Determination of the pore space parameters in microporous rocks by means of thermal methods

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ABSTRACT

The aim of the study was to examine the possibility of determining the pore space in microporous rocks using a set of methods: differential thermal analysis, retort distillation, and Dean-Stark. These methods are used for low-permeability rock containing hydrocarbons, such as shale gas, shale oil and tight gas. By using these methods it is possible to specify the amount of water contained in the sample and, consequently, determine the different levels of saturation and porosity.

The study showed shale porosity values ranging from 0% to more than 5%. It was found that the samples with the highest porosities in the combustion process evolve relatively large amounts of carbon dioxide, which indicate that the porosity is related to the presence of organic matter. There was no complete correlation between the various methods' test results. It seems that for determining the porosity of tight shale rocks, the most effective would be the use of several complementary methods.

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1. Introduction

In recent years, the high importance in fuel industry is attributed to the so-called "unconventional gas". From an economic point of view, unconventional shale reservoirs are more difficult and less profitable to operate than traditional (conventional) deposits. They are characterized by extremely low petrophysical parameters, such as porosity and permeability, representing a tremendous challenge for the oil industry. The specific nature of these reservoir rocks is determined by the analytical difficulties and technical challenges of producing natural gas.

Effective porosity, saturation of rocks with water, oil and gas, as well as the permeability of the basic reservoir parameters are necessary to evaluate the quantity of hydrocarbons and reservoir efficiency. In the case of gas accumulated in the clay-slate rocks (so-called "gas shale") the evaluation of the above parameters is a huge technical challenge. In the classical approach, shale was treated as a sealing rock, due to its very low effective porosity and permeability (from hundreds to thousands of times smaller than in conventional reservoir rocks). The consequence of low porosity is correspondingly low content of reservoir fluids. Currently, the approach to shale has changed in a fundamental way; the shale rock is treated as a source, sealing and reservoir rock. The porosity of shales also has a different character (Milner et al., 2010; Such et al., 2011). It is related to

(1) pores in the organic substance, (2) intragranular pores, and (3) intergranular pores.

n case of the first mentioned pores, in the organic matter, they refer to the isolated intrakerogen pores. As they are very small and not effectively connected to natural and hydraulic fractures, they result in huge challenges in gas production. Hence, the primary question is the separation of organic and inorganic porosity in shales. Organic porosity is critical in terms of accumulation and production of hydrocarbons, while in the pores of the inorganic genesis predominantly accumulates water (Milner et al., 2010). This separation and potential hydraulic discontinuity between brines and hydrocarbons calls into question standard concepts of pore saturation and the relative mobility of pore fluids in the rock (Handwerger et al., 2011). Another challenge in the case of shale rock is to distinguish "free" pore water from "bound" or "matrix" water. To understand the nature of unconventional reservoir rock properties there is a need not only to reconsider the meaning of previously defined concepts of the pore space, but also to develop new methods for measuring the pore space. Petrophysical analysis of fine-grained shale rocks should focus on the evaluation of actual reservoir capacity of rocks and assess the fluids transport.

In order to evaluate the shale rock hydrocarbons capacity it is essential to determine (Such and Leśniak, 2011): (1) total porosity (including isolated and interconnected pores), (2) effective porosity (sum of interconnected pore space), (3) % pore volume occupied by water, (4) % pore volume occupied by liquid hydrocarbons, (5) % pore volume occupied by dispersed organic matter.

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To test unconventional shale reservoirs, there are used traditional methods of analysis for conventional reservoir rock, modified however, for these particular needs (e.g., the Dean-Stark fluid extraction method or mercury porosimetry), as well as other methods, e.g., gas adsorption, thermal analysis or FTIR spectroscopy, used to assess the composition of fluids present in the sample. The most commonly used techniques for assessing petrophysical properties of shale are the above-mentioned methods of Dean-Stark extraction and retort extraction. These methods do not provide the most consistent results of the total porosity, and therefore there are often carried out experiments aimed to compare and link the results obtained from different methods (Handwerger, 2012).

The measurements are usually performed on core or crushed samples, and the legitimacy of the use of one selected technique is the subject of a number of comparative studies and remains controversial (Sondergeld et al., 2010; Clarkson et al., 2011). Nanopores, and virtually no diffusive flow means that in the case of tight shales the measurement of pore space is incomplete, and the results obtained are unique. It is possible, however, to obtain the parameters of pore space in the shale rocks by mercury porosimetry, according to the methodology developed at the Institute of Oil and Gas (Darłak et al., 2011). Such and Leśniak (2011) suggested to perform all analyses, except for bulk density, on the crushed material (even porosimetric measurements (Such, 2012)), which would give a better reproducibility of the results.

2. Scope and methods of the analysis

2.1. Samples of shale rocks

Seven, fine grained clastic sedimentary rock samples, were selected for the analysis. They were collected from outcrops or drill cores in Poland, Czech Republic and Estonia. The characteristic of these samples is presented in Table 1. The mineral composition presented in the table was determined basing on microscopic observations. In this table the total organic carbon (TOC) content is also included. The TOC value (wt%) is a result of Rock Eval analysis (pyrolysis technique). Gas generation potential of gas shales is mostly generated by the total organic carbon content, type and maturity of the organic matter.TOC represents the concentration of organic matter in rocks by the weight percent of organic carbon. Samples 3 and 4 have low organic carbon content ($< 1\%$), samples 1, 2 and 7 represent rocks of TOC considered the minimum for shale gas reservoirs (1–2%), while Estonian rocks' (sample 5 and 6) TOC is very high ($> 12\%$). In case of Kukersite oil shale (sample 6) most of the organic matter is derived from fossil green alga (Elenrum et al., 2008).

To complete the information on the mineral composition of the examined rocks and to determine the presence of different forms of water, the thermal analysis (TA) was performed. The analysis in a Dean-Stark apparatus was performed to determine the water content in the samples, including the capillary bound water in clays. The retort method allowed the extraction of liquid and gaseous hydrocarbons and pore water, hygroscopic and crystallization water.

2.2. Analysis of mineral composition

Thermal analysis (TA) enables determination of mineral composition of the rock samples containing clay minerals, as well as water content in the sample (hygroscopic and chemically combined). For the purpose of this research, the TA analysis was performed in the Institute of Geonics in Ostrava, with use of SETSYS 24 Evolution by Setaram. The samples of about 50 g were heated to 1200 °C with heating rate 10 °C/min.

Thermal analysis (TA) is a general term, which covers a variety of techniques, recording the physical and chemical changes in a substance as a function of temperature (Lever et al., 2014). Two of the ranges of TA techniques were applied here: thermogravimetry (TG or TGA) and differential thermal analysis (DTA). TG measures the change in mass of a material as a function of time over a temperature range, using a predetermined heating rate. DTA is a technique where the temperature difference between a sample and a reference material is measured as a function of time or temperature. A DTA curve provides data on the changes in the sample, either exothermic or endothermic (e.g., crystallization, melting, dehydration, organic matter combustion, etc.).

The interpretation of TG and DTA curves in case of rocks is not as easy as in case of pure minerals. In composite material, the decomposition temperatures could be shifted and some thermal effects overlap. However, based on examples of the use of thermal methods in geology (Földvári, 2011), particularly with regard to the interpretation of mineral composition of clay rocks, the obtained thermograms were interpreted.

2.3. Analysis in Dean-Stark apparatus

The Dean-Stark solvent extraction is applied commercially, according to the methodology outlined by the Gas Research Institute (GRI method) (Handwerger, 2012). The method enables water extraction from the sample, which helps in total porosity determination. It is possible to separate from the rock sample capillary and interlayered water associated to the clays. The GRI method is a multiple-weeks process of extraction and drying of rock core samples. The results obtained by this method are often affected by error, consisting in the extraction of more water than would be justified by taking into account free and capillary water (Handwerger, 2012). This could be explained by the contamination with atmospheric water or release of the hydroxyl water from the crystal structure of clay minerals. In the studies described in this paper, the rock material, before being placed in a Dean-Stark apparatus, was grinded. This approach is in line to the methodology proposed by Handwerger et al. (2011) as well as Such and Leśniak (2011). The fragmentation of the sample prior to extraction facilitates getting solvent (toluene) into the pores in the rock.

Upon heating, the water comes out of the sample, together with a solvent (toluene). The azeotropic mixture evaporating in the form of vapors passes into the flask and the reflux condenser, where it is condensed. The condensed mixture is collected in a vertical tube with a scale where it is partitioned into two layers by cooling to room temperature. Toluene as a liquid of lower density accumulates in the upper layer. The solvent is recycled to the reaction system automatically by the diagonal tube, whereas water can be drained down periodically into the vessel (Fig. 1). For the purpose of this study, the crushed shale samples (to a particle size from 0.5 to 2 mm) were weighed and, sequentially, placed in the Dean-Stark apparatus. Each sample was flooded with toluene and then heated to the boiling point of the solvent (in case of toluene it is 115 °C). The experiment was completed after the stabilization of the condensed water volume.

The pore volume in the rock, occupied by water, was calculated according to the following formula (API, 1998):

$$W_w = \frac{V_w \rho_w}{W_s} 100\%$$

where W_w is the pore volume in the rock, occupied by water [%], V_w is the volume of separated water [cm^3], ρ_w is the density of distilled water [g/cm^3] (0.9997 g/cm^3 in room temperature), and W_s is the initial weight of sample [g].