Research of Water Phase Composition in Zeolites

O N Kravtsova¹, N I Tappyrova¹, V A Ivanov¹

¹Department of heat and mass transfer processes, V.P. Larionov Institute of Physical-Technical Problems of the North of Siberian Branch of the Russian Academy of Sciences, Oktyabrskaya st, 1, Yakutsk, 677980, Russia

E-mail: nadejda.tappyrova@yandex.ru

Abstract. The article presents the results of experimental studies of the content of unfrozen water in the zeolite of the Honguruu deposit of the Republic of Sakha (Yakutia). The initial moisture content ranged from 6.0 to 22.4 %. To determine the amount of unfrozen water, the method of continuous heating of the sample was used. For the studied samples, the content of unfrozen water in the temperature range from -15 to 0°C does not depend on the initial humidity. In the range from -25 to -15°C, jumps in the content of unfrozen water were found.

1. Introduction

Natural zeolite is a valuable mineral with high adsorption, catalytic, cation exchange properties. Zeolites are widely used in various technological and analytical processes in the oil, gas, refrigerating, rubber industries, medicine, sewage and industrial water treatment, etc. [1-5]. For these areas, a detailed study of their adsorption, mass transfer and other properties [1, 6-9]. At the same time, the properties of zeolites have not been sufficiently studied at low temperatures. In this regard, it is of interest to determine the phase composition of water in zeolites at low temperature close to 0°C.

In 1978, in the Republic of Sakha (Yakutia), by geologists of the Yakutsk Institute of Geological Sciences SB RAS were discovered the first zeolite deposit - Honguruu in the Suntarsky district.

In this work the results of experimental studies of unfrozen water in the Zeolite field in Honguruu at initial moisture level of 6.0% to 22.4%. For measurements were used methods that made it possible to determine the amount of unfrozen water in dispersed materials developed at the Institute of Physics and Technology of SB RAS [10, 11].

2. Results of research of water phase composition in zeolites

The content of unfrozen water in the temperature range from -15°C to 0°C does not depend on the initial humidity (figure 1). In this interval, the variation of unfrozen water content in samples with different initial humidity is not limited by experimental errors. In this interval, the variation of unfrozen water content in samples with different initial humidity is not limited by experimental errors.
Figure 1. The content of unfrozen water in the zeolite at various values of the initial humidity: ○ – 13.2%; □ – 18%; Δ – 22.3%.

In the range from -25 °C to -15 °C, jumps of unfrozen water content were found (figure 1). Below are possible causes of such a stepwise variation in the temperature curve of unfrozen water.

A water adsorption by zeolites has been studied in detail [9, 12, 13]. The isotherm of water adsorption by zeolites is characterized by a sharp rise at the beginning and a long section parallel to the abscissus axis at high fillings [1]. Isotherms of water adsorption by zeolites at high fillings do not have any features in the form of steps [1, 14]. At the same time, the adsorption isotherms given in [15] have a certain stepping at high adsorption values, although the authors do not pay attention to this. This course of adsorption isotherms will also affect the temperature dependence of the unfrozen water content in the form of stepped sections [16, 17].

In the continuous heating method, the content of unfrozen water is calculated based on the thermal effect of water melting. Therefore, the correct representation of the specific heat of fusion in the calculation formulas plays an important role in reliably determining the temperature dependence of unfrozen water. During the experiment the heat of the phase transition was measured, but the humidity range in which it was determined lies much higher than the interval in which a jump in the temperature dependence of unfrozen water content is observed.

The heat of fusion at low humidity can be estimated based on the heat of adsorption. The dependence of the heat of water adsorption in zeolite on the amount of adsorbed water is very complex. These dependences are not the same for different zeolites and their different cationic forms [18]. Such a complex dependence of the heat of adsorption will make a significant error in determining the content of unfrozen water by calorimetric methods. Therefore, it is necessary to approach the results of such measurements very carefully, especially at low values of unfrozen water content.

A sharp increase in the heat of the water phase transition in comparison with the value used in the calculations will be manifested by an apparent jump in the temperature dependence of the unfrozen water content, similar to what is observed in figure 1.

Using models of regular systems to describe the phase equilibrium of pore water allowed us to identify another possible cause of this phenomenon [19, 20].

In regular systems [20] at high values of the interaction energy of solid skeleton particles and water, the temperature dependence of the unfrozen water content on the temperature in a certain interval becomes a multi-valued function (figure 2), which is associated with the appearance of an unstable state of water in the system under certain conditions. The stepwise nature of the temperature
dependence of the content of unfrozen water in zeolites may be a consequence of the appearance of such an unstable state.

![Figure 2](image.png)

Figure 2. Temperature dependence of unfrozen water content in a two-component regular rock model. Molar mass of the skeleton \( M^s_w = 4000 \text{ g/mol} \). ◊ - 0 (ideal system); Δ - 1200 J/mol; □ - -1200 J/mol.

3. Conclusion
To summarize, we can say that it is impossible to interpret the obtained results unambiguously. The complex nature of the conditions of phase equilibrium of water in zeolites at negative temperatures makes it necessary to conduct complex studies, combining various methods.

4. References
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