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Neutron scattering study of vitrinite: Insights into sub-micrometer inclusions in North American Carboniferous coals of bituminous rank

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A B S T R A C T

Results of SANS and USANS measurements performed on a series of six vitrinite samples having vitrinite reflectance (R_o) values ranging from 0.55% (high volatile bituminous rank) to 1.28% (medium volatile bituminous rank) were analyzed. Experimental data were acquired for two sample forms: platelets cut parallel to the bedding and pellets made up of randomly oriented, nearly-monodisperse particles.

Numerical analysis indicates the presence of sub-micron sized inclusions embedded in the organic matrix. For the lowest-rank vitrinites, the dominating inclusions are monodisperse are ~7–12 nm in diameter, and have concentrations of the order of 10^{17} cm^{-3}. Their shape is anisotropic, with the surface-to-volume ratio about three times larger than for a solid sphere.

The higher-rank vitrinites contain much larger monodisperse inclusions having diameters of ~50 nm, concentrations of ~10^{14} cm^{-3}, large surface-to-volume ratios, and fuzzy interfaces with the organic matrix. Inclusions of a similar size and concentration are also present in the lowest-rank sample, but are much less frequent than the small inclusions. We provisionally interpret those objects as inclusions of mineral matter, most likely associated with original plant material. The internal specific surface area (SSA) calculated for the small mineral matter inclusions is ~100 m^2/cm^3 and for the large inclusions ~2 m^2/cm^3.

1. Introduction

Over the last few decades, the small angle neutron scattering (SANS) and ultra small angle neutron scattering (USANS) techniques have been increasingly used to study porosity and pore size distribution in rocks. They have been employed in the studies of pore structure in sandstones (Radlinski et al., 1999), coals (Radlinski and Radlinska, 1999; Radlinski et al., 2001; Hinde, 2004; Radlinski et al., 2004a; Melnichenko et al., 2012) and shales (Clarkson et al., 2012, 2013; Mastalerz et al., 2012; Ruppert et al., 2013; Bahadur et al., 2014, 2015), with implications for the storage and generation of hydrocarbons. They have also been used successfully in studying properties of rocks that could be considered reservoirs or seals for CO_2 storage in geologic formations (Anovitz and Cole, 2015).

The advantage of neutron scattering techniques over other methods is that they provide pore-size-specific information for a wide range of pore sizes (diameters from ~1 nm to ~20 μm, both accessible and inaccessible) (e.g. Radlinski et al., 2004a). Importantly, SANS and USANS can also be used to quantify the pore-size-specific fraction of accessible pores under simulated reservoir conditions (Melnichenko et al., 2012; Ruppert et al., 2013). In SANS and USANS, both non-invasive techniques, the samples can have the form of solid wafers (usually of known orientation, either parallel or perpendicular to the bedding), cuttings or pellets, in the latter case averaging out the pore-orientation-related anisotropy and providing data representative for the entire sample (Radlinski et al., 2004a,b).

Small angle scattering intensity of various types of sedimentary rocks often follows the power law, which is consistent with surface fractal geometry of the pore-matrix interface (Wong et al., 1986). Low-rank coals are an exception: they exhibit markedly increased scattering in the Q-range from about 3×10^{-3} Å^{-1} to 0.1 Å^{-1} (corresponding to pore sizes of 5–100 nm) which is superimposed on the fractal scattering (Fig. 1A, B). Such "excess" scattering observed for low-rank coals is usually more pronounced in small-angle X-ray scattering (SAXS) than SANS spectra (e.g. Radlinski and Radlinska, 1999; Mares et al., 2012). Mares et al. (2012) performed quantitative analysis of SAXS data for low-ash sub-bituminous New Zealand coals (R_o varying from 0.42% to 0.45%); they determined the possible shape of the scattering objects responsible for the excess non-fractal scattering and interpreted those objects as inorganic inclusions, most likely of plant origin. That finding

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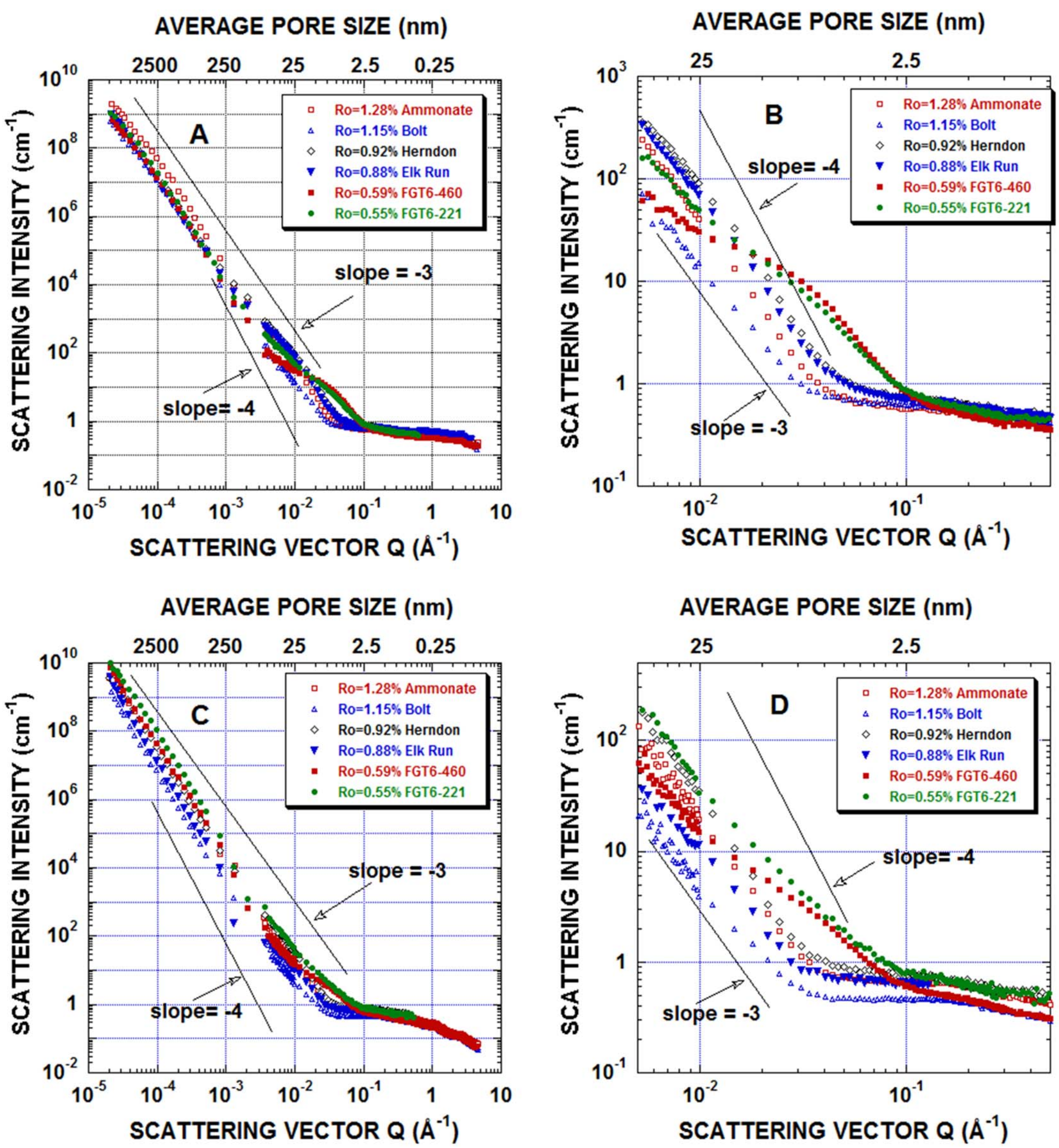

Fig. 1. A: Combined SANS and USANS data in the large-Q region for the six samples of vitrinite orientated parallel to bedding plane; B: Expanded SANS data for solid platelets; C: Combined SANS and USANS data in the large-Q region for the six pellets of vitrinite; D: Expanded SANS data for pellets. Average pore size means average pore radius calculated as $R = 2.5/Q$.

has profound consequences for the interpretation of SANS data for low-rank coals: it indicates that the mineral matter embedded in the organic matrix is organized into nanometer-scale inclusions of a particular shape and size. Scattering from these inclusions originates from the chemical inhomogeneity of the solid matrix of coal rather than the presence of porosity; it superimposes on the fractal-like scattering from the pore - organic matrix interface and, importantly, must be treated separately from the standard analysis of porosity.

This report is part of a broader study on the nature of porosity and pore size distribution in pure vitrinite, performed to eliminate the issue of maceral composition from the rank- related microstructural considerations.

2. Techniques

SANS data were acquired using the SAND instrument at the Intense Pulsed Neutron Source, Argonne National Laboratory (Thiyagarayan et al., 1998). The time-of-flight SAND instrument (now decommissioned) used a wide bandwidth of neutrons with wavelengths in the range from 1 Å to14 Å, a large position-sensitive area detector and a wide-angle bank of detectors. Neutron beam diameter at the sample position was 8 mm. Such a configuration enabled measurements up to a scattering angle of 35°, which covers a Q-range from 0.004 Å^{-1} to 4 Å^{-1} in a single run, where Q is the scattering vector.

USANS measurements were performed using instrument S18 at the High Flux Reactor in Grenoble (Hainbuchner et al., 2000). Experimental results were reduced to pinhole geometry following standard techniques (Lake, 1967). Theoretical and practical aspects of SANS and USANS techniques applied to rocks are described in detail in Radlinski et al. (2004a) and Radlinski (2006).

Ultimate analysis of the vitrinite samples was done according to the standard ASTM procedure (ASTM, 2016). For petrographic analysis, samples were mounted into polished blocks and prepared following standard procedures (ICCP, 1963).

3. Coal samples

Measurements were performed on vitrinites originating from six Carboniferous coals from the Illinois Basin and Appalachian Basin (with R_o values from 0.55% to 1.28%, corresponding to coal rank ranging