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Abstract

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STABILITY OF CALCIUM HYDROSULFOALUMINATE IN PORTLAND-CEMENT STONE

During the hardening of Portland cement, a considerable amount of calcium hydrosulfoaluminate is formed—$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$; consequently, the question of the stability of this compound in hardened Portland-cement stone is of substantial importance. The available works ([1–3]) mostly deal with the question of the stability of single crystals of calcium hydrosulfoaluminate obtained through the interaction of calcium aluminates dissolved in water and gypsum.

Studying crystals of calcium hydrosulfoaluminate by the microscopic method, O. M. Astreeva and L. Ya. Lopatnikova ([1]) observed, with time, their decomposition under ordinary conditions into gypsum, alumina hydrate, and calcium oxide. T. Yu. Lyubimova ([2]), studying the thermal stability of single crystals of calcium hydrosulfoaluminate obtained by the same method, as a function of changes in temperature and air humidity, came to the conclusion that this compound is stable only in an atmosphere of saturated vapor at 18°.

Kayonagi ([3]), examining in microscopic preparations calcium hydrosulfoaluminate obtained by dissolving Portland cement in water followed by precipitation of calcium aluminates with a $CaSO_4$ solution, records the formation, over 2–3 months, of small crystals. At the same time, supplementary chemical methods of analysis showed that the calcium hydrosulfoaluminate formed in cement stone passes with time into $4CaO \cdot Al_2O_3 \cdot nH_2O$ and gypsum.

In studying the hydration products of Portland cement containing from 2.75 to 16.5% SO_3, in the temperature interval from 25 to 100°, Kalousek and Adams ([4]), by means of differential thermal analysis, detected the formation of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ and, presumably, an analogous calcium sulfoferrite, which then pass into corresponding solid solutions of these products, subsequently transforming into phase X. Phase X, in their opinion, is a gel-like mass containing all the oxide constituents of the cement. From the review presented it is evident that, on the question of the stability of calcium hydrosulfoaluminate synthesized from solutions, as well as that formed directly in hydrated cement, there are contradictory and very limited data.

We carried out work to determine the stability of calcium hydrosulfoaluminate by chemical and X-ray methods. Calcium hydrosulfoaluminate was obtained in various ways: 1) by mixing with water Portland cement containing an increased amount of gypsum; 2) by mixing with water a mixture of finely dispersed $3CaO \cdot Al_2O_3$ and $CaSO_4 \cdot 0.5H_2O$, taken in the stoichiometric ratio required to obtain the high-sulfate form of calcium hydrosulfoaluminate; 3) by interaction of aqueous solutions of $3CaO \cdot Al_2O_3$ and $CaSO_4 \cdot 0.5H_2O$.

By the first method, to obtain calcium hydrosulfoaluminate in a hardened cement mass, two Portland cements differing in mineralogi-

chemical composition of Portland-cement clinkers: clinker from the "Gigant" plant, containing 35% C_3S, 30% C_2S, 12% C_3A, 13% C_4AF, and clinker from the "Oktyabr" plant, containing 48% C_3S, 27% C_2S, 6% C_3A, 17% C_4AF. The cements were prepared by grinding the clinker to a specific surface of 5100 cm^2/g, followed by the addition to it of finely ground hemihydrate gypsum in an amount of 6.35% as SO_3. From the resulting cements, specimens of plastic consistency of composition 1:0 were prepared at a water–cement ratio of 0.52.

According to the second method, tricalcium aluminate and hemihydrate gypsum, ground to a specific surface of about 7000 cm^2/g, were mixed in the stoichiometric ratio, gauged with 70% water, and from the resulting mixtures specimens were prepared; after one day these were demolded and placed in an atmosphere saturated with water vapor at 20–22°, where they were stored for 18 months. In the cement stone and in the synthetically prepared calcium hydrosulfoaluminate, the content of unreacted gypsum was periodically determined by the method of dissolving it in a saturated lime–water solution. The results of the determinations are given in Table 1.

Table 1

Kinetics of the interaction of gypsum with "Gigant" and "Oktyabr" cements and with tricalcium aluminate

Name of binder	Initial content of free SO_3, %	1 day	3 days	7 days	14 days	28 days	3 months	12 months	18 months
Cement "Gigant" + $CaSO_4 \cdot 0.5H_2O$	6.32	1.74	1.06	0.68	0.33	0	0	0	0

Name of binder	Initial content of free SO_3, %	1 day	3 days	7 days	14 days	28 days	3 months	12 months	18 months
Cement "Oktyabr" + $CaSO_4 \cdot 0.5H_2O$	6.34	2.19	1.77	1.28	0.90	0.62	0.21	0	0
$3CaO \cdot Al_2O_3 + CaSO_4 \cdot 0.5H_2O$	19.13	8.12	6.10	4.32	2.81	2.63	0.97	0.92	0.18

From the data in Table 1 it is evident that by the 28-day period of hydration of the "Gigant" cement, free gypsum is absent in it; the "Oktyabr" cement completely assimilates gypsum only after 3 months; the formation of calcium hydrosulfoaluminate from tricalcium aluminate and hemihydrate gypsum is likewise practically completed after 3 months.

In order to determine the stability of calcium hydrosulfoaluminate at elevated temperatures, specimens made from "Gigant" cement, and also from tricalcium aluminate and hemihydrate gypsum, after 18 months of hardening under moist conditions were subjected to heat treatment in an atmosphere saturated with water vapor at 30, 40, 60, 80, and 100° for 8 hours, and also to autoclave treatment according to the following regime: 2 hours raising the pressure to 8 atm., 4 hours holding at 8 atm., 2 hours lowering the pressure.

After water-heat treatment, the content of free gypsum in the specimens was determined by the method of dissolving it in a saturated lime-water solution. The results of the determinations are given in Table 2.

Table 2

Content of free gypsum in "Gigant" cement and in synthesized calcium hydrosulfoaluminate

Fig. 1. Powder X-ray patterns of hydrated cements and calcium hydrosulfoaluminate

Figure 1: Fig. 1. Powder X-ray patterns of hydrated cements and calcium hydrosulfoaluminate

Name of binder	Initial content SO_3, %, bound	Initial content SO_3, %, free	Free SO_3 content after treatment, %, at 30°	at 40°	at 60°	at 80°	at 100°	at 8 atm.
Cement "Gigant" + gypsum	6.320	0	0	1.069	1.194	1.345	1.644	1.697
$3CaO \cdot Al_2O_3 +$ gypsum	18.950	0.180	0.189	1.475	1.609	2.188	2.691	2.978

The data in Table 2 show that calcium hydrosulfoaluminate, stable at 20–22°, begins, as a result of water-thermal treatment, to decompose with the liberation of free gypsum at a temperature of about 40°. As the temperature is raised, the amount of gypsum released increases. Portland-cement stone and calcium hydrosulfoaluminate synthesized in the solid phase after 18 months of hydration under moist conditions were subjected to X-ray phase analysis by the powder method. For this purpose, powders dehydrated with ethyl alcohol were placed in a capillary with an internal

Fig. 1. Powder X-ray patterns of hydrated cements and calcium hydrosulfoaluminate:
a –cement from the "Gigant" plant without gypsum;
b –the same cement with gypsum;
c –cement from the "Oktyabr" plant without gypsum;
d –the same cement with gypsum;
e –$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 32H_2O$, synthesized from solutions of $3CaO \cdot Al_2O_3$ and $CaSO_4 \cdot 0.5H_2O$;
f –calcium hydrosulfoaluminate synthesized in the solid phase from $3CaO \cdot$

Al_2O_3 and $CaSO_4 \cdot 0.5H_2O$ before water-thermal treatment;
g –the same compound after treatment at 40°.

diameter of 0.5 mm, and, using copper filtered radiation, photographs were taken in an RDK camera with a diameter of 57.3 mm, with an exposure of 12 h. The tube voltage was 30 kV, and the anode current 20 mA.

The intensities of the diffraction lines and the values of the interplanar spacings of the hydrated cements "Oktyabr" and "Gigant" are given in Fig. 1.

Comparing the intensities of the diffraction lines and the values of the interplanar spacings of the "Gigant" and "Oktyabr" cements hydrated for 18 months, which do not contain gypsum, with the indices of the same cements containing gypsum introduced during mixing, it should be noted that in the latter lines are found that characterize the high-sulfate form of calcium hydrosulfoaluminate. The "Gigant" cement, containing 6.32% SO_3, in addition to the principal lines corresponding to hydrated clinker minerals, has additional lines –3.87; 3.46; 2.53; 2.11 Å. In the "Oktyabr" cement, containing 6.34% SO_3, the lines corresponding

$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ are 3.85; 3.43; 2.74; 2.53; 2.14; 1.56 Å. At the same time, both in the "Gigant" cement and in the "Oktyabr" cement, some of the lines of lower intensity corresponding to calcium hydrosulfoaluminate are superimposed on the lines of other products of cement hydration, thereby increasing the intensity of the latter. Lines characterizing the presence of free gypsum in any of its modifications were not found on the X-ray diffraction patterns.

It follows from this that phase analysis of two Portland cements differing in mineralogical composition, hydrated together with gypsum for 18 months at 20-22°, does not show decomposition of the calcium hydrosulfoaluminate formed; this, in turn, is confirmed by the results of chemical analysis (after 18 months of hydration, neither cement contained free gypsum).

Phase analysis of calcium hydrosulfoaluminate obtained in the solid phase from $3CaO \cdot Al_2O_3$ and $CaSO_4 \cdot 0.5H_2O$ shows that, after 18 months' storage of the samples under moist conditions at 20-22°, the values of the interplanar spacings (allowing for error in measuring the lines) are equal to the corresponding lines of calcium hydrosulfoaluminate obtained by the method of interaction of water-dissolved $3CaO \cdot Al_2O_3$ and $CaSO_4 \cdot 0.5H_2O$, with subsequent separation, after 7 days, from the mother liquor of the crystals of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ that had formed, as is seen in Fig. 1.

The "Gigant" cement hydrated for 18 months together with gypsum, and the calcium hydrosulfoaluminate synthesized in the solid phase, after 8 hours of treatment in an atmosphere saturated with water vapor at 30; 40; 60; 80; 100°, and also after autoclaving, were subjected to X-ray analysis in order to establish the stability of its existence at elevated temperatures. The results of the phase analysis agree with the data obtained by the chemical method of determining the decomposition temperature of calcium hydrosulfoaluminate—after hydrothermal treatment at 40°, lines 4.32; 3.06; 2.48; 2.25; 1.97 Å are detected, characterizing the presence of $CaSO_4 \cdot 2H_2O$, the interplanar-spacing values of which correspond to the tabulated values (5). The nature of the destruction of calcium hydrosulfoaluminate crystals is shown in Fig. 2 (see inset to p. 1232).

As the treatment temperature is raised, the intensity of the lines corresponding to gypsum increases, indicating a greater content of gypsum released during the decomposition of calcium hydrosulfoaluminate.

On the basis of the work carried out, the following conclusions may be drawn:
1) in a moist medium at a temperature of 20–22°, the calcium hydrosulfoaluminate formed in cement stone is a stable compound;
2) under hydrothermal treatment, calcium hydrosulfoaluminate begins to decompose at a temperature of 40°;
3) decomposition of calcium hydrosulfoaluminate during hydrothermal treatment is accompanied by the liberation of free gypsum, the amount of which increases as the temperature is raised.

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