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Full Length Article

Effect of the properties of Silurian shales from the Barrandian Basin on their methane sorption potential

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HIGHLIGHTS

- High-pressure methane isotherms were measured on Czech Silurian shale samples.
- Maximum measured excess sorption and Langmuir sorption capacity were used.
- The methane excess sorption shows a positive correlation with TOC and clay contents.
- The highest sorption capacity was in shales with the lowest volume of micropores.
- No correlation was observed between maturity and methane sorption capacity.

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ABSTRACT

High-pressure methane sorption isotherms were measured on seven representative samples of Silurian shales from the Barrandian Basin, Czech Republic. Excess sorption measurements were performed at a temperature of 45 °C and at pressures up to 15 MPa on dry samples, using a manometric method. Experimental methane high-pressure isotherms were fitted to a modified Langmuir equation. The maximum measured excess sorption parameter (n_{max}) and the Langmuir sorption capacity parameter (n_L) were used to study the effect of TOC content, organic maturity, inorganic components and pore size distribution on the methane sorption capacity. The values of n_{max} ranged from 0.050 to 0.088 mmol.g^{-1}, and the values of n_L ranged from 0.068 to 0.133 mmol.g^{-1}. The studied shale samples with random reflectance R_r of graptolite 0.56–1.76% had a very low TOC content from 0.34 to 2.37 wt% and dominant mineral fractions. Illite was the prevailing clay mineral (0–51%). Organic matter of the Silurian black shales was consisted of residues of graptolites, chitinozoans, two types of bitumen including dispersed and massive bitumens, recycled organic matter, and organic detritus. In the shales, the occurrence of fractures parallel with the original sedimentary bending was highly significant. A greater proportion of fragments of carbonaceous particles of graptolites and bitumens in the Barrandian shales had a smooth surface without pores. The sample porosity Por_{calc} ranged from 4.6 to 18.8%. In most samples, the micropore volumes were markedly lower than the meso- and macropore volumes. No relation has been proven between TOC-normalized excess sorption capacities or the TOC-normalized Langmuir sorption capacities and thermal maturation of the shales. The methane sorption capacities of shale samples show a positive correlation with TOC and a positive correlation with the clay content. The assumption that the sorption capacity is a function mainly of the microporous system of shales was not confirmed. The highest sorption capacity was observed in shale samples with the lowest volume of micropores and the highest TOC content, indicating that the organic matter content and the microporosity of clay minerals are the principal factors affecting the sorption capacity of shale samples.

1. Introduction

Although shale gas-bearing deposits have a markedly lower gas content than coal deposits, great attention has recently been paid to shale gas as a new potential source of fossil energy. Shale gas extraction is considered to be quite economical, despite the lower sorption capacity of shales, which is only about 10% of coal sorp-

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tion capacities [1]. A common feature of these unconventional sources of energetic gases – coalbed methane and shale gas – is a porous system bearing the collector properties. On the basis of present-day experience, it has been suggested that shale gas consists of a "free" gas, compressed in pores and fissures with no interaction with the shale matter, together with gas sorbed in the organic and mineral components of the rock, and gas dissolved in the deposit liquids [2,3]. The sorbed gas, which is crucial for the long-term stable production of shale gas [4], includes gas adsorbed in micropores, gas adsorbed on the surface of meso-, macro- and coarse pores, and gas dissolved (absorbed) in the macromolecular structure of kerogen and bitumen [5,6]. The sorption capacity is determined in the laboratory by measuring the amount of methane absorbed in a shale specimen at a pressure and a temperature corresponding to *in situ* conditions, using high pressure sorption. According to the principles of reversibility of adsorption/desorption, this amount should be roughly related to the amount of gas released by forced degassing.

The capacity of the porous system of shale is closely connected with its composition, i.e., with the abundance of organic (bitumen and zooclasts) and inorganic matter in a heterogeneous mixture. The organic matter is considered to be a major source of gas, which originated from thermogenic or biogenic processes. The amount of deposited gas is connected with the type and the abundance of organic matter, its degree of maturation, and its porosity. Porous clay minerals as a part of the inorganic fraction are not a source of gas, but through their sorption properties they are an important factor affecting the sorption capacity of the shale [7,8]. The total sorption capacity corresponds to the combined effect of the porosity of the organic matter and the clay minerals. Shale samples with a strong effect of total organic carbon (TOC) usually have a low concentration of clay minerals, and shale samples with a weak effect of TOC usually have a high concentration of clay mineral [2,9]. According to numerous studies, the contribution of clay minerals to the total sorption capacity is quite significant in dry shale samples with low TOC [3,10–12].

Shales have a very complex system of pores of various types and with a wide range of size classes. However, as far as sorption ability is concerned, micropores with diameters < 2 nm are generally considered to be the most important class. They have higher sorption energy than large pores [13], and therefore have a dominant effect on the shale sorption capacity. This has been confirmed by numerous studies [9,10,14,15]. Shale samples with high degrees of maturation and with high TOC levels have high sorption capacity. This can be explained by the formation of more micropores in the process of organic matter degradation and hydrocarbon formation with increasing thermal maturation [10]. Chalmers and Bustin concluded that the TOC content is the primary factor affecting the sorption capacity, and that the type of organic matter and its maturation can be considered as secondary factors [14].

The sorption capacity of clay minerals and clay-rich rocks has also been studied. It was found that the sorption affinity of methane is markedly stronger for organic matter than for clay minerals [4,12], though Ross and Bustin [10] determined that the sorption capacity of illite and montmorillonite was comparable with the sorption capacity of shales with high TOC levels. Some authors have found positive correlations between content of clay minerals and sorption capacity [3,12], while other authors have not observed a correlation of this kind [11,16].

Most published studies on the sorption capacity of shales deal with North American shales [17]. Extensive research has also been presented on Chinese shales [2,16,18–20]. Sorption experiments on European shales have only recently been reported [1,3,11,21–23]. The Czech Republic has been characterized only marginally for the potential of its shale gas deposits. The Prague Basin (Barrandian) is a locality where, according to the Czech Geological Survey, the presence of gas-bearing shales can be expected.

The present study has set out to determine the sorption capacities of selected shale samples from the Barrandian Basin, and to find connections with their petrographic, textural and mineralogical properties. The data obtained for the shales should also contribute to the European database.

2. Experimental

2.1. Samples

Representative samples of dark Silurian shales were taken from five quarries and outcrops located in the central part of the Barrandian basin (Fig. 1) from the basic Silurian lithostratigraphic formation (Fig. 2). [24,25]. Two samples were collected from the Litohlavy formation (S1 and S2), four samples from the Motol formation (S3, S5, S6 and S7), and one sample from the Kopanina formation (S4). The samples were collected after removing an approximately 50 cm upper layer of the outcrop. The basic geochemical properties are presented in Table 1.

2.2. Experimental methods

2.2.1. Petrographic analysis of dispersed organic matter

The reflectance of dispersed organic matter was measured on polished X-Y sections of rocks slabs, i. e. perpendicular to the banding or the foliation of the rocks studied here. Due to the absence of vitrinite in the Silurian Barrandian shale, the samples were measured for random reflectance (R_r%) of graptolite in normal light at λ = 546 nm, using a Carl Zeiss Axio Imager M2m microscope with a spectrometer with oil lenses (magnification of 50× and 100×). Yttrium-aluminium-garnet (R = 0.900%), gadolinium-gallium-garnet (R = 1.717%), cubic zirconia (R = 3.06%), and strontium-titanate (R = 5.34%) reflectance standards were used for calibrating the measurements. The composition of the organic particles differentiated by morphology and by optical properties into groups of graptolites, chitinozoans, bitumens, recycled organic matter and organic detritus [26–30], was determined using an Olympus BX51 microscope in normal light and fluorescence mode and with dry and oil lenses (magnification 40× and 100×) and a Pelcon point counter according to the principles of maceral analysis described in ISO 7404-3 [31]. The graptolite group contains lath-shaped fragments, a section of cortical tissues, and occasional remnants of thecae 10–300 μm in size. They were composed of a chitinous substance or a collagen-like protein that exhibited optical properties in reflected light similar to the properties of vitrinite. Chitinozoans occur as single microfossils or as chains of microfossils. They are flask- shaped or bottle-shaped, 50–250 μm in length, and they consist of an oral tube and a chamber with appendices. Massive (non-granular) and granular solid bitumen accumulates in intergranular pore spaces and microfractures. Non-granular bitumen can be observed in shales as rounded, oval or irregular bodies, while granular bitumen has an irregular formation and is also abundant as matrix bitumen. Highly reflecting fragments of zooclasts, bitumens, and other organic types of apparently allochtonous nature were classified as recycled organic matter. The last type of organic matter was organic detritus of unknown origin with particles below 10 μm in size.

2.2.2. TOC and mineralogical analysis

The elemental organic composition was determined using a CHNS/O micro-analyzer (Thermo Finnigan Flash FA 1112). TOC was determined by elemental analysis after inorganic carbonates had been eliminated with the use of 1 N HCl heated to 80 °C.