Applied Clay Science 156 (2018) 134–143

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

The influence of small pores on the anion transport properties of natural argillaceous rocks – A pore size distribution investigation of Opalinus Clay and Helvetic Marl

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ARTICLE INFO

Keywords:
NMR
NMR cryoporometry
Gas adsorption
Mercury intrusion porosimetry

ABSTRACT

The pore size distribution of two natural argillaceous rock samples, Opalinus Clay (OPA) and Helvetic Marl (HM) was investigated with five different methods: NMR, NMR cryoporometry, mercury intrusion porosimetry and CO_2 adsorption, as well as N_2 adsorption. Due to different physical principles of these methods different ranges of pore width could be detected, from micropores (< 2 nm) to mesopores (2–50 nm) and macropores (> 50 nm). The aim was to shed light on the role of small pores on the transport properties of natural argillaceous rocks, in particular to explain the differences of anion diffusion in the two argillaceous rock samples. Knowing that Helvetic Marl exhibits a stronger anion exclusion than Opalinus Clay it was hypothesized that HM (with its smaller phyllosilicate and smectite content compared to OPA) has more interlayer equivalent (ILE) pores than OPA. ILE pores are defined as pores so narrow (< 0.5 nm) that diffuse double layers, formed at negatively charged surfaces, are overlapping. Accordingly, ILE pores behave similarly as interlayer pores and may block the anion diffusion. This study could not confirm the hypothesis that HM has more ILE pores. Similar pores size distributions were determined for both materials, even with a tendency of a larger fraction of small pores in OPA as compared to HM. However, all methods have limitations in the range of very small (nm) pores.

1. Introduction

The investigation of the microstructure of argillaceous rocks and especially of the properties and connectivity of the pores is an important research activity in the field of nuclear waste management. The pore volume as well as the size and connectivity of the pores are key factors controlling the transport of dissolved radionuclides through the host rocks. Argillaceous rocks are considered as potential host rocks for deep geological repositories of radioactive waste in several countries (Andra, 2001; Ondraf/Niras, 2001; Nagra, 2002; NWMO, 2015), due to their self-sealing ability, ion transport retardation property and the low hydraulic conductivity (Sellin and Leupin, 2013). The special structure of clays, their charged surfaces and the small pores (< 10 nm) impact the anion, cation and neutral species passage through the argillaceous rocks. Particularly, the anion diffusion in an argillaceous rock is highly sensitive to the pore structure (Sposito, 2004; Bourg et al., 2008; Tournassat et al., 2009). It is expected (Wigger and Van Loon, 2017) that the anion diffusion is strongly limited by the amount of interlayer equivalent pores (ILE). Interlayer equivalent pores are formed by the very high degree of compaction of argillaceous rocks. The pores are so narrow that diffuse double layers, formed at negatively charged surfaces, are overlapping, such that the pores behave similarly as interlayer pores and become inaccessible for anions (Wigger and Van Loon, 2017). Thus, neutral and positively charged species can diffuse through the whole pore space, while the anions are strongly restricted or excluded by overlapping diffuse double layers located in narrow interlayer equivalent pores. The smaller the pores are, the larger is the chance that anions are excluded. Considering the Gouy-Chapman or a Stern model, the diffuse layer is part of an electric double (EDL) or triple layer. In the diffuse layer, the concentration of anions is lower than that of cations and the Stern layer is devoid of anions (Chagneau et al., 2015; Tournassat et al., 2016). The extent of the diffuse layer varies with ionic strength and is related to the Debye length, κ^{-1} (Appelo and Postma, 2005). Based on the assumption that the pore

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https://doi.org/10.1016/j.clay.2018.01.032
Received 4 June 2017; Received in revised form 12 January 2018; Accepted 24 January 2018

water is composed mainly of a 1:1 electrolyte and using the expression:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon * R * T}{2 * (N_a * q_e)^2 * I}} \tag{1}$$

with $\varepsilon = 6.95 \times 10^{-10}$ F/m, $R = 8.314$ J/K/mol, $T = 298$ K, $N_a = 6.022 \times 10^{23}$/mol, $q_e = 1.6 \times 10^{-19}$ C, and I expressed in mol/dm^3, the extension of the diffuse layer approximated as κ^{-1} is ~3 nm at an ionic strength of 0.01 M. Anions are partly present in the diffuse layer, and its extension cannot be uniquely defined, in principle. Nevertheless, pores with a diameter of < 6 nm are considered to be interlayer equivalent (ILE) pores at an ionic strength of 0.01 M. Based on this knowledge, the pore size distribution gives indication of the anion exclusion effects. For this reason, a solid understanding of the microstructure in natural barriers is needed. This study has the aim to investigate the pore size distribution of argillaceous rocks with different methods to better understand the transport properties in argillaceous rocks.

The most common way to measure the total porosity of a rock is the determination of the water loss upon drying. However, not only the total porosity, but also the pore size distribution (PSD) is important for diffusion related processes. The characterization of the shape, the size distribution and the connectivity of pores in argillaceous rocks is not trivial and very challenging. There are direct and indirect PSD determination methods. Among the direct methods, image analysis techniques are quite common. Straightforward physical imaging of the microstructure reveals information on the size and shape of the pores and possibly also on the connectivity of the phases. Examples are optical microscopy, scanning electron microscopy (Aligizaki, 2005), sometimes coupled as FIB-SEM (Keller et al., 2013). Microscopy techniques are very essential, but limited to large pores > 10 nm. Due to the fact that pores of low-porosity argillaceous rocks are in the subnanometer range, direct methods are ineffective. In indirect methods, an external stimulus is applied to the material and the material's response is measured using a suitable detector. Particular for argillaceous rocks, the results of porosity and PSD determinations from indirect methods vary (Horseman et al., 1999; Pearson, 1999). Some methods only access open pores, e.g. penetration and adsorption methods, while methods using radiation measure all pores. Most of indirect methods require a pre-treatment of the sample such as crushing and drying, which can modify the microstructure of the sample (Irico et al., 2013). A wide variety of techniques has been used for the characterization of the pore structure of argillaceous rocks, each of them having their advantages and disadvantages.

The most commonly used PSD measurement method is mercury intrusion porosimetry (MIP). This method was described for the first time in detail by Diamond, 1970 then used to determine the permeability of a silty clay by García-Bengochea et al., 1979. Other studies used MIP to measure the pore size distribution of compacted clay (Ahmed et al., 1974; Prapaharan et al., 1991), kaolin clay (Penumadu and Dean, 2000), Boston Blue Clay (Sridharan and Rao, 1971) and Boom Clay (Romero et al., 1999). Because mercury does not wet most substances, it will not spontaneously penetrate pores by capillary action and has to be forced into the pores of the previously dried sample by applying an external pressure. The required equilibrated pressure is inversely proportional to the size of the pore. Only a slight pressure is required to intrude mercury into large macropores, whereas much greater pressures are required to force mercury into small pores (Kaufmann et al., 2009). The main drawbacks of the MIP method are the effects arising from the large pressure and the shielding of large pores by small access throats. This effect leads to an underestimation of the intrusion volume associated with large pores and an overestimation of the intrusion volume associated with fine pores (Gane et al., 2004).

The mercury intrusion porosimetry is also used in comparison studies where MIP was combined with gas adsorption porosimetry measurements. For example (Schmitt et al., 2013) measured the pore size distribution of seal rocks with nitrogen adsorption (NAD). Kuila and Prasad, 2013 combined MIP and gas adsorption to measure the PSD of clays and shales. Brunauer et al., 1938 established a basis for the N_2 adsorption method, when they published an analysis method (BET) for determining the size of pores by gas sorption, particularly of porous solids (Kaufhold et al., 2013). The pore size distribution can be calculated from the adsorption or desorption curves. Non cylindrical pore shapes (or solid-gas interface curvature) limit the transformation of the adsorption or desorption isotherm directly into a pore size distribution (Brunauer et al., 1938; Clarkson et al., 2013). Since the pore shape in argillaceous rocks is rather poorly characterized, the pore size distribution from NAD can at the best only indicative and comparative within a series of samples (Scrivener et al., 2016). Carbon dioxide adsorption is also used to derive pore size distributions. The pore size measurements by carbon dioxide gas are based on the same principle as those using N_2, i.e., on determining the amount of the adsorbate needed to cover the surface with an adsorbate-monolayer. Carbon dioxide gas adsorption is a relatively new method in this field, and it mainly yields the pore size distribution of the micropores. Compared to the NAD method, CO_2 reaches smaller pores (< 2 nm) than N_2 due to its molecule structure. Examples of studies using carbon dioxide gas adsorption to detect micropores in shales and clays can be found in Ross and Bustin (2009) and Clarkson et al. (2013).

The pore size distribution of clays can also be determined by ^{1}H nuclear magnetic resonance (^{1}H NMR) relaxometry. The principle is to apply oscillating magnetic fields to stimulate hydrogen spins in such a way that they return a measurable signal, interpreted in terms of relaxation times of water, while every water property has a different releaxation time. Since water is the probe, ^{1}H NMR is a non-destructive and non-invasive technique which allows investigation of the pore structure without sample drying (Gallegos and Smith, 1988; Howard and Kenyon, 1992; Webber, 2010). Hinai et al., 2014 performed investigations of the PSD on shale by NMR.

NMR cryoporometry is a suitable method to determine the microstructure of cement (Mitchell et al., 2008). Hence, this method was also tested in this study for pore size distribution measurements of natural clay. It is based on recording the fractions of frozen and unfrozen liquid as a function of temperature. This method is comparably new in the field of PSD determination of clays. Only a few studies on argillaceous rock and shale samples can be found in the literature (Mitchell et al., 2008; Firouzi et al., 2014). The NMR cryoporometry study of Firouzi et al. (2014) with coal and shale samples apparently failed, because the used NMR instrumentation was limited to a minimum temperature of −20 °C; hence the small pores that could only be detected at lower temperatures were not identified.

Despite the fact that various methods were used to determine the PSD of argillaceous rocks, a comparison between the different methods is still missing for low porosity argillaceous rocks. This paper tries to address this point. The study particularly focuses on the relatively new and not often performed methods on argillaceous rocks such as CO_2-adsorption, NMR and NMR cryoporometry and compares them with well-known and established mercury intrusion porosimetry and nitrogen adsorption analysis. A stronger anion exclusion behavior has been demonstrated recently for Helvetic Marl compared to Opalinus Clay (Wigger and Van Loon, 2017), two argillaceous rocks investigated in the context of disposal of radioactive waste in Switzerland. The authors postulated that Helvetic Marl has a higher fraction of small interlayer equivalent (ILE) pores than Opalinus Clay. Here we present results of comparative pore size distribution measurements performed on these natural materials to shed light on this assumption. The information gained about the pore sizes and the structure of the low-porosity argillaceous rocks is expected to allow a better interpretation of anion exclusion effects.