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Hydrogeological Factors of the Ore Genesis in the Sedimentary Basins

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***Abstract*—**The present work was made for the purpose of evaluating the interstitial water's role in the mobilization of metal elements of clay deposits and occurrences in sedimentary formation in the hydro-geological basins. The experiments were performed by using a special facility, which allows adjusting the pressure, temperature, and the frequency of the acoustic vibrations. The dates for study were samples of the oil shales (Baltic career, O_2kk) and clay rocks, mainly montmorillonite composition (Borehole SG-12000, the depth of selection 1000–3600 m, the Azov-Kuban trough, N_1). After interstitial water squeezing from the rock samples, decrease in the original content of the rock forming components including trace metals V, Cr, Co, Ni, Cu, Zn, Zr, Mo, Pb, W, Ti, and others was recorded. The experiments made it possible to evaluate the ore elements output and organic matters with the interstitial waters. Calculations have shown that, in standard conditions, from each ton of the oil shales, 5-6 kg of ore elements and 9-10 kg of organic matter can be escaped. A quantity of matter, migrating from clays in the process of solidification, is changed depending on the lithogenesis stage: more recent unrealized deposits lose more ore and organic materials than the clay rocks, selected from depth over 3000 m. Each ton of clays in the depth interval 1000-1500 m is able to generate 3-5 kg of the ore elements and 6-8 kg of the organic matters. The interstitial waters are a freight forwarder over transferring these matters in the reservoir beds. It was concluded that the interstitial waters which escaped from the study samples are solutions with abnormal high concentrations of the metals and organic matters. In the discharge zones of the sediment basins, such fluids can create paragenetic associations of the sedimentary-catagenetic ore and hydrocarbon mineral resources accumulations.

***Keywords*—**Hydrocarbons, ore genesis, paragenesis, interstitial waters.

I. Introduction

The questions about studying the ore and hydrocarbons accumulations paragenetic interrelation in the sedimentary basins are considered by many scientists [1]-[7]. Researches of the last years showed that, under diagenesis and catagenesis of huge clay sediment sections enriched by the organic matter, interstitial waters extracting from them, can produce not only hydrocarbons but also the ore elements. By using as an example the series of stratiform fields of iron, manganese, lead and copper, it may be observed that many of these fields are spacely associated with the oil-and-gas bearing basins. It is noted about the complex metal-bearing dissolution forming, which generated in the expelled systems under the argillaceous sediments dehydration [8]-[13]. It was established that the interstitial waters extracted during the compaction of fine-grained sedimentary rocks are highly aggressive and can dissolve large amounts of organic and mineral components [14], [15].

The objective of the present work is to show the interstitial waters' role in the ore elements mass transfer during compaction and dehydration of the argillaceous masses enriched by the organic matter. For the first time, the influence of temperature-pressure and vibroacoustic effects on the interstitial fluids mobility have been experimentally studied. It makes the experimental model similar to the real geological conditions within the depression sedimentary basins.

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II. Working Procedure

The finely dispersed rocks with the high content of organic matter and different catagenetic transformation have been used for experimentation:

1) Kukersite oil shales of the Cisbaltic basin (O_2kk) are multicomponent argillaceous-carbonate rocks which contain 42–45 wt.% of concentrated organic matter; they were sampled from the open pit and under forming conditions. They are related to early catagenesis stage.
2) Clays of Azov-Kuban basin (N_2^1) are dense rocks of montmorillonite composition with the content of dispersed organic matter 2–4 wt.%; they were sampled in the depth of 1000–3600 m of the Kuban well SG-12000, and according to the forming conditions, they demonstrate the multi stage processes of dehydration and catagenesis.

The working procedure covered an experimental simulation of the argillaceous rock's thickening processes in approximately natural conditions situation. The task was being performed by using the equipment specially designed for modeling of these processes. It allows simulating these processes in the wide temperature range, pressures difference, and impulsive seismoacoustic emission.

Before starting the experiments, all samples have been normalized with the water content of 23.0%, which conforms to the half of a common value of the maximum molecular moisture capacity specific to the clays. After extracting the interstitial water, the rock's residual moisture was being decreased to 3.5–5.7%; in the other words, a high quantity of adsorbed water was involved into the dehydration process.

Four series of experiments were made in the different mode of temperature, pressure, and different frequencies acoustic vibrations exposure to the studying samples of the argillaceous rocks. In the first experiment set (mode I), continuous stepped sediments with the graded pressure built up from 0 to 20 MPa and temperature 25 °C are simulated. In the second

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experiment set (mode II), the conditions of seismic tectonic stress were created by the application of sign-variable impulsive baric influence from 0 to 40 MPa at the temperature 40 °C and acoustic vibrations 20 kHz. In the third experiment set (mode III), the temperature was increased up to 80 °C under pressure 40 MPa. Sign-variable impulsive baric loads alternations were accompanied by the acoustic background overlapping in the frequency interval 50-60 kHz with power 1 kW. In the fourth experiment set (mode IV), pressure on the rock's samples is increased to 80 MPa, while other characteristics are stayed the same.

The interstitial waters selection was carried out of fractures (under pressure 20 MPa, 40 MPa, 80 MPa). It gave the possibility to see about the interstitial waters content's change under the sediment simulation on the depth more than 3000 m. Each experiment is continued till the interstitial water's exhalation ending (120 hours).

The interest for the study of seismic impact to extraction and compositional alteration of interstitial waters within argillaceous deposits is related to the well-known facts of hydrochemical and hydrodynamic characteristics of aquifer system transformation in the area of hundreds or even thousands kilometers around the earthquake focus [16], [17]. Also, it is considered that the acoustic vibrations of the sonic frequency and ultrasonic frequency are able to change a potential of the "sample-electrolyte" system a few times, in order to stimulate the geochemical activation of the interstitial waters in the biologic and technical objects, and to force the interstitial water's possibility of a mass transfer [18]-[21]. For this reason, except the continuous thermobaric loads, the conditions of additional vibration and acoustic impacts to the samples were created in the experiments.

Basic and trace component rock's and interstitial water's compositions are analyzed by the standard chemistry quantitative method of atomic emission spectrometry with the inductively coupled plasmas. The organic carbon content in the rock is determined by the combustion method in the oxygenic atmosphere under the 800 ○C temperature, and in the interstitial waters – by a decompounding in the sulphurous-chromic concentrate mixture under the 130 ○C temperature with a coulometric ending and wet combustion under the 800 ○C temperature with following infrared detection.

The analysis results for the rock's basic and trace component composition showed that composition of the rock-forming oxides and ore elements conform to the average value in the shales and argillaceous rocks. For the distribution characteristic of the ore elements, Clarks of concentrations (Cc) were estimated (the concentration of an element in rock relative to its crustal abundance) [22]. In the kukersite oil shales, for most of the ore elements, Cc>1, and also the highest value (Cc=1.2–3.7) are noted for Sc, V, Co, Ni, Cu, Zn, As, Mo, Hf, W, Pb.

In the argillaceous rocks, Cc of the ore elements and also some less-common elements, dispersed elements, and radioactive elements increase the section from 1000 to 3600 m. For most of elements, the peak value (Cc=1.2–1.8) is accounted for the center portion of the section (1500–3000 m). In the all cases, the excess Cc>1 is confined to the rocks which are enriched by the organic matter.

III. Evaluation

The experiments with the kukersite oil-shales showed that after interstitial water's extracting, the content of many components in the test samples is decreased. Especially, such tendency is appeared in the mode III (Fig. 1). Therefore, the summarized weight content of base rock-forming oxides SiO_2, CaO, SO_3, $A1_2O_3$, Fe_2O_3, K_2O, Na_2O, MgO is decreased to 1.8-2.5 wt.% and Zn, Cu, Ni, V, Pb, Zr, Co, W, Mo, As, Rb, Sc, Y, La, Ga, etc. to 0.5–0.7 wt.%, also organic matters to 0.9–1.1 wt.%. The overall losses from oil-shales can be of 20–25 kg per ton, which includes the ore elements as high as 5–6 kg and even more essential organic matter's losses as high as 9–10 kg.

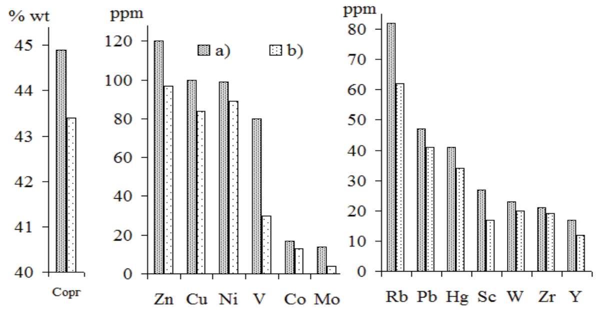

Fig. 1 The organic matter content (C_{org}) and ore elements change in the kukersite oil-shales: a) initial content of the elements in the oil-shales before experiment's start; b) content of the elements after experiment

Fluent, mineral, and organic matter's evacuation from the oil-shales is followed by its content ramp-up in the interstitial waters and reaches its maximum in the mode III under the loads simulating seismic-tectonic activity, and thermobaric influence increases (Fig. 2).

The observed high organic carbon and ore element's concentrations owe its origin not only to the mother rock's content but also to the special extracting fluid properties. Their aggressivity and solvent abilities are explained by the water's structure features in the surface force of finely dispersed atmosphere action field [23], [24]. Under a stress-pressure load which is enforced by acoustic vibrations (mode II, III), the molecule's dimeric associations role is increasing.

It facilitates the solubility of polar and nonpolar compounds significantly. Moreover, it also leads to large increase in ore elements and organic matter content. It reaches the values which are unusual for the gravity ground waters. For example, cobalt content varied from 19 to 100 ppb, nickel content varied from 20 to 70 ppb, vanadium content varied from 7 to 27 ppb, and so on. Extremely high content was noted for the following elements (ppm): iron (2–8), copper (0.06–1.7), and zinc (0.07–1.6).

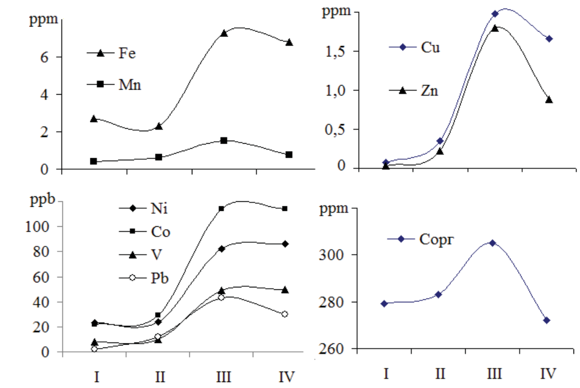

Fig. 2 The ore elements and organic carbon content changes in the interstitial waters evolving from the kukersite oil-shales in different modes: I, II, III, IV (description is on the text)

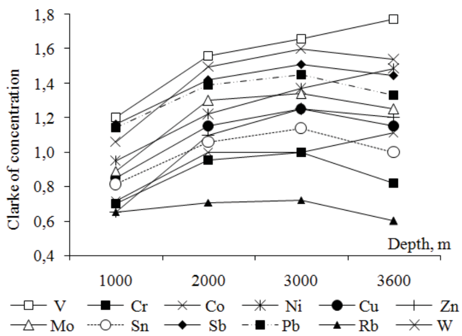

Fig. 3 Change of the Cc trace components in the argillaceous rocks (N_{1+2}) through the section of the Kuban well SG-12000

Oil-shales (kukersite) are the rocks with the concentrate organic matter. It is never subjected to the thermobaric influents in natural conditions, and they are not mature enough to generate oil [25].

Results of experiments which imitate the catagenetic loads on the oil-shales showed the ability of these rocks to generate not only hydrocarbons but also fluids enriched with the ore material. In fact, the minerals and ore matters catagenetic losses by the oil-shales formation's thickening lead to its deformation, fracturing, fault polish forming, pore-vesicular-fractures zones forming, etc. in natural conditions [26]. With the increase of migration pathways, conditions for the outflux of fluids together with mineral and organic components are created. The experiment's results prove the possibility of such mechanism.

The experiments were carried out at sufficiently low temperatures (40–80 °C) which do not match to the catagenesis ephebic stage, but the losses of organic matter were extremely essential. Therefore, even little intensity of vibroacoustic loads lead to the geochemical transformation of a source rock and they are comparable with the catagenesis thermobaric factors in term of effectiveness. Besides the mineral and organic matter's subtraction from the argillaceous rocks to adjoining environment, the reprecipitation processes of the salts and naftides occurred. For this reason, the metal sulfides precipitation and authigenic minerals crystallization accompany the naftides and ore occurrence. It is noted that under the pressure rising to 80 MPa, the organic carbon content and some ore elements contents in the extracted interstitial waters do not increase, but they decrease. We assume that the laboratory analogue of the generative potential realization of the rocks in the conditions simulating the deposits submersion to the depth of 3000 m was obtained. Many researches consider that this depth corresponds to the main zone of argillaceous deposits dehydration and organic matter's catagenesis. It must be emphasized that in the specified baric interval, there is an obvious tendency for the variation of the organic carbon and porphyric metals (Ni, Co, V) content.

It can also be noted that the ore element's concentrations dissolved in the interstitial waters are quite comparable with the metal's field areas waters, fumarole therms and hydrotherms. The presented dates indicate the important role of interstitial waters in the organic and mineral components migration from the argillaceous rocks. Catagenetic losses of the organic matter in the oil-shales formations are long-familiar. For example, according to [27], in the cis-Caspian depression on the depth 1–2 km, the shales volume is decreased to 60% because they contain the organic matter and carbonate rock, which cannot lose only volume, but also can lose mass by the thickening.

The most probable is that the migration's basic form of the ore elements in the extracted interstitial waters is complex metal-organic compounds of increased solubility forming of chelate ring. They have high migrational capability compared to nonorganic complexing compound subject to hydrolysis, hydrolytic polymerization, and to other processes which promoted their depositing.

The results of interstitial waters extracting process simulation from the Neogene age clays of the Kuban well SG-12000 are discussed below. In this series of experiments, the samples collection of the argillaceous rocks obtained from 1000 to 3600 m interval was analyzed. It is considered that in the West Pre-Caucasian region, where one of the most stressful pressure-and-temperature conditions for Russian oil-and-gas bearing basis exits, the Miocene and Pleiocene deposits realized its oil-and-gas generation potential [28]. It was confirmed by the obtained results. Initial content of the rock's forming oxides and ore elements in the upper level clays (1000–1500 m) are compared to the values of Clarks. A content of the silicon oxide, aluminic oxide, ferrous oxide, sulfur oxide and manganous oxide increases with depth. Cc of the ore elements, less-common elements, and rare-earth elements in the 1500–3000 m interval rise steeply (Fig. 3). However, from there on the depth more than 3000 m a rise of their content are decelerated on the reached values level or even decreased. Only nickel, vanadium, and cobalt's concentrations continue to rise. Apparently such porphyrinic type elements' behavior relates with oil-and-gas generation processes upgrading. A biogenic migration of these elements' existence in the shape of the stable organic-mineral complexes is emphasized once again.

The organic matters and the mineral components, which were determined in the experiments with oil-shales earlier, are repeated in the experiments with the clays samples of the Kuban well after interstitial waters extracting. Through the deposits section, the highest losses of a rock's components total weight in 1500–3000 m interval are fixed. The mineral and organic matters subtraction is decelerated below this depth. Rapid reduction of extracted substances mass is observed in the interval 2500–3000 m (Fig. 4).

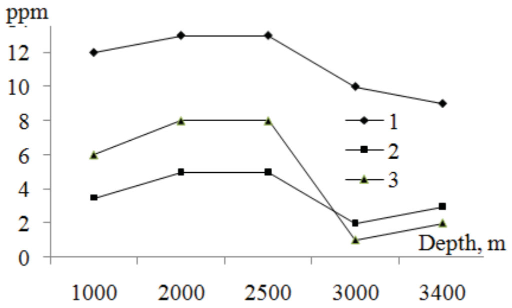

Fig. 4 The mineral and organic matters losses after interstitial waters extracting from the argillaceous rocks (Kuban well SG-12000, N_{1+2}) in depending of the occurrence depth: 1 – extracting minerals mass; 2 – extracting ore elements mass; 3 – extracting organic matters mass

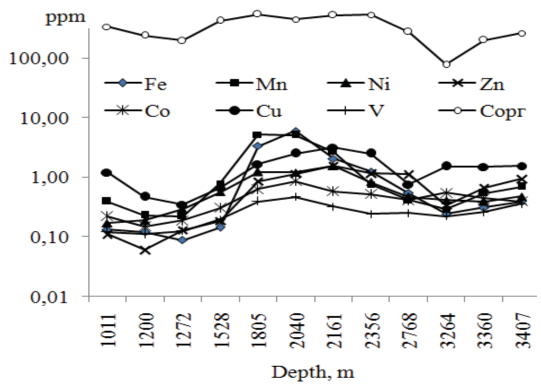

Fig. 5 Organic carbon and ore elements content change in the interstitial waters extracted from the argillaceous rocks from Kuban well SG-12000

It may be that on this depth, the hydrocarbons generation comes to an end. The micro-oil migration processes are activated, and along with it, ore elements are deleted to the ambient interstitial space. Performing calculations (in difference between initial content in the rock and final – after interstitial waters extracting) showed that the common mass of all the matters migrating from clays under its thickening is changing depending on a sampling depth; in the other words, lithogenesis stage.

In the interstitial waters extracted from the argillaceous rocks with different catagenetic maturation degree, the maximum ore elements and organic matters content is occurred in 1500-3000 m interval (Fig. 5). Metal content within the interstitial waters decreases along with the rock's mobilization capacity decrease. On the depth over than 3000–3500 m, the metal-intension is stabilized in spite of temperature increasing to 80 °C and pressure to 80 MPa. However, it does not mean that the ore elements and organic matters wasting process is finished. It can be believed that their further migration can activate again under the rock's crystalline texture rearrangement due to harder thermobaric conditions and seismic acoustic phenomena.

During the change of simulation conditions from slight impact on the samples to gradual increase of the thermobaric and seismic acoustic loads, the organic carbon concentrations in extracted interstitial waters increase. It is interesting that the maximum ore components contents are confined to the same depth's intervals. It can indicate to their migration processes union.

The research results revealed that the appropriate catagenic conditions of interaction between the interstitial waters and mineral matrix of finely dispersed deposit rocks were the important factors of the mass transfer and depositing of ore and hydrocarbon components into the ambient area (reservoir rocks and excessive fissuring zones). The transfer proportions of the dispersed-scattered organic-mineral components under the argillaceous deposits dehydration depend on not only thermobaric factors but also on a seismic activity degree and geo-dynamic potential stress in the sedimentary basins. The change of redox conditions along the interstitial fluid flow, the interaction between the fluids, rocks and waters of the other geochemical ambiences create good conditions for extracting the dissolved organic matter, liquid, and gaseous hydrocarbons, as well as the oil-and-gas formations and metals deposition. It is caused by the sudden pressure decrease leading to the disequilibrium in the catagenic system "rock-interstitial fluids". West Siberian, Volgo-Ural, Azovo-Kuban, Dneprovo-Donetsk, and West Canadian basins can be noted as the examples of paragenesis of naftide and ore occurrences, associated to the selvedges of troughs of petroleum basins, where there are no volcanic sequences [11].

IV. Conclusions

The dehydration processes of the argillaceous rocks, interstitial waters extracting and their reforming to the naftide- and ore-produced dissolutions go permanently during a long geological history. A transit system is forming:

Argillaceous rocks enriched by the organic matter and ore components contained on the Cc level ⇒ adsorbed and film (osmatic) interstitial waters ⇒ naftide- and ore-produced dissolutions ⇒ discharge zones of the expelled waters ⇒ sediment-catagenetic fields of the fossil fuels and fossil minerals.

The organic matters and ore elements extracting from the interstitial waters synchronism under the argillaceous rocks thickening indicates that the ore-produced dissolutions generation is not associated with the magma chambers. The ore elements are extracted together with interstitial (aggressive bound) waters from finely dispersed deposits with the sub-Cc of metals.

Accomplished investigations are aimed at the development of theoretical basis and methodological approaches to the study of paragenetic relation between the ore and oil-and-gas formation processes, and at the discovery of the regularities of the hydrocarbons fields with the commercial ore fields collocation.

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