UDC 533.9.004.14; 621.039.6

A. Drobyshev*, A. Aldiyarov, K. Katpaeva, E. Korshikov, V. Kurnosov,
A. Shinbayeva, D. Sokolov, A. Timchenko

Al-FarabiKazakh National University, Almaty, Kazakhstan,
*E-mail: Andrei.drobyshev@kaznu.kz

Physical modeling of the formation of the clathrate hydrates of methane

Nowadays natural gas hydrates attract special attention as a possible source of fossil fuel. According to various estimates, the reserves of hydrocarbons in hydrates exceed considerably explored reserves of natural gas. Due to the clathrate structure the unit volume of the gas hydrate can contain up to 160-180 volumes of pure gas.

Key words: hydrate, methane clathrate, energy.

А. Дробышев, А. Алдияров, Т. Кожамкулов, К. Катпаева, Е. Коршиков, В. Курносов,
А. Шинбаева, Д. Соколов, А. Тимченко

Физическое моделирование формирования клатратов гидратов метана

В настоящее время природные газовые гидраты привлекают особое внимание как возможный источник ископаемого топлива. По разным оценкам, запасы углеводородов в газовых гидратах значительно превышают разведанные запасы природного газа.

Ключевые слова: гидрат, метан, клатрат, энергетика.

А. Дробышев, А. Алдияров, Т. Кожамкулов, К. Катпаева, Е. Коршиков, В. Курносов,
А. Шинбаева, Д. Соколов, А. Тимченко

Метан гидратының клатраттарының қалыптасуын физикалық модельдеу

Қазіргі кезде табиғи газ гидраттар қазбалы отынның мүмкін көзі ретінде ерекше назар аудартып отыр. Әртүрлі бағалаулар бойынша газды гидраттардағы көмірсулардың қорлары барланған табиғи газдың қорынан асып отыр.

Түйін сөздер: гидрат, метан, клатрат, энергетика.

Nowadays natural gas hydrates attract special attention as a possible source of fossil fuel. According to various estimates, the reserves of hydrocarbons in hydrates exceed considerably explored reserves of natural gas. Due to the clathrate structure the unit volume of the gas hydrate can contain up to 160-180 volumes of pure gas. In recent years interest to a problem of gas hydrates has considerably increased. Such changes are connected with the progress of searches of alternative sources of hydrocarbonic raw materials in countries that do not possess the resources of energy carriers. Thus gas hydrates are nonconventional sources of the hydrocarbonic raw materials which can be developed in the near future.

At the same time, mechanisms of methane clathrate hydrates formations have not reached an advanced level, their thermophysical and mechanical properties have not been investigated profoundly [1]. Regarding this experimental modeling of the processes of formational clathrate hydrates of methane in water cryomatrix in the process of co-condensation from gas phase on cooled substrate was carried in the range of temperatures T=(12-60) K and pressures P=(10^{-4}-10^{-6}) Torr. Methane concentration in water varied in the range of 5-90%. The thickness of a film was 30-60 mcm. The vibrational spectra of two-component thin films of cryovacuum condensates of CH_4+H_2O were measured and analyzed. According to the comparison of thermal desorption curves and changes in the absorption amplitude of characteristic frequencies of methane vibrations, we made some assumptions relatively the state of methane molecules in the «matrix» of water. We assume, that under these conditions cryoprecipitated methane in solid solution with water can exist in three states. The most significant and interesting temperature ranges are the following:

1. Temperature range from 30 K to 58 K – is the range of solid methane evaporation. This assumption is consistent with the values of methane equilibrium parameters (pressure, temperature) on the phase diagram.

2. Temperature range from 60 K to 130 K – is the range of decrease in the adsorption capacity of amorphous water film at higher temperatures.

3. Temperature range from 130 K to 145 K – is the range of the restructuring of solid phase from water – amorphous state (ASW) through the intermediate state super cold liquid (SCL) to cubic ice [2].

4. In the range from 145 to 160 K the methane concentration in the sample is almost stable. At these high temperatures, methane can exist in the film only in bound state with water, namely in the form of clathrates. Increase of the temperature above 160 K leads to a decrease of methane concentration, which is connected with the transition of cubic ice I_c to regular hexagonal state I_h, which is apparently accompanied by a partial destruction of the clathrates. Narrow temperature range of 172-176 K with constant values of the methane concentration is related with the existence of hexagonal ice containing methane clathrates. Further increase in the temperature leads to evaporation of water film with simultaneous change of methane concentration. The fact that methane evaporates from the sample together with water confirms methane clathrates presence in the samples.

References

1 Aldiyarov, A. Drobyshev, E. Korshikov, V. Kurnosov, and D. Sokolov. Physics of the Solid State.–2012.–Vol.**54**.–No.7.–pp. 1475–1479

2 Debenedetti P.G. Supercooled and glassy water //J. Phys. Cond. Matter.-2003.- vol**15**.-pp. 1670-1721