Fluid inclusions in vein calcite from the productive reservoirs of the Astrakhansky gas condensate field

N V Sokerina1, S N Shanina1, M Yu Sokerin1, A N Kolchugin2, S I Isaenko1

1 Institute of Geology, FIC Komi Scientific Center, Ural Branch of the Russian Academy of Sciences, Syktyvkar, Russia
2 Kazan Federal University, Kazan, Russia

E-mail: sokerina@geo.komisc.ru

Abstract. Fluid inclusions from calcite veins were studied the Astrakhanskoye gas condensate field. It was done for the identify the conditions for the formation of oil reservoirs located in bioclastic recrystallized limestones with vertically oriented fractures. Samples were selected from the core material of one studied well in interval 4215-4217 m. Two types of syngenetic inclusions were found in calcite: gas and gas-liquid inclusions. The homogenization temperature of gas inclusions is from -16.9 to 40 °C. Studying the gas phase by Raman spectroscopy show the presence of methane and hydrogen sulfide. Carbon dioxide, ethane, and propane were found in smaller quantities. The homogenization temperature is 100-130 °C of two-phase fluid inclusions. Probably, it is close to the temperature of the vein calcite aggregates. The aqueous phase of inclusions is represented by solutions of magnesium chloride. The gas-phase was not studied by Raman spectroscopy because of mobility. The total composition of inclusion gases in calcite is represented mainly by carbon dioxide, methane, and hydrogen sulfide, according to gas chromatography. Ethane, propane, and isobutane are present in smaller amounts. The concentration decreases from ethane to butane. Also, ethylene, propylene, and butylene were identified in very low concentrations. A characteristic feature of hydrocarbon gases is a decrease in concentrations from ethane to propane and from propane to butane, and it is typical for gas condensates.

1. Introduction

The study of fluid inclusions in minerals and rocks allows determining the conditions of mineral precipitation. Such studies were rarely done in minerals from reservoir intervals of oil and gas deposits, due to the inaccessibility of rock samples. We studied fluid inclusions from calcite veins and host rocks, represented by bioclastic recrystallized limestones with widely vertically oriented fractures. It has done for the reconstruction of conditions of the formation of an Astrakhanskoye gas condensate field. Fractures are filled by calcite. Calcite was selected from vein 2 cm thick. It is represented by milky-white fine-crystalline aggregates in the boundary between the vein and host rocks and transparent crystals up to 4 mm in the open part of the fractures. Studied interval form top part of the reservoir, in Bashkirian units, as part of the Cheremshan horizon. Deposits belong to the Cheremshansky horizon. The studied samples were selected from the well, on the depth of 4215-4217 m. Details on the geological structure of the studied field can be found in publications [1, 2, etc.].
2. Methods

Microthermometric investigations of calcites were elaborated using a Linkam THMSG600. It used double-polished thick sections for homogenization and cryometry temperatures. The method allows measuring temperatures from -196 to 600 °C. The salt composition of the inclusions was determined by the eutectic temperature of the water-salt system [3].

The gas composition of individual inclusions was studied by Raman spectroscopy. The Raman spectroscopy studies were conducted by a LabRam HR800 (Horiba Jobin Yvon) high-resolution Raman spectrometer (600 g/mm; confocal hole size – 300 μm; slit – 100 μm; objectives: ×50, ×100) at the CCU Geoscience (Syktyvkar, Institute of Geology, FRC Komi Science Center, UB RAS). We used Ar⁺ laser (λ=514.5 nm, laser power: 0.01, 1, 10, 100 mW). The spectra were recorded at room temperature. The quantitative content of individual gases was carried out according to the method of Ernst [4].

The study of the gross analysis of gas compositions was carried out using a Tsvet-800 gas chromatograph equipped with a pyrolysis unit. The instrument allows determination of the contents of the most abundant inorganic gases and relatively light-saturated and undersaturated hydrocarbons. The decrepitation of fluid inclusions was performed in a pyrolysis reactor, a quartz ampoule into which helium carrier gas is injected through a quartz tube [5], which is connected to a metal capillary with a Teflon clamp in the upper unheated part of the ampoule. It should be noted that this reactor type contains no metal parts that could serve as sources of xenogenic gases or could promote secondary reactions. The sample (0.5 g) was heated up to 500°C in a microfurnace. Gases were accumulated in a stream of the carrier gas and frozen out in the precolumn, which provided the separation of gases with low boiling temperatures. Gases were determined using a thermal conductivity detector (katharometer) for the registration of inorganic gases and water and a flame ionization detector (FID) for the registration of hydrocarbon gases. The duration of decrepitation was 3 min. Previous experience [5] indicated that this time is sufficient for the opening of inclusions in the samples but too short for the occurrence of secondary gas-forming reactions. The size of the analyzed particles was 0.25 +0.5 mm. Impurities were preliminarily removed from the carrier gas in a guard column immersed in liquid nitrogen. Then, helium was introduced into the pyrolysis block and transferred into the precolumn filled with the polysorb-1 sorbent through a heated three-way valve. The gas from the precolumn was injected through a warmed adapter into the analytical column of a chromatograph GS-Q (30 m × 0.53 mm × 40 μm) and then sequentially transferred into the heat capacity and flame ionization detectors. The flow rate of the helium carrier was 18 ml/min, the detector current was 140 mA, and the temperature of the katharometer and FID was 150°C. The peaks were analyzed using the TWS-MaxiChrom program. Using the described pyrolysis–gas chromatography procedure, H₂, N₂, CO, CH₄, CO₂, C₂H₄, C₂H₂, C₃H₆, C₃H₈, C₄H₁₀, iC₄H₁₀, H₂O were determined. The contents of gases were estimated using a calibration factor. The standard gas mixture was injected into the reactor through a metering valve. The relative uncertainty of the method was 16%.

3. Results and Discussion

It was studied thick sections from vein calcite and host limestones. Recognizable inclusions were found only in calcite. They can be divided into two types. The first type is represented by gas inclusions. Upon freezing, gas-phase becomes heterogeneous in some crystals, and inclusions freeze at about -120 °C. Upon subsequent heating, the contents are melted at temperatures of -87 °C (3 measurements), -94 ± 4 °C (23 measurements) and -103 ± 3 °C (13 measurements), homogenization vary from -16.9 to 40.0 °C. Inclusions are usually found in small groups or singly and have an irregular or rhombic shape. Their size does not exceed 30 microns, usually about 10 microns. Sometimes two-phase fluid inclusions are containing liquid hydrocarbons and gas [6]. The second type is represented by two-
phase gas-liquid fluid inclusions with a gas phase of not more than 5 vol.%. The eutectic temperature is -33 ± 1 °C of the water-salt solution, which may indicate the presence of a solution of magnesium chloride in the liquid phase. During freezing, gas hydrates are usually formed and melt temperatures vary from -0.7 to +4.0 °C. The homogenization temperature of inclusions varies in the range of 100-134 °C. Usually, inclusions have a rhombic shape, size up to 30 microns (usually no more than 10 microns), are found in small groups or singly. The number of measurements is 14.

Thus, two types of primary inclusions were found gas and gas-liquid. They probably have different sources. Gas-liquid inclusions were captured at the initial stages of the formation of the deposit during the filling of the pore space with aqueous calcium-hydrogen carbonate solutions mixed with magnesium chloride. The homogenization temperature of gas-liquid inclusions varies from 100 to 134 °C. Probably, it can be temperatures of the precipitation of calcite veins (without pressure correction data). It should be noted that current temperatures in the gas condensate field at this depth are 100 ÷ 120 °C [2]. Gaseous inclusions were also captured at the time of mineral formation from the solutions enriched by the gas component.

The gas composition of individual inclusions was analyzed by Raman spectroscopy. It was established, that gases are present in the inclusions in form CO₂, H₂S, CH₄, C₂H₆, C₃H₈ (fig. 1). Luminescence was observed, during the study, which indirectly indicates the presence of organic matter inside the inclusion. Due to luminescence, these data may be distorted and less pronounced peaks may be hidden of other substances caused by an increased background.

![Figure 1. Average gas content in fluid inclusions, according to Raman spectroscopy; * - recalculation has done according to σ 488 nm.](image)

In individual inclusions, the content was transformed with the formation of a soot-like substance, under the action of a laser (fig. 2 a, b). In some inclusions with liquid hydrocarbons, we obtained a completely illuminated spectrum, when using a laser with a power of 0.01 mW. The content changed color to black when the laser power was increased to 1 mW or more.
Figure 2. An example of conversion of fluid inclusion contents: a - before laser exposure; b - after laser exposure.

Studying of the Raman spectra show an often shift of the peaks to the left. It, probably, indicates a significant heating of the contents of the inclusions under the action of laser radiation (fig. 3). This is more typical for the peaks of H$_2$S, CH$_4$, C$_2$H$_6$, and C$_3$H$_8$, less for CO$_2$. A shift in the Raman spectrum was not observed in the host mineral (calcite).

Figure 3. An example of the shift of the Raman spectrum. In front of the brackets is the actual value, in brackets is the ideal value.

The gas composition of the inclusions in vein calcite and limestone. The results are shown in Table 1. Methane, carbon dioxide, hydrogen sulfide, ethane, propane, butane, and isobutane are present in inclusions in calcite. A characteristic feature is a decrease in concentrations from ethane to propane and from propane to butanes and it is typical for gas condensates [7]. It should be noted, the composition of the gases of fluid inclusions from vein calcite fully corresponds to the composition of
the reservoir waters [8]. The data of gas chromatography differs from the results obtained by Raman spectroscopy. It depends on the peculiarity of these studies.

**Table 1.** The gas composition of inclusions from host limestone and vein calcite, according to gas chromatography data

|          | CO  | CO₂ | CH₄ | C₂H₆ | C₃H₈ | C₄H₁₀ | i-C₄H₁₀ | n-C₄H₁₀ | H₂S | Σ  |
|----------|-----|-----|-----|------|------|-------|--------|--------|-----|----|
| Host limestone | 6.4 | 86.7 | 4.05 | 0.10 | 0.18 | 0.06  | 0.12   | 0.01   | n/o | 2.38 | 100 |
| Vein calcite   | n/o | 44.3 | 44.9 | 0.02 | 1.65 | 0.01  | 1.41   | 0.07   | 0.01 | 1.15 | 7.78 |

The gas composition of inclusions in limestone is characterized by a high content of carbon dioxide and the presence of carbon monoxide with a small amount of methane and hydrogen sulfide. There are some differences in the content of saturated and unsaturated hydrocarbons of the number of C₂-C₄. In general, the composition of gases in inclusions of limestone is very different from the veins of calcite and the composition of the reservoir fluid. Especially content of methane in limestone is eleven times lower than in vein calcite.

**4. Conclusions**

It was found that the precipitation of calcite vein was in temperatures close to 130 °C. At the initial stages of formation of the gas condensate field realized the process of filling by calcite of the pore space from aqueous solutions enriched with calcium hydrogen carbonates and magnesium chlorides. The composition of gases from limestone and vein calcite indicates the presence of migratory hydrocarbons in inclusions. The obtained distribution of hydrocarbon gases in calcite indicates the same composition with a fluid of gas condensate field.

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