New data on the composition of organic matter of deep-seated rocks of Bashkortostan by NMR in a low magnetic field

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Abstract. The study of the organic matter of Riphean-Vendian deposits, the features of its distribution are the subject of research by many authors. The problem of hydrocarbon of these deposits remains relevant. We have conducted studies of deep-seated rocks of the Lower Riphean of the kaltasinskaya suite of the Eastern-Askinskaya area, with an increased content of organic matter in individual intervals. In addition to standard research methods, the method of nuclear magnetic relaxation in a low magnetic field was used. This method allows determining the phase state of organic matter in the original rock without any impact and after isothermal heating of the rock at 350°C. The free induction signal and the type of solid-phase signal, which corresponds to the waveform for the asphaltene component of the oil, were analyzed. The predominant part of the liquid-phase signal - about 35%, is characterized by a transverse relaxation time of 540 μs, corresponding to the resinous component of organic matter. The quantitative ratio of asphaltenes before and after heat treatment was also analyzed. A significant decrease in its amount was recorded. During thermal exposure, more than 55% of light, more mobile hydrocarbon molecules are formed in the liquid-phase part of organic matter.

1. Introduction. Setting goals and objectives

The problem of depletion of oil reserves has become increasingly relevant in recent years. As there is a shortage of hydrocarbon reserves arises, unconventional and heavy oils, including bitumen and shale, are the focus of extensive research. Quantitative characterization of the component composition of organic matter directly in the rock and assessment of the ability to generate hydrocarbons becomes a key task in creating of technologies for identifying such objects and the possibilities of its extraction. A special NMR-SARA technique was created for component analysis of heavy oil [1].

The aim of our research was to evaluate the application of the method of nuclear magnetic relaxation (NMR) in a low magnetic field to analyze the state of organic matter in rocks, in particular, rocks of the lower Riphean of the of the kaltasinskaya suite of the Eastern-Askinskaya area of Bashkortostan [2].
2. Object of research

The industrial hydrocarbon content of the sedimentary cover of the Riphean of Bashkortostan, localized within the Volga-Ural oil and gas province, is known only in the form of small accumulations of heavy, degassed oil [2]. Prospects of hydrocarbon content are associated with the upper zones of the upper Precambrian sublevels.

The rocks of the Lower Riphean of the Eastern-Askinskaya area studied by us are massive, dense, composed of marl dolomites with sites of recrystallization of carbonate components with the formation of block calcite. The lower intervals of the area (lower Riphean, upper kaltasinskaya suite) are characterized by an abundance of organic residues (Fig. 1a, b). The inner zones of organic residues are composed of block calcite, which formed in the processes of recrystallization of a substance (Fig. 2a, b). According to published data, the Lower Riphean deposits of the studied territories have a low background porosity of about 5-10%, and the porosity in some intervals decreases to 1-5%, only in 3% of the rocks did the porosity exceed 10% [2].

The rocks of the studied area are almost impenetrable and low capacity; they are characterized by an increased amount of organic matter. The porosity of the samples is associated with single small isolated pores, voids of corrosion and leaching, as well as sites of recrystallization of the substance, during which secondary porosity is formed [3].

![Figure 1: Eastern-Askinskaya area, Lower Riphean, top of the kaltasinskaya suite, well 1, sample 4, depth 3908.5 m. a) Nicole II, b) Nicole +. Plots of recrystallization of carbonate rocks with a high content of organic matter, the formation of large-block calcite.](image)

Earlier, in order to elucidate the features of the mineral composition and its relation with type and phase state of organic matter, we performed studies by EPR spectroscopy [3]. The presence of syngenetic calcite is recorded not only by the presence in the EPR spectrum of an impurity manganese ion in the Ca position, but also by the EPR lines of the impurity radical-ions of SO₂⁻, SO₃²⁻ and PO₃⁻ in the position of the anionic groups CO₃⁻ (Fig. 3a). The presence of sulfur ions, phosphorus indicate an early diagenesis of carbonate silts with the participation of organic matter. To clarify the features of organic matter, the carbonate part of the rock (diluted with hydrochloric acid) was removed. The obtained results indicate that the lines of Corg – of the organic radical, Rbit of the bitumen radical and E' - center in the structure of quartz (Fig. 3b) are fixed on the EPR spectra [3].
Isometric heating at 350°C was carried out in a horizontal furnace of the SUOL type, to which hydrogen was supplied, the initial rock was analyzed in a hydrogen atmosphere for 30 minutes in order to study organic matter capable of generating oil molecules. The symmetric EPR line of the free radical C_{350} with a line width of 0.6 mT is a marker for the appearance of oil molecules (Fig. 3c). Subsequently, the investigated rock with the tube was heated to 350°C.

**Figure 2.** Eastern-Askinskaya area, Lower Riphean, top of the kaltasinskaya suite, well 1, sample 3, depth 3908.5 m. a) Isolation of block recrystallized calcite. Magn. 300x; b) Secondary porosity in sites of recrystallization of organic residues. Magn.1000x.

**Figure 3.** Overview EPR spectrum ion-radical region: a) nature; b) after HCl demineralization; c) new free radical C_{350} as anneal at 350°C during 30 min.

3. **Experimental results of NMR relaxation**

The measurements were performed on “Chromatec – Proton 20M” NMR analyzer, which operates at a frequency of 20 MHz with using a specially designed program for controlling and processing experimental data [1].

A quantitative assessment of the petrophysical properties of rocks containing organic matter of the bitumen and oil series is impossible without a quantitative description of the properties of organic matter; therefore, the creation of methods for its determination directly in the rock by non-invasive methods is current interest. The first step in this direction was the application of the NMR-SARA method for the initial rock, similarly to the analysis of the SARA component of heavy oils [1]. The technique of
preliminary sample preparation is the same as for EPR studies. Warming was also carried out in a SUOL oven at 350°C; the experiment time was 5 hours; after cooling, the sample was ready for NMR measurements. An important parameter is the weight characteristic of the studied sample subjected to minimal changes. The results of NMR studies are presented in Figure 4, reduced to a unit of weight, typical decays of the signal of free induction (SFI) of organic matter in the initial sample 1–3 (depth 3908.5-3913.5 m) and after pyrolysis at 350°C for 5 hours in a hydrogen atmosphere.

The obtained results (Fig. 4) indicate that the two experimental curves of SFI a) and b) are close in the fast-falling section and differ in the slowly falling section.

![Figure 4. Typical decays of the signal of free induction of organic matter. a) initial rock; b) after heating at 350°C. Semilogarithmic scale. In the inset, the initial section of the decay of the solid phase is up to 100μs.](image)

Components with different rates or relaxation times are observed on the shape of the relaxation curves. For a complete description of the shape of this signal, the model consisting of Gaussian and exponential functions turned out to be the most adequate. Such model is usually represented as the sum of mathematical functions describing the relaxation of each components of the decline (Table 1).

In this table: $A_{0S}$, $A_{0LM}$ and $A_{0LL}$ (%) denote the intensities of fast- falling (solid-phase in the sense of NMR analysis) and slowly falling (liquid-phase) components, respectively. The relaxation times (μs) correspond to: $T_{2LM}$ and $T_{2LL}$ of the liquid-phase component, and $T_{2sc}$ and $T_{2sam}$ are the relaxation times of the Gaussian and exponential components of the solid-state decay. Moreover, the coefficient fam characterizes the fraction of the amorphous phase. The total true intensity of the SFI $A_0$ is nothing more than the sum of the liquid phase $A_{0L}=A_{0LM}+A_{0LL}$ and the solid phase $A_{0S}$ taking into account the calibration of the device per 1 mg of water, corresponds to the proton content or proton index HI (mgN/g).
Table 1. Table of results of the analysis of relaxation curves of organic matter in the rock before and after heating at 350°C

| Solid Phases (Gauss+Exp) | Liquid Phases (Middle and Long) | A0 |
|-------------------------|---------------------------------|----|
|                         |                                 |    |
| A0S T2sc fam T2sam A0LM T2LM A0LL T2LL HI |                         |    |
| Riphean 64,01 20,16 0,39 60,97 35,18 541,23 0,81 1000 0,52 |                         |    |
| 350°C 39,64 17,72 0,90 36,13 4,76 363,02 55,6 20000 0,42 |                         |    |

4. Discussions

From the analysis of the decay components of the signal of free induction of a natural rock sample it follows by analogy [1, 4], that the solid phase is represented by asphaltenes 62.01%, in which the proportion of the amorphous part is 0.39, the liquid phase consists mainly of resins and corresponds to heavy oil - bitumen. Isothermal pyrolysis was accompanied by cracking of the solid phase, which occurs with an increase in the proportion of the amorphous part from 0.39 to 0.9, and the long-time liquid phase to 55.6%. In addition, the pyrolysis process occurred with the loss of hydrogen atoms and proton density by 0.1 due to the carbonization process.

5. Conclusions

The value of the proton index HI=0.52 of the initial sample is consistent with a small value of hydrogen atoms equal to 0.84 in the rock and, accordingly, a small line width (0.09 mT) of the EPR signal of bitumen. The formation of bitumen is accompanied by the carbonization of hydrocarbon molecules (loss of hydrogen atoms), the rate of which depends on time and external conditions.

The amount of the solid-phase component 64.01% in the initial sample is comparable with the value of 39.64% after pyrolysis (350°C; 5 hours) and characterizes the dispersed organic matter of the rocks (DOM) as the oil source organic matter. A control of this assumption is a decrease in the EPR line width of the radical C350 with an increase in the pyrolysis time from 0.6 mT of an oil molecule (30 minutes) to 0.12 mT of a bitumen molecule (5 hours).

A quantitative assessment of the petrophysical properties of rocks containing organic matter of the bitumen and oil series is impossible without a quantitative characterization of the properties of organic matter and the creation of methods for its determination directly in the rock by non-invasive methods. The first step in this direction was the application of the Low-Field NMR method for rock, similarly to the analysis of SARA components of heavy oils [2]. This method was used to study the dispersed organic matter of samples of deep-seated rocks of Lower Riphean; the results show the component composition of organic matter of the initial rock and the ability of these rocks to generate hydrocarbons.

Acknowledgements

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