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Bridging Pore and Macroscopic Scale - Scanning SAXS-WAXS Microscopy Applied to Shales

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SUMMARY

The determination of fabric and pore structure of shales remains a challenging task which is mainly due to the wide range of pore sizes (and shapes) ranging from molecular dimensions to microns. High resolution imaging techniques fail to provide information over representative regions of interest, while more conventional characterization techniques may only assess volume averaged properties of the pore systems. Thus, open questions remain regarding the effects of the multi-scale pore network of shales in the retention and transport of hydrocarbons during unconventional production processes. We apply scanning small- and wide-angle X-ray scattering (SAXS and WAXS) microscopy to obtain averaged but detailed information from the micro- and meso-pore structures of shales. By combining SAXS/WAXS with raster-scanning microscopy, we obtain local scattering information from 1-100 nm-size pores in micrometer-size volumes over a large (2 x 2) mm² scanning area. We derive porosity, pore size distribution and orientation, as well as mineralogy of specially prepared thin section samples, covering length scale ranges of nm to sub-microns and from microns to millimeters, with a gap that can potentially be closed. The method further enables the linking of porosity to shale matrix components, which is integrated in a multi-scale imaging workflow involving μCT, and SEM/EDX analysis, aimed at allowing for the full pore network characterization of shales.
Introduction

Modern advanced imaging techniques, like TEM (Keller 2013) or Helium Ion microscopy (King et al. 2015) allow assessing micro (<2 nm) and meso (2 – 50 nm) pores (Sing et al. 1985) of the shale matrix giving most valuable insight to the pore morphology and pore network fabric. A statistically relevant pore network, however, cannot be extracted due to the limited field of view of these techniques (see e.g. Keller et al. 2013b). Other analytical tools, such as low pressure gas adsorption (Clarkson 2013) or small angle scattering techniques (Radlinski 2006) are capable of probing micro and meso pores in a representative sample volumes but only providing volume averaged information about the pore systems. Consequently, currently used experimental techniques fail in bridging the gap between micro and meso porous structures and the macroscopic scale. The distribution of properties on this mesoscopic scale might be important for a quantification of fluid saturations and fluid-transport processes. The main focus of this contribution is to attempt closing this gap by applying scanning small- and wide-angle X-ray scattering (SAXS-WAXS) microscopy over a suite of natural shale thin section and porous glass samples. The measurements were performed in a raster scanning mode. For each pixel, simultaneously SAXS and WAXS patterns are obtained from volumes as small as 10x25x30 μm over a 2x2 mm² total area. Thus measurements give both localised and representative information of the micro and meso pore scale in terms of pore size distribution, surface area, pore orientation, porosity (SAXS) and mineralogy (WAXS). Registering the data to μ-CT SEM/EDX measurements, we demonstrate that method can be directly implemented into a multi-scale imaging workflow.

Materials and Methods

A scanning SAXS-WAXS experiment is performed to retrieve information on size distribution, orientation of the scatterers and mineralogy form the targeted sample volume. The experiments were performed at the cSAXS beamline at the Swiss Light Source, Paul Scherrer Institute. The experimental setup is explained in detail in Figure 1. A parallel monochromatic X-ray beam with a photon energy of 11.4 keV (λ = 0.1088 nm) has been trimmed to a spot size of 10x25 μm². With the collimated beam we scanned the sample (X-ray transmission microscopy) with a pixel size of 10x10 μm² causing elastic scattering from the illuminated small sample volume. Photons were detected in a small angular interval with respect to the initial beam (small angle scattering). The scattering angle (2θ) to which photons are scattered corresponds to the objects size; small objects, i.e. small pores scatter to large angles and vice versa. The scattering intensity is measured in two different geometries using different detectors corresponding to different pore-size ranges. The scattering vector q as calculated from the scattering angle by $q = \frac{4\pi}{\lambda} \sin(\theta)$ refers to the invers of the size of the scattering object by $d=2\pi/q$. WAXS assesses crystal lattices and SAXS pores from 1-100 nm. Applied to rocks for the mineral quantification (Wenk et al. 2008) and pore size distribution (Radlinski 2006) models are fitted to the radially integrated intensity distribution $I(q)$. 
Figure 1 The left combined figure shows the experimental setup at the cSAXS beamline. The scattered photons are detected on a WAXS and a separate SAXS detector. The Intensity as function of scattering vector $q = \frac{4\pi}{\lambda} \sin \theta$ plot is utilized to determine size distributions. From the SAXS pattern (a and b) orientational information can be retrieved via the shift ($\Theta_s$), average scattering and amplitude of the cosine function approximating the intensity distribution of the scattering pattern (modified after Bunk et al. 2009). An isotropic scattering pattern does not contain information on orientation (curve a).

Structurally ordered scatterers cause anisotropy of the scattering pattern (Fonseca et al. 2009). From the anisotropy of the SAXS pattern and its orientation the orientation and degree of orientation of scatterers can be inferred (Bunk et al. 2009, Giannini et al. 2013). When mapping the intensity distribution as a function of the azimuthal angle $\Theta$ on the detector panel the distribution can be approximated by a cosine function (Figure 1). The shift $\Theta_s$ of the function represents the average orientation of the scattering pattern which is 90 degrees shifted to the real orientation of the scatterers. The amplitude $a_1$ of the function of the function represents the oriented part of the scattering pattern where $a_0$ is the average scattering. From the ratio ($a_1/a_0$) of the two a degree of orientation can be measured. A value close to 1 represents a highly ordered structure (Figure 1 b), meaning that the scatterers show preferential orientation. A value close to 0 represents a structure without preferential orientation (Figure 1, a). Thus, if an isotropic scattering pattern is present no orientation can be measured (Figure 1a). The measurements are performed in a raster scanning mode with a step width of 10 μm. If sufficient measurements are performed a representative sample area is mapped.

Conclusions

We show the application of scanning SAXS-WAXS microscopy on shale thin sections, bridging a resolution gap from the micro and meso pore range to the macroscopic scale. The new aspect of the technique is that small volumes are assessed which allows studying heterogeneity by localising information. The measurements combine SAXS and WAXS. We explore the technique to extract volumetric properties from the SAXS pattern and mineralogical information from the WAXS pattern. In addition we investigate the technique to retrieve local information on pore orientation. The method is capable of resolving representative areas for it is operated in a raster scanning mode.

References


