Thermal properties of the bituminous sandy rocks of the Volga-Ural oil and gas province.

A I Mullakaev¹ and R R Khasanov¹

¹ Institute of Geology and Petroleum Technologies, Kazan Federal University, Kazan, Russia

E-mail: almazmullakaev@gmail.com, rinat.khassanov@kpfu.ru

Abstract

Natural accumulations of bitumen in the Volga-Ural oil and gas province are unconventional sources of hydrocarbons. They are mainly concentrated in the Republic of Tatarstan and are confined to psammitic (sandy) rocks of lower Permian age (Sheshmian Horizon of Ufimian Stage). Sands and sandstones belong to the greywacke group, so rock-forming minerals are represented by quartz, feldspars and effusive fragments. The internal structure of the bitumen-containing reservoir is characterized by an extreme degree of lithological and mineralogical heterogeneity, which is the result of the imposition of a whole complex of processes. Since the beginning of the development of bitumen deposits by thermal methods, the issues of studying the internal heterogeneity and its influence on the production process become particularly acute. Internal reservoir heterogeneity may prevent uniform heating and the formation of a full-fledged steam chamber. Sands and sandstones of the productive part are divided into three rock types (bituminous sands, bituminous sandstones and residual bituminous sandstones). Thermal studies using methods of thermogravimetry (TG) and differential scanning calorimetry (DSC) showed differences in rock types in terms of the decomposition of mineral and organic components, as well as the removal of gaseous components. As a result of thermal studies, it was found that not only loose, bitumen-saturated sands, but also denser, cemented rock types can serve as a reservoir for hydrocarbons. This is due to the conservation of hydrocarbon fractions in the intergranular space during the formation of carbonate cement.

1. Introduction.

The development of oil fields in the Volga-Ural oil and gas province has been underway for more than 60 years. For the most part they are exhausted and in the final stages of development. The increase of the raw material base occurs due to the intensification of the involvement in the operation of new sources of hydrocarbon raw materials, which include accumulations of natural bitumen in the territory of the Republic of Tatarstan. They are confined to sandy rocks of the Permian age (Sheshmian Horizon of the Ufimian Stage) [1]. The bituminous psammitic deposits of the Sheshmian Horizon occur in the east of the East European Platform within the Volga-Ural oil and gas province. They are tectonically confined to the western slope of the South Tatar arch, which is one of the largest positive structures in the region. The bodies of the tar sands form a system of linearly located elongated elevations, which are morphologically distinctly expressed on the surface of the sheshmzan Horizon.
Discussions about the nature of sand bodies have been going on for quite a long time, but there is no consensus on their nature. Various assumptions have been made: deltaic, coastal-sea-bar, alluvial, etc. [1, 2]. According to recent studies [3], sand deposits may have a complex genesis involving aeolian processes, which has led to their two-tier structure. The detrital material was originally carried by river water flows to the flat areas from the zone of the collapsing mountain system of the ancient Urals [4]. After that, the upper part of the sandy mass was above sea level and groundwater level and underwent aeolian processing, which led to the formation of linear dunes. These processes explain the two-tiered structure of the Horizon with the division into the lower sand-clay layer and the upper sand layer. The sandy layer is devoid of clay components, which was removed as a result of wind activity. Further, the studied strata was covered with a thick layer of clays and became an excellent reservoir for future penetration and accumulation of hydrocarbons (HC) [3].

Sands and sandstones belong to the greywacke group, rock-forming minerals are mainly represented by quartz, feldspars and effusive fragments [5]. Their mineral composition is determined by the composition of the feeding provinces, paleogeographic and facial features of sedimentation [4, 6]. The reservoir rocks in the productive Horizons of bitumen deposits are sands and sandstones of varying degrees of strength. The reason for the high porosity of sands and sandstones is that detrital grains loosely contact and form communicating pores [6]. The use of thermal technologies for the development of superviscous oil fields [7] dictates the need to control the circulation of high-temperature fluids [8]. In this regard, the requirements for studying the internal structure of bitumen-containing sediments are increasing. It is characterized by an extreme degree of lithological and mineralogical heterogeneity. The nature of the heterogeneity is complex and is the result of the imposition of a whole complex of sedimentological, postsedimentological and diagenetic processes [9]. Tectonic movements also make a major contribution to the development of internal heterogeneity [10]. The technology of steam assisted gravity drainage involves the creation of a steam chamber in the reservoir, within which a viscous oil-bituminous substance is mobilize and acquires flowable properties. Internal reservoir heterogeneity, which complicates the circulation of fluids, may interfere with the uniform heating and formation of the steam chamber. According to mineralogical and lithological features, various rock types are distinguished among the sands and sandstones of the productive part of the Sheshmian Horizon of the Ufimian Stage, which are characterized by different fluid permeability. The main purpose of this work is to clarify the role of various sandy differences during thermal effects on the reservoir.

2. Methodology

Studies of the composition, structural and textural features of sands and sandstones were carried out using petrographic and mineralogical methods. At the first stage, an optical-microscopy study of rocks in transparent thin sections was carried out. The samples were examined in transmitted light using a Carl Zeiss Axio Imager A2 polarization microscope. Mineralogical studies of the fine components of sands and sandstones were studied using an FEI XL-30 ESEM scanning electron microscope with an energy dispersive spectrometer. The method allows to identify fine-sized mineral phases and to establish their chemical composition. As a result of the studies, a typification of the studied sands and sandstones was carried out based on the degree of carbonate cementation and saturation with oil-bitumen fractions. At the second stage, the analysis of rock types of sands and sandstones was carried out using thermogravimetry (TG) and differential scanning calorimetry (DSC). Thermal
analysis of sandy rocks and hydrocarbons containing them was carried out on a synchronous thermal analysis device with highly sensitive sensors - NETZSCH STA 449 F3 Jupiter. The analysis interval was set in the temperature range from 30 to 1000 °C with a heating step of 10 °C per minute. The analysis was performed in air and using powder preparations. Data processing and calculations were carried out using the software package NETZSCH. The choice of TG and DSC as a laboratory method of research is due to the fact that the initial typification of samples into three main rock types was made according to the degree of bitumen saturation and cementation. The TG and DSC methods were used to determine the content of carbonate cement and hydrocarbon substances, as well as its fractional composition in various sand and sandstone rock types [11].

3. Results and Discussions

The whole variety of Sheshmian sands and sandstones can be divided into three main rock types [12]. The allocation of rock types is based on two main macro signs: cementation and bituminous saturation. According to these signs, bituminous sands, bituminous sandstones and residual bituminous sandstones are distinguished. Below is their detailed description.

**Bituminous sands** are black loose sands, the color of which is due to the presence of a bituminous substance. The most bituminous intervals of the Horizon are characterized by the lowest consolidation of rocks. The mineral composition is represented by rock-forming grains of quartz, feldspar and effusive rock fragments. They differ from cemented differences by the almost complete absence of carbonate cement, which is found only in rare strata and is not the main cement for the rock-forming minerals of this rock type. The role of cement in them is carried out by oil-bituminous substance. Weakly consolidated fragments of bituminous sands easily collapsing with little pressure on them. This rock type can be called the most important among all since it is the main object of industrial development.

**Bituminous sandstones** are represented by quite strong black and dark brown sandstones. The mineral composition is represented by the same rock-forming detrital minerals, which are cemented by carbonate minerals. The cement is predominantly calcite with a small proportion of authigenic dolomite. Dolomitization of calcite occurred under the influence of incoming groundwater from the lower sulfate-carbonate Horizons. Cement mainly pore and contact. Bitumen saturation is determined by the developed porous-permeable properties. This rock type has lower bitumen saturation values relative to bituminous sands, which is explained by the presence of carbonate cement, which displaces and prevents the penetration of oil-bituminous substances.

**Residual-bituminous sandstones** are the most consolidated types of rocks. They are painted in colors ranging from gray and greenish gray to light brown. The mineral composition is composed of the same rock-forming detrital minerals as other rock types. Carbonate cement, less often clay-carbonate, according to the nature of filling is basal, pore. The minerals of carbonate cement are calcite and dolomite. Dolomitization is more developed than in bituminous sands. With an increase in the depth of occurrence, the proportion of dolomite increases. This is due to the fact that the magnesium-containing water necessary for the formation of authigenic dolomite, penetrated from the underlying Lower Permian sulphate-carbonate sediments [10]. This rock type is characterized by the highest content of carbonate minerals in its composition and, visually, the lowest content of bituminous substance. For this reason, the rocks are usually light, but the areas contain signs of residual oil saturation as
traces of saturation and characteristic odor. Signs of oil saturation increased in samples of strong cemented differences during sample preparation and heating, which suggests the presence of fractions of the light, non-dense, dark colored hydrocarbons sealed in the cement material. To confirm these findings samples of the above-described rock types were analyzed by thermal methods (TG and DSC). In the course of the experiment, samples were heated to high temperatures (up to 1000 °C) necessary for the decomposition of mineral and organic components. At the same time, the change in the sample mass and the change in the magnitude of the thermal effect (enthalpy) of the reaction were recorded. Comparison of the curves of change in mass and the magnitude of the thermal effect in certain temperature ranges allows us to draw accurate conclusions about the material composition of rocks in terms of the destruction temperatures of minerals and hydrocarbon fractions. It is noteworthy that all selected rock types have a characteristic behavior of the curves of mass loss and enthalpy.

Typical thermograms of the bituminous sands rock type are shown in Fig.1. This rock type has a high HC content and low carbonate content. Oil saturation is measured according to the mass loss curve (TG line) and exothermic reaction effects (DSC line) in the temperature range from 200-250 °C to 600 °C. The decomposition of carbonates takes place at about 650–750 °C and in this rock type is characterized by a slight decrease in the sample mass and a negative value of the reaction enthalpy. This is due to the fact that almost all carbonates decompose at the same temperature, and is accompanied by heat absorption (i.e., the reaction is endothermic), while the combustion process of the HC is stretched in the temperature range, the mass loss is smooth, and the reaction occurs with the release of heat (exothermic reaction). Smooth mass loss is due to the fact that the hydrocarbons in the studied samples are characterized by heterogeneity of the fractional composition. Conventionally, they can be divided into light and heavy.
hydrocarbons. Light hydrocarbons begin to burn at the beginning of the temperature range of 200-600 °C, while heavy ones react later. The fractional heterogeneity of the HC also explains the rather wide reaction interval of almost 400 °C. In this case, the oil saturation varies between 8-12\% by weight. Carbonate level 1-2\%.

The thermogram of the bituminous sandstone rock type is shown in Fig. 2. From thermograms, it is clearly seen how the rock type “bituminous sands” differs from the rock type “bituminous sandstones”. The proportion of carbonate material increases significantly, while oil saturation decreases. For the samples, the oil saturation varies within 3-5\%, and carbonate content - 8-10\%.

![Thermogram of bituminous sandstone rock type](image)

Pic.2 Typical thermogram of the bituminous sandstone rock type: 1 – weight loss curve, 2 - reaction enthalpy curve

The thermograms of the residual-bituminous sandstone rock type are shown in Figure 3. This rock type is characterized by a significant increase in the proportion of carbonates associated with the cement of rocks (18-20\%). At the same time, the sample is characterized by a high hydrocarbon content of up to 4-5\%. This rock type is characterized by the greatest density and consolidation. However, the external signs of oil saturation in it appear much weaker than in other rock types. High hydrocarbon contents in it apparently explained by their conservation in the pore and intergranular space of the mineral substance with cement

It should be noted that the studied rock types of sands and sandstones differ in fractional diversity of the hydrocarbon substance. In rock type “bituminous sandstone”, a curve of the magnitude of the exothermic reaction with a small amplitude is observed, which is typical for heavy hydrocarbons. In the littotype “residual-bituminous sandstones”, bright exothermic effects appear, which may serve as a sign of the presence of not only heavy hydrocarbons, but also much more active light ones.
**Pic.3.** Typical thermogram of the residual-bituminous sandstone rock type: 1 – weight loss curve, 2 - reaction enthalpy curve

**4. Conclusions**

As a result of the research the following conclusions were made. All selected rock types of sands and sandstones have a similar mineral composition of detrital material and differ from each other only in the content of cement carbonate minerals. The content and composition of hydrocarbon fractions is controlled by the substance of cement, which is caused by epigenetic processes proceeding under the influence of many factors. The main among these factors is the chemistry of the environment. The introduction of hydrocarbon fluid and changes in the chemical composition of the contacting water are the main cause of variations in the chemical environment, which results in different degrees of cementation and oil saturation. It has been established that part of the hydrocarbon fractions can be conserved in the mineral matrix. Due to isolation from hypergenic destruction, preserved hydrocarbons retained the original fractional diversity. The reservoir for hydrocarbons can serve not only loose bituminous sands, but also denser, cemented rock types. The preservation of hydrocarbon fractions in the intergranular space of sandstones may occur during the formation of carbonate cement. The results obtained can be used in the calculation of reserves and involvement in the development of dense sandstone differences.

*This study was funded by the subsidy allocated to Kazan Federal University as part of the state program for increasing its competitiveness among the world’s leading centers of science and education.*

**References**

[1] Troyepolskiy V.I., Lebedev N.P. Produktivnyye bituminoznyye tolschchi permskikh otlozheniy Melekesskoy vpadiny i Tatarskogo svoda. Kazan: Izdatelstvo Kazanskogo universiteta, 1982. – 104. (In Russian)
[2] Uspenskiy B.V., Valeyeva I.F. Geologiya mestorozhdeniy prirodnvykh bitumov Republik Tatarstan. Kazan: Izdatelstvo OOO "PF "Gart", 2008. - 348. (In Russian)

[3] Mullakaev Almaz, Khasanov Rinat. The Aeolian factor in the formation of the Sheshmian Horizon sands and sandstones in the Permian of the South-Tatar Arch / In book: Barclay, M., Nikolaeva, S., Silantiev, V. (Eds.) Kazan Golovkinsky Stratigraphic Meeting, 2017: Advances in Devonian, Carboniferous and Permian Research: Stratigraphy, Environments, Climate and Resources. Filodiritto International Proceedings, Bologna, Italy, pp. 381-385.

[4] Khasanov R.R., Mullakaev A.I. Paleogeographic factors of the formation of Permian reservoir rocks of bitumen deposits in the east of the Russian plate (Russia) /International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM Volume 1, 2016, 469-474 pp. DOI: 10.5593/SGEM2016/B11/S01.059

[5] Khasanov R.R., Mullakaev A.I., Dusmanov E.N. The structure of sandstones in productive horizons of the Permian bituminous deposits of Tatarstan (Russia). Uchenye Zapiski Kazanskogo Universiteta. Seriya Estestvennye Nauki, 2017, vol. 159, no. 1, pp. 164–173. (In Russian)

[6] Pettijohn F.J., Potter P., Siever R. Sand and Sandstone. New York, Springer, 1972. 618 p.

[7] Muslimov R.Kh., Romanov G.V., Kayukova G.P., et al. Integrated Development of Heavy Oils and Natural Bitumens of the Permian System of the Republic of Tatarstan. Kazan, Fen, 2012. 396 p. (In Russian)

[8] Korolev, E.A., Khramchenkov, M.G., Khramchenkov, E.M., Eskin A.A., Gabdulvalieva R.R., Garina A.N. Modeling of the suffusion cavities development in bitumen saturated sandstones of Ashchalinskoye deposit under SAGD technology application // Neftyanoe Khozyaystvo – Oil Industry. – 2018. – 1. – P. 55-57.

[9] Korolev, E.A., Bakhtin A.I. Eskin A.A., Hanipova R.R. Diagenetic changes of sandstone reservoir of Ashchalinskoye bitumen deposit // Neftyanoe Khozyaystvo – Oil Industry. – 2016. – 10. – P. 26-28.

[10] Mullakaev A.I., Delev A.N., Usmanov S.A., Sudakov, V.A., Khasanov R.R. Tectonic causes of uneven cementation zones distribution in the bituminous sandstones productive part of the Sheshminsky Horizon of the South Tatar arch // Neftyanoe Khozyaystvo - Oil Industry. - 2018. - Vol., Is.2. - P.23-25. DOI: 10.24887/0028-2448-2018-2-23-25

[11] Yusupova T.N. Identifikatsiya nefti po dannym termicheskogo analiza / Yusupova T.N., Petrova L.M., Ganeyeva Yu.M., Lifanova Ye.V., Romanov G.V. // Neftekhimiya -1999. -№ 4. -S. 254-259. (In Russian)

[12] Mullakaev, A.I, Khasanov, R.R., Galiullin, B.M. Mineralogy of sandstones and localization of oil matter in productive Horizons of high-viscosity oil in permian deposits of the Volga-Ural region (Russia)/ 17th International Multidisciplinary Scientific GeoConference SGEM 2017, SGEM2017 Conference Proceedings, 29 June - 5 July 2017, Vol. 17, Issue 11, 353-358 pp. DOI:10.5593/sgem2017/11.