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REGULATING THE PROCESSES OF HYDRATION STRUCTURE FORMATION OF A CARBONATE-GYPSUM MIXTURE ON A BASE IN BINDER SYSTEMS

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Abstract:

The study of the structure formation features of various gypsum binders showed that, despite the formation of the same phase $CaSO_4 \cdot 2H_2O$ during the hydration of various low-temperature binders, they differ in strength and kinetics of its growth. The results of thermogravimetric and X-ray phase analyzes of the hydration products of carbonate-gypsum binder are presented.

Keywords: Gypsum, calcium carbonate, hydration, binders, aluminate, silicate, diffraction pattern, structure formation.

The interaction of the clay component of gypsum with calcium carbonate during high-temperature firing can serve as a source of calcium aluminates and silicates, which have the ability to formation of hydration hardening structures. However, due to the low content of calcium carbonates in the original gypsum, the number of hydraulically active compounds arising in this case is small. Meanwhile, from the point of view of obtaining moisture-resistant, sufficiently strong structures, they are of the greatest interest. Therefore, we conducted a series of experiments with compositions composed of natural gypsum with the addition of calcium carbonate and fired in the temperature range of 500–1100°C. Carbonate was introduced into the mixture in amounts of 10 and 20%. The resulting products were subjected to X-ray phase and chemical analysis and studied in the form of diluted and concentrated suspensions (pastes) [2, p. 47–49; 4, p. 84–87].

It has been established that starting from 700° free calcium oxide appears in all mixtures, formed due to the thermal decomposition of $CaCO_3$. With increasing firing temperature at 30-minute exposure, the content of CaO_{free}. increases in mixtures from 10% $CaCO_3$ to 900 °C, from 20% $CaCO_3$ to 1000 °C. With an increase in firing duration to 2 hours, the maximum CaOfree. moves towards lower temperatures.

The very presence of a maximum in CaO_{free} content. on the curves confirms that calcium oxide released during the decomposition of calcium carbonate is bound into new formations, similar to what happens when firing natural loess-like loams [5, p. 55–56]. The composition of the resulting products was studied using X-ray phase analysis, the degree of decomposition of calcium carbonate was determined by thermogravimetric analysis (Table 1), which shows that the decomposition of calcium carbonate begins in both mixtures at temperatures significantly lower than what occurs in a one-component system of $CaCO_3$.

10% $CaCO_3$ introduced into the mixture completely decomposes as a result of 2-hour firing at a temperature of 800°, 20% at 900°C. Approximate calculations show that minus CaO_{free}. up to 6-7% CaO is bound into new phases.

Influence of the mixture firing mode on the residual $CaCO_3$ content

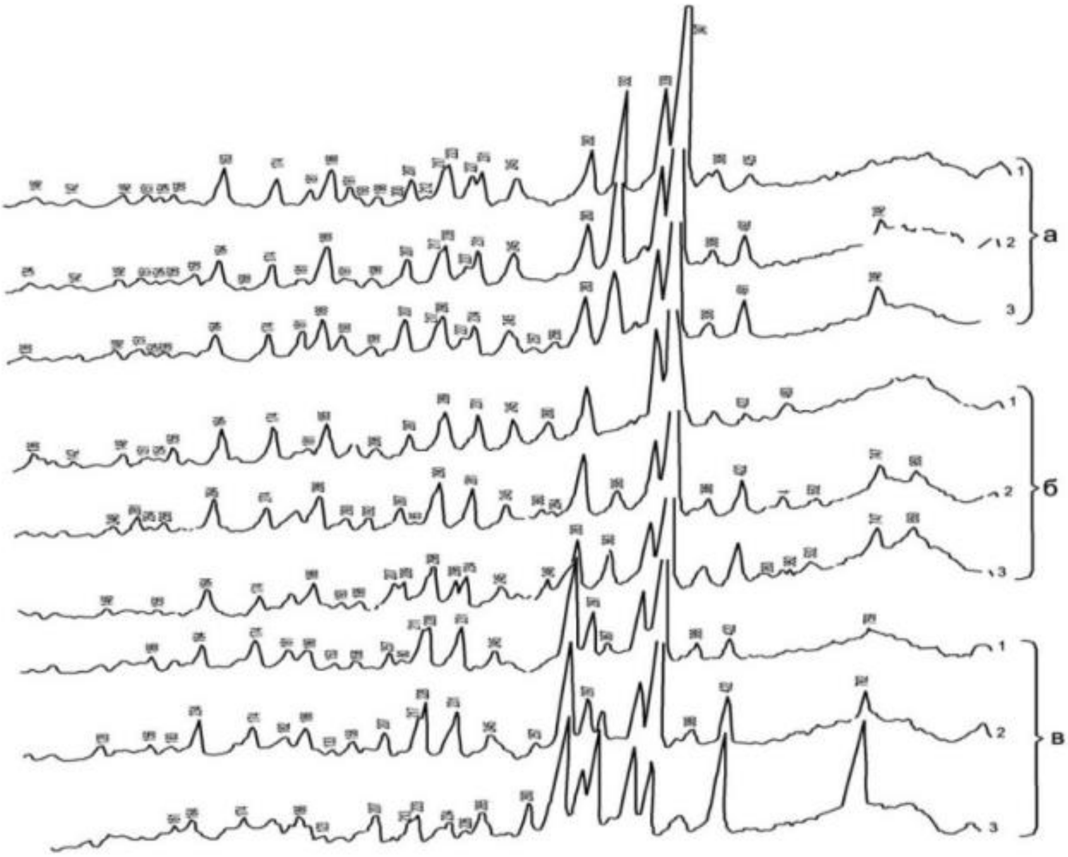
Exposure time	90 % gypsum + 10 % $CaCO_3$			80 % gypsum + 20 % CaCO3		
	Firing temperature, °C	Weight loss, %	Residual $CaCO_3$ content, %	Firing temperature, °C	Weight loss, %	Residual $CaCO_3$ content, %
30 minutes	600	5,5	7,60	30 minutes	600	12,45
	700	5,5	7,60		700	12,45
	800	2,6	3,83		800	11,03
	900	1,6	2,01		900	5,00
	1000	0	0		1000	0
2 hours	600	5,5	7,60		1100	0
	700	5,5	7,60	2 hours	600	12,45
	800	0	0		700	10,65
	90	0	0		800	5,30

					900	0

Diffraction patterns of the products of firing mixtures of 10 and 20% $CaCO_3$ confirm the formation of new phases due to the interaction of carbonate with gypsum at temperatures above 800°. The result of firing at lower temperatures (500–700°C) is mainly the decomposition of gypsum, clay and carbonate components. The resulting finely dispersed products are represented by anhydrous calcium sulfate, anhydrite, very active calcium oxide, which is intensively hydrated even during the preparation of the sample for analysis due to air moisture and, accordingly, is detected on diffraction patterns in the form of $Ca(OH)_2$; dehydrated kaolinite is X-ray amorphous and cannot be determined by X-ray phase analysis [1, p. 47–48].

With increasing temperature and firing time, the anhydrite remains practically without noticeable changes, calcium carbonate completely disappears depending on its concentration in the mixture at 900°C (10% $CaCO_3$) or 1000°C (20% $CaCO_3$) with a firing duration of 30 minutes and at 800 and 900°, respectively, with increasing exposure to 2 hours.

The presence of dicalcium silicate is not clearly established. As is known, it is the first phase formed in carbonate-silica compositions, and with an increase in temperature above 900°C it turns into hydraulically inactive β $CaO{\cdot}SiO_2$ [3, p. 162–165] – wollastonite. The latter is also well identified in the products of firing gypsum with 10 and 20% $CaCO_3$ at temperatures of 1000 and 1100° (3.05; 2.95 Å). Among the aluminosilicates, gehlenite (3.69; 3.07; 2.83 Å) was found in the products of firing gypsum with 10 and 20% $CaCO_3$ at a temperature of 1000°C for 2 hours (pic. 1).



picture 1. Diffraction patterns of hydration products of carbonate-gypsum binder obtained by temperature: 600 (a); 800 (b); 1100 (c) after 6 hours (1); 7 days (2); and 28 days. (3) hardening

Measurements of the kinetics of structure formation of concentrated pastes from the products of firing carbonate-gypsum compositions showed that, within the temperature range of 500–1100°C, a whole series of binders with different properties are formed depending on the phase composition of the initial product, determined by the firing regime.

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Starting from 550°C, in all cases the paste acquires noticeable strength only after a day or later. The character of the Pm-т kinetic curves characteristic of low-temperature gypsum binders-an avalanche increase in strength in the early stages-is partially preserved only for short-term firing products at 500°C.

With increasing firing temperature, the rate of hardening of the paste decreases to a greater extent, the higher the temperature and firing time, regardless of the $CaCO_3$ content in the mixture. This pattern persists until free calcium oxide and the products of its interaction with the clay component appear in the system.

Starting from 700°C, depending on the $CaCO_3$ content and firing time, an increase in the strength of structures and an acceleration of their formation are noted. Then, with a further increase in the firing temperature above 900°C, the strength decreases again, which indicates the formation of hydraulically inactive reaction products in the form of wollastonite and aluminosilicates.

Thermogravimetric and X-ray phase (pic. 1) analyzes of hydration products in kinetics confirm that the formation of a hardening structure in firing products up to 600°C is determined by the hydration of insoluble anhydrite and ultimately the crystallization of gypsum dihydrate.

The slow occurrence of this process, reflected in the insignificant content of hydration water in the hydration products (in 6 hours, for example, it reached only 1.5%), also determined the insignificant strength of the structure in the first stages of hydration. Only by the 28th day is complete hydration of the gypsum part in these mixtures achieved; Accordingly, by this time the strength reaches its greatest value.

For fired products, starting from 700°C and especially from 800°C, hydration of anhydrite occurs in the presence of free lime formed during the decomposition of carbonate. In this case, the composition of high-temperature gypsum binder with the addition of $Ca(OH)_2$, described above, is reproduced.

The resulting structure is formed both due to the hydration of anhydrite, which becomes noticeable only by the 7th day, and due to the participation in the reaction of free calcium hydroxide, the amount of which gradually decreases with time, as well as due to the hydration of calcium silicates and aluminates formed during the firing process.

Influence of firing temperature on the kinetics of the formation structure (Pm kgc/cm^2) of a mixture of 80% gypsum + 20% $CaCO_3$, W/S = 0.38

Firing temperature, °C	Test period											
	minutes				time				Day			
	1	5	15	30	1	2	4	6	1	7	14	28
30 minutes												
500	0,90	7,0	9,5	9,0	0,6	11,0	13,5	18,6	47,3	144	136	90
550	0,2	0,15	0,12	0,18	–	0,40	0,90	1,4	4,5	5	131	176
600	0,05	0,12	0,3	0,1	0,12	0,21	0,20	0,41	2,5	17	150	239
700	0,13	0,20	0,22	–	0,22	0,24	0,18	0,26	2	60	133	131
800	0,11	0,15	0,10	0,13	0,16	0,17	0,17	0,26	0,63	68	104	16
900	0,15	0,13	0,16	0,21	0,22	0,30	0,33	0,40	0,52	17	309	368
1000	0,12	0,17	0,18	0,23	0,24	0,43	1,8	1,6	2,5	19	303	312
1100	0,10	0,11	0,11	0,15	0,16	0,20	0,17	0,36	0,36	10,5	53,1	168
2 hours												
500	0,10	0,15	0,15	0,4	0,21	0,32	0,41	0,43	1,5	15	34,4	161
550	0,12	0,15	0,20	0,20	0,22	0,23	0,41	3,1	6,3	16,3	25,4	33
600	0,10	0,14	0,20	0,31	0,30	0,41	0,53	0,70	7	42	47,0	52
700	0,11	0,20	0,14	0,15	0,15	0,20	0,40	0,32	2,3	60	75,5	81
800	0,10	0,12	0,17	0,19	0,21	0,33	0,40	0,50	0,02	101	132	164
900	0,10	0,10	0,13	0,11	0,10	0,13	0,20	0,23	0,30	94	311	421
1000	0,13	0,15	0,29	0,49	0,58	0,60	2,0	3,3	4,5	27	56	170
1100	0,15	0,18	0,18	0,32	0,33	0,36	13,4	–	–	–	–	–

The presence of the latter is confirmed by the formation of calcium hydrosulfoaluminate, well identified by X-ray phase analysis (9.50; 5.52; 5.02); indirect confirmation of the presence of dicalcium silicate can be the high final strength of the structure at later stages, which increases with increasing degree of participation of calcium carbonate in the processes of formation of new phases during firing.

A further increase in the firing temperature to 900°C for a low-carbonate mixture and to 1000° for a high-carbonate mixture leads to an even greater slowdown in the hydration of the gypsum part and a decrease in the degree of participation of $Ca(OH)_2$ in hydration processes; calcium hydrosulfoaluminate is not formed. A sharp drop in the final strength values indicates a decrease in the role of dicalcium silicate in structure formation [6, p. 17–21; 7, p. 64–68].

Thus, as a result of high-temperature firing (800–900°C) of carbonate-gypsum mixtures, a binder material with the ability to hydraulically harden can be obtained. Physico-mechanical tests have shown its sufficient stability both in air and in humid water hardening conditions. Consequently, this material can occupy an intermediate position between air gypsum binders and hydraulic binders that harden in water.

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