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Research paper

Impact of sand content on solute diffusion in Opalinus Clay

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ABSTRACT

The mesostructure (micro to millimeter scale) of clay rocks was considered as a two-component mixture consisting of impermeable non-clayey sand grains embedded in a permeable clay matrix. Provided that representative diffusion properties can be defined, the clay matrix can be treated as a continuum. Under these conditions diffusion at larger scales will depend on geometric properties of the mesostructure. The objective of this study, then, is to analyze geometric parameters, which control diffusion at larger scales. In a first step a set of different clay matrix mesostructures were reconstructed on the base of synchotron X-ray computed microtomography applied to clay rock samples from northern Switzerland (e.g. Opalinus Clay). In a second step mesostructural effects on diffusion were quantified by applying diffusion simulations to reconstructed mesostructures. Further analysis revealed that constrictivity is the most dominant parameter, which controls diffusion on the millimeter scale in Opalinus Clay. Regarding diffusion, the mesostructure of the clay matrix is near isotropic. Hence, the reason for anisotropic diffusion in Opalinus Clay must be searched on the nanometer to micrometer scale and it is caused by anisotropic pore path tortuosity related to shape preferred orientation of clay platelets.

1. Introduction

Low-permeability clay rock formations are considered as potential hosts for radioactive waste (Nagra, 2002, 2004; Andra, 2005). Clay rocks typically have a very low hydraulic conductivity and the transfer of radionuclides will be largely controlled by diffusion. Diffusion depends strongly on geometric parameters, which in turn are intimately related to the microstructure. Clay rocks are natural multiphase composite materials with microstructural properties at different length scales. At the millimeter to centimeter scale, clay rocks consist of non-clayey grains embedded in a matrix of fine-grained clay platelets. At the nano to micron scale microstructural investigations revealed that geometric incompatibilities along grain boundaries of different clay platelets form the interparticle pore space (e.g. Keller et al., 2013). Preferred orientation of clay platelets attained during sedimentation and compaction (e.g. Lash and Blood, 2004; Wenk et al., 2008) is likely the cause for anisotropic diffusion due to an anisotropy pore path tortuosity (Van Loon et al., 2004). Anisotropic pore path tortuosity was documented on the base of a 3D investigation of the nano-porosity in Opalinus Clay (Keller et al., 2011). At least in case of porosity it was demonstrated that if a sufficiently large volume of clay matrix is considered, porosity is spatially homogenous enough so that the porous clay matrix can be treated as a continuum with defined porosity properties (Keller et al., 2013). In addition, high-resolution tomographic investigations showed that the nanoporosity in non-clayey components (i.e. carbonates) is low and that the pore space consists of isolated pore objects, which are not connected (Keller et al., 2013). Consequently, non-clayey materials can be treated as largely non-porous (see also Robinet et al., 2012). Taking all these observations into account, a clay rock at the millimeter scale consists essentially of a permeable clayey matrix with inter dispersed and non-permeable non-clayey sand grains. In such a case transport properties of clay rocks depend on the amount of sand grains dispersed in the clay matrix (Revil and Cathles, 1999). In particular, diffusion at the millimeter scale is likely controlled by the mesostructure of the clay matrix treated as continuum. On this length scale, diffusion will not only depend on the continuum diffusion properties of the clay matrix but also on its mesostructure and following the theory of diffusion in porous media, the clay matrix content (ϕ), tortuosity (τ) and constrictivity (δ) are usually considered as the most important geometric parameters (e.g. Van Brakel and Heertjes, 1974; Horseman et al., 1996). In the past these parameters were used in many different concepts for characterizing transport pathways (see Holzer et al., 2013 for a review). Here these parameters are understood as purely geometric factors that can be extracted from reconstructed 3D microstructures (Gommes et al., 2009; Holzer et al., 2013). Quantifications of geometric parameters related to a continuous clay matrix based on real clay rock microstructures are rare. Applying synchrotron XCT to a Callovo-Oxofordian clay-rich rock sample and on the base of resulting 3D reconstructions of the continuous clay matrix, Robinet et al. (2012) investigated the influence of the presence of non-clayey grains on diffusion. Thereby, mesostructural effects on diffusion in the continuous clay matrix were considered by a single geometric parameter. No attempts have been made to distinguish between effects

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of different geometric parameters. Knowing the influence of different geometric parameters eases the interpretation of experimentally derived diffusibilities (Van Brakel and Heertjes, 1974). In addition, the relationship between tortuosity/constrictivity and the clay matrix content remains unclear. Robinet et al. (2012) applied basic morphological image techniques (i.e. dilation and erosion) to the voxel representation of the mesostructure to investigate effects as a function of the clay matrix content. The relevance of these modified mesostructures in terms of a natural occurrence is, however, unclear.

This work is an attempt to extract and define geometric parameters, which measure the geometric properties of clay matrix mesostructures and can then be used to determine macroscopic diffusion properties of clay rocks. Since geometric parameters depend on clay matrix content, synchrotron X-ray computed tomography (XCT) was applied to clay rock samples with different clay contents. The determination of the clay matrix content ϕ on the base of reconstructed 3D microstructures is straightforward, which, however, is not the case for tortuosity τ and constrictivity δ. Diffusion modeling was applied to 3D microstructures, which allowed determining values of the geometric factor G. G accounts for the total mesostructural effects on diffusion but gives no indications on the actual geometric control of diffusion Then, using the well-known relation $G = \delta / \tau^2$ (Van Brakel and Heertjes, 1974; Horseman et al., 1996; Van Loon et al., 2004) and by accepting a given definition of geometric tortuosity allowed to define a procedure to extract values of geometric constrictivity. The procedure is such that values of geometric tortuosity and contrictivity can be determined on the base of 3D microstructures. All geometric parameters (i.e. G, τ and δ) are functions of clay matrix content and the presented results allow estimates on geometric parameters provided the clay content of a sample is known. In this way it will possible to evaluate the impact of non-clayey sand content on diffusion.

2. Samples

In order to investigate mesostructural properties of the clay matrix in shales, samples with different clay contents were selected (Table 1). Two out of the three samples are from the Schlattingen borehole SLA-1. The location of the borehole is in the Swiss Molasse basin near the town of Schaffhausen. The sedimentary sequence at SLA-1 includes marine limestones, marls and shales, which are unconformably covered by Tertiary rock of the Alpine Molasse. Miocene thrusting related to the formation of the Jura Mountain did not affect rocks at SLA-1. Sample BD-7 is a calcareous marl taken at a depth of 781 m. Sample Opa-3 was taken from Opalinus Clay unit and is an argillaceous marlstone taken at depth of 837 m. For samples BD-7 and Opa-3 mineral contents were determined by X-ray diffraction (XRD) analysis at University of Bern, Switzerland (Table 1). In order to cover a wider range of clay contents and related mesostructures a third sample BWS was taken at Mont Terri rock laboratory in northwestern Switzerland (see Bossart and Thury, 2008 for geological details). This sample contains the highest content of non-clayey grains and was taken from sandy facies of Opalinus Clay (Table 1). Illite and kaolinite dominate the clay mineral composition of the samples. Mixed-layer illite–smectite and chlorite are also present.

3. Imaging methods

3.1. Synchrotron X-ray imaging

The measurements were performed at the synchrotron X-ray imaging station of the Helmholtz Centre Berlin for Materials and Energy (HZB, BAMline, Germany). The X-ray detection system consists of an optical setup (Optique Peter) and of a PCO4000 CCD area detector with 4008 × 2672 pixels. A CWO scintillator screen with a thickness of 50 μm was used. The obtained pixel size was 438 nm. A W-Si multilayer monochromator with an energy resolution of about $dE / E = 10^{-2}$ was used to obtain a monochromatic X-ray beam. An X-ray energy of 19 keV was chosen for optimal image contrast. 1800 radiographic projections were taken for the reconstruction of the tomographic 3D data set. The exposure time was 3 s. All images were dark field and flat field corrected. A filter back projection algorithm was used for mathematical data reconstruction.

3.2. Image processing

The reconstructed XCT raw image stacks have volumes in the order of 2600^3 voxels, of which one sub-volume was selected and analyzed (Table 1). The size of the analyzed volumes is documented in Table 1. Multi-phase segmentation of the XCT image stacks is a crucial step and the results were evaluated by comparing the determined content of major constituents to estimates obtained on the base of XRD.

Based on visual inspection, image contrast of XCT images allows the distinction of 5 phases: i) Brightest grains are heavy minerals such as pyrites and siderites, ii) bright-grey grains are carbonates but image contrast did not allow distinguishing between calcite and aragonite, iii) dark-grey grains are likely tectosilicates such as quartz and feldspar, iv) black parts of the images correspond mainly to organic material and to a few small cracks and v) the remaining volume fraction corresponds to the clay matrix consisting mainly of fine-grained clay minerals. High-resolution focused ion beam nano-tomography revealed that the clay matrix contains also small carbonate and quartz grains, which cannot be resolved by XCT (Keller et al., 2013). As a consequence of the presence of small non-clayey grains within the clay matrix, XRD and XCT measurements yielded different results. This particularly refers to the fine-grained clay matrix, of which volume fraction as determined by XCT is only roughly equivalent to the clay content determined on the base of a bulk XRD analysis. However, in order to compare the two methods, the wt.% mineralogy related to XRD was recalculated into vol.% by assuming typical mineral densities (Table 1).

Table 1
Modal amounts obtained on the base of XRD and XCT.

Method	Sample	Size	Quartz, feldspar	Carbonates	Heavy minerals	Organic	Sheet sillicates
			wt.%	wt.%	wt.%	wt.%	wt.%
XRD (University of Bern)	BD-7		21	33	6.1	0.1	43
	OPA3		19	16	1.7	0.4	63
			vol.%	vol.%	vol.%		vol.%
	BD-7		19.7	30.9	3.1	–	46.3
	OPA3		17.8	15.0	0.9	–	67.8
			Quartz, feldspar	Carbonates & micas	Heavy minerals	Organic	Clay matrix
			vol.%	vol.%	vol.%	vol.%	vol.%
	BWS	0.5 × 0.22 × 0.4 mm	33.0	53.0	0.6	0.4	13.0
XCT	BD-7	1.0 × 0.8 × 0.3 mm	9.6	30.5	4.5	0.4	55
	OPA3	0.8 × 0.8 × 0.3 mm	14.3	12.1	0.6	3	70