Geochemistry of radioactive elements in bituminous sands and sandstones of Permian bitumen deposits of Tatarstan (east of the Russian plate)

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Abstract.

The article investigates geochemical features of Permian (Cisuralian, Ufimian Stage and Biarmian, Kazanian Stage of the General Stratigraphic Scale of Russia) bituminous sands and sandstones located on the territory of the Volga-Ural oil and gas province (Republic of Tatarstan). Natural bitumens are extracted using thermal methods as deposits of high-viscosity oils. In the samples studied, the specific activity of natural radionuclides from the $^{238}$U ($^{226}$Ra), $^{232}$Th, and $^{40}$K series was measured using gamma spectrometry. As a result of the precipitation of uranium and thorium and their subsequent decay, the accumulation of radium ($^{226}$Ra and $^{228}$Ra) has been shown to occur in the bituminous substance. In the process of exploitation of bitumen-bearing rock deposits (as an oil fields) radium in the composition of a water-oil mixture can be extracted to the surface or deposited on sulfate barriers, while being concentrated on the walls of pipes and other equipment. This process requires increased attention to monitoring and inspection the environmental safety of the exploitation procedure.

Key words: bitumen sands, bitumen sandstones, tar sands, radioactive elements, concentration

1. Introduction.

Within the Volga-Ural oil and gas province, there are deposits of natural bitumen [1,2,3], dated to the Ufimian and Kazanian deposits of the Permian period. Reduction of the reserves of light oil facilitates the introduction of new technologies for extracting hard-to-recover hydrocarbons, including natural bitumen. In the territory of the Republic of Tatarstan, the resources of bitumen-bearing rocks vary from 1.5 to 10 billion tons. More than 150 deposits and manifestations of natural bitumens are confined to Ufimian and Kazanian deposits, where they occur from the Earth’s surface to depths of 400 m. At present, efforts are being made in...
Tatarstan to develop bitumen deposits as high-viscosity oils. The complexity of their development is due to the fact that in the natural state they do not have the necessary parameters of viscosity and density to be extracted by traditional well methods. Thermal methods are used to achieve the necessary production conditions. Bituminous rocks are warmed by heated steam [3]. As a result, the bitumen substance acquires fluid properties and is extractable to the surface. In this connection, the study of the nature of the chemical changes occurring in the formation during the interaction of steam and oil fractions, as well as the trace element composition of the bitumen-bearing rocks, is of particular importance. The change in physical and chemical conditions of the environment for recovered hydrocarbon fractions during the exploitation of oil fields causes an undesirable concentration of metal compounds in the pipes.

One of the important geochemical problems in petroleum geology is an uncontrolled concentration of radioactive elements and, mainly, radium [4]. The nature of radium concentration is as follows. The most common isotopes in natural environments (sediments, rocks) are uranium 238 and thorium 232. Radium 226 is a product of the decay of uranium 238, which is mobile in an alkaline environment and can concentrate on acid barriers. In oil-bearing deposits uranium is concentrated in the zone of water-oil contact, where as a result of its decay, the concentration of radium 226 occurs. Part of the radium is also accumulated as a result of sedimentation from the groundwater of the enclosing sediments. During the exploitation of the oil field, radium in the water-oil mixture enters the surface, where it is deposited on sulfate barriers in the composition of sulfate compounds. As a result, areas with increased radioactivity may be formed, causing environmental problems.

The purpose of this work is to study the activity of natural radionuclides in bitumen-bearing rocks.

2. Methodology

To solve environmental problems arising during the exploitation of bitumen-bearing rocks by thermal methods, was made mineralogical and geochemical research of bitumen-containing rocks of the Sheshmian horizon (Ufimian Stage of Permian Period). Petrographic research has been carried out using methods of traditional polarization microscopy in transmitted light. To determine the composition of the finely dispersed mineral substance of cement and the type of organic matter, the electron paramagnetic resonance (EPR) method has been used. EPR [5,6] studies diamagnetic crystals in which the paramagnetic centers are impurity ions of Fe$^{3+}$, Mn$^{2+}$ in calcite, dolomite, electron-hole centers in them, free radicals of organic matter of coal and oil series. These paramagnetic centers reflect the conditions and environment of formation of minerals, the degree of degradation of the syngenetic material of rocks, reflecting different stages of catagenetic transformation of rocks. In calcite ions Mn$^{2+}$ are replacing calcium ions (Ca$^{2+}$), and in the dolomite they replace ions Ca$^{2+}$ and Mg$^{2+}$ in two structurally nonequivalent positions. In bitumen-containing sands and sandstones, the content
of natural radionuclides from the $^{238}\text{U}$ ($^{226}\text{Ra}$) series, as well as $^{232}\text{Th}$ and $^{40}\text{K}$, was estimated by gamma spectrometry. The specific activity of natural radionuclides is measured in Bq / kg. Analyses were performed in the Institute of Environmental Sciences, KFU. The content of uranium and thorium was determined using ICP-MS in the laboratory of the Institute of Geology and Petroleum Technologies. The results of the analyses are shown in table 1.

Table 1

| №  | Sample | Lithology types                          | $^{40}\text{K}$, Bq/kg. | $^{226}\text{Ra}$, Bq/kg. | $^{232}\text{Th}$, Bq/kg. | U, ppm | Th, ppm |
|----|--------|------------------------------------------|--------------------------|---------------------------|---------------------------|--------|---------|
| 1  | C 5    | bituminous cemented sandstones           | 190,00                   | 9,68                      | N/A                       | N/A    | 0       |
| 2  | C 8    | bituminous cemented sandstones           | 235,60                   | 8,93                      | N/A                       | N/A    | 1,36    |
| 3  | C 13   | bituminous cemented sandstones           | 170,70                   | N/A                       | 9,40                      | N/A    | N/A     |
| 4  | C 16   | bituminous cemented sandstones           | 199,40                   | 9,36                      | N/A                       | N/A    | 1,48    |
| 5  | C 21   | cemented sandstones                      | 168,00                   | 3,24                      | N/A                       | N/A    | N/A     |
| 6  | C 22   | cemented sandstones                      | 179,10                   | 6,28                      | N/A                       | N/A    | 1,47    |
| 7  | C 28   | cemented sandstones                      | 167,70                   | 5,44                      | N/A                       | N/A    | N/A     |
| 8  | C 35   | cemented sandstones                      | 358,00                   | 6,59                      | 7,98                      | N/A    | 2,29    |
| 9  | D 1    | cemented sandstones                      | 193,90                   | 7,27                      | 6,41                      | N/A    | N/A     |
| 10 | D 3    | bituminous cemented sandstones           | 166,60                   | 6,18                      | N/A                       | N/A    | N/A     |
| 11 | D 7    | tar sands                                | 212,10                   | 13,30                     | N/A                       | N/A    | 1,63    |
| 12 | D 10   | tar sands                                | 193,50                   | 29,53                     | N/A                       | N/A    | N/A     |
| 13 | D 11   | bituminous cemented sandstones           | 196,20                   | 6,05                      | N/A                       | N/A    | N/A     |
| 14 | D 14   | bituminous cemented sandstones           | 206,20                   | 5,96                      | N/A                       | N/A    | 1,36    |
| 15 | D 19   | tar sands                                | 206,30                   | 5,21                      | 2,89                      | 3,92   |         |
| 16 | D 24   | bituminous cemented sandstones           | 187,00                   | 12,18                     | N/A                       | N/A    | 1,66    |
| 17 | D 27   | bituminous cemented sandstones           | 266,00                   | 7,12                      | 1,49                      | 1,6    |         |
| 18 | D 31   | cemented sandstones                      | 268,70                   | 15,47                     | N/A                       | N/A    | N/A     |
| 19 | D 32   | cemented sandstones                      | 167,20                   | 7,54                      | 1,94                      | 9,35   |         |
| 20 | D 38   | cemented sandstones                      | 239,80                   | 6,43                      | 4,73                      | N/A    | 1,98    |
| 21 | D 46   | cemented sandstones                      | 193,70                   | 6,02                      | N/A                       | 18,18  | N/A     |

N/A-data not available or below the detection limit of the device

3. Results and Discussions

According to the mineral composition, the investigated sandstones are polymictic and belong to the greywack group [1,7]. In the clastic material of sandstones, there can be found grains of quartz, feldspar, mica, as well as particles of magmatic rocks, the source of which were the magmatic rocks of the Ural Mountains destroyed in the Permian period. Particles of acidic rocks predominate among the magmatic fragments. The clastic material is not sufficiently sorted out, it is dominated by uncoated, angular fragments that indicate the short duration of the process of their washing and transfer [8]. The rocks of the Sheshmian horizon are represented by loose uncemented varieties (sands) and dense, hard-cemented sandstones. The cement in dense sandstones is clayey-carbonate, sometimes carbonate, proportion of
which in sand and sandstones can be more than 30%. The presence of clayey components and carbonate minerals that were difficult to determine in the sandstones was confirmed by the EPR method. The EPR spectra in the rock revealed Fe$^{3+}$ signals associated with clay minerals, as well as Mn$^{2+}$ signals typical of dolomite and calcite. An important component of the studied sandstones is the organic matter, the forms of its presence in rocks are also confidently fixed by the EPR method [9]. There are two types of organic matter - the oil and coal series in the studied samples. The oil substance has a migration nature and, apparently, is associated with an influx of water-oil fluid from deeper horizons (Carboniferous sediments). The organic matter of the coal series is the syngenetic remains of plants deposited together with the primary sediments. In loose sands the role of cement is played by a bitumen substance that envelops fragments of quartz, feldspar and other minerals. The element composition of the organic matter in the samples studied has the values: C (72.05-83.31%), H (10.08-11.62%), N (0.20-0.50%) [7]. The bulk of the samples is characterized by similar parameters which indicates the homogeneity of the composition of bitumen.

Due to the scale of their presence, the $^{238}$U ($^{226}$Ra) and $^{232}$Th ($^{228}$Ra) and $^{40}$K radionuclides have a significant influence on the geochemical behavior of the petroleum substance, which is unevenly distributed in the studied rocks [11]. Depending on the content of organic matter, the rocks studied were divided into three groups - tar sands, bituminous cemented sandstones and cemented sandstones [8].

The structure of bituminous deposits is characterized by vertical zoning. The horizons of loose sands are located mainly in the upper sections of the productive horizon, and strong differences are in the lower horizons. This pattern can be explained by cementation of rocks below the zone of water-oil contact [12], where geochemical contrasts arose between the oil waters and the waters of the enclosing strata. Secondary mineral formation in the zone of water-oil contact was accompanied by cementation of the parent rocks with calcite (and dolomite). The underground water of the underlying sulfate-carbonate Early Permian deposits are quite likely to be the source of calcium for the crystallization of dispersed calcite in the porous space of sandstones. The groundwater is characterized by favorable for the migration of calcium and magnesium alkaline properties.

Different types of studied sandstones are characterized by different activity of the radionuclides considered, which is explained by their different geochemical behavior and forms of location. It is known [13] that uranium in sedimentary rocks is mainly associated with organic matter and partly with apatite and calcite, thorium with clay minerals, and potassium with clay minerals and potassium feldspar. The correlation of radioactive elements between each other indirectly reflects their connections with the mineral components of rocks (Table 2). However, it should be noted that due to the low content of uranium and thorium in the rocks, the correlation bonds are weakly expressed and can be used only to reveal general patterns.
Table 2

Correlation matrix of specific activity of radionuclides and concentrations of uranium and thorium

|       | $^{40}$K | $^{226}$Ra | $^{232}$Th | U   | Th   |
|-------|---------|-----------|-----------|-----|------|
| $^{40}$K | 1,00    | 0,10      | 0,33      | -0,08 | 0,03 |
| $^{226}$Ra | 0,10    | 1,00      | -0,32     | -0,12 | -0,09|
| $^{232}$Th | 0,33    | -0,32     | 1,00      | -0,15 | -0,08|
| U      | -0,08   | -0,12     | -0,15     | 1,00  | 0,04 |
| Th     | 0,03    | -0,09     | -0,08     | 0,04  | 1,00 |

In the rocks being studied, we can identify association of potassium with sands and sandstones greatest values of which occur in bitumen-bearing varieties and decrease in clays and clayey rocks. The reason for this is that potassium is found primarily in potassium feldspars, and potassium feldspars are a constant component of the clastic material of the examined sandstones. An increase in the values of the specific activity of potassium in rocks with organic matter should be attributed, apparently, to its precipitation on acid barriers. And the origin of the reactive dissolved potassium - with the processes of leaching in the zones of water-oil contact.

Thorium ($^{232}$Th) is a natural radionuclide. Thorium does not form elevated concentrations in the rocks under consideration (table 1). Some increase in its concentrations is associated with the sites of rock carbonatization. In nature, it occurs mainly in acidic magmatic rocks, while in sedimentary rocks it concentrate in combustible shales [13]. It can be assumed that the introduction of the bulk of thorium into the Ufimian deposits occurred as part of fragments of igneous rocks, and it enters the composition of groundwater during the decomposition of carrier minerals. In the rocks under consideration, its enhanced correlation with Uranium is noted. Apparently, this is due to its deposition in small quantities on acid barriers in the zone of water-oil contact, where it accumulates along with uranium on cementation zones.

A subject of great interest is radium characterized by a non-uniform distribution with increasing specific activity in rocks containing hydrocarbon fractions, especially in tar sands with bitumen (Table 1). In cemented rocks, its activity is much lower. Radium is a product of the decay of uranium and thorium. The uranium content in sands and sandstones is low and is within the clarke of concentration for sedimentary rocks (2-4 ppm) and below the sensitivity threshold of the method. Its concentration is connected, apparently, with acidic barriers in the
zone of water-oil contact. Radium accumulates in oils as a result of the constant addition of uranium from surrounding rocks and its further decay. The negative bonds of radium (\(^{226}\text{Ra}\)) with uranium concentrations should be attributed to a decrease in uranium concentrations as a result of its decay and the increase in activity of the resulting radium.

4. Conclusions

Summarizing all the above, we can state the following. In the zone of water-oil contact, where potassium is affected by groundwater, potassium is likely to be dissolved and be carried over with redepositing in the other parts of the section. Such areas could be zones of sandstone cementation where mass calcite precipitation has been found to occur. Links with other radionuclides, especially with thorium, are not explicit. This is due to the fact that the content of radionuclides in different parts of the section is affected by oil and associated waters.

It appears to occur the accumulation of radium (\(^{226}\text{Ra}\) and \(^{228}\text{Ra}\)) as a result of the decay of uranium and thorium in bitumen substance. Thus, in the process of exploitation of deposits of bitumen-containing rocks as deposits of highly viscous oils, phenomena similar to those observed in oil fields may occur [4]. Radium constituting the water-oil mixture can be extracted to the surface and deposited on sulfate barriers concentrating on the walls of pipes and other equipment. This process requires increased attention to monitoring and inspection the environmental safety of the exploitation procedure.

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