STUDY OF THE STATE OF WATER SORBED ON CALCIUM HYDROSILICATE BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE

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Abstract

Full Text

PHYSICAL CHEMISTRY

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STUDY OF THE STATE OF WATER SORBED ON CALCIUM HYDROSILICATE BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE

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As was shown previously (ˆ1), on the dehydration isotherms (desorption of water) for a number of samples of low-temperature calcium hydrosilicates, a characteristic vertical section is observed at a relative pressure $P/P_s = 0.35$ (Fig. 1).

Isothermal dehydration at constant vapor pressure may indicate both the dissociation of a definite crystalline hydrate and the release of water sorbed by the zeolite-like structure of the hydrosilicate. These two ways of interpreting the data obtained do not exclude one another; however, the difference lies in the degree of localization of the water molecules in the structure. To clarify the nature of the bonding of water in the hydrosilicate in the range of P/P_s values from 0.5 to 0, we used the method of nuclear magnetic resonance of protons (n.m.r.).

As the object of the investigation, a sample with $CaO/SiO_2 = 0.8$ (ˆ1) was chosen. To measure the n.m.r. spectrum, portions of the powder were placed in special ampoules connected with the apparatus on which the adsorption measurements were carried out. By successive sealing-off of ampoules as water was desorbed, 6 samples were obtained corresponding to points of the isotherm shown in Fig. 1. The n.m.r. spectra were recorded on an apparatus described earlier (ˆ2). All n.m.r. measurements were carried out at room temperature.

Fig. 1. Desorption isotherm of water vapor at 18°C on a sample of calcium hydrosilicate (ˆ1). The points mark the numbers of the samples on which the

Fig. 2

Figure 2: Fig. 2

n.m.r. spectra were studied.

It is known that n.m.r. spectra change sharply depending on the aggregate state of a substance (ˆ3). In a liquid, owing to the great mobility of the molecules, the local magnetic fields arising from neighboring dipoles are greatly reduced, and the absorption line narrows, amounting to fractions of a gauss. For solids with a rigid lattice, where the nuclei occupy certain fixed positions, the n.m.r. signal has a width of several gauss. The n.m.r. signals obtained for all samples are shown in Fig. 2a. Samples 1 and 2 give a complex absorption line which apparently consists of two Lorentzian lines of different widths*. These lines are shown by dashed curves in Fig. 2b. The narrow line, about 0.15 G wide, corresponds to the most mobile water molecules contained in these samples; the other has a width of 0.25 G. As water is desorbed in the region $P/P_s < 0.35$, the first line disappears, while the second is characteristic of

* The line width is defined as the distance between the maxima of the derivative of the absorption signal.

Fig. 2. *a* –derivatives of the proton NMR absorption signals for all the samples studied. (The numbers by the curves correspond to the sample numbers in Fig. 1. The black dots are derivative values for Lorentzian lines); *b* –decomposition of the signal from sample No. 2 into components; *c* –example of a recording of the derivative NMR signal (sample No. 3); modulation amplitude H_m 0.025 G, phase-detector time constant 2 sec, field sweep rate 0.33 G/min.

samples 3, 4, and 5. The results of the study of sample 6 do not differ in any way from the spectrum obtained earlier for tobermorite ([4]).

The broadening of the absorption line for water remaining at $P/P_s < 0.35$ indicates a certain decrease in its mobility compared with the water contained in samples 1 and 2. As follows from the data obtained (Fig. 2), samples 1–5 give narrow (0.15–0.25 G) absorption lines instead of the lines of width 10–12 G usually observed for crystalline hydrates ([5]). It follows from this that the water molecules sorbed by the hydrosilicate are not part of its crystal lattice, since they have a mobility close to that of molecules in liquid water. From the width of the observed line one can determine the correlation time of such motion. As shown in ([6]),

$$\pi\Delta\nu_{\frac{1}{2}} = \frac{\langle\sigma_0^2\rangle}{3}\left[3\tau_c + \frac{5\tau_c}{1+\omega^2\tau_c^2} + \frac{2\tau_c}{1+4\omega^2\tau_c^2}\right],$$

where $\Delta\nu_{\frac{1}{2}}$ is the absorption-line width, $\langle\sigma_0^2\rangle$ is the second moment of the absorption line for the corresponding rigid lattice, in our case for ice, ω is the

Fig. 3

Figure 3: Fig. 3

resonance frequency, and τ_c is the correlation time. For samples 3–5, allowing for field inhomogeneity, we obtain for τ_c the value $1.7 \cdot 10^{-7}$. For the more mobile water, $\tau_c = 7.8 \cdot 10^{-8}$ sec. It should be noted that this value is approximate, since the influence of field inhomogeneity in this case is considerable.

If there were no change in the mobility of the water at different P/P_s, the line width would remain constant, and the magnitude of the maximum of the derivative absorption signal would increase in proportion to the amount of water contained in the samples. In Fig. 3a the dependence is given of the relative magnitude of the maximum of the derivative absorption signal on the relative water content in the samples, where $I/I_{\max}$ is the ratio of the maximum value of the pro–

Fig. 3. Dependence of the relative magnitude of the maximum of the derivative absorption signal on the relative water content in the samples.

of the initial NMR absorption signal of the given sample to the maximum value for sample 1, and $n/n_{\max}$ is the ratio of the amount of water in the given sample to the water in sample 1 (allowing for structural water). As can be seen from Fig. 3a, the curve consists of two sections with different slopes. Let us conventionally call water having a definite mobility and, consequently, a definite NMR line width a phase. Then, in the process of water desorption, at the points where the curve breaks and where it intersects the abscissa axis, there occurs a successive disappearance of the more mobile phases, i.e., a change in the state of the water in the hydrosilicate. These points correspond to a total water content in the sample of 2.4 and 1.07 H_2O/SiO_2. If, however, one plots the dependence of the relative magnitude of the signal corresponding to a given phase on the relative content, then all the points lie on a single straight line (Fig. 3b). For samples 3, 4, and 5, the data for sample 3 were chosen as unity, and for samples 1 and 2, the data for the more mobile water in sample 1.

On the basis of consideration of all the experimental data obtained in the present work, it may be concluded that, upon sorption of water on the calcium hydrosilicate sample studied, no ordinary crystalline hydrate is formed. In the range of P/P_s values from 0.5 to 0 there occurs only a change in the character of the motion of the absorbed water toward a decrease in its mobility. Additional data on the nature of water in this system can be obtained by studying NMR spectra at various temperatures.

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Note: Figure translations are in progress. See original paper for figures.