



The Effect of Temperature on the Kinetics of the Structure Formation of a Carbonate-Gypsum Mixture Based on A Natural Gypsum Binder

Abilova Amina Janabaevna

Karakalpak Research Institute of Natural Sciences, Karakalpak Branch of the Academy of Sciences of the Republic of Uzbekistan, Republic of Uzbekistan, Nukus

Bekbosinova Risgul Jiemuratovna

Karakalpak Research Institute of Natural Sciences, Karakalpak Branch of the Academy of Sciences of the Republic of Uzbekistan, Republic of Uzbekistan, Nukus

Mnajov Amaniyaz Nietbaevich

Karakalpak Research Institute of Natural Sciences, Karakalpak Branch of the Academy of Sciences of the Republic of Uzbekistan, Republic of Uzbekistan, Nukus

ABSTRACT

The article studies the influence of temperature on the kinetics of the structure formation of a carbonate-gypsum mixture and the features of the structure formation of various gypsum binders. Despite the formation of the same $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ phase during hydration of various low-temperature binders, they differ in strength and kinetics of its increase.

The results of thermogravimetric analysis of hydration products of carbonate-gypsum binder are presented. The analysis of hydration products in kinetics confirms that the formation of a hardening structure in firing products up to 600°C is determined by the hydration of insoluble anhydrite and the crystallization of ultimately two-water gypsum, and as a result of high-temperature firing of carbonate-gypsum mixtures, it is possible to obtain a binder capable of hydraulic hardening.

Keywords:

gypsum, calcium carbonate, hydration, binders, aluminates, silicate, diffractogram, structure formation, firing, temperature, mixture.

Introduction. The processes of structure formation in the gypsum binder system are very important. Therefore, much attention is currently being paid to the stability of the structure in various conditions and the ability to recover under the influence of temperature and humidity changes. The structure-forming abilities of gypsum binders depend on the composition of the original natural raw materials and the method of its processing (firing conditions, fineness of grinding, etc.).

Heat treatment of gypsum is associated with the occurrence of deformations that contribute to the weakening and destruction of bonds in the crystal lattice of gypsum and the emergence of active centers of an acidic or basic nature. A review of the literature shows

that the magnitude and kinetics of deformation development should differ for different types of structures, which in turn depend on the morphological features of crystals, as well as on the presence of impurities and their quantities. [1, pp.47-49;].

However, due to the low content of calcium carbonates in the initial 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. In this regard, a study was conducted to study the kinetics of structure formation in concentrated suspensions of binders obtained at different temperatures.

Research methods. A study of the kinetics of structure formation in concentrated suspensions was carried out using X-ray and thermogravimetric analysis methods.

Thermogravimetric studies were performed on a Paulik-Paulik-Erdey system derivatograph. The heating rate of the samples was 10 °C/min, and the weight of the sample was 100 mg. Differential thermal analysis simultaneously gives the direction and magnitude of the enthalpy change, the differential curve of weight loss. These analyses are universal and by now more modern methods of studying the compositions of solid minerals.

Results and discussions. A series of experiments were conducted with compositions made 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 an amount of 10 and 20%. The obtained products were subjected to X-ray phase and chemical analysis and examined in the form of dilute and concentrated suspensions (pastes) [2, pp. 84-87].

It was found that starting from 700 °C, free calcium oxide appears in all mixtures,

formed due to the thermal decomposition of CaCO_3 . With an increase in the firing temperature at a 30-minute exposure of the content of the CaO_{free} increases in mixtures from 10% CaCO_3 to 900 °C, from 20% CaCO_3 to 1000 °C. With an increase in the firing duration up to 2 hours maximum according to CaO_{free} moves towards lower temperatures.

The very presence of a maximum in terms of the content of the CaO_{free} the curves confirm that the calcium oxide released during the decomposition of calcium carbonate binds to neoplasms, just as it occurs during the firing of natural loess-like loams [3, pp. 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 it occurs in a single-component system of CaCO_3 .

The 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 % of CaO binds to new phases.

Table 1.

The effect of the firing mode of the mixture on the residual content CaCO_3

Exposure time	90% gypsum +10% CaCO_3			80% gypsum +20% CaCO_3		
	Temperature of the firing, °C	Weight loss %	Content of residual CaCO_3 , %	Firing rate, °C	Weight loss %	Content of residual CaCO_3 , %
30 minutes	600	5,7	7,61	30 minutes	9,7	12,43
	700	5,7	7,61		9,7	12,43
	800	2,7	3,80		8,5	11,03
	900	1,8	2,02		3,94	5,02
	1000	0	0		0	0
2 hour's	600	5,4	7,61	2 hour's	0	0
	700	5,4	7,61		9,7	12,44
	800	0	0		8,4	10,64
	900	0	0		0	5,31

Diffraction patterns of firing products of 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 °C. The result of firing at lower temperatures (500-700 °C) is mainly the decomposition of gypsum, clay and carbonate components. The resulting fine products are represented by anhydrous calcium sulfate, anhydrite, very active calcium oxide, intensively hydrated even during the preparation of the sample for analysis due to air moisture and, accordingly, detected on diffraction patterns in the form of $\text{Ca}(\text{OH})_2$; dehydrated kaolinite is X-ray amorphous and is not determined by X-ray phase analysis [4, pp. 47-48].

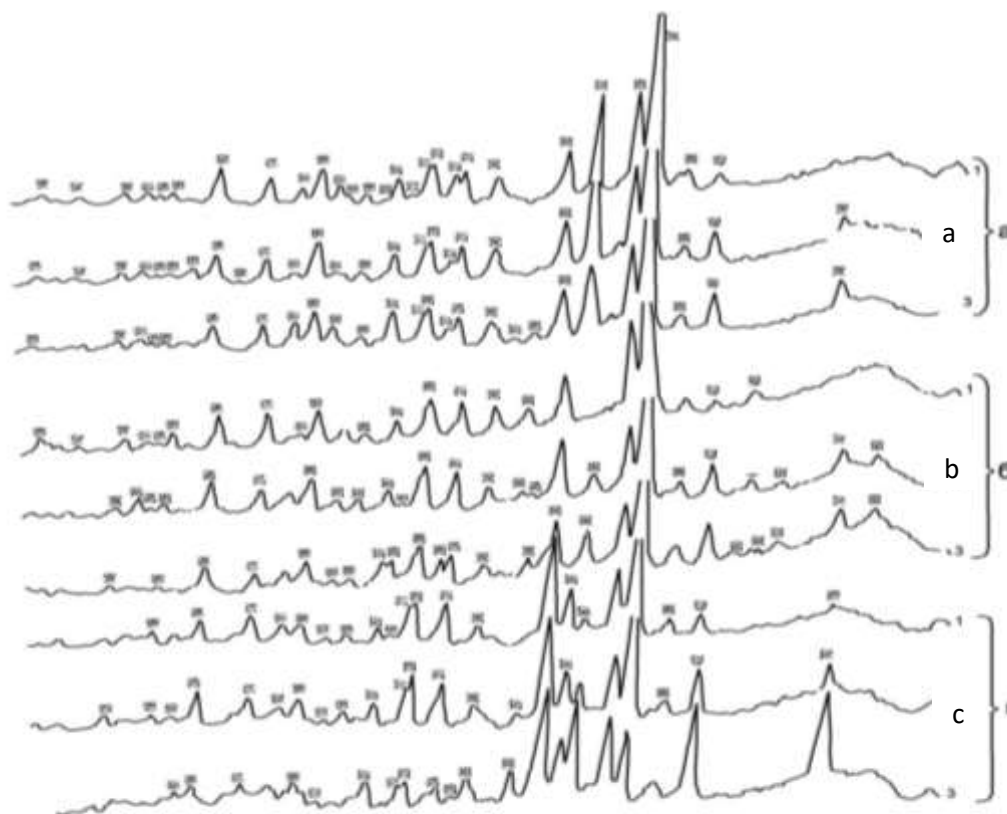
With an increase in temperature and firing time, anhydrite remains almost without noticeable changes, calcium carbonate completely disappears depending on its concentration in the mixture at 900 °C (10% CaCO_3) or 1000 °C (20% CaCO_3) with a firing duration of 30 minutes and at 800 and 900 °C, respectively,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

The presence of bicalcium 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 ° it turns into the hydraulically inactive β $\text{CaO}\cdot\text{SiO}_2$ [5, pp. 162-165] - wollastonite. The latter is also well identified in gypsum firing products with 10 and 20% CaCO_3 at temperatures of 1000 and 1100 °C (3,05; 2,95 Å). Gelenite (3.69; 3.07; 2.83 Å) was found among the aluminosilicates in gypsum firing products with 10 and 20% CaCO_3 at a temperature of 1000 °C exposure for 2 hours (picture.1).

Measurements of the kinetics of the structure formation of concentrated pastes from the firing products of carbonate-gypsum compositions showed that a whole series of binders with different properties is formed within temperatures of 500-1100 ° depending on the phase composition of the initial product determined by the firing mode.

Starting from 550 °C, in all cases, the paste acquires noticeable strength only after a day or later. The character of the kinetic curves $P_m\text{-}\tau$ characteristic of low-temperature gypsum binders - avalanche strength growth in the first terms - is partially preserved only for products of short-term firing at 500 °C.



Picture. 1. Diffractograms of hydration products of a carbonate-gypsum binder obtained at a temperature of 600 (a); 800 (b); 1100 (c) after 6 hours (1); 7 days. (2); and 28 days. (3); hardening.

With an increase in the firing temperature, the hardening rate of the paste decreases to a greater extent, the higher the temperature and firing time, regardless of the content of CaCO₃ 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 content of CaCO₃ and the firing time, there is an increase in the strength of structures and acceleration of their formation. Then, with a further increase in the firing temperature above 900 °C, the strength decreases again, which indicates the formation of hydraulically inactive interaction products in the form of wollastonite and aluminosilicates.

Table 2.

Effect of firing temperature on kinetics structure of formation (P_m kgc/sm²) mixtures of 80% gypsum + 20% CaCO₃, W/S = 0,38

Te mpera of the firing tour, °C	Test period									
	Min			Hour				day		
		5	0						4	8
30 minutes										

		,90	,0	,5	,0	,6	1,0	3,5	8,6	7,3	44	36	0
	500	,2	,15	,12	,18		,40	,90	,4	,5		31	76
	550					,12					7	50	39
	600	,05	,12	,3	,1		,21	,20	,41	,5			
	700					,22					0	33	31
	800	,13	,20	,22			,24	,18	,26				
	900				,13	,16				,63	8	04	6
0	100	,11	,15	,10	,13	,16	,17	,17	,26				
					,21	,22	,30	,33	,40	,52	7	09	68
0	110	,15	,13	,16	,21	,22	,30	,33	,40	,52	7	09	68
		,12	,17	,18	,23	,24	,43	,8	,6	,5	9	03	12
		,10	,11	,11	,15	,16	,20	,17	,36	,36	0,5	3,1	68
2 hour's													
		,10	,15	,15	,4	,21	,32	,41	,43	,5	5	4,4	61
	500	,12	,15	,20	,20	,22	,23	,41	,1	,3	6,3	5,4	3
	550												
	600	,10	,14	,20	,31	,30	,41	,53	,70		2	7,0	2
	700												
	800	,11	,20	,14	,15	,15	,20	,40	,32	,3	0	5,5	1
	900												
0	100	,10	,12	,17	,19	,21	,33	,40	,50	,02	01	32	64
0	110	,10	,10	,13	,11	,10	,13	,20	,23	,30	4	11	21
		,13	,15	,29	,49	,58	,60	,0	,3	,5	7	6	70
		,15	,18	,18	,32	,33	,36	3,4					

Thermogravimetric and X-ray phase (picture1) analyses 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 crystallization, ultimately, of two-water gypsum.

The slow course of this process, reflected in the insignificant content of hydrated water in the hydration products (for example, it reached only 1.5% in 6 hours), also caused the insignificant strength of the structure in the first periods of hydration. Only by the 28th day the complete hydration of the gypsum part in these mixtures is achieved; accordingly, by this time the strength reaches the highest value.

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

The resulting structure is formed both due to hydration of anhydrite, which becomes noticeable only by 7 days, 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 hydration of calcium silicates and aluminates formed during the firing process.

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

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

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

List of literature:

1. O. Asamatdinov, A. Jiemuratov, F.L.Glekel'. Vyajushie na osnove gancha Karakalpakii // Tashkent, 1977. - P. 47-49
2. Aray L.Ya. Napravlenie issledovaniy v oblasti ximii gipsa // Sekkoto Sekkay. - 1998.-№ 167 - P.9-16.
3. Voljenskiy A.V. Ferronskaya A.V. Gipsovie vyajushie izdeliya //M. Stroiizdat.1994. - P. 55-56.
4. Abilova A.J., Xamraev S.S., Vyajushie materialı na osnove gipsovix mineralov Respubliki Karakalpakstana // Ximicheskaya promishlennost'. - Rossiya, 2016. - № 2. - P. 47-48

5. Budnikov P.P. Gips, ego issledovanie i primeneniye / - M.- L., Stroyizdat 1950. - P. 162-165.
6. Abylova Amina Zhanabaevna, Turemuranov Sharibay Nauryzbaevich, Bekbosynova Rysgul Zhyemuratovna. Development of technology for producing cementitious composites based on minerals in Karakalparstan // Austrian Journal of Technical and Natural Scitnces, Vienna 2019, #7-8, - P. 17-21.
7. Turemuranov Sharibay Nauryzbaevich, Abylova Amina Zhanabaevna. Study of the processes of hydration structure formation in lime-belite binders on the basis of marls of the republic of Karakalpakstan // Vienna 2019, #7-8, - P. 64-68.