K. G. KRASILNIKOV

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Abstract

Full Text

K. G. KRASILNIKOV

ON CALCULATING THE SPECIFIC SURFACE AREA OF TOBERMORITE FROM THE PARAMETERS OF ITS CRYSTAL LATTICE AND ADSORPTION DATA

(Presented by Academician P. A. Rehbinder, December 6, 1962)

The principal products of hydration hardening of silicate cements under ordinary conditions are Ca hydrosilicates of the tobermorite group. Like most Ca hydrosilicates, tobermorite, $Ca_{10}[Si_{12}O_{31}](OH)_6 \cdot nH_2O$, has a layered crystal structure. This layered character is due to the structure of the silicic-acid radical $[Si_{12}O_{31}]_{\infty,\infty}$, which is a two-dimensional corrugated network (^{1}). The elementary crystal cell of tobermorite is characterized by the parameters a = 11.3 Å, b = 7.2 Å, c = 18.6—28 Å (depending on the water content in the hydrosilicate) (^{2}) and includes, along the c axis, two such networks (elementary plates). Sorption of water vapor on tobermorite occurs by penetration of water molecules along the cleavage planes of the layered crystal and is accompanied by its swelling. In this, the mobile layered structure of tobermorite differs from the rigid three-dimensional structures of zeolites, whose adsorption data were compared with the structure of the framework in works (^{3,4}).

Fig. 1. Model of a swelling layered structure

Starting from the model of a swelling layered structure shown in Fig. 1 and having the corresponding values of the density of the crystals, one can calculate the limiting value of their specific surface area

$$s_d = \frac{2}{c/2 \cdot d},$$

where d is the density of the crystals. To determine the density, we used the results of a dilatometric study of the process of tobermorite formation during the interaction of silica gel and $Ca(OH)_2$ in aqueous solution. Calculated weighed portions of silica gel and $Ca(OH)_2$ were placed in glass dilatometers, the capillaries of which had been calibrated. The samples were evacuated on a vacuum apparatus and filled in vacuum with previously degassed water. The displacement of the menisci in the capillaries was measured at $20 \pm 0.05^\circ$ with a cathetometer. Observations were carried out for 6 months, until the reaction was completed. Fig. 2 gives the decrease in the volume of the system, $-\Delta V$, calculated per 1 mole of SiO_2 for initial compositions with different CaO/SiO_2 ratios. The obtained values of $-\Delta V$ represent deviations of the molar volumes of the initial components from additivity during hydrosilicate formation. Taking the tabulated density values of $Ca(OH)_2$ as 2.24 and of silica gel as 2.20 g/cm^3, for a sample of composition $CaO/SiO_2 = 0.8$ the density of the crystals formed was calculated at a water content $H_2O/SiO_2 = 2.5$,* as was the value of their surface area s_d (Table 1). Taking into account that the surface of the plates does not depend on the degree of hydration of the crystals, one can determine their density at $H_2O/SiO_2 = 1$ (Table 1). Hence the density of water sorbed in the interlayer– pore spaces of the structure in the range $H_2O/SiO_2 = 1.0$—2.5 is $d_{H_2O} = 1.35$ g/cm^3.

As was shown (5), the step on the desorption isotherms of water vapor at $p/p_s = 0.35$ is characteristic of the layered structure of the hydrosilicates studied. Point 1 on the desorption isotherm (Fig. 3) corresponds to a degree of hydration of the crystals $H_2O/SiO_2 = 2.5$. Knowing the volume of desorbed water Δv, starting from this point, and the corresponding change in the distances between the elementary plates of individual crystals Δl, one can determine their surface:

$$s_v = \frac{2\Delta v}{\Delta l} \cdot \frac{n}{n-1},$$

where n is the average number of plates in unit crystals. The distance between plates l can be obtained according to Fig. 1 if it is assumed that the thickness of one plate is determined by the smallest interplanar distance $c/2 = 9.3$ Å, found for these crystals (2) (Table 1). The appearance of a step on the desorption isotherm, corresponding to a sharp decrease in the volume of sorbed water, in the case of a mobile layered structure of the sorbent must also be accompanied by an abrupt decrease in the interplanar distance. Indeed, as the calculation shows, the lattice parameter c at points 1 and 2 of the isotherm (Fig. 3) changes from 28 Å to 24.6 Å. Such a change in the lattice parameter of the crystal can evidently be regarded as a phase transition. The constancy of the vapor elasticity in this case corresponds to the condition of coexistence of two hydrates and will persist until one of them disappears, in this case the hydrate with $c = 28$ Å. On the other hand, study of the state of water sorbed on the same hydrosilicate sample by the NMR method (6) showed that water molecules at $H_2O/SiO_2 > 1$ do not enter the structure of the crystal lattice, possessing a

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* It was assumed here that the density of water sorbed above the indicated ratio, according to the isotherm in Fig. 3, practically does not differ from its bulk value.

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

mobility close to that in liquid water. If the layered crystal of tobermorite is considered as an assembly (packet) of elementary crystallites bonded along the basal planes, the characteristic step on the desorption isotherm (Fig. 3) is explained by the release of sorbed water from the interplanar spaces.

Fig. 2. Decrease in volume during the interaction of $Ca(OH)_2$ and silica gel in an aqueous medium

The geometric surface of silicate corrugated nets can also be determined directly from the lattice parameters. According to the model of the tobermorite structure ([1]), the surface of one unit cell is $2 \cdot 108$ $\mathring{A}^2$, whence the internal surface of crystals of a sample with $H_2O/SiO_2 = 1$, $s = 910$ m^2/g. Thus, independent determinations of the total surface of tobermorite give on average a value of 880 m^2/g. This value is characteristic of the model of the crystal structure adopted in the calculations and does not depend on their dimensions.

Fig. 3. Sorption isotherm of water vapor at 18° on a tobermorite sample with $CaO/SiO_2 = 0.8$. Black points—desorption

The desorption isotherm presented in Fig. 3 satisfies the BET equation within the range 0.04—0.3 p/p_s with the values of the equation constants $a_m = 4.90$ mmol/g and $C = 32$. In order to calculate on the basis of

from these data the crystal surface accessible to water, it is necessary to know the value of the area occupied by a water molecule, ω_{H_2O}, which in the present case can be obtained only from independent determinations. If one uses the surface value given above, then the effective value is $\omega_{H_2O} = 29$ $\mathring{A}^2$. Studying the sorption of water on a disaggregated sample of highly basic tobermorite, the authors of ([7]) "calibrated" ω_{H_2O}, proceeding from the surface value determined from nitrogen adsorption, and obtained $\omega_{H_2O} = 11.4$ $\mathring{A}^2$ and $s_{H_2O} = 337$ m^2/g*.

Table 1

H_2O/SiO_2	c, Å	l, Å	d, g/cm^3	S_d, m^2/g	S_ω, m^2/g
1.07	20.8	1.1	2.22	870	880
1.9	24.6	3.0	2.12	770	–
2.5	28	4.7	2.00	712	720

In accordance with the formula for tobermorite, of the 10 Ca^{2+} ions entering into the unit cell, 7 are bound to the silicic-acid radical, and the remaining 3 are compensated by OH^{1-} ions. According to the calculation, the value a_m corresponds to 7 water molecules per one elementary plate. Taking the Ca^{2+} ions to be sorption centers for water molecules and distributing the water molecules between the two indicated types of bonding of Ca^{2+} ions in the crystal cell, one can obtain a consecutive series of changes in the coordination number of the Ca^{2+} ions (Table 2) in accordance with the desorption isotherm (Fig. 3) and the known data on the hydration of these crystals (^{2}).

Table 2

H_2O/SiO_2	Number of H_2O molecules per Ca^{2+} ion bound to: $^1/_7[Si_{12}O_{31}]^{-41}$	Number of H_2O molecules per Ca^{2+} ion bound to: $2OH^{-1}$
0.5	0	1
1.08	1	1
1.66*	2	1
1.9	2	2
2.5	3	2

* Value corresponding to the value of a_m by BET.

Unlike water, nitrogen molecules do not penetrate into the interplanar spaces of the layered structure of tobermorite, since these spaces are filled with water molecules and decrease upon dehydration of the hydrosilicate (Table 1). Therefore, from low-temperature nitrogen adsorption isotherms one can obtain only the external surface of the crystals. For the sample studied by us, $s_{N_2} = 52\ m^2/g$. From this one can determine the average number of plates in a unit packet: $n = s_{H_2O}/s_{N_2} = 17$. The value of n increases noticeably for pressed samples and samples hardened naturally. Evidently, n characterizes the degree of intergrowth of elementary crystals in the polycrystalline structure.

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Moscow State University
named after M. V. Lomonosov

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* On the basis of the data of (^{7}) the conclusion was drawn that water sorption occurs on doubled plates. However, the authors do not present any evidence attesting to the completeness of disaggregation of the layered structure in their experiments.

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

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