Free and Bound Water Content in Tight Rocks of Bazhenov Formation

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Abstract. The paper presents data on water content separated into free, physically and chemically bound types for a collection of core samples from the Bazhenov formation. The rock samples came from 3 wells of Nizhnevartovsk arch, Western Siberia, Russian Federation. Each rock sample was a part of whole core with the maximum preserved natural water content. A suite of modern laboratory techniques includes evaporation method, derivatographic, and hygrometric studies. The results show that the content of chemically bound water (0÷6.4 wt.%) exceeds that of free (0÷1.87 wt.%) and physically bound (0÷1.0 wt.%). For the first time, we present the water content of mono-, poly-, and capillary condensation water obtained from the interpretation of adsorption isotherm. These data made it possible to draw a meaningful conclusion on mixed wettability of Bazhenov formation rocks.

1. Introduction

According to the EIA, Bazhenov Formation (BF) contains the most considerable amount of technically recoverable oil resources in the world [1]. The BF occupies a territory of the West Siberian Plate in the Russian Federation at depths of 2÷3 km with a relatively stable thickness of 15÷50 m [2]. The sediments of the BF are represented by black bituminous, predominantly siliceous deposits, sometimes flaggy, more often massive with a certain amount of fish detritus along bedding planes, with phosphorite imprints, and interlayers of clayey limestone in the bottom part [3, 4]. To date, a reliable determination of water saturation and content is one of the important, but unsolved problems in the development of oil assets within the BF. Therefore presented research aimed at improving the efficiency of using its enormous potential is of indisputable relevance.

Over the entire period of oil field development within the framework of BF, neither water-saturated interval nor water-oil transition zone of the reservoir was identified anywhere in producing wells. The majority (75÷80%) of BF rock samples are considered to be hydrophobic [5, 6]. Based on this experience, one can assume that BF rocks can hold only bound water of clay minerals and organic matter. However, it is not possible to formally establish the absence of pore solutions in BF rock samples of “dry” state, since the rock samples have a finite electrical resistivity (less than 800 Ohm·m according to available lateral log data), that is, conduct an electric current and salts cover a large number of BF rock samples after drying. Thus, the presence of various types of water, including both free and bound, can be expected in BF rocks.
The free water is a most loosely held and may be producible as a liquid or condensate water during production. The loosely bound water, although almost impossible to recover, has hydrogen, and so neutron porosity logs are sensitive to it. It is essential to know its volume to make neutron logs more useful to measure the “total” water and organic content, to quantify the hydrocarbon saturation and effective rock porosity [7-9].

Chemically bound water is part of the crystal structures of minerals and is firmly held there due to the chemical forces. The content of strongly bound water does not contribute to resource assessment and reserves estimation but has a significant influence on heat and mass transfer processes in rocks.

The goal of the study is to reliably quantitatively determine content of various water types using a suite of laboratory methods in a representative collection of 22 whole core samples (Ø 10 cm) with the maximum preserved natural pore water content.

2. Materials
The representative collection of 22 whole core samples (Ø 10 cm) with the maximum preserved natural pore water content formed a test based for investigation. The core samples came from 3 fields (Well 1, Well 2, Well 3) of BF located in the West Siberia (Russian Federation). A sampling interval was about 1 m, depth more than 2.5 km, age J3v. After sampling, all the whole cores were immediately tightly wrapped in plastic film and waxed (Figure 1a). The specimens were taken from the central part of the whole cores and analyzed within the day of paraffin shell opening to exclude the effect of drilling fluid.

Multiple core studies delivered water content that is mass fractions of water in a studied sample. The total water content separated into two parts: free water and part of physically bound water. One may trivially convert water content to water saturation by using open porosity and bulk density of the sample.

3. Methods

3.1. Water content determination
Determination of pore water content was performed using widely known methods of analysis but adapted for the BF rocks. The suite of laboratory methods includes thermogravimetric analysis (TGA), evaporation method (EM) and hygrometric method (sorption isotherm).

3.1.1. Evaporation method. EM-based on the retort principle, but featuring more accurate and reliable results [10, 11]. EM consists of taking the crushed rock sample (near 50 g), putting it in a Teflon cuvette and heating to extract the fluids, captured in a test-tube. The heating includes two pre-defined temperature steps: at 121 °C to extract the free water and at 250 °C to extract the loosely bound water. The measurement results deliver the residual pore water (total content of free and loosely bound water).
bound water) content. The salinity of the residual water was estimated using a water extract method [12].

3.1.2. Thermogravimetric analysis. We used the TGA to estimate the chemical bound water content. The measurements were carried out on a NETZSCH STA 449C Jupiter thermal analyzer combined with a Bruker Tensor 27 FT-IR spectrometer. The sample weight was 30±3 mg. The measurements were carried out in the temperature range of 40÷1200 °C in a dynamic air atmosphere. The setup recorded IR-spectra of the emitted gases at wave numbers 650÷4000 cm⁻¹ with a resolution of 4 cm⁻¹.

3.1.3. Hygrometric method. Obtaining the adsorption isotherm by the hygrometric method is based on the study of the equilibrium of the studied rock with water vapor above the sample. Due to the lack of core material, the studies covered only 19 BF rock samples. At each step, an aqueous electrolyte solution fills the bottom of the exciter. After some time in the closed volume of the exciter at a constant temperature a particular (user-defined) pressure ratio P/Pₚ (P — the pressure of water vapor in equilibrium with the rock at a given temperature; Pₚ — the pressure of saturated water vapor at the same temperature) develops. The value of P/Pₚ varies from 0 (for absolutely dry air) to 1 (for extremely water-saturated air). An operator places the sample understudy in the desiccator above the solution level and determines its moisture content at a given P/Pₚ over time. Thermodynamic equilibrium delivers a strictly specified point of the adsorption isotherm. Then the same sample is transferred to another desiccator (with a different known value of P/Pₚ), get the second point, and so on for the entire range of values of P/Pₚ. As a result, the content of mono-bound, poly-bound water, and capillary condensation water can be determined [13, 14].

3.2. Mineral composition

3.2.1. X-Ray Diffraction. Rock mineral composition of the studied samples was determined by the XRD method on an automated X-ray diffractometer Bourevestnik DRON-3m (Russia). The XRD practices [15-20] suggested optimal specimen preparation technique, including crushing, mixing and drying.

4. Results and discussion

Gross mineral composition (crystalline minerals only) of the target BF rocks samples is relatively consistent with the exception of a few highly carbonate siltstone samples (carbonate content of more than 50 wt.% and clay content of 0 wt.%): silica, clay, carbonate minerals, as well as plagioclase, pyrite and rest. XRD analysis of clay-sized fractions indicates that hydrous micas (illite) are the dominant clay mineral in all wells. All samples do not contain either smectite or montmorillonite.

The free water locates in the pore space of the rocks and reduces its permeability to oil. According to the EM, the free water content varies from 0.88 to 1.87 wt.% for Well 10÷0.78 wt.% for Well 2 and 0÷1.28 wt.% for Well 3 (Figure 2). The residual water content for all samples of the target core collection changes from 0.05 to 2.34 wt.% (Figure 2) and there is no relationship between the residual pore water content and depth for the target wells. The residual water salinity reaches for Well 1 9.3±18.36 g/l, Well 2 1.23±8.75 g/L and Well 3 2.03±35.98 g/l.

Unfortunately, it is practically impossible to separate tightly bound physical and chemically bound water according to the TGA results, since the clay minerals of BF samples have different dehydration and dehydroxylation temperatures [10]. Roughly, a temperature of less than 400 °C leads to release of the crystallized chemically bound water, while at a temperature of more than 400 °C the constitutional water. The amount of chemically bound water according to TGA measurements lies in range 0.28÷1.71 wt.% for Well 1, 0.5÷6.4 wt.% for Well 2 and 0÷1.96 wt.% for Well 3 and significantly exceeds the free and loosely clay bound water content (Figure 2). The chemically (tightly) bound water comes as part of the clay structure and should be considered as part of the rock matrix, rather than a component of the saturating fluids existing in the pore network.
Figure 2. Content of free, loosely clay-bound and chemically bound water for BF rock samples from Well 1 (a), Well 2 (b) and Well 3 (c).

All the obtained sorption isotherms have S-shaped form, i.e., two inflexion points are determined by which the amount of mono-bound, poly-bound water, and capillary condensation water can be determined (Figure 3). The amount of mono-bound water in the samples ranges from 0.01 to 1.2 wt.% (average 0.4 wt.%). The amount of poly-bound water in the samples reaches values from 0.02 to 1.6 wt.% (average 0.8 wt.%). Capillary condensation water amounts from 0.15 to 3.9 wt.% (mean value 1.8 wt.%).

Figure 3. Content of mono-bound, poly-bound water, and capillary condensation water for BF rock samples from Well 1 (a), Well 2 (b) and Well 3 (c).

The content of loosely bound water in the BF rock samples of Well 1 is 0.47±0.77 wt.%, Well 2 — 0.1±1.0 wt.% and Well 3 — 0±0.99 wt.% and generally represents the lower values of the physically bound water content, which can be measured using the EM. The amount of mono-, poly- and capillary condensation water obtained by the hygrometric method characterizes the higher moisture adsorption potential of the BF rock samples and should include residual water. The confirmation of this is a correlation between the content of mono-bound water and residual water. So the hygrometric method gives the upper bound of physically bound water content — from 1.5 to 3 wt.% The free and bound water content varies spatially with depth (Figure 2) due to heterogeneity of the properties and composition of BF rocks even within the one well. The same behaviour for mono-, poly- and capillary condensation water can be observed (Figure 3).

To understand the water nature, we correlated free, loosely clay bound water and chemical bound water with obtained sample characteristics including XRD clay content for the target collection of BF rock samples. The absence of correlations for free water content proves that the mobile pore water was extracted and not water released due to clay dehydration. Probably a relationship between porosity and free water volume can be found. Further research in this direction is a topic for future publication. The functional correlations between loosely clay-bound and chemically bound water content with the XRD total clay content (Figure 4) suggest that the bound water source is the clay minerals. For the Well 1 was found a strong correlation between the content of clays and the mono-bound water ($R^2=0.78$) (Figure 4a).
Figure 4. Cross plots of loosely clay bound water, chemically bound water and water monolayer content versus clay mineral content for the studied BF rock samples from Well 1 (a), Well 2 (b) and Well 3 (c).

It turns out that on the surface of the BF minerals both hydrophobic and hydrophilic sites are distributed, the number of which and the alternation depend on the nature of rock-forming minerals, physical and chemical properties of saturating liquids and the content of residual water. In general, the obtained results make it necessary to revise the widely accepted statement about the hydrophobicity of BF rocks and show the novelty and topicality of the studies.

5. Conclusions
The research delivered reliable data on the content of free, loosely and chemically bound water in the BF rock samples of low porosity (gas porosity less than 5%). The dataset provides inputs for both reliable estimations of hydrocarbon reserves (oil, gas, bitumen) and development of adequate petrophysical models for well log interpretation, including the spontaneous potential, electric, dielectric, neutron, and nuclear magnetic resonance logging methods. Moreover, the obtained results on the residual water content and water of mono-, poly- and capillary condensation form a basis to review ideas about the predominant hydrophobicity of the BF rocks.

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