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WETTABILITY OF SHALE ROCK AS AN INDICATOR OF FRACTURING FLUID COMPOSITION

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Abstract: Shales have become one of the main unconventional gas resources in the world. However, physicochemical properties of rocks are still at the center of research. There have been conducted major researches in wettability of shales by fluids and advances in understanding and control of shale rock wettability. Also influence of interfacial phenomena on a production capacity of reservoirs have been made. The aim of this study is to find a relationship between type of fracturing fluid used during shale gas recovery and shale rock wettability. The study is the first step to evaluate conditions, under which wetting occurs most intensely, how it can be controlled by changing a composition of fracturing fluid and how this composition effects the wetting mechanism. We present a characterization of porous materials by a capillary rise method to study shale wettability by water, oil and other fluids. This work describes the experimental contributions to understand the shale rock/fluid interactions through inquire of fluid role in wettability of shale rock.

Keywords: *shale rock, wettability, porous materials, hydraulic fracturing, contact angle*

Introduction

This paper investigates interaction of shale rocks and liquids that may be used as a base of fracturing fluid. So far, such studies have not been conducted using Polish shales due to lack of shale gas recovery in Poland. Recently, exploration boreholes, which allow acquiring of this type of samples, have been drilled. Their analysis is required before conducting applied research. Shale rocks wetting by fracturing fluids should be fully described, what would help to avoid application of unsuitable technologies resulting in decrease of shale gas recovery. Nowadays, the relevance of wettability parameter is more explicitly recognized. Most national laboratories do not pay much attention to wettability of shale rocks. However, it should be noted that wettability plays the major role in gas recovery. This parameter can be considered relevant due to the fact that a large surface area per unit volume of shale rock is exposed to the

fluids (Raza et al., 1968). Therefore, this paper focuses on influence of selected experimental fluids on reservoir to understand wettability of the Polish shale rock.

Many factors have the influence on the shale rock/liquid interactions during fracturing. Considering the intricacy of reservoir, each reservoir system should be taken as an individual case, since intelligibility of these interactions leaves many doubts (Cuiec, 1984). The leading property of rocks is wettability, which affect the choice of an appropriate method for fracturing and amount of hydrocarbon recovery. Hydraulic fracturing (HF) is a method widely used for fracturing rocks in the production of natural gas (Howard et al., 1970). It is based on pumping to a drillhole the fracturing fluid under high-pressure containing a proppant as well as other additives. The first stage of gas recovery from a reservoir is drilling of wells into a gas-bearing rock. This is achieved by rotary drilling using the drilling fluid (Jones et al., 1996) that must fulfil functions such as cooling the drill, having the correct rheology and right physicochemical characteristics and environmental requirements. The use of water-based drilling muds is preferred (Maitland, 2000). The fracturing fluid consists mainly of water and proppant (99.5%) and chemical additives (0.5%). The most general fracturing fluids use natural polymers, such as guar (Gittings et al., 2000). These fluids are injected under high pressure to the rock generating the fractures. The proppants like sand, ceramic materials or resin coated sand are introduced to keep the induced hydraulic fractures open (Mader et al., 1989).

Hydraulic fracturing is an advanced technology, commonly used for many decades with lot of successes. However, the method is subjected to numerous disadvantages that should be eliminated. They include the liquid waste management, investment and environmental costs, risk of contamination of surface water and groundwater, methane emission and wide social misunderstanding over any activities related to extraction of shale gas (Piszczyk et al., 2014). However, some of them generate the economic, environmental and social problems. The main technological problem of extracting gas from the Polish shales is a fracturing fluid compatibility with the shale reservoir (Rogala et al., 2013). This applies both to stimulation of reservoir to the gas flow and prevention of the flow blocking. Due to fracturing fluid/shale rock compatibility issues, the estimations of amount of gas contained in the fractures and available to extraction are not precise. Brown (1956) was one of the first, who found out that differences in shale gas recovery from various reservoirs may, in part, be a result of narrow differences in wettability.

Wettability

In this study, wettability is primarily discussed in the context of shale gas recovery using hydraulic fracturing. Hydraulic fracturing has been widely used for over sixty years and accounted the most of world gas production (Morrow, 1990). Wettability of reservoir is not easily defined property. Classification of shale reservoirs as either water-wet or oil-wet is an appreciable oversimplification. Borysenko et al. (2009) demonstrated that the shales become oil-wet due to the presence of organic matter or

subjection to polar compounds in the water reservoir. Consequently, there is a risk that one would be unable to choose the proper fracturing fluid, and gas production could be lower than expected. There are many factors which have significant impact on wettability, such as the surface roughness, contaminations, fluid composition, etc. The differences in wettability may result from differences in the part of the surface that has preferentially oil-wet and water-wet (Brown, 1956). Many reservoir engineers consider in practice that most reservoirs are strongly wet by water (Morrow, 1990). The scientific substantiation for the Morrow (1990) work was that water preferentially filled the reservoir trap. Also, adsorption of polar compounds from the fluids largely effects on the wetting properties of reservoir surfaces. The capillary forces keep water in the fractures (Morrow, 1990), and the films on the porous surface indicated that wetting property of solids is prevailed by the outermost layer of particles. The further research discovered some rocks, which had flow properties indicating that they were oil-wet (Brown, 1956). The certain reservoirs have multiphase flow properties, which signify that they characterize intermediate wettability. Borysenko et al. (2009) examined that many shales differ in terms of wettability. Also the differences in mineralogy and texture of shale rock influence variant affinity for water and oil, ranging from hydrophilic to hydrophobic. Dixit et al. (1997) studied the influence of the heterogeneity on wettability in the reservoir on two phase oil–water flow. They elaborated a three-dimensional network model which entertains wettability changes as a phase trapping, film flow and variations in the advancing and receding contact angles. They discovered, that applying various combinations of fluid displacement mechanisms with properties of the porous material allowed them to reproduce the extensive variety of the oil–water system. This indicates, that the progress relates to the interfacial phenomena, surface chemistry and flow nature for oil–water systems in the porous media.

Contact angle - capillary rise method

Wetting and adhesion phenomena play an important role in nature and technological processes, such as beneficiation of materials. In all these processes, the free surface and interfacial energies, that result from the non-compensated phase interactions at the surface interface, play the fundamental role. Many physical and chemical processes occur either at the interfaces or surfaces. The wettability of surface depends on the surface tension of liquid, surface free energy of solid and solid-liquid interface. Contact angles formed by gas, liquid and solid phases play an important role in many fields of science and technology as well as in nature (Kowalczyk and Drzymala, 2011).

Wetting of a solid surface is described by the Young equation, which determines the equilibrium relationship between the contact angle (θ) and three interfacial surface tensions (σ_{lg} , σ_{sl} , σ_{sg} of the liquid-gas, solid-liquid and solid-gas, respectively) (Adams, 1990):

$$\cos \theta = \frac{\sigma_{gs} - \sigma_{sl}}{\sigma_{lg}} \quad (1)$$

When the liquid easily spreads the solid surface it means that the contact angle is zero and the solid is hydrophilic. On the other hand, when the liquid runs off the solid surface, the contact angle is greater than 0° and the solid surface is hydrophobic (Adamson and Gast, 1997; Drzymala, 2007).

The Young equation is applicable only on homogenous and flat surfaces. If we want to use the Young equation for a solid surfaces with mechanical roughness and chemical heterogeneity, then we have to add an aforementioned corrections factors into this equation.

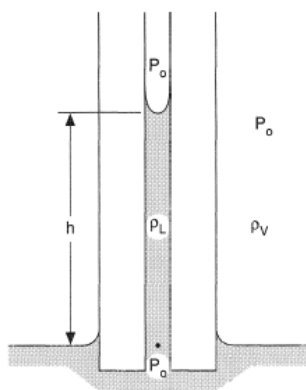


Fig. 2. Capillary rise method

There are many methods of contact angle measurements including sessile drop, drop shape on the solid surface, captive bubble, capillary rise, capillary pressure, force of detachment of air bubble from solids in liquid and many others (Drzymala, 2007; Chau, 2009). This paper is focused on a capillary rise method (Fig. 2) called the Washburn method (1921). The method depends on water saturation measurements and related capillary pressures and provides that fluid movement in the capillary occurs under the capillary pressure. The Washburn method is based on the relationship between time of penetration and wettability of solid. The wettability test method proposed in this paper is based on the macroscopic observation of affinity of liquid to the shale rock. The surface properties of solids are defined by using the contact angle of liquid or critical surface tension. For the same material, the value of contact angle depends on the pore diameter and roughness. For contact angle determination the modified Washburn equation was used (Holownia-Kedzia, 2012):

$$\cos \theta = K \cdot \frac{t_0}{t_1} \quad (2)$$

where

$$K = \frac{\gamma_0 \cdot \eta_1}{\gamma_1 \cdot \eta_0}, \quad (3)$$

and t is time of penetration, γ surface tension, η viscosity of reference (0) and investigated (1) liquids. To have the accurate determination of a contact angle it is necessary to select a suitable reference liquid. The reference liquid is the one with known value of contact angle (Chander et al., 2007; Kowalczyk and Drzymala, 2012).

Material and method

This work is based on shale rock samples originated from Baltic Basin, Pomerania, Poland, derived from the Ordovician period. Shales are source rocks for unconventional hydrocarbons. Shales are characterized by dark color (Fig. 3) and relatively high fragility that usually indicates a high content of natural gas.



Fig. 3. Shale sample from the Baltic Basin, Pomerania, Poland

The contact angle experiments by the capillary rise method were carried out by an apparatus shown in Fig. 4. All the experiments were conducted at temperature 273 K. All shale rock samples (with the fraction less than 0.425 mm) were inserted into capillary tubes with an inside diameter of 4 mm. The samples in the glass capillaries were accurately weighed (each capillary tube was filled by the same portion of porous material), and then was packed with a shaking machine until to obtain the same height in all capillaries. The capillary tubes were placed in a stand and the measurement was started. The measurements were recorded by a computer software (SNC Program Standard Radwag). The results are presented in numbers as square of mass gain in capillaries as a function of wetting time. The contact angles were calculated using Eq. 2.

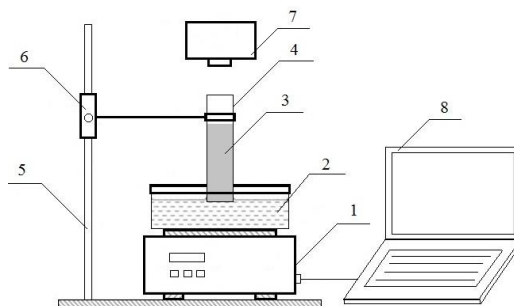


Fig. 4. Laboratory set-up used for measurements of contact angle by capillary rise method
 1 – electronic balance, a covered container with wetting liquid, 3 – shale particle bed, 4 – column,
 5 – stand, 6 – micrometric screw, 7 – camera, 8 – computer (Dang-Vu et al., 2005)

Results

Most petroleum engineers accepted hypothesis, that all reservoirs are water-wet. Problems with shale gas extraction led to the focus on the properties of rocks. Many attempts were made to determine whether reservoirs are strongly water-wet. The wettability of porous materials proved that wettability of the porous matrix medium depends on the distribution of liquid in the pores. This process has influence on the conditions, in which gas is extracted.

Table 1. Contact angles determined by sessile drop method to choose reference liquids

| Fluid | Contact angle, deg |
|-----------------|--------------------|
| Cyclohexane | 4 |
| Water | 82 |
| Diesel oil | 45 |
| Methanol | 32 |
| Aniline | 49 |
| Benzyl alkohol | 40 |
| Ethanolamine | 52 |
| Ethylene glycol | 63 |
| Hexanol | 20 |

The success of the capillary rise method relies on the correct choice of the reference liquid. Therefore, the first step was to determine the reference liquid essential for the Washburn technique. The measurements were achieved by simply sessile drop method. In this experiment, the shale sample was mechanically compressed to obtain the pastille. Then, the contact angles formed by sessile liquid drops on the smooth homogeneous solid surface were determined. Table 1 shows the contact angle of shale in the presence of different liquids. Among all the examined liquids, cyclohexane with a low surface tension of 25.3 mN/m has the lowest contact angle and wets the shale

rock best. In the literature, it is reported that cyclohexane is the most commonly used reference liquid (Yuan and Lee, 2013). Cyclohexane was chosen among the examined liquids as the reference liquid to find out if tested shale rock is oil-wet or water-wet.

It is important to notice that the wetting velocity depends on the liquid density, viscosity and surface tension. There are two steps of shale rocks wetting. The first step is when liquid fills the pores vertically and the second when it moves horizontally filling all volume of shale particle bed until the mass is constant (Fig. 5). Table 2 presents physicochemical properties and contact angles of tested fluids.

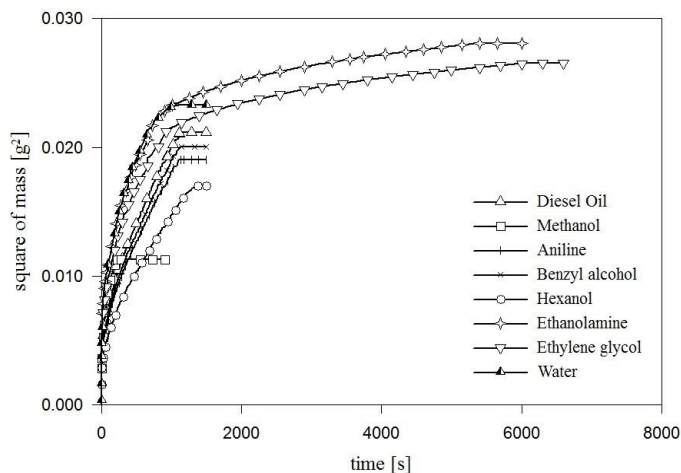


Fig. 5. Square of mass as a function of wetting time for all tested in this work liquids

Table 2. Physicochemical properties and calculated contact angles of shale in the present of different tested liquids for cyclohexane as reference liquid

| Tested liquid | Viscosity, η , mPa·s | Surface tension, γ , mN/m | Penetration time, t , s | K (Eq. 3) | $\cos\theta$ | Calculated contact angle, θ , deg (Eq. 2) |
|-----------------|------------------------------|--|------------------------------|----------------|--------------|--|
| Cyclohexane | 0.980 | 25.3 | 257 | reference | 1 | 0 |
| Water | 1.005 | 72.6 | 1102 | 0.36 | 0.083 | 85 |
| Diesel oil | 3.450 | 28.4 | 1120 | 3.14 | 0.720 | 44 |
| Methanol | 0.614 | 22.6 | 220 | 0.70 | 0.819 | 35 |
| Aniline | 4.40 | 42.90 | 1103 | 2.65 | 0.617 | 52 |
| Benzyl alcohol | 5.04 | 39.00 | 1120 | 3.34 | 0.766 | 40 |
| Ethanolamine | 24.10 | 48.89 | 5313 | 12.73 | 0.616 | 52 |
| Ethylene glycol | 21.00 | 47.00 | 6115 | 11.53 | 0.485 | 61 |
| Hexanol | 4.59 | 24.00 | 1343 | 4.94 | 0.945 | 19 |

Contrary to expectations, investigated shale rock is oil-wet. This observation was explained by the differences in oil-water wetting properties of solid surface. The contact angle for diesel oil is almost two-fold smaller (44°) than that for water (85°). Taking into account only wettability, the best choice would be fracturing fluid based on

the diesel fuel. However, during shale gas extraction it is avoided to use of hydrocarbons as a base fracturing fluid. The lowest contact angle is observed for methanol (35°). Also, for hexanol and benzyl alcohol, the values of the contact angles were low against the background of the tested liquids. It is better to use an aqueous fracturing fluid containing e.g. methanol (which has smaller angle than the diesel oil) and/or surfactants.

Conclusions

In this work wettability of Polish shale rocks using the capillary rise method was presented. The results showed that the investigated shale rock is oil-wet. This observation was explained by the differences in oil/water wetting properties of solid surface. The contact angle for diesel oil was almost two-fold smaller (44°) than that for water (85°). The lowest contact angle was observed for methanol (35°). It is better to use an aqueous fracturing fluid containing e.g. methanol (which has smaller angle than the diesel oil) and/or surfactants. This work can help to determine the direction of future research to find a way to get the most effectively control of reservoir wettability as well as whether the substances, which are currently used during hydraulic fracturing, are suitable for Polish shale and their components have beneficial effect on wettability behavior.

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