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RESEARCH HYDRATION STRUCTURE FORMATION OF HIGH-TEMPERATURE GYPSUM BINDERS ON THE BASIS OF KHUJAKUL DEPOSITS

Turemuratov Sh. N.,
Karakalpak Scientific Research Institute of Natural Sciences of the Karakalpak Branch of the Academy of Sciences of the Republic of Uzbekistan, Nukus.

Bekbosynova R. Zh.,
Karakalpak Scientific Research Institute of Natural Sciences of the Karakalpak Branch of the Academy of Sciences of the Republic of Uzbekistan, Nukus.

Abilova A. Zh.,
Karakalpak Scientific Research Institute of Natural Sciences of the Karakalpak Branch of the Academy of Sciences of the Republic of Uzbekistan, Nukus.

Khozhametova B. K.,
Karakalpak State University named after Berdakh, Nukus.

Sadikova A. M.
Karakalpak State University named after Berdakh, Nukus.
e-mail: amina.abylova@mail.ru, +998977881900

Annotation.

The article discusses the processes of high-temperature gypsum binder from the Khujakul deposit of the Republic of Karakalpakstan, in the temperature range of 550-1000°C and simulating the decomposition of its compositions, the phase composition of the resulting products, the main patterns of structure formation are established depending on the phase composition of the original binder.The results of the influence of the concentration of $Ca(OH)_2$ on the strength of the structure in concentrated suspensions of gypsum at different temperatures are presented.

The ways of regulating the properties of various gypsum binders with the help of additives and rational use of natural gypsum for the production of high-temperature gypsum binder for rocks with a predominance of the clay-carbonate part have been determined.

As a result of high-temperature firing (800-1000°C) of carbonate-gypsum mixtures, a binder material with the ability to hydraulic hardening can be obtained.

Key words: binder, calcium hydroxide, roasting, strength, concentration, hydration, additive, mineral, wet, air mixture.

INTRODUCTION.

Gypsum is a fairly widespread breed, it can serve as a basis for obtaining local binders. Therefore, monomineral gypsum binders have long attracted the attention of researchers involved in hydration and hardening processes.

The relatively high solubility, the clearly expressed crystalline structure of the hydrated phases, the formation of which is not complicated by hydrolysis, makes gypsum binders a convenient object of study. [1, 5]. Gypsum, which is a natural mixture of gypsum dihydrate with clay minerals, belongs to such a binder object. Using the example of the products of the thermal decomposition of gypsum, which sharply changes the phase composition in the temperature range of 550–1000°C, forming products with significantly different physicochemical properties, it is possible to trace the relationship between them and the kinetics of formation and strength of hydration hardening structures.

MATERIAL AND METODS.

The research material in this work was gypsum minerals from the Khujakul deposits and mineral fillers from the Beltau and Khujakul deposits. Experimental data on the study of various binders based on gypsum rocks of the Khujakul deposit are summarized. In composition, it is close to high-grade, so it can be used to obtain binders with high physical and mechanical properties. Using the example of semi-aqueous calcium sulfate, the effect of the type and concentration of finely dispersed fillers of different nature - carbonate, clayey, on the properties of coagulation and hydration structures in their aqueous suspensions at different water-solid ratios was studied.

RESULTS AND DISCUSSIONS.

On the properties of high-temperature gypsum binder (HBB), where the clay part of the gypsum acquires significant importance and the formation of the hydration structure, lime has a significantly greater and qualitatively different effect than on the low-temperature gypsum binder. In this case, $Ca(OH)_2$ acts not only as a regulator of the dissolution and hydration of calcium sulfate, but also as a participant in a chemical reaction with the formation of hydrated calcium phases, which are sources of additional strength. [7, 9].

The dehydrated clay part of gypsum in this case has the properties of alumina-containing active mineral additives, the processes of interaction of which with $Ca(OH)_2$, as is known, are accompanied by the formation of sufficiently strong but relatively slowly formed hardening structures. As a result of dehydration of the dihydrate, depending on the conditions of the process, various products can be formed, which are very significantly different in composition, structure and properties. Their numbers and nature are still a subject of discussion and are interpreted in different ways [3, 4].

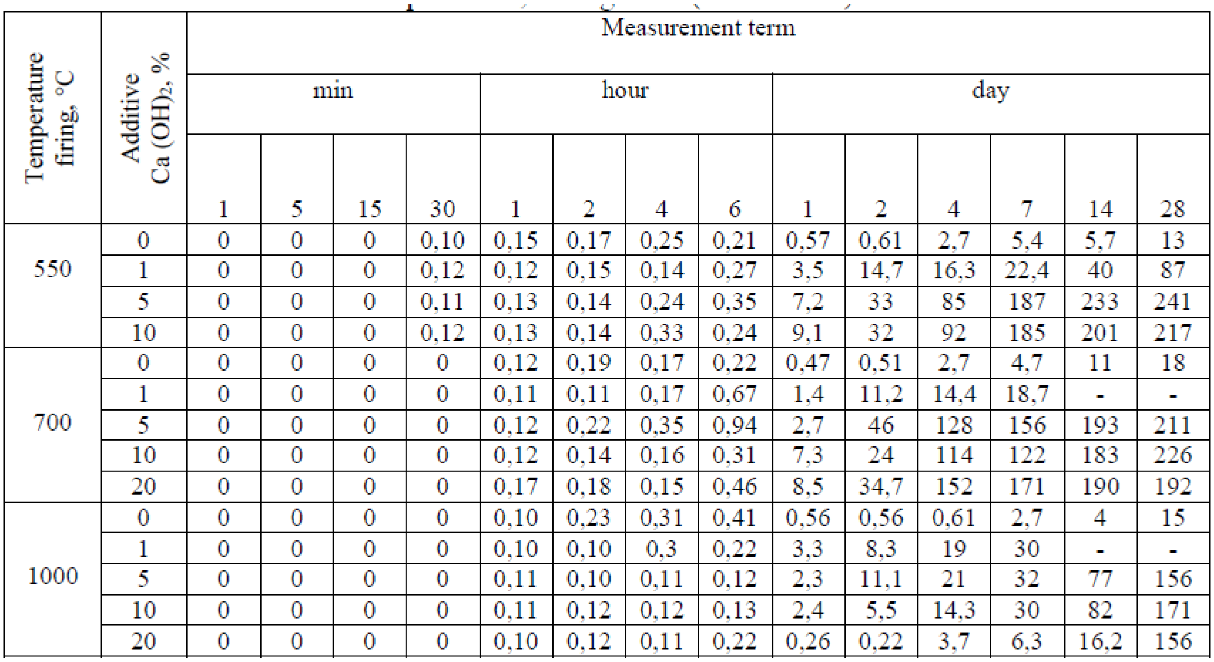
Measurements of the kinetics of structure formation and concentrated suspensions with the addition of calcium hydroxide (1-20 %) showed (Tab. 1) that the presence of lime in the system begins to manifest itself only after 24 hours.

Strength will increase as the content of $Ca(OH)_2$ in the mixture increases, passing through a maximum at the higher lime concentrations, the higher the activity of gypsum, which is determined by the temperature of its firing (Fig. 1).

Gypsum as a monomineral binder, the hydration processes of which are not complicated by hydrolysis, seems to be a very convenient object of research. On his example, the basic laws of the formation of crystallization hardening structures were studied (2, 6, 8).

Table 1

Influence of $Ca(OH)_2$ on the kinetics of structure formation of gypsum fired at different temperatures, Pm kgf/cm² (W/T = 0.50)



Temperature firing, °C	Additive $Ca(OH)_2$, %	Measurement term													
		min				hour				day					
		1	5	15	30	1	2	4	6	1	2	4	7	14	28
550	0	0	0	0	0,10	0,15	0,17	0,25	0,21	0,57	0,61	2,7	5,4	5,7	13
	1	0	0	0	0,12	0,12	0,15	0,14	0,27	3,5	14,7	16,3	22,4	40	87
	5	0	0	0	0,11	0,13	0,14	0,24	0,35	7,2	33	85	187	233	241
	10	0	0	0	0,12	0,13	0,14	0,33	0,24	9,1	32	92	185	201	217
700	0	0	0	0	0	0,12	0,19	0,17	0,22	0,47	0,51	2,7	4,7	11	18
	1	0	0	0	0	0,11	0,11	0,17	0,67	1,4	11,2	14,4	18,7	-	-
	5	0	0	0	0	0,12	0,22	0,35	0,94	2,7	46	128	156	193	211
	10	0	0	0	0	0,12	0,14	0,16	0,31	7,3	24	114	122	183	226
	20	0	0	0	0	0,17	0,18	0,15	0,46	8,5	34,7	152	171	190	192
1000	0	0	0	0	0	0,10	0,23	0,31	0,41	0,56	0,56	0,61	2,7	4	15
	1	0	0	0	0	0,10	0,10	0,3	0,22	3,3	8,3	19	30	-	-
	5	0	0	0	0	0,11	0,10	0,11	0,12	2,3	11,1	21	32	77	156
	10	0	0	0	0	0,11	0,12	0,12	0,13	2,4	5,5	14,3	30	82	171
	20	0	0	0	0	0,10	0,12	0,11	0,22	0,26	0,22	3,7	6,3	16,2	156

Most researchers agree that the hydration of hemihydrate gypsum proceeds according to the liquid-phase mechanism; however, there are opponents of this point of view, who believe that the addition of water to the hemihydrate proceeds without intermediate dissolution, i.e. according to the solid-phase scheme [10, 11].

For compositions based on gypsum fired at 550°C and 700°C containing the clay component in the most active form, the maximum strength is achieved in mixtures with 5-10 % $Ca(OH)_2$.

With an increase in the gypsum firing temperature to 1000°C, the optimal dosage of $Ca(OH)_2$ in the initial period shifts to the region of lower concentrations of 1-5 %, increasing to 10 % over time. This is in line with a sharp decrease in the activity of the clay part, which, as noted in works on alumina-containing additives, is a consequence of high-temperature firing.

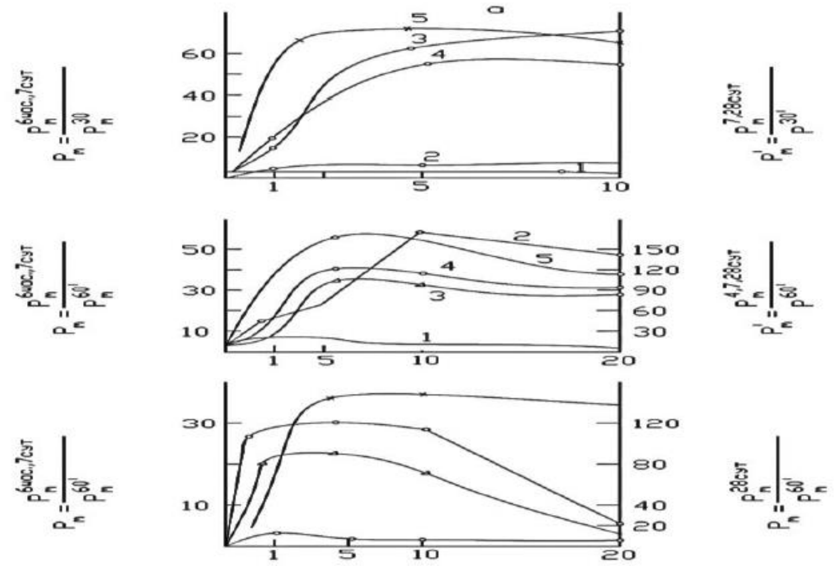


Fig. 1. Influence of $Ca(OH)_2$ concentration on structure strength in concentrated gypsum suspensions (a) 550 °C, (b) 700 °C and (c) 1000 °C after 6 hours (1), 1 day. (2), 4 days. (3). 7 days (4), 28 days. (five).

The same patterns are manifested in clay-gypsum mixtures (Tab. 2) where structures of noticeable strength appear in the presence of $Ca(OH)_2$ already in the first hours. As calcium hydroxide reacts with dehydrated kaolin, the maximum Pm values shift towards compositions with high lime concentrations (Fig. 2).

Table 2

Influence of $Ca(OH)_2$ on the structure formation of a clay-gypsum mixture Pm, kgf/cm² (W/T = 0.50)

Temperature firing, °C	Additive $Ca(OH)_2$, %	Measurement term													
		Min				Hour				day					
		1	5	15	30	1	2	4	6	1	2	4	7	14	28
550	0	0,01	0,08	0,09	0,10	0,15	0,17	0,48	0,65	20,2	35	38	33	35	31
	1	0,11	0,13	0,27	0,65	5,2	5,6	8,9	23	39	42	43	69	69	-
	5	0,10	0,14	0,14	0,22	0,48	2,1	5,1	6,6	45,3	84,4	85,23	90	90,3	152
	10	0,11	0,12	0,13	0,22	0,41	0,41	1,8	4,7	38,5	79,7	122	180	216	233
700	0	0,01	0	0	0	0,17	0,14	0,17	0,22	0,55	1,44	2,35	7	7	17,4
	10	0,12	0,17	0,21	0,22	0,27	0,31	0,33	0,38	12,2	36	64	187	217	222
1000	0	0,01	0	0	0	0,15	0,14	0,15	0,16	0,23	0,54	1,44	2,35	7	17,5
	10	0,11	0,12	0,13	0,21	0,22	0,28	0,28	0,29	0,67	1,8	4	16,1	-	95

In mixtures containing gypsum calcined at 1000°C, the formation of hydrosulfoaluminate was not observed for 28 days. The calcium hydroxide introduced into the system remains free in the hydration products (4,8; 2,0 A°, etc.), only slightly decreasing in quantity, as follows from the weight loss data (Tab. 3) in the region of 490-520°C from thermogravimetric curves.

It can be assumed that in these compositions part of the lime is associated with the active silica of the clay component of gypsum into colloidal calcium hydrosilicates.

As can be seen from the above data, gypsum fired at 700°C has the highest lime binding activity.

Calcium hydroxide added to HBV also affects the kinetics of hydration of its gypsum component. As a result of interaction with aqueous anhydrite, which is part of gypsum, fired at 550°C and above, a dihydrate is formed. For a composition with 550°C gypsum, the appearance of the dihydrate in the solid phase is unambiguously recorded already after 5 minutes from the beginning of hydration. In mixtures with gypsum 700°C, the induction period, during which anhydrite gradually dissolves in water, forming supersaturated solutions and precipitating into a solid phase, increases to several days.

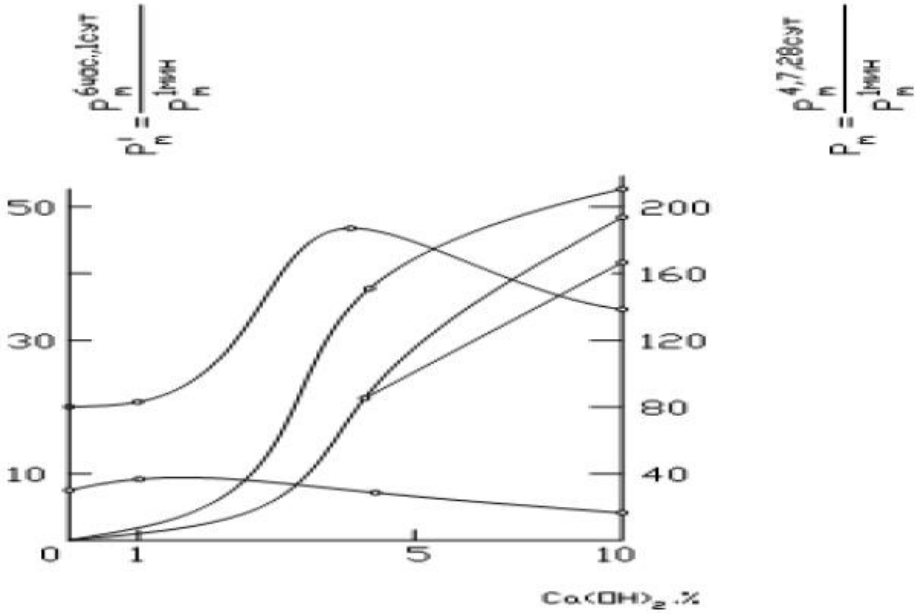
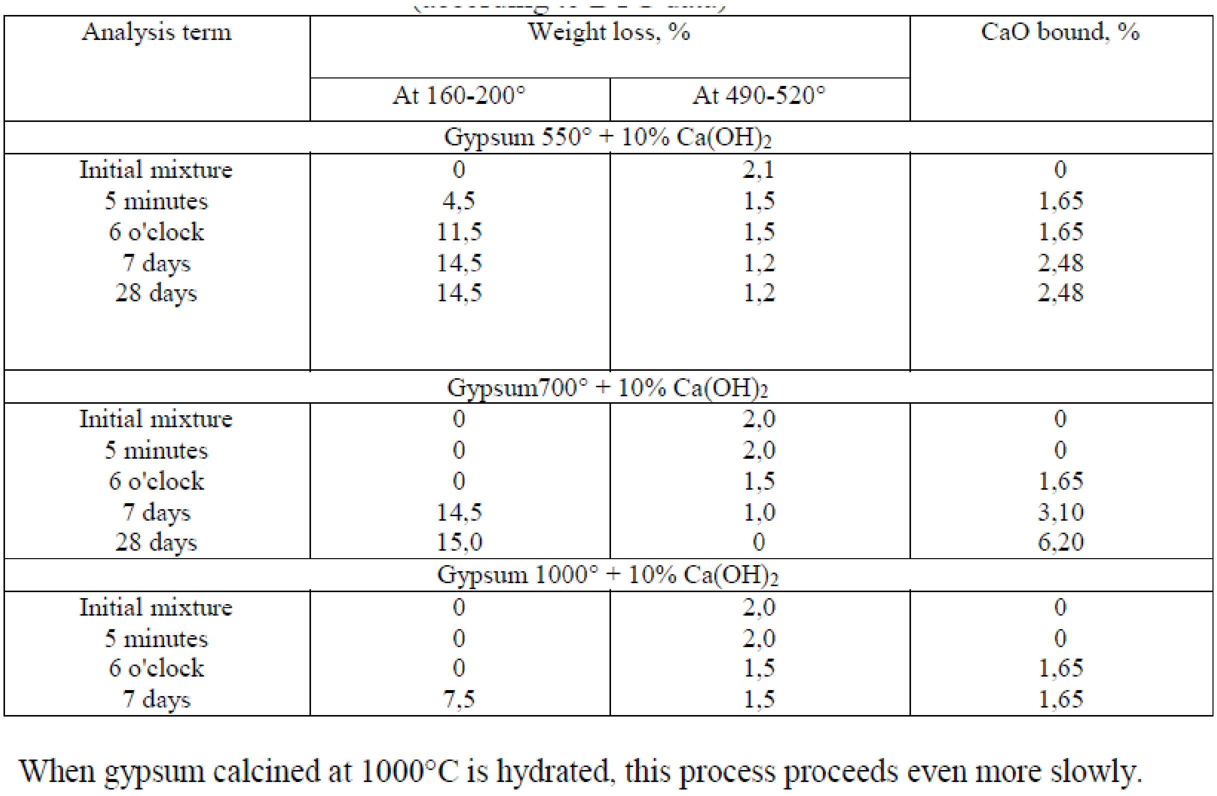


Fig. 2. Influence of the concentration of $Ca(OH)_2$ on the strength of the hardening structure of the clay-gypsum mixture fired at 550°C 1-6 hours, 2-1 days, 3-4 days, 4-7 days, 5-28 days

Table 3. Kinetics of hydration and binding of $Ca(OH)_2$ to gypsum calcined at different temperatures (according to DTG data)



Analysis term	Weight loss, %		CaO bound, %
	At 160-200°	At 490-520°	
Gypsum 550° + 10% $Ca(OH)_2$			
Initial mixture	0	2,1	0
5 minutes	4,5	1,5	1,65
6 o'clock	11,5	1,5	1,65
7 days	14,5	1,2	2,48
28 days	14,5	1,2	2,48
Gypsum700° + 10% $Ca(OH)_2$			
Initial mixture	0	2,0	0
5 minutes	0	2,0	0
6 o'clock	0	1,5	1,65
7 days	14,5	1,0	3,10
28 days	15,0	0	6,20
Gypsum 1000° + 10% $Ca(OH)_2$			
Initial mixture	0	2,0	0
5 minutes	0	2,0	0
6 o'clock	0	1,5	1,65
7 days	7,5	1,5	1,65

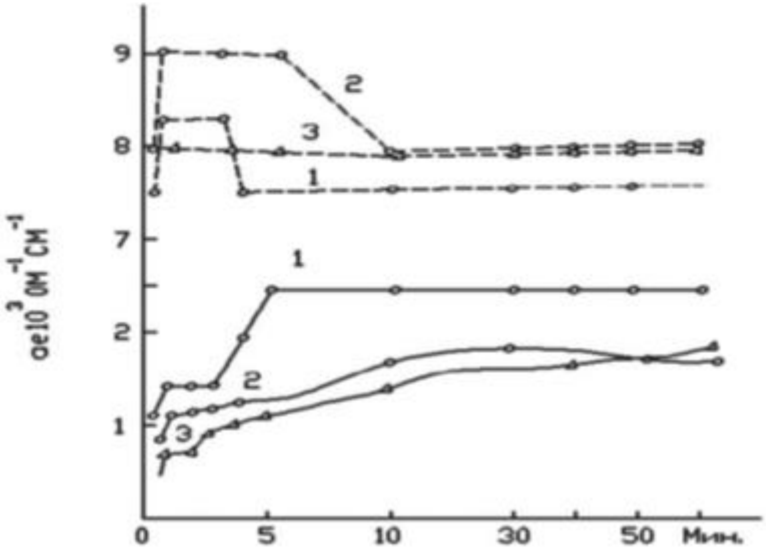
When gypsum calcined at 1000°C is hydrated, this process proceeds even more slowly.

When gypsum calcined at 1000°C is hydrated, this process proceeds even more slowly. The nature of the conductometric kinetic curves for HBB suspensions in the presence of lime indicates that, in this case, in contrast to low-temperature gypsum, calcium hydroxide intensifies the dissolution of anhydrite, accelerates the formation of solutions supersaturated with respect to dihydrate and the release of the latter into the solid phase. So, dashed curves 1, 2 in Fig. 3 for suspensions with $Ca(OH)_2$ rises steeply after 30 seconds, showing a rapid saturation of the solution with mobile ions Ca+2, S-24, and then after 3-6 minutes (for gypsum 550° and 700°C, respectively) fall sharply and a consequence of the precipitation of the hydration phase from the solution. In the absence of $Ca(OH)_2$, a supersaturated solution appears only after 3 and 10 minutes for gypsum 550° and 700°C, respectively, and during an hour low drops of the x-r curves associated with the release of dihydrate are not observed. Small plateau during 1-3 min. For gypsum 550°C and 1-5 min.

For gypsum 700°C in suspensions with $Ca(OH)_2$ is replaced by a horizontal course of the curve during the entire period (5-60 min) for suspensions of ganch fired at 550°C, and a gradual gentle rise of curves for suspensions of less active gypsum 700°C without lime. For gypsum 1000°C, even in the presence of $Ca(OH)_2$, supersaturated solutions are not formed during the first hour.

However, it should be noted that the specific contribution of the processes of hydration of the gypsum part of high-temperature gypsum to the strength of the resulting structures, even in the presence of lime, is significantly less than the processes associated with the chemical interaction of the clay component of gypsum with lime. A comparative analysis of the kinetic curves of Pm-r leads to a similar conclusion.

As shown by the results of physical and mechanical tests of high-temperature gypsum binders with the addition of $Ca(OH)_2$ (Tab. 4) under various storage conditions, it is the clay component that determines in this case the main properties of the cement stone.



While in air storage conditions gypsum at 550 ° and 700 °C, in contrast to gypsum binders based on hemihydrate, practically does not harden, the addition of 10 % $Ca(OH)_2$ contributes to the production of a cement stone with significant strength, increasing from 3 to 6 months three times. Under humid conditions of hardening, there is no drop in strength characteristic of low-temperature gypsum over time; on the contrary, it reaches higher values than in air, so that the moisture resistance coefficient K_{wlazh}/K_{vozd} in the presence of lime additives is higher than 1.

Similar results were obtained when testing artificial clay-gypsum and gypsum-loess (Tab. 5) compositions subjected to high-temperature firing.

Table 5.

Influence of firing temperature on the compressive strength of a mixture of 60 % gypsum + 40 % loess (cubes 3x3x3 cm) depending on the conditions of hardening, kgf/cm²

Firing temperature (holding 30 min.) °C	Test period, days				
	1	3	7	28	90
Air storage					
180	51	52	54	56	49
550*	-	4,2	4,2	2,8	2,8
700	-	3,5	9	2,6	2,8
1000	-	1,4	1,6	2,2	2,8
Wet storage					
180	12	14	17	18	14
550*	-	2,8	9,7	22,4	28
700	-	6,8	8,2	42	38
1000	-	1,12	1,12	21	28
Water resistance coefficient					
180	0,23	0,27	0,22	0,32	0,29
550*	-	0,66	0,23	8	10
700	-	1,8	0,9	16	13
1000	-	0,8	0,7	0,5	10

* Mixture fired at high temperature, tested after 3 days

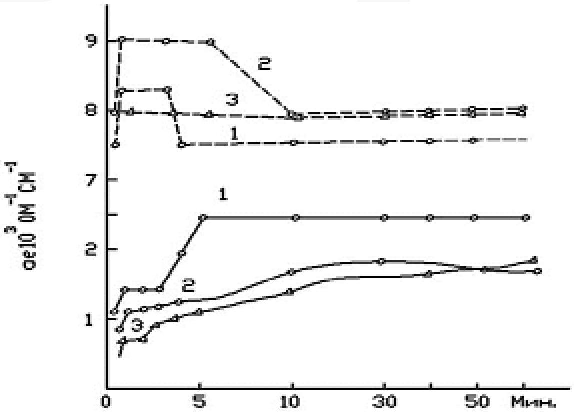
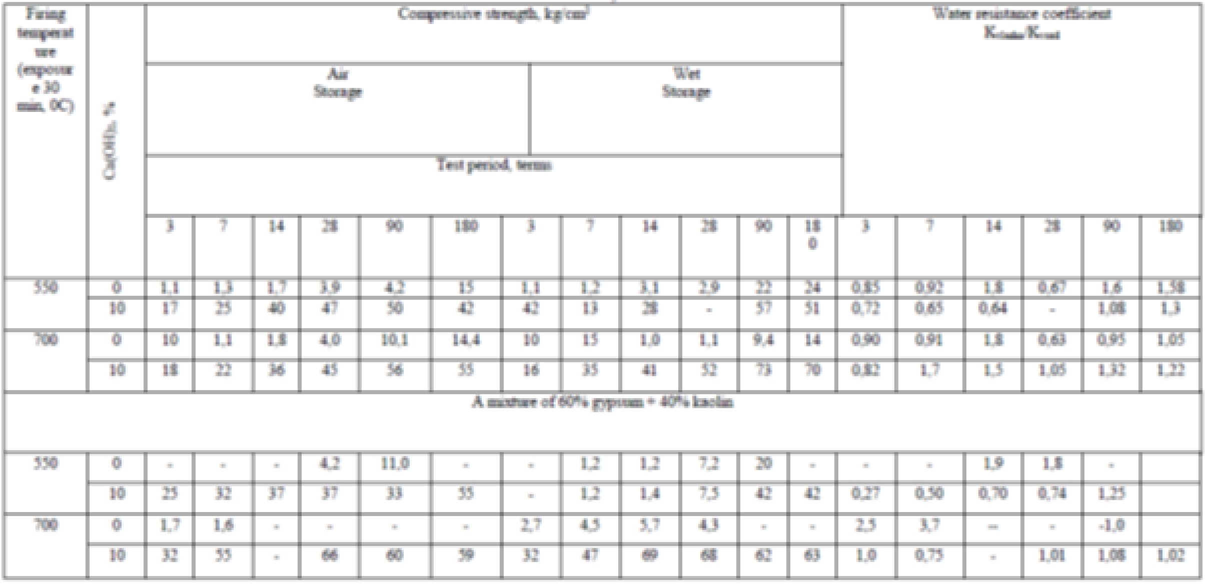


Fig. 3. Influence of $Ca(OH)_2$ on the kinetics of electrical conductivity of suspensions of high-temperature gypsum, fired at 550° (1), 700° (2), 1000° (3). Dotted line - with 10% $Ca(OH)_2$, solid lines - without lime

Table 4.

Influence of $Ca(OH)_2$ on the strength of high-temperature gypsum binder (sample cubes, 3x3x3 cm).



Firing temperature (exposure 30 min, 0C)	$Ca(OH)_2$, %	Compressive strength, kg/cm²												Water resistance coefficient [illegible]					
		Air Storage						Wet Storage											
		Test period, terms																	
		3	7	14	28	90	180	3	7	14	28	90	180	3	7	14	28	90	180
550	0	1,1	1,3	1,7	3,9	4,2	15	1,1	1,2	3,1	2,9	22	24	0,85	0,92	1,8	0,67	1,6	1,58
	10	17	25	40	47	50	42	42	13	28	-	57	51	0,72	0,65	0,64	-	1,08	1,3
700	0	10	1,1	1,8	4,0	10,1	14,4	10	15	1,0	1,1	9,4	14	0,90	0,91	1,8	0,63	0,95	1,05
	10	18	22	36	45	56	55	16	35	41	52	73	70	0,82	1,7	1,5	1,05	1,32	1,22
A mixture of 60% gypsum + 40% kaolin																			
550	0	-	-	-	4,2	11,0	-	-	1,2	1,2	7,2	20	-	-	-	1,9	1,8	-	
	10	25	32	37	37	33	55	-	1,2	1,4	7,5	42	42	0,27	0,50	0,70	0,74	1,25	
700	0	1,7	1,6	-	-	-	-	2,7	4,5	5,7	4,3	-	-	2,5	3,7	–	-	-1,0	
	10	32	55	-	66	60	59	32	47	69	68	62	63	1,0	0,75	-	1,01	1,08	1,02

CONCLUSION

Features of structure formation determine the ways of regulating the properties of various gypsum binders using additives

High-temperature gypsum binder of Khujakul marl, obtained by firing 550-700°C, natural gypsum, with the addition of $Ca(OH)_2$, acquires increased water resistance compared to conventional gypsum binders, while maintaining air resistance at the same time. This quality may be of interest in the practical use of large reserves of "low-grade" natural gypsum with a low gypsum concentration and an increased content of the clay part.

The introduction of calcium carbonate into gypsum prior to heat treatment makes it possible to increase the concentration of structure-forming minerals and obtain, as a result of firing at 800-900°C, a hydraulic binder with a sufficiently high strength in air and water hardening conditions (carbonate-gypsum binder).

Thus, the ways of rational use of natural gypsum are determined by its composition, for the production of high-temperature gypsum binder - rocks with a predominance of the clayey carbonate part.

Thus, a high-temperature gypsum binder obtained by firing 550-700°C of natural gypsum, with the addition of $Ca(OH)_2$, acquires increased water resistance compared to conventional gypsum binders, while maintaining air resistance at the same time. This quality may be of interest in the practical use of large reserves of "low-grade" natural gypsum with a low gypsum concentration and an increased content of the clay part.

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