

## Co-deposition of gas hydrate and oil wax from water-in-crude oil emulsion saturated with CO<sub>2</sub>

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**Abstract.** Samples of water-hydrate-paraffin sediments with the regions of different colored were obtained by passing the emulsion of CO<sub>2</sub>-saturated water into oil through a cooled tubular reactor. Each of the regions was characterized by means of powder X-ray diffraction. It was shown that prevailing joint deposition of paraffins and hydrate occurs at some regions; complicated water-hydrate-paraffin agglomerates containing almost no admixture of the colored oil components. The possibility to form these agglomerates should be taken into account in the development of the methods preventing the deposition of hydrates and paraffins under real conditions.

### 1. Introduction

Gas hydrates are widespread natural clathrate compounds in which the host framework is composed of hydrogen-bonded water molecules, while the guest components occupy the cavities of this framework [1]. Technological attention to gas hydrates is due to the possibility of the formation of hydrate plugs in the equipment of gas and oil producing facilities and in pipelines. For this reason, hydrate prevention is an urgent subject for investigation in oil and gas industry [2-4]. Hydrate formation occurs during oil production when multiphase flows coming up from the wells are cooled (oil, water/brine and associated petroleum gas) directly in boreholes or in field pipelines. According to the most widespread model, hydrate formation occurs during the reaction of associated petroleum gas dissolved in oil with water emulsified in oil [1,2,5]. The mechanisms of hydrate formation in emulsions were considered in [6,7]. The major stages of this process include hydrate nucleation on the surface of water – oil contact, rapid growth of hydrate film on the entire surface of water drops, and slower ingrow of the hydrate inside the drop. The latter process is limited by gas diffusion through the ice layer which has already been formed. Most frequently thermodynamic inhibitors (methanol, glycols) are used to prevent hydrate formation. The addition of these inhibitors into the multiphase



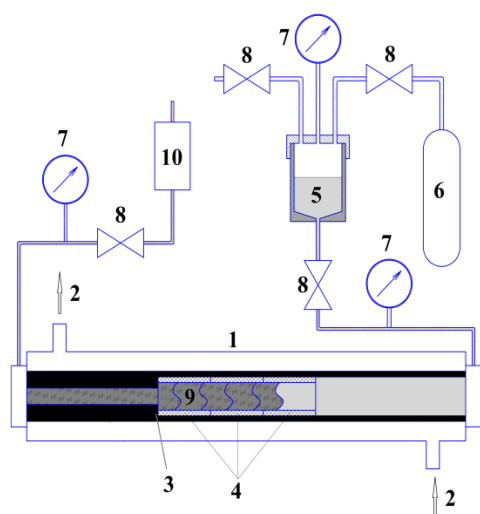
flow causes a shift of the equilibrium conditions of hydrate formation to the region of low temperatures/high pressure. Increasing application is won by so-called low-dose inhibitors of hydrate formation: their action is due to their adsorption on the surface of hydrate particles. This slows down the nucleation of the hydrate phase (kinetic inhibitors) and prevents the agglomeration of hydrate particles with each other (anti-agglomerating agents), which allows preventing pipeline blocking in many cases [8,9].

It is well known that, in addition to gas hydrates, paraffins present in oil can also form deposits on pipeline walls (for example, [10,11]). There are some data that evidence in favor of the mutual effect of hydrate particles formed in the multiphase flow and depositing paraffin species. It was shown in [12] that the formation of gas hydrate particles in the flow promotes the precipitation of paraffins. In turn, paraffin deposition promotes the agglomeration of the formed hydrate particles. The possibility of the formation of hydrate-paraffin agglomerates was demonstrated. The authors of [13,14] state that the presence of paraffin crystals in the oil phase decelerates hydrate nucleation. Paraffin deposition on the surface of water drops and hydrate particles was discovered, and these agglomerates were observed to stick together. In the opinion of the authors of [14], adhesion of the hydrophobic paraffin particles on the hydrophilic surfaces is provided by the presence of surface-active species in the system. There is a trend to an increase in the rate of hydrate growth with an increase in the concentration of paraffin crystals in oil. In addition, the presence of paraffin crystals causes an increase in the viscosity of hydrate suspensions, which points to higher agglomeration of the particles in the presence of paraffins. Paraffins promote hydrate formation in dispersions stabilized with solid particles with highly and moderately hydrophobic surface; the situation is inverse for the particles with low hydrophobicity [15]. So, by present the major regularities of the processes involved in the formation of hydrate-paraffin agglomerates in multiphase systems hydrate – water – hydrate-forming gas have been already studied. At the same time, we are unaware of any works considering the structure and phase composition of these agglomerates. In the present work we report on the first results on the formation of hydrate-paraffin agglomerates in a flow reactor and describe the results obtained in the investigation of the resulting hydrate-paraffin agglomerates.

## 2. Experimental section

A schematic of the experimental set-up is shown in figure 1. The inner diameter of the tubular reactor is 6 mm (the wide part) and 2 mm (the narrow part), the site in which the reactor width changes is marked as (3); the length of the reactor is 500 mm. All parts of the set-up except the tubular reactor (1) were kept at room temperature; the necessary low temperature in the reactor (1) was maintained with the help of the fluid cryostat pumping the coolant through jacket (2). The formation of paraffin-hydrate plug (9) occurred in the narrowing spot (3) of the tubular reactor. To simplify the extraction of plug (9) from the reactor, in some experiments teflon bushings (4) with the total length of 100 mm and inner diameter 4 mm were placed next to the insertion (3).

During the experiment, CO<sub>2</sub>-saturated emulsion of water (50 wt%) in paraffin-containing oil (paraffin content 3.7 mass %, density 826 kg/m<sup>3</sup>, the size of drops in the emulsion 72±14 μm) was pressed from the pressure cylinder (5) under the action of gas pressure created by the gas from gas vessel (6) through reactor (1), then the mixture was depressurized through a fine-adjusting regulating valve (10). Valve (10) allowed controlling the rate of emulsion flush through the reactor. Pressure at the reactor inlet and outlet, as well as in the pressure cylinder (5), was measured with the help of pressure sensors (7) with the accuracy of 0.03 MPa. Experiment management was performed with the help of cutoff valves (8). Before experiment, the emulsion was charged into the pressure cylinder (5) in which the pressure of CO<sub>2</sub> was maintained at a level of 5.5 MPa at room temperature. For saturation, the emulsion was kept before experiment under pressure for 24 h. The necessary reactor temperature (-1.5 or -5.0°C) and the rate of emulsion flush ~2.5 ml/min were set at the beginning of the experiment. Flow rate was decreased almost to zero during several hours, and then it was again set at the previous level. The pressure difference at the inlet and outlet of the tubular reactor was recorded during the experiment.



**Figure 1.** Schematic view of the experimental set-up: (1) Tubular reactor, (2) cooling jacket, inlet and outlet of cooling liquid into the jacket of the reactor, (3) site in which the section of the reactor narrows, (4) tubular teflon inserts, (5) pressure reservoir with the emulsion saturated with gas, (6) vessel with gas, (7) pressure sensor, (8) valves, (9) the formed plug, (10) microadjusting valve to control the flow of the emulsion through the tubular reactor.

### 3. Results and discussion

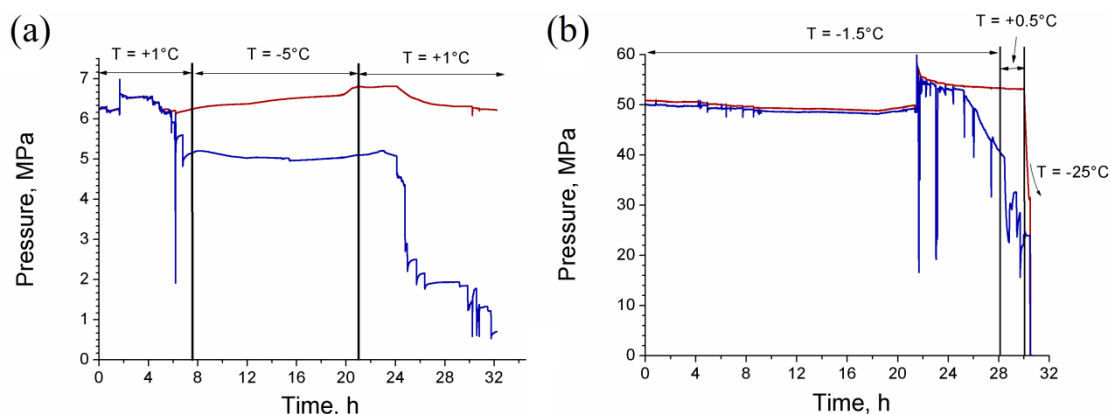
Six independent experiments on the formation of paraffin-hydrate plugs were carried out. The appearance of the samples and the results of their investigation turned out to be similar in all experiments, so below they will be considered jointly. Typical pressure curves at the reactor inlet and outlet are shown in figure 2. In the case of the free flow of the emulsion through the reactor the pressure difference was close to zero. The flow of the emulsion through the reactor was hampered with the formation of the paraffin-hydrate plug, and thus the pressure difference occurred. The formation of agglomerates started within several hours after temperature was decreased to  $-1.5$  -  $-5.0^{\circ}\text{C}$ , and manifested itself as the pressure drop and the reactor outlet, while the pressure at the reactor inlet remained unchanged or decreased to a smaller extent (figure 2). At a temperature of  $+1^{\circ}\text{C}$ , pressure change and plug formation were not observed during pumping for a long time (up to 24 h). It was stressed that, as a rule, plug formation occurred during several hours after the flow of emulsion through the reactor was stopped. To exclude the participation of ice in plug formation, reactor temperature was increased to  $+0.5$  -  $+1^{\circ}\text{C}$  for about 1 hour before the end of the experiment, and pressure difference either remained at the former level or increased (most likely due to additional growth of the plug). This points to the fact that ice, if any, was present in the reactor at that moment, it did not play the major role in the formation of the agglomerate. At the end of the experiment, temperature was decreased to  $-25^{\circ}\text{C}$ , and after that the residual pressure was released, the resulting sample was taken out of the reactor and immediately frozen in liquid nitrogen.

The samples taken from the zone of teflon inserts ((4) in figure 1) and from the wide part of the reactor differed from each other substantially (figure 3). In all cases, the samples from the wide part of the reactor were uniformly colored, with porosity visible for unaided eye (region (5) in figure 3). We suppose that these samples correspond to the frozen dispersion of hydrate particles and ice in oil. Gas bubbles could be formed during oil degassing at the stage of freezing / pressure release. The samples from the narrow part of the reactor, as a rule, consisted of several regions differing from each other in appearance; their porosity was not visible for unaided eye (figure 3). In the region which was nearest to the wide part of the reactor, as a rule, three types of regions were interchanging (figure 3): a light region, which was non-transparent, with white dull surface, sometimes contaminated with oil (III) in figure 3, a dark region – non-transparent, with nonuniform dark color on the surface, without light spots (II) in figure 3; spotty – with nonuniform dark color of the surface and with visible light spots on this surface (IV) in figure 3. The transparent part of the sample (region (I) in figure 3) was formed in the region which was the closest to the narrow part of the tubular reactor. ((3) in figure 1).

Light regions verged on the wide part of the reactor, further on the regions of different types were interchanging.

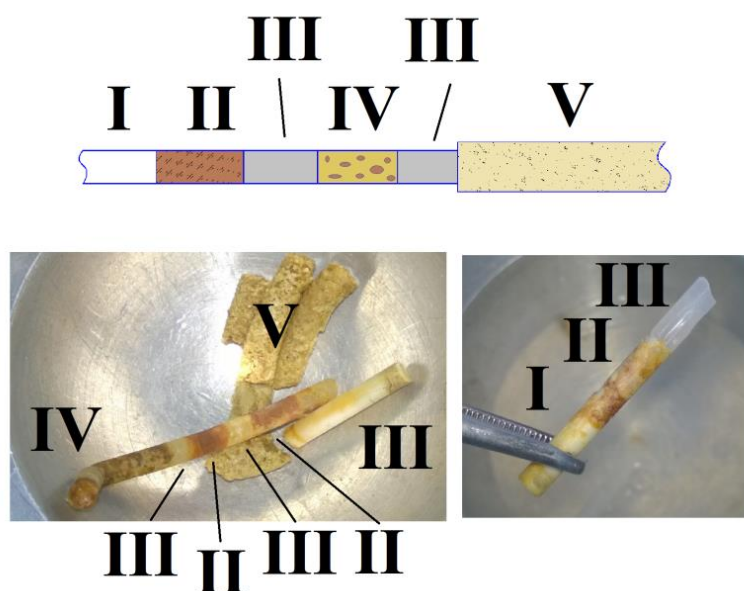
Each region of the sample was characterized by means of powder X-ray diffraction. Typical diffraction patterns are shown in figure 4. In all cases, three phases are revealed in the diffraction patterns: ice, hydrate of carbon dioxide, and crystalline oil paraffin. The reflections related to ice and hydrate were assigned relying on the data reported in [16] and [17], respectively. According to the data of [18,19], there are two reflections of oil paraffins in the angle range  $2\Theta$  ( $\text{CuK}\alpha$  radiation) shown in figure 4:  $2\Theta = 21\div 22$  and  $24\div 25^\circ$ . Their positions depend on temperature and composition of the mixture of paraffins. The small amount of substance in the sample available for us does not allow us to apply the known procedures of quantitative X-ray analysis to the examination of our sample. For this reason, we only compared relative amounts of different phases in different regions of the sample. One can see in the powder X-ray diffraction patterns that the transparent regions (I) in figure 3 contain mainly ice, with small admixtures of hydrate and paraffin (weak reflections of paraffin and hydrate at the background of strong reflections of ice). For the samples from the wide part of the reactor and for spotty (IV) in figure 3 and dark (II) in figure 3 regions, the intensities of reflections from all phases are comparable; the most intensive reflection from ice is somewhat larger than the most intensive reflections of paraffin and hydrate. It may be assumed that these regions contain all three phases in comparable amounts. Finally, the situation is quite contrary for light regions (III). Here the most intensive reflection of ice is weaker than the most intensive reflections of paraffin and hydrate, while the relative intensity of the ice and hydrate reflections varies. So, the light regions contain mainly paraffin and hydrate, the transparent regions contain mainly water, while in other regions the amounts of these phases are comparable. According to the data of thermovolumetric analysis of averaged samples from the dark, light and spotty regions, the average hydrate content in the mixture varied within the range 6-9 mass %. More detailed analyses of the composition of different regions will be carried out in future.

We suppose that the most interesting result of the present work is experimental confirmation of the possibility of the joint deposition of pure agglomerates of water, hydrate and oil paraffins in the reactor channel. It is known [2] that the paraffin-hydrate plugs are formed most frequently in the points of channel narrowing or bending, which is observed in our case. It may be assumed that the deposition starts at the walls of the channel and then reaches its center. Alternating formation of light, dark and spotty regions may be connected with the different manners of the joint crystallization of paraffins and hydrate depending on the concentrations of components present in a given point of the reactor, and on the degree of thermodynamic supersaturation. We suppose that the crystallization of pure paraffins capturing hydrate and water into their volume (all components are not colored, that is why light regions are formed) takes place in the sites with the highest supersaturation of the emulsion

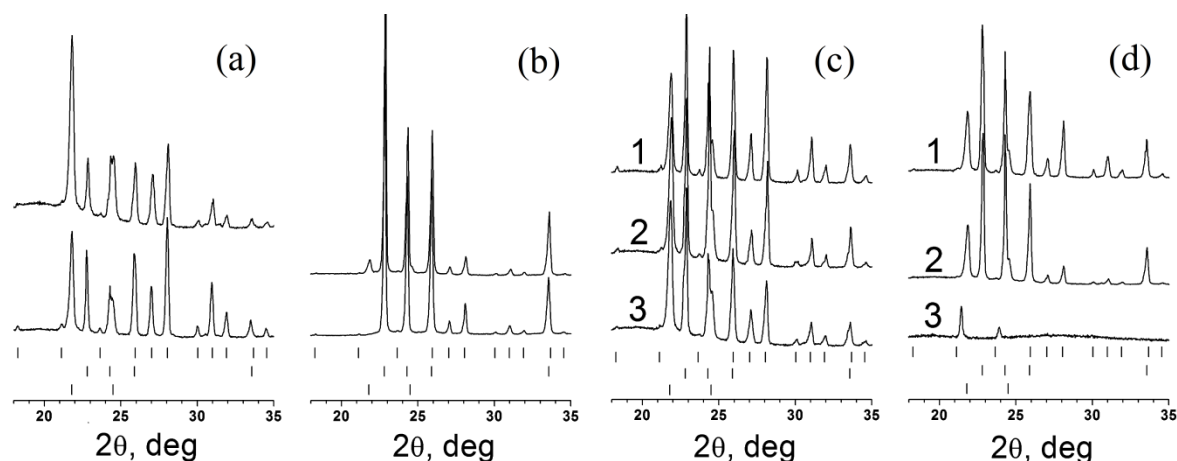


**Figure 2.** Typical time dependencies of pressure at the inlet of the tubular reactor (red line) and at the outlet of it (blue line). The intervals of time during which the corresponding temperature was kept in

the reactor are shown. Pressure drop in experiment (a) is jumpwise (connected with an increase in the rate of liquid phase discharge from the reactor), pressure decrease in experiment (b) is smooth. The regions of a sharp pressure increase on the curves correspond to gas pumping into the pressure cylinder.



**Figure 3.** Different regions of the samples of paraffin-hydrate plugs obtained in the experiments. Regions: (I) transparent, (II) dark, (III) light, (IV) spotty, (V) from the wide part of the reactor. Corresponding regions are also marked in photographs.



**Figure 4.** Typical powder diffraction patterns of different regions of frozen water-paraffin-hydrate agglomerates. (a) Light regions, (b) transparent regions, (c) 1 and 3 – spotty regions, 2 – dark region, (d) 1 – sample from the wide part of the reactor, 2 – spotty region at  $-100^{\circ}\text{C}$ , 3 – spotty region at  $0^{\circ}\text{C}$ . Strokes mean the expected positions of the reflections from different phases: upper position -  $\text{CO}_2$  hydrate, middle position - ice, lower position – paraffins.

with the hydrate-forming gas and paraffin. In this situation, water – hydrate – paraffin agglomerate is formed due to hydrophobization of the hydrophilic surfaces of water and hydrate by surfactants that are present in oil. Due to this, the surface of water drops and hydrate particles has good adhesion to paraffin, and they are capable of joint deposition. The mechanism is similar to that considered previously in [20]. Enrichment of the light regions with water and paraffin proceeds due to pushing the

major part of oil further along the reactor. After the deposition of a substantial amount of water – hydrate – paraffin agglomerate, colored oil components start to get included into the deposit; so spotty and dark regions are formed. A detailed mechanism leading to the formation of differently colored regions is still unclear at present, and the amount of data is insufficient to discuss these questions. Finally, because of the deposition of emulsion-stabilizing components, water which remains not included into the agglomerates and the hydrate phase is separated from oil and pushed into the peripheral part of the sample where it forms a transparent region. In this region, hydrate is formed from dissolved CO<sub>2</sub> dissolved in water; paraffin particles are brought mechanically from preceding regions.

Thus, the possibility of spontaneous formation of water – hydrate – paraffin agglomerates in oil dispersed systems is demonstrated experimentally in the work. This possibility should be taken into account when developing the methods against the formation of hydrate-paraffin deposits during oil production in the regions with cold climate.

### Acknowledgements

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