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Abstract

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ON THE COMPOSITION AND STABILITY OF CALCIUM HYDROSILICATES UNDER HYDROTHERMAL TREATMENT AT 700 atm and 200°

In ultradeep oil wells the temperature reaches 200°, and the pressure 700 atm. During their cementing, hardening of the binder must take place under particularly severe conditions. To study the influence of these conditions on the hardening of binders, we investigated at the Scientific-Research Institute of Cement the composition and degree of stability of calcium hydrosilicates obtained by synthesis from a mixture of lime and quartz sand with the ratio $CaO : SiO_2 = 2;\ 1;\ 0.8$, at a temperature of 200° and 700 atm, and, for comparison, at 200° and 16 atm. For the synthesis, chemically pure calcium oxide and quartz sand washed and ground in a porcelain mill to $S = 3500$ cm^2/g (by Tovarov) were used.

The prepared mixtures were gauged with distilled water until a paste of plastic consistency was obtained, and were poured into molds measuring $1 \times 1 \times 3$ cm. Part of the specimens in the molds was placed in a specially adapted high-pressure autoclave of the GROZNII system, where hardening proceeded at 200° and 700 atm. Another part of the molds was placed in an autoclave, where synthesis proceeded at 200° and 16 atm. The holding time of the specimens at the stated parameters was determined by the conditions of the experiment. At the end of the experiment the strength of the specimens was determined.

The phase composition was established by X-ray, thermal, and petrographic methods. X-ray patterns were taken on a URS-50I diffractometer, and thermograms on a Kurnakov pyrometer. The X-ray and thermal characteristics of the synthesis products were taken according to works ($^{1-4}$).

During hydrothermal treatment of the mixture with $CaO : SiO_2 = 2$, both at low and at high pressure, hydrosilicate $C_2SH(C)$ is formed (Table 1), identified on the X-ray patterns by lines with $d = 5.43;\ 4.06;\ 3.82;\ 3.60;\ 3.34;\ 3.04;\ 2.91;\ 2.84;\ 2.70;\ 2.56;\ 2.51$ Å and others. Its presence is also confirmed by endothermic effects on the DTA curves at 680 and 730°.

Under the microscope the synthesis products appear as an extremely fine-grained, almost isotropic mass (Fig. 3a). Free lime and unreacted quartz were not found in the specimens. The calcium hydrosilicates obtained had practically no binding properties. Autoclaving the mixture with CaO : SiO_2 = 1 for 3 days led to the formation of a phase consisting almost entirely of xonotlite. Its synthesis proceeds through calcium hydrosilicates that are metastable under these conditions and are formed at early times (Table 1, Figs. 1 and 2).

Hydrothermal treatment for more than 3 days does not noticeably change the phase composition. However, with an increase in the duration of autoclaving, the flexural strength of the specimens decreases sharply, which may be explained by the growth of xonotlite crystals in the medium of water superheated at 700 atm.

Table 1

Phase composition, optical constants, and strength of specimens from mixtures of lime and quartz sand

No.	Pressure, ati	Duration, h	Flexural strength, kg/cm^2	Compressive strength, kg/cm^2	N_{avg}	Phase composition
						CaO : SiO_2 = 2
1	16	72	0	0		$C_2SH(C)$; $C_2SH(B)$
2	16	120	0	0		Same
3	16	168	0	0		$C_2SH(C)$
4	700	72	0	0		Same
5	700	120	0	0		» »
6	700	168	0	0	1.630-1.635	» »
						CaO : SiO_2 = 1
7	16	3	27	130		$C_2SH(C)$; CSH(B); C : S = 0.8, 1.25; $C_4S_5H_5$; $Ca(OH)_2$; SiO_2

No.	Pressure, ati	Duration, h	Flexural strength, kg/cm^2	Compressive strength, kg/cm^2	N_{avg}	Phase composition
8	16	24	34	122		$C_2SH(C)$; CSH(B); C : S = 0.8; $CSH_{0\cdot18}$; $CSH_{0\cdot18}$
9	16	72	29	125		Same
10	16	120	–	127		Same
11	16	168	26	124		» »
12	700	3	19	83		$C_2SH(C)$; CSH(B); C : S = 0.8; $C_4S_5H_5$; $Ca(OH)_2$; SiO_2
13	700	24	9	75		CSH(B); C : S = 0.8; $CSH_{0\cdot18}$;
14	700	72	brittle	75		$CSH_{0\cdot18}$
15	700	120	»	70		Same
16	700	168	»	75	1.579 ± 0.003	» »
						CaO : SiO_2 = 0.8
17	16	3	25	110		$C_4S_5H_5$; $CSH_{0\cdot18}$; CSH(B); C : S = 1.25; SiO_2
18	16	24	–	85		$C_4S_5H_5$; $CSH_{0\cdot18}$; CSH(B); C : S = 0.8; SiO_2
19	16	72	30	75		Same
20	16	120	35	92		» »
21	16	168	23	95		» »

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

No.	Pressure, ati	Duration, h	Flexural strength, kg/cm^2	Compressive strength, kg/cm^2	N_{avg}	Phase composition
22	700	3	21	105		» »
23	700	24	30	100		» »
24	700	72	22	130		» »
25	700	120	31	110		» »
26	700	168	24	120	1.564 ± 0.003	» »

On the DTA curves for specimens consisting of xonotlite $CSH_{0 \cdot 18}$, thermal effects of low intensity are observed at (+) 755° and (−) 770° (Fig. 2, 2, 3, 5). On the X-ray patterns there are lines with $d = 2.62$; 1.676; 1.562; 1.514; 1.426 and 1.385 Å, which so far have not been identified.

The synthesis product obtained at 700 ati over 7 days is a fine-crystalline mass of comparatively homogeneous composition (Fig. 3b). The hydrosilicate obtained has the form of extremely fine, nearly isotropic grains, often cemented together with the formation of granules, at the center of which there is a spherulite with high birefringence.

When a mixture with $CaO : SiO_2 = 0.8$ is autoclaved for 1 day, a practically constant ratio of hydrosilicates is obtained: xonotlite, tobermorite, and fibrous CSH(B), the amount and crystallization of which do not change appreciably as the duration of treatment is increased (Figs. 1 and 2, 6-10). The strength of the specimens likewise does not change substantially, which indicates preservation of the structure of the hardened intergrowth. On the DTA curves, the presence of tobermorite is confirmed by an endothermic effect at 230°; the presence of hydrosilicate CSH(B) $C : S = 0.8$ is determined by an exothermic effect at 845°.

Residues of unreacted quartz were detected by X-ray and petrographic analyses.

Under the microscope the synthesis products are characterized by an extremely fine-crystalline structure, consisting of the finest grains,

Fig. 1. X-ray diffraction patterns of the synthesis products from lime and quartz sand with $CaO : SiO_2 = 1$ (curves 1-5) and with $CaO : SiO_2 = 0.8$ (curves 6-10), treated at 200° and 700 atm: 1, 6—3 hours; 2, 7—1 day; 3, 8—3 days; 4, 9—5 days; 5, 10—7 days.

Fig. 2. Thermograms of the synthesis products from lime and quartz sand. The designations of the curves are the same as in Fig. 1. Thermograms of samples synthesized at 16 atm are denoted by dashed lines.

sometimes intergrown, with the formation of small scales or granules. In addition, small spherulitic formations, usually accompanying xonotlite, were observed in all specimens.

The processes of synthesis of calcium hydrosilicates at 700 atm gauge and 200° differ qualitatively and quantitatively from the processes occurring at 16 atm gauge and the same temperature. This is seen especially clearly in the example of a mixture with

Fig. 3. Microstructure of calcium hydrosilicates obtained at 200° and 700 atm gauge for 7 days at the initial ratio of the mixture: *a*—$CaO : SiO_2 = 2$; *b*—$CaO : SiO_2 = 1$; *c*—$CaO : SiO_2 = 0.8$. Without analyzer. 600×

$CaO : SiO_2 = 0.8$, upon autoclaving of which for 3 h at 700 atm gauge CSH(B), $C : S = 0.8$, is formed, whereas at 16 atm gauge–CSH(B), $C : S = 1.25$ (Fig. 2, *b*).

At subsequent treatment times the amount in the specimens of CSH(B) (exothermic effect at 845°) and tobermorite (endothermic effect at 230°) depends on the magnitude of the pressure (Fig. 2, 7—10).

The X-ray diffraction patterns of specimens obtained at 700 atm gauge are characterized by a larger number of lines of greater intensity, defining individual compounds, than the X-ray diffraction patterns of specimens treated for the same interval of time at 16 atm gauge.

Calcium hydrosilicates synthesized at 16 atm gauge are distinguished by still finer and less distinct crystallization of the minerals and by a more heterogeneous composition.

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