameter of 24 mm and a depth of 8 mm (volume of 3.9 cm^3). The powdered bentonite samples were carefully packed into the wet-cell holder using a metal brass rod, producing a rough texture parallel to the upper surface of the sample holder. The amount of clay powder in the cells varied between 4.45 to 4.48 g for IBECO and 3.67 to 3.68 g for TIXOTON experiments. Assuming an average mineral density of 2.35 g/cm^3, the initial dry packing densities of the powders ranged between 0.94 and 1.15 g/cm^3 (Table 3). These values are lower than the highly compacted commercial bentonite (>1.2 g/cm^3) used in other studies (e.g. Bradbury and Baeyens, 2003; Muurinen and

Table 1
Mineral assemblage and properties of the bentonites used in this study

	Montmorillonite (%)	CEC (meq/100 g)	Layer charge (eq/$(Si, Al)_4O_{10}$)	Mica (%)	Calcite (%)	Feldspar (%)	Quartz (%)
Na-bentonite (Ibeco-seal-80)	>80	82	0.33	<3	8–12	<3	–
Ca-bentonite (Tixoton-TE)	>80	71	0.29	1–2	1	5–6	8–9

CEC = cation exchange capacity, meq = milli-equivalent per 100 g, eq = equivalent per formula unit (data from Hofmann et al., 2004).