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Experimental Treatment of Polymictic Sandstones with Hot Solutions Saturated with Carbon Dioxide. Results and Practical Importance

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Abstract: *The purpose experiments was to test the hypothesis of the attack of overheated water solutions saturated with carbon dioxide on kerogen-containing sandstones for formation of local rock deconsolidation and increasing the mobility of associated bitumoids. During experiments of the first series, samples of sandstones were saturated with a solution of predetermined mineralization and carbon dioxide, and underwent a pressure typical of a depth of 5000 m for 40 days. During the second series sandstone samples experienced pressure of 150 at and a temperature of 85 °C in the first stage and at a pressure of 500 at and T = 135 ° C - in the second stage (during 10 days each stage). After the hydrothermal influence at a pressure of 150 at and T=85o C, deconsolidation of rocks took place as well as the formation of additional void, the creation of additional quantities of authigenic kaolinite, quartz, albite, transition of associated bitumoids to the mobile state. After testing the open porosity of sandstones increased to 8.7-10.6%, i.e. reservoirs were transferred to the rank of commercial. The obtained results are important in the development of methods for increasing of oil recovery enhancement in the extraction of heavy high-viscosity oils.*

Keywords: **:** *experiments, sandstones, positive pressures, temperatures, hydrothermal solutions, carbon dioxide, porosity, reservoirs, hydrocarbons.*

1. INTRODUCTION

The study is topical due to the fact that today the production of hydrocarbons in major petroleum provinces of West Siberia *gradually decreases* [1]. Thus, in the Khanty-Mansi Autonomous Region, the field production has been yearly decreasing by 25 mln tonnes since 2015 [2]. Soon the resource base recovery by moving down to a depth of 3–4 km will be inefficient. Therefore, it becomes even more topical to put deep horizons of the sedimentary cover into commercial production. Careful analysis of available cores with estimating the impact of secondary transformations of oil-bearing rocks is required to substantiate the discovery of new fields. The study of the latter, in particular, enables defining the lower limit of high-yield reservoirs existence and estimating the impact of deep faults on reservoir properties. The structure of oil reserves of Russia considerably worsened in the last decades of the 20th century. *About 65% of the remaining reserves are hard to recover* [1, 3]. Therefore, the development of new technological solutions and methods of stimulating high-viscosity heavy oil production is topical for the Russian oil and gas industry. The main objective point of the study was to experimentally prove the possibility of secondary porosity formation and the increase in reservoir quality under the influence of overheated water solutions saturated with carbon dioxide.

2. MATERIALS & METHODS

The author modelled sandstone deconsolidation under increased temperature and pressure conditions in the carbon dioxide environment. The experiments were conducted in the laboratory of IPGG SB RAS using a tool to study silicate systems under the pressure of water and carbon dioxide, based on the application layout by H.J. Greenwood [4], fig. 1. To enhance the reaction of mineralisation, the crashed samples of 0.25–0.1 mm and less than 0.01 mm in gold ampoules were placed in the reactor together with a sample. Then samples and powders were saturated with a solution with specified mineralisation and carbon dioxide with the following exposure to high temperatures and pressure. The conditions of the experiment are given in the table (table 1). Before and after testing, the quantity of intergranular contacts and catagenesis coefficients were calculated in thin sections. The structure of void space in coloured thin sections was studied. The storage capacity of rocks was studied by standard methods and by mercury injection on the device "Micrometric auto-pore – 9200" by Cultronics (France). The mineral rock density was determined using "Autopicnometr" of the same company. The porosity calculated by mercury injection data was defined by the formula:

$Kn = [(ng \cdot v^{)-1} + 1]^{-1}$, *where* ng – mineral rock density, g/cm^3; v - total intrusive rock volume, cm^3.

The X-ray analysis of powders, chemical silicate analysis of solutions, and quantitative spectrum analysis of samples were conducted. The study included **two testing series.**

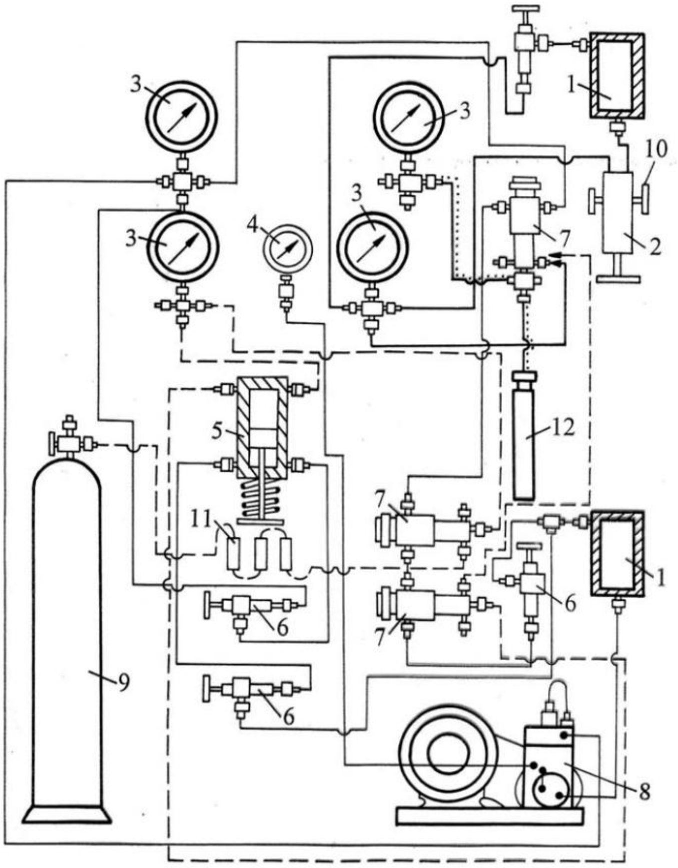

Fig1. *Diagram of Installation for Testing Silicate Systems under Water and Carbon Dioxide Pressure (ATC–1000)*

1 – reservoirs for oil and water; 2 – hydraulic press; 3 – gauges; 4 – pump capacity gauge; 5 – gas/oil separator; 6 – needle valves; 7 – hydraulic valves; 8 – pump; 9 – CO_2 bulb; 10 – hydraulic press tap; 11 – drier with magnesium perchlorate and activated carbon; 12 – reactor.

Table1. *Testing Conditions*

Series 1	Series 2	
P = 1.500 at		P = 150 at
T = 160 °C	Stage 1	T = 85 °C
pH = 8.8		$[CO_2]$ = 40 %
M = 8.3 g/l		t = 10 days
$[CO_2]$ = 45%		solution parameters are the same
XCO_2 = 0.43 m/l	Stage 2	P = 500 at
[NaC1] = 2.633 • 2 g/l		T = 135° C
$[NaHCO_3]$ = 1.517 • 2 g/l		$[CO_2]$ = 40%
t = 40 days		t = 10 days
		solution parameters are the same

<u>The first series</u> was conducted with the aim of the thermodynamic conditions modeling of the Urengoi zone at a depth of more than 4 km. Two sandstone samples with a similar material and granulometric composition, but with different quantities and types of cement (table 2), taken from the depths of 4,481 m and 3,828 m, were treated at a temperature of 160 ^{0}C and a pressure of 1,500 at, calculated by the Burch method [5] for a depth of 5 km. The testing lasted 40 days.

Table2. *Lithologo-mineralogical Description of Sandy Rocks before Testing*

Series	Well No.	Sample No.	Coring interval, m	C	Md	Material composition, %			Composition of rock fragments	Cements, %					Argillaceous minerals composition from XRDA
						Quartz	Feldspar	Rock fragments		Cal Dol	Chlorite-hydromica	Quartz	Albite	H-oxides Fe, epidote, pyrite	
Series 1	Urengoyskaya 414	21	4888-4902 8.7 nl	1.5	0.57	35.2	16.4	48.4	Flint, quartzite, clay shale, pegmatite, acid effusives	$\frac{5-7}{3-5}$	+	3-5	1-2	1-2	H+H-M+Ch+ dickite
	Yuzhno-Chaselskaya 15	40	3820-3828 2.3 nl	1.4	0.60	39.7	13.0	38.7	Flint, quartzite, siltstone, chert, pegmatite, acid effusives	10-15	1-2	5-6	2-3	—	H+H-M+Ch+K
Series 2	Doroninskaya 275	23	292-298 1.1 nl	1.33	0.63	22	15	62	Flint, quartzite, clay, chert, siltstone, acid and medium effusives	$\frac{2-3}{3-5}$	—	2-3	—	1-5	H+V-Ch+V+K
	Doroninskaya 275	29	328-330.7 1.0 nl	0.57	0.19	20	10	70	Mica and clay shales, kaolinised sandstone, mudstone, acid effusives.	$\frac{0}{2-3}$	5-7	1-2	—	2-4	H+V-Ch+Ch?+K

Legend: C – maximum diameter, Md – medium diameter of fragments; Cal - calcite, Dol - dolomite; XRDA - X-ray diffraction analysis; H - hydromica, H~M – alternating-layer mica-montmorillonite mineral, Ch - chlorite, K - kaolinite, V - vermiculite, V ~ Ch - alternating-layer vermiculite-chlorite mineral.

<u>The second series</u> of testing involved the Lower Jurassic sandstone samples from a depth of 292–330 m, which were placed at a depth of 3 km under conditions of the initial subzone of deep catagenesis at a pressure of 150 at and a temperature of 85°C (table 1), and then at a depth of 5 km in the zone of deep catagenesis at a pressure of 500 at and a temperature of 135^0 C. The testing lasted 10 days at each stage.

3. RESULTS AND DISCUSSION

As a result of conducted testings, the following changes have been registered: 1 - ***in the structure of void space*** (morphology, pore sizes, open porosity ratio, porosity effectiveness and fracturing ratio, change in the volume and in total pore space surface and pore channels); 2 - ***in the mineral rock composition*** (in the appearance of new mineral phases, additional formation of authigenic minerals, crystalline transformation of minerals***); in structural transformations of the rock clastics*** (overconsolidation, deconsolidation of cataclasis, dissolution under pressure, recrystallization, plastic deformations of fragmental grains, changes in the ratios of intercrystalline contact types and coefficients of catagenesis).

Structural transformations of the clastic part and void space have become more apparent as a result of a 40-day test of rock samples from deep depths with maximum pressures (1500 at) at 160 °C, i.e. under conditions typical for deep catagenesis at CO_2 concentration in solution of 45%. The appearance of new mineral phases was not recorded in this test mode.

<u>After the first series of testing,</u> a part of calcitic cement in sandstone no. 40 dissolved, which caused the ***emergence of marmorised sites***. Besides, the connectivity increased, the volume of large pores and the specific surface of small-diameter pores in sandstone no. 21 became larger (fig. 2), the number of primary contacts sharply decreased, and the number of secondary contacts rose due to regeneration of quarts and albite, the number of plastic deformations of feldspars and effusites as well as suture contacts also increased. Sandstone no. 21 deconsolidated due to dissolution and cataclasis of feldspar. At the same time, coefficients A (number of contacts per grain) and Cc (compaction coefficient) considerably decreased (table 3).

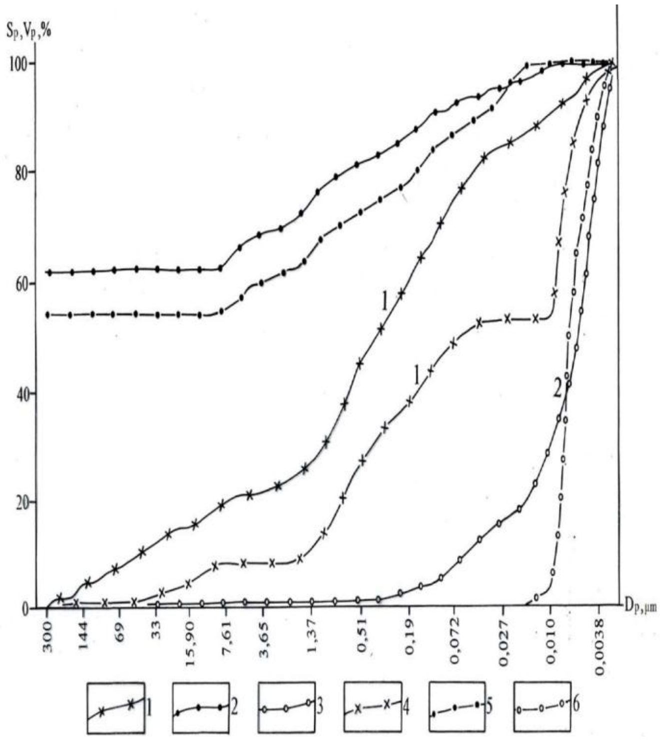

Fig2. *Cumulative curves of 1 – volume and 2 – pore surface depending on pore diameter before and after the first series of testing (Urengoyskaya 414 well, sample 21)*

Legend: Curves: 1 – mercury insertion; 2 – mercury displacement; 3 – changes in pore surface before testing; 4 – before mercury insertion; 5 – before mercury displacement; 6 – changes in pore surface after testing. Vp – pore volume; Sp – total pore surface; Dp – pore diameter

Table3. *Interrelation of Intergranular Contact Types and Catagenesis Coefficients of Sandy Rock Samples Before and After Testing*

				% of content	Types and quantity of intergranular contacts, %																Catagenesis coefficients			Porosity from mercury injection, %
	Well, №		Coring depth, м								Mechanical adaptation		Plastic deformation				Quartz regeneration	Quartz solution under pressure (full/not full)	Chemical dissolution	Structure-stylolite	Number of contacts per grain A	Catagenesis intensity I	Compaction coefficient Cc	
Series, stage		Sample No.			Pointy primary	secondary	Linear primary not full	full	Linear secondary not full	full	full	not full	mica	clay and clay shale	chert	effusive								
Series 1	Urengoyskaya 414	21	4888-4902	1	$\frac{5.0}{2.5}$		$\frac{10.1}{40.5}$		$\frac{2.5}{2.5}$		4.4	19.6	—	—	4.4	—	2.5	$\frac{1.2}{1.8}$	$\frac{3.1}{4.3}$	0.6	5.1	5.9	3.8	7.5
				2	$\frac{3.5}{2.1}$		$\frac{18.7}{24.4}$		$\frac{3.5}{2.8}$		4.3	12.3	—	0.7	3.5 fs	2.8 0.7	5.7	$\frac{0.7}{3.5}$	$\frac{1.4}{1.4}$	4.9	4.6	5.8	1.6	7.9
	Yuzhno-Chaselskaya 15	40	3820-3828	1	$\frac{9.7}{0.7}$		$\frac{28.3}{17.3}$		$\frac{2.9}{2.2}$		6.7	11.9	—	2.2	2.2	0.7	3.7	$\frac{1.4}{2.9}$	$\frac{0}{4.4}$	3.7	4.5	5.2	0.8	6.6
				2	$\frac{10.7}{0.82}$		$\frac{20.6}{8.3}$		$\frac{11.5}{5.7}$		6.6	3.3	—	—	6.5 fs	3.3 4.1	5.9	$\frac{2.5}{0.8}$	$\frac{1.6}{0.8}$	7.4	4.0	5.5	0.7	7.0
Series 2, stage 1	Doroninskaya 275	23	292-298	1	$\frac{3.7}{1.7}$		$\frac{6.4}{33.5}$		$\frac{1.7}{2.5}$		3.1	19.8	—	—	16.1	3.7	1.7	$\frac{0}{0.6}$	$\frac{0.6}{5.5}$	1.2	5.4	6.6	4.7	5.3
				2	$\frac{5.1}{0}$		$\frac{17.3}{29.7}$		$\frac{0.7}{0.7}$		2.9	16.6	1.4	8.7	5.8	1.4	2.9	$\frac{1.4}{0}$	$\frac{0.7}{3.8}$	0.7	5.1	6.0	1.5	10.6
	Doroninskaya 275	29	328-330.7	1	$\frac{12.8}{0.6}$		$\frac{21.9}{31.7}$		$\frac{1.2}{0}$		1.2	10.3	0.6	8.5	4.2	1.2 fs	1.8	$\frac{0.6}{0}$	$\frac{0}{4.2}$	—	5.3	5.8	1.6	6.5
				2	$\frac{4.5}{0}$		$\frac{17.7}{28.3}$		$\frac{1.9}{0.6}$		4.6	10.5	2.5	2.5	10.5	1.9 fs	5.0	$\frac{1.9}{1.3}$	$\frac{0}{4.6}$	0.6	5.1	6.0	2.0	8.7

% of content: 1 – before testing, 2 – after testing.

After the first stage of the second series testing at a temperature of 85^{0}C and a pressure of 150 at, the sandstone **no. 23** deconsolidated (fig. 3),. ***Its pore space was filled with liquid hydrocarbons*** and it became unfit for subsequent testing. The total weight of extracted bitumen made up 0.206 g. In **sandstone no. 29**, which was more argillaceous, structural transformations were not so pronounced (fig. 4). *As a result, porosity in sample no. 29 increased by 1.8% and made up 8.7%, and in sample no. 23 it increased more sharply (from 5.3% to 10.6%*, (table 3). After testing, the diffraction pattern of argillaceous minerals changed: in the medium-sandy fraction of sample 29 the structure imperfection of hydromica increased, its basal reflexes improved, and the structure of albite improved as well (reflex of 3.24 A^o), fig. 5.

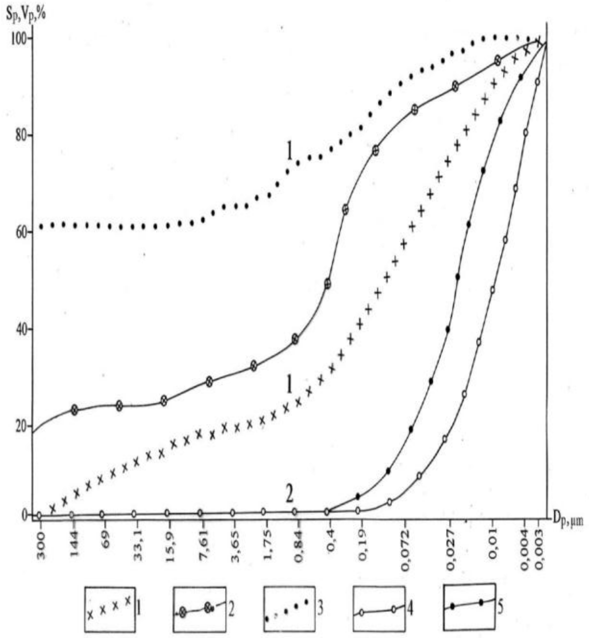

Fig3. *Cumulative curves of dependence of 1 – pore volume on pore diameter; 2 – pore surface on pore diameter before and after testing, series 2, stage 1 (Doroninskaya 275 well, sample 23)*

Legend: mercury insertion curve: 1 – before testing; 2 – after testing; 3 – mercury displacement curve. Changes in total pore surface; 4 – before testing; 5 – after testing. Vp – pore volume; Sp – total pore surface; Dp – pore diameter

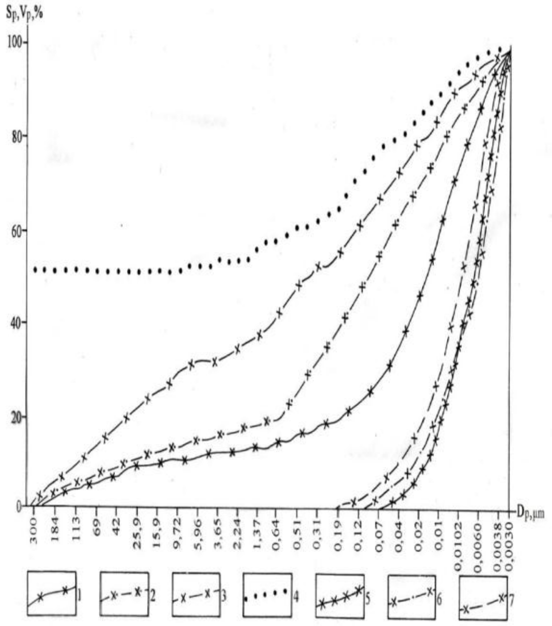

Fig4. *Cumulative curves of volume and pore surface depending on pore diameter before and after the second series of testing (Doroninskaya 275 well, sample 29)*

Legend: mercury insertion curve: 1 – before testing; 2 – after testing (stage 1); 3 – after testing (stage 2). Mercury displacement curve: 4 – before testing. Changes in pore surface: 5 – before testing; 6 – after testing (stage 1); 7 – after testing (stage 2). Vp – pore volume; Sp –pore surface; Dp – pore diameter

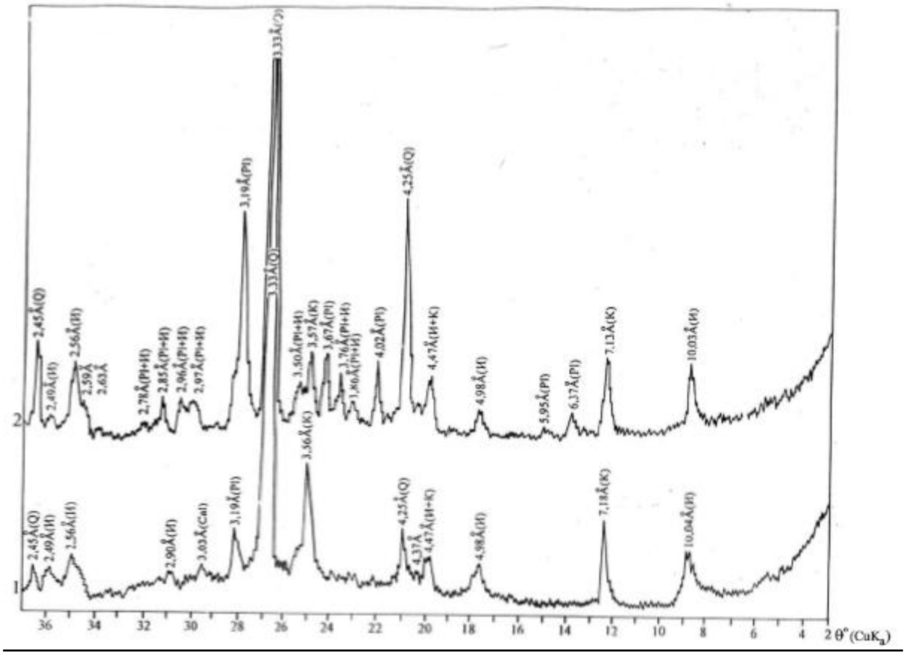

Fig5. *X-ray diffraction patterns fragment of the fraction of 0.25–0.1 mm of sample 29 (Doroninskaya 275 well), treated with 1N HCl (1 – before and 2 – after testing, series 2, stage 2)*

Legend: Q – quartz, I – illite, Pl – plagioclase, Cal – calcite, K – kaolinite. Recording conditions: DRON – 3, CuK$_a$, 40 mA. Analysis by N.T. Mandrikova

After the second stage of the second series testing, at a temperature of 135°C and a pressure of 500 at, ***sample no. 23 entirely crumbled***. In powder no. 23, the disorder and structure imperfection of argillaceous minerals increased (fig. 6). Layers with defect brucite networks appeared in chlorite structure. *Additional quartz, kaolinite, chlorite, hydromica, and albite formed in the samples*. Previously a number of researchers have reported on the possibility of synthesizing these minerals from overheated water solutions of alkaline composition [6 - 9, etc.].

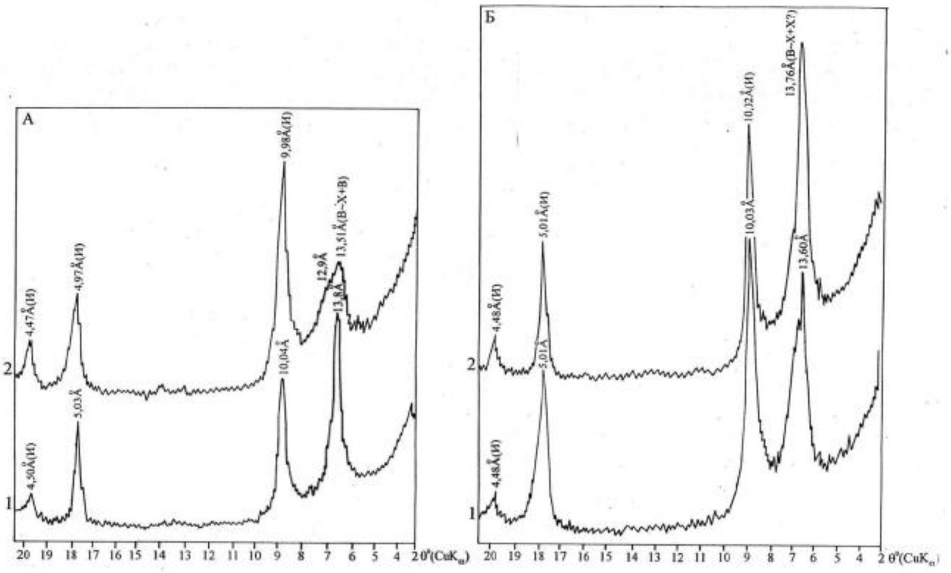

Fig6. *X-ray diffraction patterns fragment of the fine fraction of samples 23 (A) and 29 (Б), Doroninskaya 275 well, calcined at T = 550 ºC during 2 hours (1 – before and 2 – after testing, series 2, stage 2)*

Legend: Q – quartz, B – vermiculite, X – chlorite, B ~ X - alternating-layer vermiculite-chlorite mineral. Recording conditions: DRON – 3, CuK$_a$, 40 kV, 40 mA. Analysis by N.T. Mandrikova.

Despite little testing time, ***the rate of mineral alteration was quite high***, which is due to a great influence of hydrolysis and ion exchange between rock components and hydrothermal solution and above all, the presence of alkaline feldspars, hydromicas and mixed lattice phases. The chemical analysis of solutions after the 1st and 2nd stages of the second series testings showed that the concentration of *Ca, Mg, Fe and Mn* ions after hydrothermal influence with the participation of CO_2 increased sharply, and the *K* and *Na* ions decreased. This is obviously related to mechanical capture or sorption, in particular, of potassium ions by the structure of hydromicas and the liberation of calcium ions in the process of ion exchange.

Thus, the first series of testing resulted in more intense structural transformation of **greywacke sandstone no. 21 with a small cement content, obtained from deep subsurface**. After 10 days of hydrothermal influence at a pressure of 150 at and a temperature of 85^o C, the rocks deconsolidated, and additional volume appeared as a result of aluminosilicate rock matrix dissolution. During the second series of testing, most pronounced transformation was indicated in sandstone after the second stage of testing under severe conditions ($T^o = 135^oC$, $P = 500$ at). After hydrothermal treatment with the involvement of CO_2, ***the effective porosity of sandstones rose by 2.5–3.5%, so the reservoir became commercial.*** A practically important result was that associated bitumoids gained the capacity for migration at hydrothermal impact in carbon dioxide environment. ***This means that the presence of carbon dioxide in the solution stimulates the growing mobility of bitumoids.***

The experimental modelling confirmed the assumed formation of deconsolidated rocks and better reservoirs in tectonically active zones as a result of hydrothermal effect of hot solutions saturated with carbon dioxide on polymictic sandstones. It was proven that the presence of carbon dioxide in the solution favours the transitions of associated bitumoids to a movable state, which is of great practical importance in choosing an optimal well exploitation regime when producing high-viscosity oil.

4. CONCLUSION

1. More intense structural transformations were identified in greywacke sandstone with little cement content sampled from a deep depth. The most intense structural and mineral transformations of sandy rocks from shallow depths occurred after the second series of testing after the second testing stage at $T = 135^o$ C and $P = 500$ atm. Even after 10 days of hydrothermal influence at a pressure of 150 at and a temperature of 85^0 C, the rocks deconsolidated and additional voids were formed due to leaching of feldspar and mica, as well as new mineral phases – kaolinite, quartz, and albite – were synthesised.

2. Despite relatively low temperatures and short duration of testing, the rate of mineral transformations was rather high. The formation of additional quantity of authigenic albite and protodolomite was indicated as early as after 10 days of hydrothermal influence on sandy rocks at a temperature of 85^o C and a pressure of 150 at. This was due to a great impact of hydration, hydrolysis, and, especially, ion exchange between rock components and hydrothermal solution.

3. The testing resulted in the increase of effective porosity of polymictic greywacke sandstones by 2.5–3.5%, which indicates a principal possibility of the reservoir properties improvement in tectonic dislocation zones, with the involvement of hydrothermal solutions saturated with carbon dioxide.

4. After testing at a pressure of 150 at and a temperature of 85^o C, in the carbon dioxide environment of sandstone no. 23 containing residual bound asphalt-resin substances, after 10 days bitumoids became movable, which resulted in filling of the entire void space with liquid oil. This result is of a practical interest, as it indicates that the presence of carbon dioxide in the solution stimulates increase in bitumoids movability. This becomes very important in the development of technology and the choice of an optimal regime of producing high-viscosity and hard-to-recover oil.

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