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The microstructure of rocks and small-angle and ultra-small-angle neutron scattering: the coming of age of a new technique

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I. Background

The micro-architecture of sedimentary rocks is a scientifically fascinating subject of profound practical importance. The geometry and topology of pore space on a linear scale varying from angstroms to millimetres governs the transport and retention of formation waters and hydrocarbons, and determines the internal surface area available for adsorption of gases. Subsurface hydrology, petroleum geology, petroleum engineering, adsorption and desorption of methane in coal seams, and sequestration of greenhouse gases into geologic formations are all directly influenced by the rock microstructure.

In the 1980's, a number of pioneering papers were published where a connection was made between the fractal geometry and the microstructure of heterogeneous surfaces, including internal surfaces of sedimentary rocks. These studies used SEM and optical microscopy [1-3], molecular adsorption [4], SAXS [5] and SANS [6]. Early on it has been established that fractal characteristics of coarse sedimentary rocks may extend over length scales from angstroms to about 0.1mm [1, 6]. Cohen developed a theoretical model of various morphological regimes in sedimentary rocks [7] and theoretical tools, for the interpretation of scattering data, have been worked out [5, 6, 8, 9].

In recent years, combined SANS and USANS emerged as a multi-scale, non-invasive method ideally suited for probing rock microstructure in various practical applications. This was made possible by the construction of absolutely calibrated high-flux SANS instruments and, remarkably, the development of wing-free, Bonse-Hart geometry USANS facilities [10, 11]. Modern SANS and USANS machines combined, provide a continuous Q-range from 10^{-5}Å^{-1} to 4 Å^{-1}, which covers a linear pore size range of several angstroms (lower pore size limit in sedimentary rocks) to about 30 μm. This spans the entire pore size range for many sedimentary rocks, with the notable exception of coarse sandstones.

II. Geological applications of SANS and USANS

II.1. Microstructure of sandstone reservoirs

Owing to their importance in reservoir engineering, the microstructure of sandstones has been extensively studied using various methods. The tools of choice traditionally have been SEM, optical microscopy and mercury porosimetry [12]. Chemically, sandstones are dominated by quartz and are perceived by neutrons as a simple two-phase, rock matrix - pore space system. Fractality of sandstones has been first demonstrated using microscopy [1], observed with SANS [6] and confirmed later using combined SANS and USANS [13]. A combination of SEM, SANS and USANS experimental data, interpreted along the lines of a polydisperse spherical pores model, has furnished detailed microstructural information on scales from angstroms to millimetres: pore size distribution, specific surface area as a function of probe size, synthetic mercury injection curve and the correlation function. This information is consistent with, but often surpasses results obtained using other methods like mercury porosimetry, microscopy and NMR relaxometry [14].

II.2. Microstructure of coals

II.2.1. General

Compared to thermally stable and chemically simple inorganic sandstones, coals occupy the opposite end of the sedimentary rock spectrum. Coals are geo-polymers, comprised of thousands of species of large organic molecules originating from higher plants. These molecules may be thermally altered to various degrees depending on burial history, resulting in coals of different rank. Macroscopically different bands in coal, comprised of different organic entities (macerals), are common. Sorbates like water, CO_2, CH_4, N_2 and other fluids, can interact with the coal matrix leading to microstructural modifications manifested as swelling [15]. Coal may also contain significant amount of inorganic matter (ash).

Remarkably, calculations of neutron scattering contrast for coals of various ranks show

that contrast between different macerals comprising the coal matrix is very small compared to the contrast between the coal matrix and pore space. Contrast between the organic matrix and ash is also small. Therefore, neutrons used in SANS experiments perceive coal as a two-phase (solid matrix – pore space) system. The situation is different for SAXS, as X-ray contrast between the ash and organic matrix is similar to the X-ray contrast between the organic coal matrix and void, and X-rays perceive coal as a three-phase system [16].

II.2.2. Gas adsorption capacity of coals

At shallow depths and at relatively low pressures below the critical point, gases like methane and carbon dioxide are stored within the pore space of coal predominantly as a liquid-like monolayer adsorbed directly on the coal-pore interface. In these conditions, the volume fraction of gas contained in the bulk of the pore space is small compared to the volume fraction of adsorbed monolayer. Consequently, the gas adsorption capacity of coal is then determined by the internal surface area available for monolayer coverage.

The SANS/USANS method provides access to micropores, mesopores and macropores (up to about 30 μm diameter) in coal in one experiment. Radlinski et al. used a polydisperse spherical scatterers model to fit SANS/USANS data for coals ranging from high volatile bituminous to anthracite rank (vitrinite reflectance range from 0.55% to 5.15%) and computed the pore size distribution, total porosity and internal specific surface area for objects of varying sizes [17]. All coals turned out to be characterised by very wide, power-law-like pore size distributions and had total porosities consistent with the world-wide trend [18]. Specific surface areas for a probe size of 4Å, calculated from SANS/USANS data, have been in excellent agreement with nitrogen adsorption data independently obtained for the same samples of coal and individual macerals.

II.2.3. Coal as a source of oil and gas

Only a few published studies have demonstrated that coals have sourced significant volumes of hydrocarbons. The evidence has been mostly geochemical [19], although it is well established that the microstructure of coal abruptly re-arranges as its thermal maturity reaches the stage corresponding to a vitrinite reflectance value of about 0.6%. It has also been suggested that, prior to oil expulsion, the micropores are progressively clogged with thermally generated bitumen as rank increases [20].

Boreham et al. combined geochemistry and SANS to study hydrocarbon generation within a natural maturity series of ash-free Early-Middle Eocene coals (vitrinite reflectance range from 0.37% to 1.2%) originating from two wells in the Bass Basin,

Australia [21]. The rank (and sample depth) at the onset of hydrocarbon generation determined geochemically coincides with re-arrangement of micropores and mesopores observed by SANS. SANS also provides direct evidence for progressive saturation of micropores and mesopores with increased rank, up to the full saturation at the oil expulsion threshold corresponding to a vitrinite reflectance value of about 0.75%.

III. Generation of hydrocarbons in clastic source rocks

The processes of hydrocarbon migration and expulsion occur at the subsurface in the pore space of mudstones containing dispersed organic matter from which the hydrocarbons are thermally generated. The pore-size-specific migration of fluid phases with depth (or, in general, with increased thermal maturity of organic matter) can be observed using SANS and USANS due to the evolution of the scattering contrast between the inorganic rock matrix and the pore space filled with different formation fluids like brine, generated bitumen and generated hydrocarbons with varying content of the asphaltene, polar and aromatic fractions.

The application of SANS/USANS to the detection of hydrocarbon generation and expulsion in clastic source rocks has developed over the last 10 years, from case studies of a natural maturity series of source rocks [22] and artificial maturity series of source rocks [23] to a basin-wide evaluation of Cretaceous source rocks in the Browse Basin, Western Australia [24]. Modern SANS/USANS data analysis software [25] enables routine fits of experimental neutron scattering data to a polydisperse spherical pore model followed by computations of (1) absolute scattering intensity versus depth for selected pore sizes, (2) pore size distribution, (3) internal specific surface area, (4) pore number density versus depth for selected pore sizes, and (5) total porosity versus depth. These plots are used to determine the depth of the onset of hydrocarbon generation, onset of expulsion and the onset of oil-to-gas cracking while monitoring the properties of inorganic rock matrix, like compressibility and porosity. The major advantage of the SANS/USANS method over the geochemical approach is its ability to directly and non-destructively monitor the migration of generated hydrocarbons through the pore space of a source rock in a pore-size-specific manner.

IV. SANS versus SAXS: why use neutrons and not X-rays?

For strictly two-phase systems (rock matrix – pore space in this case) the microstructural information obtained from SANS is equivalent to that gained from SAXS. Therefore, for sedimentary rocks like sandstones, lean shales and ash-free coals, the choice between neutrons and X-rays involves considerations about the form in which a rock sample is available, maximum sample size and minimum sample thickness, and – in some cases – the desirability of contrast-matching experiments [26]. With the advent of synchrotron hard X-ray SAXS facilities the limited penetration depth of classical

X-ray sources becomes less of a concern.

Sedimentary rocks, with both organic and inorganic components (with the minority phase constituting more than about 1 wt %) are perceived as approximately two-phase by neutrons and three-phase by X-rays [16, 22]. In applications involving hydrocarbon generation and expulsion SANS would be a preferred experimental method [22], but there are cases where juxtaposition of SANS and SAXS results reveals microstructural detail not easily interpretable when one only method is used. One example is SANS/SAXS identification of clay-clogged lamellar micropores in coal [17].

V. Practical aspects of using SANS/USANS in industrial applications

In industrial applications a large number of samples may need to be prepared, analysed using SANS/USANS and interpreted with appropriate software. For example, in a recent multi-client study of hydrocarbon generative potential of source rocks in the Bass Basin, Australia, a total of 165 potential source rock samples, originating from nine commercial exploration wells, were prepared and analysed by SANS and 46 of these samples were analysed by USANS [24]. The turnaround time was 12 months.

There were three major steps in this project: (i) well and sample selection, (ii) sample preparation for SANS/USANS and (iii) data processing and interpretation. The latter two steps are well documented now and can be performed routinely [24].

The selection of wells was based on general geological knowledge of the basin (including position of the depocentre, source rock richness, maturity of the organic matter, and the presence (or absence) of hydrocarbon shows and/or discoveries). Sample (depth) selection for each well was based on wireline logs and other specific information provided in well completion reports. Particular attention was given to lithological homogeneity of the entire depth series of rocks selected for SANS/USANS work. Both cuttings and side-wall core material were used.

Selected rock samples (mostly cuttings) were gently crushed, sieved to a grain size fraction of 355 - 475 μm and potted in resin. After curing, two 25 mm diameter slices (about 1 mm thick for SANS and about 0.4 mm thick for USANS) were cut off with a precision diamond saw. This step turned out to be more time consuming than the actual acquisition and interpretation of SANS/USANS data.

SANS experiments were performed at the Argonne National Laboratory IPNS facility (instrument SAND [27]) and USANS experiments were done at the Austrian Beam Line, Grenoble Research Reactor (instrument S18 [11]). Raw data were reduced using the routine instrument software these sites. Further processing and analysis was performed using the publicly available PRINSAS software [25].

VI. Conclusion

Insight into the microstructure of sedimentary rocks gained using SANS and USANS is unique. It enables a non-invasive determination of the pore size distribution and specific internal surface area, computation of the correlation function and construction of a mercury porosimetry curve in the linear scale range from angstroms to tens of micrometers. Pore-size-specific detection of formation fluids migrating through the pore space is also possible. The method has been tested on many rock types for several specific applications. Both core and cuttings material can be used for sample preparation. Numerous SANS and several USANS facilities worldwide are available for external users. User-friendly, Windows-based SANS/USANS data processing software, for geological applications, is available in the public domain. Sedimentary rocks generally are strong scatterers and a throughput of 20 samples per day (for SANS) and 5 samples per day (for USANS) is achievable with modern apparatus. All this makes SANS/USANS an attractive option for microstructural studies of rocks.

VII. References

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