

Experimental study of influence of oil-cracking processes in hydrothermal solutions on formation of various types of oil-and-gas deposits

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Introduction. Cracking of crude oil and its medium and heavy fractions is the basic industrial process of reception of light gasoline-kerosene fractions and other oil-products which are widely used in the petrochemical industry. At the same time, it seems likely, that cracking to some extent it should be shown directly in natural conditions at influence on crude oil of high temperatures and pressures. Moreover, to it, according to a number of researchers [Simoneit, 1995; Bazhenov and Lein, 2002; etc.] are caused by features of composition and other characteristics of so-called hydrothermal oil in areas of modern volcanic and hydrothermal activity, in which the temperature quite often reach 400°C and above. If cracking oil really takes place in the nature it in many respects can explain features of distribution in the interior of the Earth of various types of oil-and-gas deposits. Earlier experimental studies confirm possibility in principle of realization oil-cracking processes in the hydrothermal systems close on thermo baric parameters [Bjoroy et al, 1992; Huang, 1999; Huang et al, 2001; etc.]. Especially convincing in this respect were experiments in which comparison of parent and residual oil was spent, as well as with the hydrocarbons trapped in synthetic fluid inclusions in quartz [Teinturier et al, 2003]. It has allowed the specified authors to show, that oil-cracking processes practically does not occur at temperature 250°C and pressure 212 bars. But it is actively shown already at temperature 350°C and pressure 400 bars.

In the presented work experimental study oil-cracking processes for the purpose of finding-out of influence of their on formation of oil-and-gas deposits of various types is undertaken. Researches were carried out in a complex, but basically with use growth aqueous-hydrocarbon inclusions in the quartz which has been grown up simultaneously with realization of interaction of hydrothermal solutions with crude oil in a wide range of temperatures and pressure.

Methods, equipment and materials. Experiments were carried out by a hydrothermal method of temperature gradient in the heat resisting autoclaves in volume 30, 50 and 280 ml made of stainless steel and Cr-Ni of an alloy. The diaphragm dividing zones of dissolution of charge and growth of crystals, in an autoclave was absent. It created conditions for continuous convective mixing of solutions during all experiment and formation of fluid inclusions on all length of grown crystal. Autoclaves heated up in mine electric furnaces with two independent heaters. Accuracy of definition of temperatures was $\pm 2^\circ\text{C}$. Pressure was set by pouring of a solution with mark-to-space ratio to be determined by P-V-T diagrams for corresponding or relatives to composition of solutions, but in absence of such diagrams by PVT dependences for pure water. The initial water-in-oil mixes for experiments were prepared from oils, selected from various oil-and-gas bearing deposits of Russia, and neutral (10 and 25 wt. % NaCl), alkalescent (5 and 10 wt. % NaHCO_3) and alkaline (3.0, 5.0 and 7.5 wt. % Na_2CO_3) aqueous solutions. The share of oil in the water-in-oil mixes changed from 0.01 to 50 vol. %. In some experiments instead of oil were used in its average and heavy fractions whose share in mixes made from 12 to 36 vol. %. In bottom (hotter) zone of an autoclave it was established from four to six charge quartz bars in the size 2 x 4 x 80 mm. One more quartz bar of ZY-orientation, in the length from 140 to 208 mm (depending on the size of autoclaves), was suspended on a framework in top, less hot zone of autoclave, and served as seed

for growth of quartz with fluid inclusions. The autoclave was filled in with consistently by water solution and liquid hydrocarbons in the set proportions.

Experiments were carried out at temperatures from 220/260°C to 490/500°C and fillings of autoclaves from 50 to 80 %. After end of experiments, products of interaction of oil and its fractions with hydrothermal solutions were studied under binocular and polarizing microscopes, were exposed X-ray, fluorescence and microprobe analysis. Initial and residual oil and its fractions were characterized by IR spectra recorded on a spectrometer Avatar 320 FT-IR of firm Nicolet, and chromatograms, received on chromatograph Perkin Elmer Clarus 5000 using of capillary column Solgel of 60 cm, gas-carrier - helium. From the grown quartz prepared the polished plates of thickness 0.5-2.0 mm for studying of fluid and solid inclusions. Phase states and fractional composition of hydrocarbons were defined visually and on temperatures of the over point at heating of inclusions in measuring microthermometry complex THMSG-600 of firm Linkam, microscope Amplival, supplied with a set long-focus objectives, a video camera and operating computer. Liquid and gaseous phases in individual fluid inclusions were identified on fundamental bands of absorption of IR spectra in a range of 6000-2600 cm^{-1} recorded by means of IR microscope Continuum and single-beam FT-IR of spectrometer Nicolet, Nexus with the minimum size of the aperture 5 microns (resolution of 4 cm^{-1}). Distribution of hydrocarbons in inclusions was supervised using micro spectrophotometer marks QDI 302, firms CRAIC, on the basis of microscope LEICA DM 2500 P.

In total, more than 100 experiments were carried out by duration from 14 till 30 days.

Results and discussion. Fluid inclusions in the quartz formed at interaction of hydrothermal solutions with crude oil and its basic fractions at relatively low temperatures (220-3320°C) and pressure of about 5-50 MPa, are characterized by two-phase (L1+G) - or three-phase (from $L1 \geq G > L2$ to $L2 \geq L1 > G$) states (where L1 - a aqueous solution, G - a gas phase and L2 - liquid hydrocarbons (oil or its fractions)). In a gas phase, except aqueous vapor, gas hydrocarbons it is not fixed. In case of increase of temperature and pressure in inclusions, as a rule, in the beginning disappears the gas phase with transition of the fluid to two-phase liquid state with correlation of phases from $L1 > L2$ to $L2 > L1$ (depending on predominance of corresponded phase in initial inclusion). The existence of such two-phase aqueous-oil liquid fluids without a free gas phase in the conditions of short-term heating in a heat chamber is tracked to 385-405°C (fig. 1).

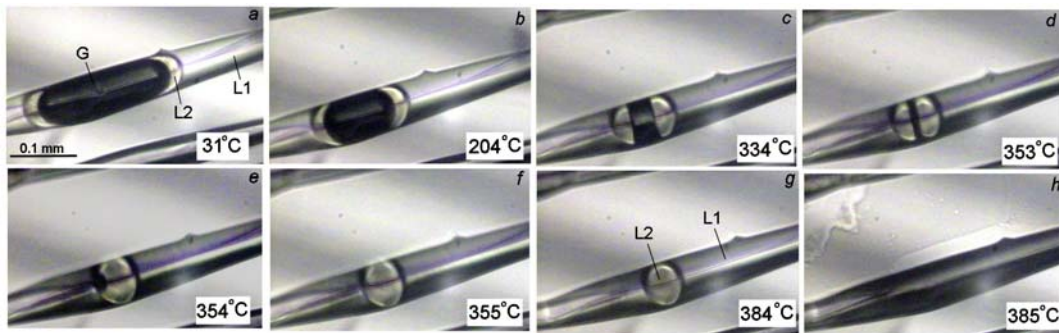


Fig. 1. Transformation three-phase gas-liquid ($L1 > G > L2$) fluid in liquid two-phase ($L1 > L2$) aqueous-oil fluid in process of rise in temperature (and, accordingly, pressure). At 385°C has occurred depressurization inclusions.

It testifies about possibility of existence in the Earth interior at the indicated TP-parameters of aqueous-oil fluids without a free gas phase. The contents dissolved in an aqueous phase liquids hydrocarbons before depressurization of the inclusions is about of 8-10 vol. %. Taking into account average values of geothermal gradients and hydro and litho static pressures such fluids without free gas can exist in the Earth interior at depths about of 3.5-4.5 km.

Other phase composition and other character of phase transformations have place in fluid inclusions in the quartz crystals grown at higher temperatures (330-490°C) and pressure (traced up to 120 MPa). In usual conditions such inclusions are multiphase essentially liquid ($L1 \geq G > L2 > SB$) or essentially gas ($G \gg L1 \approx L2 > SB$), where L1 - aqueous solution, G - gas hydrocarbons, mainly methane, L2 - liquid

hydrocarbons (oil or its fractions) and SB - solid bitumen (asphalt). Besides in such inclusions additional liquid phases L3 and L4 are often observed (fig. 2).

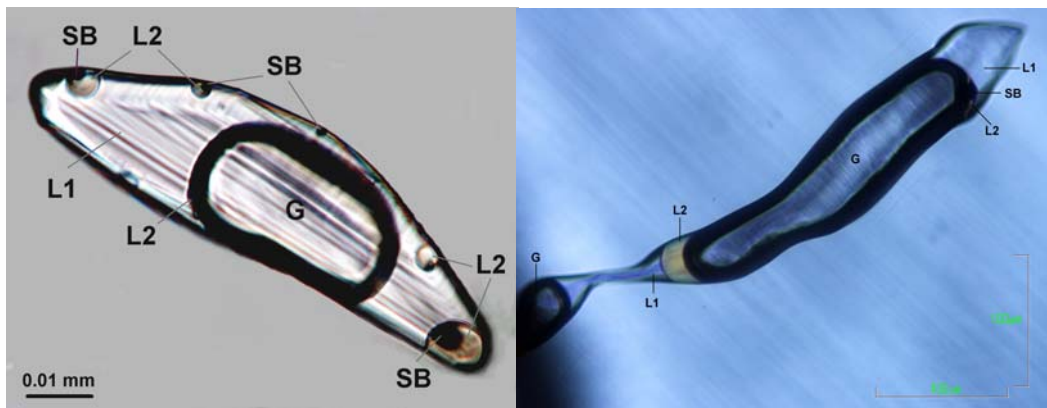


Fig. 2. Essentially liquid (at the left) and essentially gas (on the right) aqueous-hydrocarbon inclusions in which liquid hydrocarbons (L2) are presented gasoline-kerosene fraction, gas (G) - basically methane, and solid bitumen (SB) - asphalt.

These phases are dissolved in phase L2 at 94 and 127°C, respectively, and phase L2 is completely dissolved in gas hydrocarbons in the range of temperatures 240 – 280 °C with formation of two-phase gas-liquid fluid (L1> G) (fig. 3).

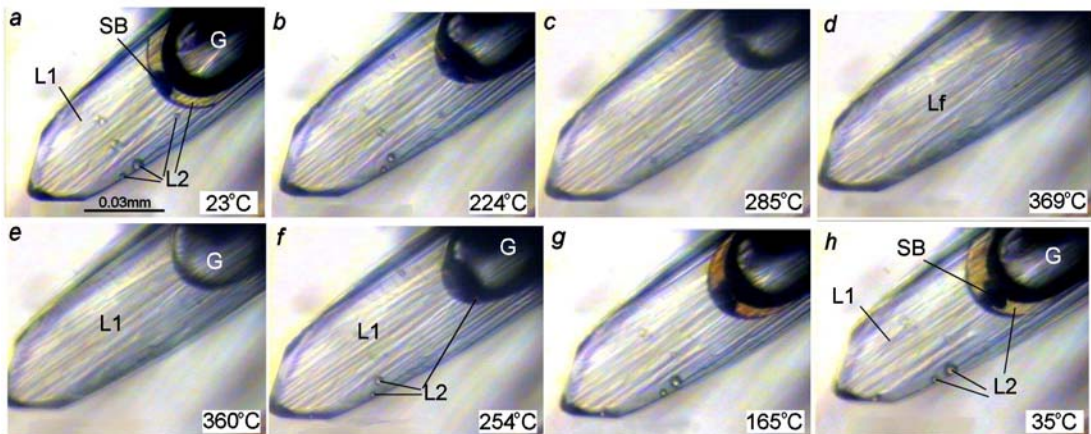


Fig. 3. Transformation of multiphase essentially liquid fluid (L1> G>> L2> SB) in process of rise in temperature (and, accordingly, pressure) in two-phase gas(hydrocarbon)-aqueous fluid with completely dissolved liquid gasoline-kerosene fractions (L1> G) with further (369-372 °C) transition in homogeneous supercritical state. Cooling restores original state of fluid.

It essentially distinguishes them from the two-phase liquid aqueous-oil fluids in inclusions of low temperature quartz. Oil (especially its medium and heavy fractions) in high-temperature (from 330 to 500°C) hydrothermal solutions are actively being cracked with formation easy gasoline-kerosene fractions that are fixed on vigorous boiling at temperatures from 60 to 240 – 270°C, and also by chromatograms initial oil and its medium and heavy fractions. As a whole, this process, possibly, reflects conditions at which are formed condensate pools and oil-gas condensate deposits. Heating of such fluids to the temperatures close to a critical point of water, leads to their transition into homogeneous supercritical state. It specifies in possibility of existence and carrying over in the interior of the Earth of enormous quantities of the liquid hydrocarbons enriched by light and medium oil fractions, in the form of

supercritical fluids. Taking into account representations about average geothermal gradients and hydro- and litho static pressures, aqueous-hydrocarbon fluids in such state should be at depths of 12-15 km.

Conclusion. Carried out researches testify to essential differences phase states of hydrocarbons in the fluids generated at interaction of oil and its fractions with hydrothermal solutions at temperatures below 320°C and above 330°C (basically 350 – 500°C) and pressure of saturated steam and above.

These differences are consequence of oil-cracking processes (to be exact, its medium and heavy fractions) with formation mainly gasoline-kerosene fractions, gas hydrocarbons, basically methane, and residual solid bitumen. Temperature and pressure in interior of the Earth are defined by real thermo gradient and hydro- lithostatic by pressures. The same parameters, taking into account composition and relation of phases in water-hydrocarbon fluids, define finally, phase states and opportunities of oil-cracking. It inevitably should result by formation of various types of oil-and-gas deposits.

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