

Laboratory modeling of hydrate formation in rock specimens (*a review*)

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Abstract

We present a review of the literature on the methods of modeling of sedimentary rocks containing gas hydrates with the aim of a subsequent study of their physical and mechanical properties. The attention is focused mainly on the non-Russian researches carried out in the last 15 years. The review includes description of corresponding setups and modeling techniques. The dependence of the morphology of hydrate present in the specimen on the specimen preparation technique is reviewed in detail. In addition, the structure and texture of synthetic and natural hydrate-containing rock specimens are briefly reported, as well as the regularities of formation and dissociation of gas hydrates in the Earth's crust.

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Introduction

Natural gas hydrates are widespread in the Earth's upper crust and are the most sensitive to changes in environmental conditions (pressure and temperature) among its components (Ginsburg and Soloviev, 1994; Istomin and Kvon, 2004; Istomin and Yakushev, 1992; Kuznetsov et al., 1997, 2003; Safronov et al., 2010; Sloan and Koh, 2008). They can exist in nature under the following conditions: (1) high pressure, (2) low temperature, (3) presence of free water, and (4) presence of free (or water-dissolved) hydrate-forming gas in contact with the latter. In most of its natural accumulations hydrate gas consists of predominant methane (98–99%) and traces of ethane, propane, butane, CO₂, H₂S, nitrogen, etc. In some cases, the content of these traces reaches tens of percents. In the Earth's crust, gas hydrates can accumulate within the hydrate stability zone (HSZ), i.e., in the depth range where the temperature is rather low and the pressure is high enough for the existence of hydrates at this temperature. In water areas, the minimum depth favoring the existence of hydrate below the bottom level is ~200 m in the Arctic regions and 500–700 m in the equatorial ones. The HSZ thickness there reaches 1 km. Hydrates can exist only in bottom deposits,

because the concentration of dissolved gas necessary for hydrate formation cannot be reached in water. In permafrost rocks the HSZ thickness is 400–800 m (and, in places, >1 km), and the depth of location of the upper boundary of this zone is ~250 m. Above the HSZ, the so-called relict hydrate accumulations can form as a result of self-preservation of metastable hydrates in the permafrost rocks (Yakushev, 2009).

The known estimates of the total amount of natural gas present as hydrates in the Earth's crust differ by three orders of magnitude. As the knowledge about natural gas hydrates grows, the forecast assessments of hydrate gas reserves diminish. The most realistic assessments were made by Soloviev (2002, 2003): 2×10^{14} m³ of gas in deep-seated accumulations of subaqueous hydrates and $\sim 10^{13}$ m³ of gas in subbottom hydrates. The hydrate gas resources in permafrost rocks of Russia estimated by the Gazprom VNIIGAZ specialists are within 7.2×10^{12} – 1.7×10^{13} m³ (Yakushev, 2009). These forecast assessments are based on analysis of subaqueous-hydrate accumulations known by that time, i.e., are apparently minimum, but even these reserves of hydrate gas are nearly equal to the gas reserves explored in conventional gas fields by now. The most large-scale and successful experiments on pilot gas production from gas hydrate accumulations in permafrost rocks were performed in the Mallik field (Mackenzie River delta, northern Canada) in 2002–2008 (Dallimore and Collett, 2005; Dallimore et al., 2008; Nu-

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masawa et al., 2008), and similar gas production from subaqueous gas hydrate accumulations was made in the area of the deep-water Nankai Trough (near the Japanese Islands) in 2013 (Yamamoto, 2014). Also, successful experiments on the extraction of gas from subbottom gas hydrate accumulations were carried out. The production of gas from subaqueous gas hydrate accumulations was performed with application of the thermal and decompression methods of hydrate decomposition (Khlystov et al., 2014). In the first case, hydrate accumulations are heated (e.g., by injection of hot water into the well) to a temperature above the hydrate dissociation temperature, and the evolved gas is pumped off. In the second case, dissociation of gas hydrates is achieved by reducing the well pressure.

In addition to problems of gas production from natural gas hydrates, the scenarios of their possible participation in global processes in the upper crust are actively discussed. One of them is the possible decomposition of accumulated gas hydrates caused by the growing average annual temperature of the Earth's surface as a result of the greenhouse effect. In this case, the atmosphere receives an additional amount of methane, which is a more effective greenhouse gas than carbon dioxide, and the atmosphere warming might become a self-accelerating process. There are also discussions about the possibility of permafrost or ocean floor disposal of industrial carbon dioxide in the form of hydrate. For example, a global field experiment on the replacement of methane in hydrate accumulation by carbon dioxide was successfully performed in 2012 (Schoderbek et al., 2013). Thus, it is obvious that gas hydrates are a widespread natural object, which is of crucial importance not only as the potential source of natural gas.

Today, serious efforts are made to search for and explore natural gas hydrate accumulations and fields, both continental and aqueous ones. The prospecting works include drilling, sampling of bottom deposits by corers, and application of geophysical (mainly seismic and electrical) methods. Development and verification of remote sensing methods for search for gas hydrate accumulations need special (mostly laboratory) studies of the physical properties of hydrate-containing rocks (Gabito and Tzouris, 2010; Riedel et al., 2010; Waite et al., 2009). The knowledge of these properties is also of crucial cognitive importance, because it permits one to elucidate the regularities of formation and dissociation of gas hydrates in the Earth's crust, elaborate more realistic models of gas hydrate accumulation in different geologic conditions, and make prerequisites for the development of new technologies for exploration of gas hydrate accumulations. Special laboratory setups are designed for modeling of hydrate-containing specimens (HCS) and measurement of their parameters. The most complicated problem is modeling of synthetic HCS similar to real geologic objects. A large number of techniques for modeling of HCS were proposed by researchers, but no single approach has been developed yet. This is, first of all, due to the diversity of natural objects (rocks of different compositions, textures, and structures). In this review we consider the most interesting techniques for modeling of hydrate-containing rocks that were implemented in the last

10–15 years. Special attention was focused on non-Russian publications, because it is non-Russian researchers who achieved the greatest success in this scientific field. To understand the HCS modeling techniques, a reader must orient himself in the present-day scientific information about the mechanisms of hydrate formation in sedimentary rocks and the structure and morphology of hydrate inclusions. Unfortunately, such information is scarce in Russian literature. Therefore we think it is necessary to review briefly these issues.

Models of natural hydrate accumulation

Natural gas hydrates form by the following major mechanisms: (1) during the rise of gas-saturated fluids in the HSZ (predominantly in marine sediments), (2) from biogenic gas produced in the HSZ (the formation process can run only in a homogeneous aqueous solution, because the rate of formation of biogenic gas is low), and (3) from frozen sedimentary rocks containing gas and water (Ginsburg and Soloviev, 1994; Hyndman and Davis, 1992; Kvenvolden and Barnard, 1983; Spangenberg et al., 2015; Waite et al., 2009; Yakushev, 2009).

The rise of a gas-saturated fluid flow is accompanied by its cooling and a pressure decrease. Several scenarios of these processes are possible, both with and without hydrate formation, depending on the starting concentration of gas in the fluid and the relative rates of its cooling and pressure decrease. The major ones are schematically shown in Fig. 1.

The scenario *A* takes place when the concentration of gas dissolved in the fluid is low. Although the cooled fluid gets into the stability field of hydrate (P – T projection of the diagram), the T – X projection shows that the aqueous solution of methane remains strongly diluted, and formation of methane hydrate is impossible. A small amount of hydrate would be expected to form during the freezing of this solution, i.e., a temperature decrease below the ihg curve. In fact, this is possible only in the case of freezing of sedimentary rocks lacking free gas. In the scenario *C*, the concentration of hydrate-forming gas in the fluid is higher than its maximum solubility in a liquid, and the fluid contains free gas. Therefore, the formation of hydrate can begin when the fluid gets into the HSZ, i.e., intersects the lhg curve (hydrate forms at the gas–liquid boundary). In the scenario *B* corresponding to intermediate concentrations of gas in the fluid, the starting fluid contains only dissolved gas, but as the temperature and pressure decrease and intersect the lh curve, the solution becomes oversaturated with methane, thus favoring the formation of gas hydrate. In this case, hydrate forms at somewhat lower temperatures than those expected from the lhg curve and, correspondingly, above the HSZ boundary. It forms from a homogeneous aqueous solution. At 5 MPa and 0 °C, up to 5 g of hydrate can be produced from 1 L of an aqueous methane-saturated solution. Note that depending on the relative rates of pressure and temperature decrease, the formation of hydrate can be preceded by the release of bubble gas from

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