Pore Water Characterization of the Tight Rocks of Bazhenov Formation Using the Water and Salt Extracts

E S Kazak¹², Ya V Sorokoumova¹²

¹Geology Department, Lomonosov Moscow State University, Moscow 119234, Russian Federation
²Center for Hydrocarbon Recovery, Skolkovo Institute of Science and Technology (Skoltech), Moscow 121205, Russian Federation

E-mail: Kanigu@mail.ru

Abstract. The paper presents the results of the pore water composition investigation of tight shales of the Bazhenov Formation rocks of Western Siberia, obtained by integrated interpretation of the experimental data of the water and salt extracts. The two methods of cation exchange capacity (CEC) measurement were applied – Pfeffer and Hexaamminecobalt trichloride method. Both of them showed similar results. CEC varies from 3.45 to 4.53 meq/100 g by Pfeffer method and from 3.51 to 4.35 meq/100 g by Hexaamminecobalt trichloride method. Ca, Na, Mg, K form exchange complex of all studied core samples. According to interrelation (rNa+rK)>rCa the exchange complex type is marine and was inherited from the composition of the paleobasin seawater. It was found that water extract composition depends on the core mineral content, except chlorine, which originates from the pore water. Using the thermodynamic modelling in PHREEQC program, next ratio of exchange cations was found: Na (up to 91%), Mg (up to 5.6%), Ca (up to 2.6%) and K (up to 0.8%). According to the calculation using the water extracts results, the pore water salinity changes from 1.23 to 21.96 g/L.

1. Introduction

At present, there are just a few studies about Bazhenov formation (BF) tight shales ion-salt complex [1-3]. Rock’s ion-salt complex consists of minerals, exchangeable cations, and pore solution. The water and salt extracts are the main instruments for its investigation.

The pore water composition is caused by rock formation conditions and post-diagenetic transformations that is why its exploration helps to retrace these processes. Another reason for ion-salt complex exploration is its usefulness for well logging materials interpretation, paleohydrochemical studies of petroleum-bearing regions, and thermodynamic models verification.

Ion-exchange interactions are incongruent processes in the multi-component heterogeneous system «water-rock-gas-organic substance». It is assumed that an exchange complex formed due to a presence of uncompensated charges on minerals crystal lattice where pore water ions of the opposite charge could adjoin. Pore water cations can partially or completely replace the cation exchange complex of rock. The total amount of exchangeable cations is called a cation exchange capacity (CEC). CEC depends on granular and mineral rock composition, clays content, pH value of pore solution, electrochemical conditions, pressure, and temperature. It changes in a wide range – from 0 (quartz granules) to 900 cmol/kg (soil organic matter), K⁺, Na⁺, Ca²⁺, Mg²⁺ are its main cations [4].
Current work is focused on the BF shales ion-salt complex characterization, which includes mineral composition determination, exchangeable cations concentration evaluation, and then the pore water salinity and composition calculation using the thermodynamic modeling.

2. Materials
The research was provided on 6 core samples of BF rocks with the maximum preserved natural pore water content. The core samples were collected from 3 BF fields located in the central part of the West Siberia (Russian Federation). A sampling interval was about 1.5 m, depth more than 3.0 km, formation age is J3v. The central part of the whole cores was used for analysis (Figure 1, b) to exclude the drilling fluid effect.

3. Methods

3.1. Water extracts
The ion-salt complex of BF rock samples was investigated by water extracts method [5] which based on distilled water – powdered rock interaction (Figure 1, c) during 3 min with a weight ratio «rock : water» as 1:3 and further components determinations in the gathered solution.

3.2. CEC and exchangeable cations measurement
CEC measurement was provided by two methods:
- Hexaamminecobalt trichloride method commonly used in world research practice [6]. This method is based on exchangeable cations replacement by hexaamminecobalt from hexaamminecobalt trichloride aqueous solution (with pH value ~7) during 60 min. The CEC value is obtained by determining the difference between the initial cobalt amount in the solution and the remaining amount in the extract after the exchange reaction.
- Pfeffer method often applied for soil investigation, but also sufficient for BF rocks studies [7]. This method is based on exchangeable cations replacement by ammonium from Pfeffer reagent (70% ammonium chloride alcoholic solution with pH value ~7) during 60 min. The CEC value is obtained by summation of K+, Na+, Ca2+, Mg2+ concentrations in the extract after the exchange reaction. The ion concentrations were performed by inductively coupled plasma atomic emission spectrometry method by an iCAP 7600Duo spectrometer (Thermo Scientific Corporation, USA).

3.3. Mineral composition
Rock mineral composition of the studied samples was determined by the XRD method on an automated X-ray diffractometer Bourevestnik DRON-3m (Russia). Specimens for XRD were prepared according to the suggested practices [8-13], including crushing, mixing, and drying.

4. Results and discussion
The mineral composition of investigated BF core samples is presented (Figure 1): silicate minerals — 33±83 wt.%; clay minerals — 4±30 wt.%; carbonate minerals — up to 6 wt.%; pyrite up to 14 wt.%; plagioclase — up to 16 wt.%; potassium feldspar — up to 8 wt.%. According to geochemical studies, the samples have a high organic carbon content (TOC) — up to 15.09 wt.%; enriched with kerogen, which, when thermally decomposed, provides up to 93 mg HC/g rock.

BF rocks are regional aquitard, but in the geological past, they were a recharge zone that supplied elision water to the Upper Jurassic hydrogeological complex. Till the end of Cenomanian time, 50÷70 % of water was squeezed out of Bazhenov and Georgiev waterproof clays, and 20÷37 % of water was pressed out during the Cenozoic Era [14]. Nowadays the BF sediments are almost entirely consolidated. Residual water content in measured samples of BF rocks is from 0 to 2.34 wt.% [15, 16], which is more than 98% of the total pore water.
Figure 1. XRD composition of BF rock samples.

It was defined by Pfeffer method that total CEC varies from 3.45 to 4.53 meq/100 g, and from 3.51 to 4.35 meq/100 g by Hexaamminecobalt trichloride method (Table 1). Results for 4 out of 6 samples are shown convergence within an error of 0.5 meq/100 g. There was not found any correlation between CEC and organic matter and clay content. Obtained CEC values for BF rocks also correspond to other tight shale formations - Bakken 5.4±10.5 meq/100 g, Haynesville – from 2±4 meq/100 g [17].

BF samples exchange complex consists of Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), Na\(^+\), according to determination by Pfeffer method (Table 1, Figure 2). Na\(^+\) is a predominant cation in all investigated samples and changes from 2.83 to 3.96 meq/100 g that is more than 75±88% of CEC value (Figure 2).

Table 1. Cation exchange composition, CEC and salinity of the studied samples.

| Sample ID | Oil Field | Ca\(^{2+}\) by Pfeffer Method (meq/100g) | Mg\(^{2+}\) by Pfeffer Method (meq/100g) | Na\(^+\) by Pfeffer Method (meq/100g) | K\(^+\) by Pfeffer Method (meq/100g) | CEC by Pfeffer Method (meq/100g) | CEC by HexaammineCo Trichloride Method (meq/100g) | Salinity as NaCl (g/L) |
|-----------|-----------|----------------------------------------|----------------------------------------|--------------------------------------|----------------------------------|---------------------------------|-----------------------------------------------|-----------------|
| O2        | 1         | 0.33                                   | 0.16                                   | 2.83                                 | 0.13                             | 3.45                            | 4.15                                                   | 1.23            |
| U8        | 2         | 0.29                                   | 0.11                                   | 3.02                                 | 0.13                             | 3.55                            | 3.99                                                   | 21.96           |
| U12       | 2         | 0.20                                   | 0.22                                   | 3.38                                 | 0.08                             | 3.87                            | 3.94                                                   | 2.03            |
| U13       | 2         | 0.31                                   | 0.15                                   | 3.96                                 | 0.10                             | 4.53                            | 4.35                                                   | 16.38           |
| N21       | 3         | 0.09                                   | 0.60                                   | 2.83                                 | 0.10                             | 3.62                            | 3.51                                                   | 9.75            |
| N23       | 3         | 0.43                                   | 0.32                                   | 3.00                                 | 0.21                             | 3.95                            | 3.74                                                   | 18.36           |

Figure 3 presents the water extracts composition. All water extracts samples have near-neutral pH value (6.89±7.42). Na\(^+\) is a dominant cation in water extract composition excluding samples N21 and U12, which have Ca\(^{2+}\) as the dominant cation in solution (Figure 3, a). The sample U12 has different anion composition in comparison with other samples (Figure 3, b). The correlation between chlorine content and free water amount (R²=0.76) indicates that the pore water is the most probable chlorine source. The chlorine concentrations are quite low (Figure 3, b)
Figure 2. Composition of the exchange complex of the studied BF core samples.

It is known [18, 19] that the ions of the water extracts are defined by the rock mineral composition, except Cl\(^-\) and Br\(^-\) content. According to a correlation analysis, we assumed that main K\(^+\) source for the water extracts is K-feldspar (R\(^2\)=0.83). The SO\(_4\)\(^2-\) concentration is controlled by high pyrite content (up to 14 wt.% (Figure 2)), the Ca\(^{2+}\) and Mg\(^{2+}\) contents have the likeliest origination from the exchange complex.

Figure 3. Composition of the water extract solutions of the studied BF core samples.

There are two types of exchange complex – marine ([rNa+rK]<rCa) and continental ([rNa+rK]<rCa) [4, 20], and all tested samples are related to the first one. The BF rocks accumulated in the deep-water conditions of Bazhenov sea with a salinity about 35 g/L [21], with Na\(^+\) as a predominant ion [14], that is why Na\(^+\) dominates in exchange complex even after katagenesis.

The cation exchange reactions proceed on the «pore water-rock» contact. BF rocks have a low water content that is why exchange processes active only in the water-occupied interstices and seemed to be very local. Under equilibrium conditions, cation concentration in solution depends on their ratio in exchange complex but not on exchange capacity. The main cations ratio in pore water under equilibrium conditions with the rock was calculated using the experimental data of exchange complex composition (Table 1). As a result of modeling in PHREEQC program [22] it was established that Na\(^+\) makes up to 91%, Mg\(^{2+}\) (up to 5.6%), Ca\(^{2+}\) (up to 2.6%) and K\(^+\) (up to 0.8%), which means that the pore water composition should have Na\(^+\) as a predominant cation. Taking into consideration that the exchange complex composition depends on salinity, we provide calculations with different salinity values but with the same cations ratio. It was found that Na\(^+\) also increases in exchange complex with the higher ionic strength.

The Neocomian and Upper Jurassic aquifers of Western Siberia belong to a Na-Cl group with salinity 10.84±26.63 g/L and 2.6±49 g/L [14, 23, 24]. According to the modeling results, the BF pore water should have sodium composition predominantly. The chlorine content in pore water can be measured and calculated using the water extracts data taking into account water content in rock. We calculated salinity of pore water according to chlorine concentration and sodium content, which equivalent to Cl\(^-\) amount. The salinity as NaCl for samples changes from 1.23 to 21.96 g/L (Table 1).
These values are the lower boundary of possible salinity range of BF pore water and mainly match with the results of the BF pore water salinity of Salmanovskoye field [25].

5. Conclusions
The CEC value varies from 3.45 to 4.53 meq/100g (by Pfeffer method), and from 3.51 to 4.35 meq/100g (by Hexaamminecobalt trichloride method). Na is a dominant cation in the exchange complex of all investigated samples, which means that all of them belong to the marine type. It was established that both Pfeffer and Hexaamminecobalt trichloride method could be used for CEC determination in BF rocks.

Water extracts composition is more heterogeneous then exchangeable complex structure due to minerals anisotropy of the core samples. Correlation analysis showed that the chlorine ion concentration in water extracts is strongly related to the test core pieces free water content (R²=0.76). It was shown that applying the water and salt extracts can help in the pore water composition and salinity assessment in cases where a direct pore water analysis is not possible.

As a result of experimental study and thermodynamic modelling, it was established that pore water of BF rocks has mainly Na-Cl composition and salinity 1.23±21.96 g/L. The BF pore water solution is the result of complicated processes of water-rock interaction and mixing with the squeezed bounded water. That is why its composition may differ significantly from the initial sediment basin water towards a decrease in salinity (mainly due to incoming of bounded water), a reduction of the Ca²⁺ and Mg²⁺ content and an increase in the Na⁺ and bicarbonates amount.

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