Microporous and Mesoporous Materials 170 (2013) 83–94

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

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

Characterization of multi-scale microstructural features in Opalinus Clay

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ARTICLE INFO

Article history:
Received 26 March 2012
Received in revised form 2 November 2012
Accepted 9 November 2012
Available online 3 December 2012

Keywords:
Shales
Porosity
Microstructure
Imaging methods

ABSTRACT

STEM-, FIB- and X-ray tomography were applied to a sample taken from the Opalinus Clay unit. This allowed characterization of the pore structure in the fine-grained clay matrix at different levels of microstructural detail. On the level of detail that can be resolved by FIB-nt, the observed pore space is largely unconnected and the resolved porosity was in the 2–3 Vol.% range. At higher optical magnification but for smaller sample sizes, STEM tomography resolved a porosity of around 13 Vol.%. This suggests that the transition from an unconnected to a connected pore space in the shale sample occurs on the few nanometer scale. Geometric analyses of larger pores as visualized by FIB-nt revealed that dilation induced formation of bridges of only a few hundred nanometers between tips of neighboring pores may lead to a coalescence of larger pores. The resulting large pore network may allow for gas transport in the fine-grained clay matrix.

1. Introduction

In the context of the disposal of radioactive waste, the production of shale gas and CO_2 sequestration gas transport along the intergranular pore space in clay rock formations is an important issue. The present investigation focused on 3D visualization and characterization of potential gas transport pathways and their connectivity. This information is required for the validation of the isolation potential of a host rock for radioactive waste and also for a better understanding of gas-deliverability of shale gas reservoirs. A microstructural investigation of shales poses challenges because there are microstructural features on a wide range of scales. On the macroscopic scale, the geometry of compositional layering may control transport properties. At the same time, however, the transport properties of different layer materials are controlled by their structures at the microscopic and submicroscopic scale. Here, we focused on the pore structure related to a clay-supported shale-microstructure consisting of isolated non-clayey mineral grains distributed within a matrix of fine-grained clay minerals. In such case, it is known that the intergranular pore system is dominated by pores with radii on the nanoscale [1–3]. Thereby, it is proposed that gas flow is controlled by the geometry of comparably larger pores (i.e. radii >10 nm) [4]. Besides these larger pores, a major fraction of the pore space is characterized by radii <10 nm [e.g. 2]. These few nanometer wide pores likely connect larger pores and may control connectivity of the pore network [e.g. 2]. Hence, the structure of the pore space may be seen as having different levels of geometrical details (i.e. microstructural levels). In the case of shales, the pore size range covers several orders of magnitude and thus, cannot be visualized in 3D by one single tomographic method. Therefore, we applied and tested several tomographic methods, which cover a resolution range from a few nanometers to the millimeter scale. The following tomographic methods provide increasing resolution but decreasing sample size: X-ray tomography (XCT), focused ion beam nanotomography (FIB-nt) [5] and scanning transmission electron microscopy (STEM) tomography. All of these methods were applied to a shale sample from the Opalinus Clay unit. The 3D geometry of nanoporosity in the clay matrix was investigated by FIB-nt and STEM tomography. Unfortunately, the sample size that can be analyzed by these methods is rather small (see below). In the case of an inhomogeneous distribution of nanoporosity, for example because of the presence of non-clayey minerals grains, in the sample it is useful to perform large-scale scanning electron microscopy (SEM) imaging of broad ion beam (BIB) polished surfaces [6] prior to the application of FIB-nt. This allowed a 2D characterization of the microstructure on the mm-scale and the selection of specific sites, which can subsequently be investigated by FIB-nt. For this study two specific target volumes were selected for FIB-nt analysis: (i) a volume that corresponds to a pressure shadow around a larger grain and (ii) a volume that is located at some distance from larger grains.

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1387-1811/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.micromeso.2012.11.029

Performing more than one FIB-nt realization gave some ideas on spatial porosity fluctuations. In order to resolve more geometrical detail of the pore space than it is possible with FIB-nt, we also prepared TEM foils and small cylinders (i.e. diameter 200–300 nm) which were investigated by TEM imaging and STEM tomography.

In addition, we provide a detailed geometric analysis of the shale pore microstructure in order to address the nature of potential gas transport pathways through shales. Commercial analytical tools allow the extraction of some well-known parameters (e.g. porosity, pore surface area etc.) but they lack options for the quantification of important parameters such as pore path length, pore path tortuosity and the spatial distribution of these quantities. Furthermore, gas migration studies suggest that gas percolation may be associated with the formation of a small number of pathways that are induced by pressure dilation [7]. However, the extent of dilation necessary to form a connected network of larger pores is largely unknown. For example, it is possible that dilation occurs predominately between tips of larger isolated pore objects, which would lead to a coalescence of the larger pore objects and to an interconnected pore space. Therefore, the distance between pore tips and the geometry of the interconnected pore network is of major interest. Thus, in addition to the spatial distribution of pore path geometrical properties [2,3], we analyzed the relationship between different distance distributions that correspond to the distances between grain boundaries of neighboring non-clayey grains (i.e. carbonates/quartz), pore lengths and distances between pore tips of neighboring pores. Based on this geometric information, we analyzed the effects of potential pathways dilation and associated coalescence of larger pores.

2. Methodology

2.1. Sample

All methods described herein were applied to the same rock sample (i.e. sample BDR1_oc) that was collected from the Opalinus Clay rock unit at the Mont Terri rock laboratory in northwest Switzerland (Canton Jura, Switzerland; [8]). This laboratory is located adjacent to the safety gallery of the Mont Terri motorway tunnel. Sedimentation of Opalinus Clay occurred around 174 my ago in a shallow marine basin. After sedimentation the rock unit underwent two stages of burial with a maximum burial depth of about 1350 m. Folding of the mountain belt occurred between 10.5 and 3 my ago. The Opalinus Clay can be subdivided into three main facies: shaley facies, sandy facies and carbonate rich sandy facies. The sample was taken from the shaley facies about 250 m below the surface. The shaley facies of Opalinus Clay typically contains 66% clay minerals, 13% calcite, 14% quartz, 2% feldspars, pyrite and organic carbon [8].

On the macroscopic scale, the analyzed shale sample contains fine whitish, presumably carbonate-rich layers on the mm-scale and sub mm-scale. On the microscopic scale, the prepared and analyzed samples can be subdivided into a matrix composed of fine-grained clay minerals and within this matrix there are numerous isolated non-clayey minerals (Fig. 1). For the analyzed sample, data from nitrogen adsorption analysis are available [2]. BET surface is 20.0 (m^2/g) and the calculated porosity is 11.5 Vol.% (see [2] for more discussion).

2.2. Sample preparation

Electron microscopy (FIB/SEM/TEM) requires drying of the samples prior to analysis. Conventional drying and/or freeze-drying of moist clay may cause preparation artifacts such as drying shrinkage (conventional drying), ice formation during freeze drying. Special methods such as high-pressure freezing and subsequent freeze-drying were used to avoid these artifacts. The sample preparation includes the following steps: Clay slabs with a thickness of 200–300 μm and a diameter of 5–6 mm were cut with the help of a saw with a very fine (thickness of saw blade = 200 μm) diamond blade parallel to the bedding plane. Then, the slabs were frozen under high pressure (2100 bar) and within milliseconds by using the HPM 100 high-pressure freezing system. Freezing at high pressure occurs by the injection of pressurized liquid nitrogen. This treatment prevents the formation of ice-crystals and thus preserves the delicate framework of the pore space. Then, the vitrified water was sublimated under high vacuum using a system for freeze-drying [2,9]. Details of high-pressure freezing techniques and their application for cryofixation are given by [10]. To stabilize the dry clay slabs, they were sandwiched between two 50 μm thick glass discs which were glued together with epoxy. Then, a cross-section was cut with a diamond saw perpendicular to the bedding plane. The surface of this cross-section was polished by using a broad ion beam (BIB) instrument and subsequently investigated by SEM and FIB-nt. SEM imaging of BIB polished clay samples is used for a material characterization on the mm-scale (for comparison: typical sample size of the FIB-nt analyzed volume is a cube of 10–30 μm edge length). Such extended SEM images are the basis for the localization of distinct pore microstructures, which can subsequently be investigated by FIB-nt. The SEM images were processed as follows: First several SEM images were stitched together which results in a single high-resolution panoramic image. Second, pores were segmented by grey level thresholding from extended SEM images.

2.3. X-ray tomography

The clay sample was scanned with a X-ray micro tomography cone beam setup consisting of a μm spot size X-ray tube "XT9160-TXD" from Viscom, a rotation table "UPR-160F air" from Micos and a X-ray flat panel detector "C7942 CA02" from Hamamatsu covered with a 1 mm thick Al plate. A voltage of 40 kV was applied to accelerate the electrons which impacted on a tungsten target with diamond support. The projection images were taken at angles uniformly distributed over 2π, whereby the last projection served to determine the quality of the measurement (the projections at 0 and 2π should be equal). To correct for dark counts and inhomogeneity of the detector a dark and a flat image were acquired with total integration times of 32 and 64 s, respectively. The projection images were corrected for bad pixels, beam hardening and ring artifacts before a standard filtered backprojection algorithm was used for reconstructing the $1120 \times 1120 \times 1184$ voxels 3D absorption image. Based on the detector pixel size and the magnification, the resulting voxel edge length of the reconstructed 3D image is 2.56 μm, which was larger than the focal spot size and ensured that the image was not blurred (Table 1).

2.4. Focused ion beam nanotomography

FIB-nt is done with dual beam FIB–SEM instruments, in which an ion beam and an electron beam focus intersect at a point on the sample surface. 3D information can be obtained by acquiring a sequence of cross sectional images spaced evenly through a region of a bulk specimen, and reconstructing those two-dimensional images into a three-dimensional representation of the sampled volume. The process begins by the milling of a wedge shaped trench in the sample. One wall of the trench is vertical (i.e. normal to the specimen surface) and becomes the initial cross section imaged by the electron beam [5]. After imaging, the ion beam is used to remove a layer of uniform thickness of material from this wall,