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REGULATION OF THE PROPERTIES OF HYDRATION STRUCTURES IN CLAY GYPSUM COMPOSITIONS

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Abstract

The purpose of this study was to study the properties of various binders based on gypsum rocks of the Ustyurt deposit. The ways of regulating the properties of various gypsum binders using additives and rational use of natural gypsum for the production of a low-temperature binder with a gypsum type of hardening and a high-temperature gypsum binder for rocks with a predominance of the clay-carbonate part are determined.

The processes of thermal decomposition of gypsum in the temperature range of 100–1000 °C are considered and its modeling compositions, the phase composition of the products formed, the basic patterns of structure formation depending on the phase composition of the initial binder are established. Heat treatment of clay gypsum (100–1000 °C) allows you to change the nature of the structure-forming component, including the sulfate or clay part in the hydration process

Keywords: Hydration, structure formation, clay-gypsum, additive, strength, roasting, solution, heat treatment, alumina, gypsum binder, surfactants

Introduction:

Scientific and practical results have been achieved in the Republic in obtaining new local materials and directional changes in the properties of existing compositions.

Karakalpakstan is a republic of a country remote from industrialized regions. There is no production of cement and surfactants, and their transportation is economically impractical. At the same time, the territory of Karakalpakstan is rich in raw materials for

the production of local binders and mineral additives to Portland cement, in particular gypsum, limestone, etc (Segalova, 1963, Voljenskiy, 1971) In this regard, scientific work is developing the direction of obtaining gypsum-based binders of various nature and in-depth study of the processes of their hydration structure formation and their properties. The formation of hydration hardening structures, depending on the type, nature and composition of the binder, are present in

the additive system. This is largely due to the complex nature of the processes occurring in nonequilibrium multicomponent systems consisting of polymineral binders.

The processes of hydration of clinker and other minerals included in the composition of binders, as well as hydration structure formation (hydration structure formation) in these systems are interrelated (Mixeev, 1957; Ferronskoy, 2004).

Objects and methods of research

The objects of research in this work were gypsum minerals of the Ustyurt deposit (Republic of Karakalpakstan). Gypsum stones of the studied deposits of the Republic of Karakalpakstan belong to rocks of sedimentary origin, the content of calcium sulfate in them ranges from 60 to 98%. Meanwhile, the large reserves of clay gypsum explored on its territory remain unused for the time being due to the low concentration of gypsum in the rock (Turemuratov, 2019; Abilova, 2019).

Gypsum, which is a natural mixture of two-water gypsum with clay minerals, belongs to such binders. Of particular interest is for Karakalpakstan, where it uses imported gypsum materials. The relatively high solubility, well-defined crystal structure of hydrate phases, the formation of which is not complicated by hydrolysis, makes gypsum binders a convenient object of study.

Thermogravimetric research methods were performed on a Paulik-Paulik-Erdey system derivatograph. The method allows us to qualitatively and quantitatively determine the changes in the characteristic enthalpy, the heat content of substances.

Comprehensive laboratory studies included the study of structure formation in concentrated suspensions (pastes), the interaction of additives with the liquid phase and the determination of the phase composition of the resulting products using thermographic methods. The process of hydration of the sulfate and clay parts in the heat treatment of clay gypsum (100–1000 °C) allows you to change the nature of the structure-forming component.

Results and their discussions

Heat treatment of clay gypsum at a temperature (100–1000 °C) allows you to change the nature of the structure-forming compo-

nent, including the sulfate or clay part in the hydration process. This serves as a determining factor in the kinetics of formation and the properties of emerging structures. In accordance with the peculiarities of the chemical nature of the structure-forming component, the regulation of these processes should be carried out in various ways (Asamatdinov, 1977; Abilova, 2018).

For low-temperature gypsum binders, the hardening of which is based on the interaction with water of the semi-hydrate, the determining factor limiting the maximum strength that can be provided by the nominal composition of the binder is the stresses caused by the rapid release of hydrate in volume at high supersaturation. The reduction of the latter, therefore, must be considered as the main task in regulating hydration structure formation in this case. In practice, it can be solved by influencing the processes of dissolution of the semihydrate in the direction of slowing down.

In our experiments, such minerals as calcium hydroxide were used as additives affecting the dissolution of semihydrate, which were introduced in amounts from 0.5 to 10% into dry binders or with mixing water.

Measurements of the kinetics of structure formation in concentrated suspensions with the addition of $\text{Ca}(\text{OH})_2$ (1–20%) showed that its presence in the system begins to manifest itself after 24 hours (Table 1). At the same time, the strength increases as the content of $\text{Ca}(\text{OH})_2$ in the mixture increases, passing through the maximum at higher concentrations than The activity of the clay part of gypsum is higher, which is determined by the temperature of its firing (Picture 1). For gypsum-based compositions (550 and 700 °C) containing a clay component in the most active form, maximum strength is achieved in mixtures with 5–10% $\text{Ca}(\text{OH})_2$.

Conductometric studies and analyses of the liquid phase of semi-hydrate suspensions or low-temperature gypsum binders in the presence of $\text{Ca}(\text{OH})_2$ indicate a slowdown in the release of dihydrate into the solid phase due to lower supersaturation, and thermogravimetric analysis showed a decrease in the degree of hydration of the binder in the presence of $\text{Ca}(\text{OH})_2$. In correlation with this, there is also a sharp inhibition of structure

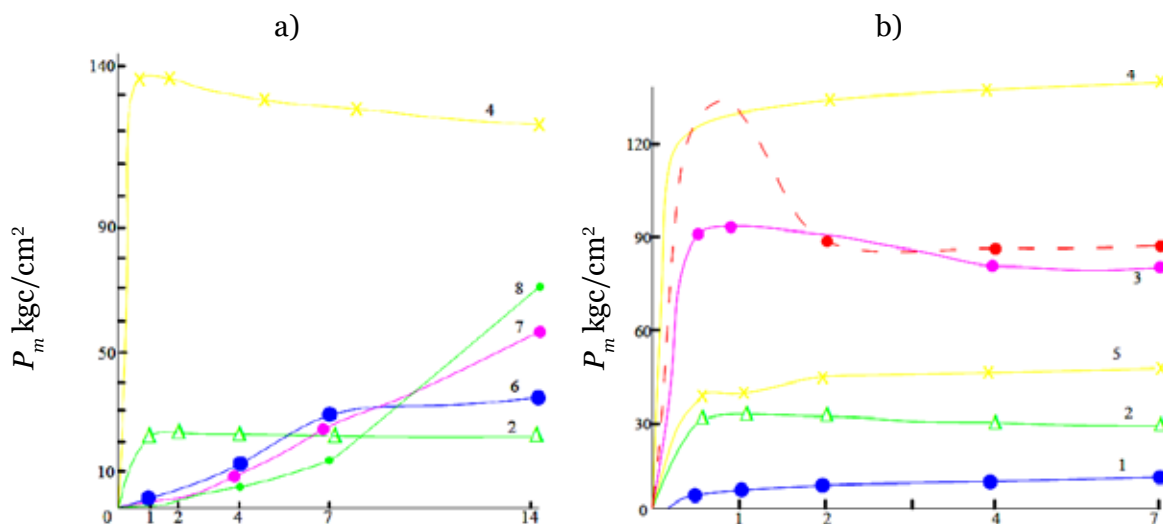
formation with this additive. Over time, the role of lime in the processes of gypsum structure formation changes qualitatively. If at the initial moment the additive serves as a retarder of the hydration of the gypsum part,

then over time it begins to exhibit the properties of the chemically active component in relation to the clay reagent, contributing to the formation of additional hydration structures due to interaction with it.

Table 1. Effect of $\text{Ca}(\text{OH})_2$ on the kinetics of structure formation of gypsum fired at different temperatures, $R_m \text{ kgf/cm}^2$ ($W/H = 0.50$)

Firing temperature, °C	Supplement $\text{Ca}(\text{OH})_2, \text{ n}\%$	The timing of the measurement													
		Min				Hour				day					
		1	5	15	30	1	2	4	6	1	2	4	7	14	28
500	0	0	0	0	0.11	0.17	0.19	0.27	0.30	0.63	0.69	2.9	5.8	6.2	14
	1	0	0	0	0.14	0.16	0.19	0.21	0.28	3.9	15.6	17.1	23.3	41	85
	5	0	0	0	0.13	0.15	0.16	0.27	0.36	7.6	35	87	189	232	239
	10	0	0	0	0.11	0.12	0.14	0.31	0.35	8.5	31	90	183	198	214
	0	0	0	0	0.06	0.13	0.21	0.23	0.25	0.49	0.55	2.8	4.6	12	19
700	1	0	0	0	0.06	0.11	0.14	0.17	0.64	1.3	11.5	14.1	18.5	18.9	-
	5	0	0	0	0.09	0.16	0.27	0.39	0.97	2.9	48	125	154	191	209
	10	0	0	0	0.07	0.12	0.17	0.19	0.32	7.2	23	112	120	181	221
	20	0	0	0	0.08	0.16	0.19	0.15	0.47	8.7	34.9	153	174	189	191
	0	0	0	0	0	0.10	0.22	0.29	0.38	0.51	0.52	0.61	2.6	3.8	14
1000	1	0	0	0	0	0.09	0.11	0.2	0.23	3.1	8.2	17	27	-	-
	5	0	0	0	0	0.10	0.11	0.11	0.13	2.2	11.1	20	29	75	152
	10	0	0	0	0	0.09	0.11	0.11	0.12	2.3	5.3	14.1	29	80	167
	20	0	0	0	0	0.08	0.12	0.12	0.20	0.21	0.20	3.2	6.1	15.3	153

Picture 1. Kinetics of structure formation in concentrated gypsum suspensions depending on the firing temperature: 1–130 °C, 2–150 °C, 3–160 °C, 4–190 °C, 5–250 °C, 6–600 °C, 7–800 °C, 8–1000 °C



In compositions hardening on the basis of insoluble anhydrite, on the contrary, unlike semi-hydrate, stress does not play a significant role, achieving maximum strength

is limited by low supersaturation and, accordingly, very slow hydrate formation. Therefore, an increase in the solubility of the structure-forming phase is of the greatest

importance for such systems (Ivanov, 2008; Abilova 2019). The strength of high-temperature gypsum binders depends mainly on the number and composition of hydraulically active phases. For the Ustyurt gypsum we are considering, it is limited by the low content of calcium compounds in the sulfate part.

With an increase in the firing temperature of gypsum to 1000 °C the optimal dosage of Ca(OH)₂ in the initial period shifts to the area

of lower concentrations (1–5%), increasing to 10% over time. This is in accordance with a sharp decrease in the activity of alumina and its transition to inactive β and α modifications during heat treatment, as well as with alumina-containing active mineral additives.

The same patterns are manifested in clay-gypsum mixtures (Table.2) where structures of noticeable strength arise in the presence of Ca(OH)₂ already in the first hours.

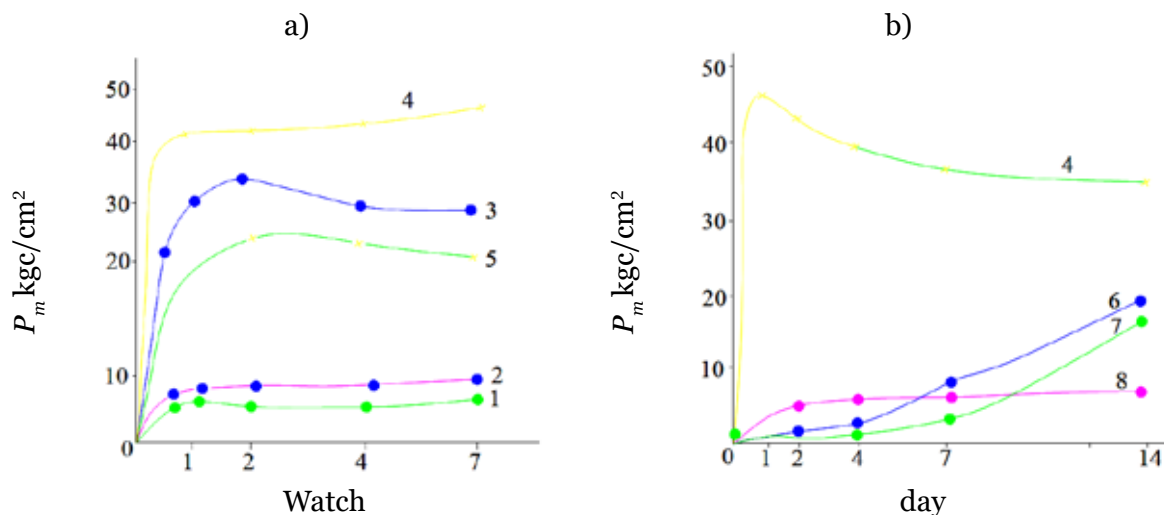
Table 2. The effect of Ca(OH)₂ on the structure formation of clay-gypsum mixture P_m , kgs/sm² (W/H = 0.50)

Firing temperature, °C	Supplement Ca(OH) ₂	Timing measurement													
		min				hour				day					
		1	5	15	30	1	2	4	6	1	2	4	7	14	28
550	0	0.01	0.09	0.10	0.11	0.17	0.18	0.45	0.61	20.9	36.2	39	34	36	32
	1	0.10	0.12	0.25	0.61	5.1	5.5	8.7	22	38	41	42	68	68	–
	5	0.09	0.13	0.15	0.24	0.51	2.3	5.2	6.8	45.5	84.6	85.	90.5	91	151
	10	0.12	0.14	0.16	0.24	0.45	0.46	1.9	4.8	38.9	79.8	123	182	218	236
700	0	0.01	0.01	0	0.06	0.19	0.15	0.18	0.21	0.53	1.42	2.25	7.4	7.1	17.2
	10	0.11	0.17	0.23	0.21	0.26	0.33	0.35	0.39	12.3	36.4	65	189	218	223
1000	0	0.03	0.02	0	0	0.16	0.15	0.16	0.17	0.24	0.56	1.6	2.32	7.1	17.8
	10	0.10	0.14	0.15	0.22	0.23	0.25	0.27	0.28	0.65	1.9	4.2	16.6	–	96

As can be seen from (picture. 2), the course of the kinetic curves $P_m - \tau$ changes significantly: as the semihydrate disappears in the mixture, instead of a steep rise, indicating the avalanche nature of the process at the initial stages, as a result of the instantaneous occurrence of high supersaturation in suspensions

β-CaSO₄ · 0.5H₂O, a slow, a gradual rise in the late stages of hydration, indicating a change in the nature of the structure-forming component. In firing products above 450 °C, this component is soluble anhydrite, which does not give solutions supersaturated in dihydrate at the first stages of interaction with.

Picture 2. Kinetics of structure formation in concentrated suspensions of clay-gypsum mixture depending on the firing temperature: 1–130 °C, 2–150 °C, 3–160 °C, 4–190 °C, 5–250 °C, 6–600 °C, 7–800 °C, 8–1000 °C

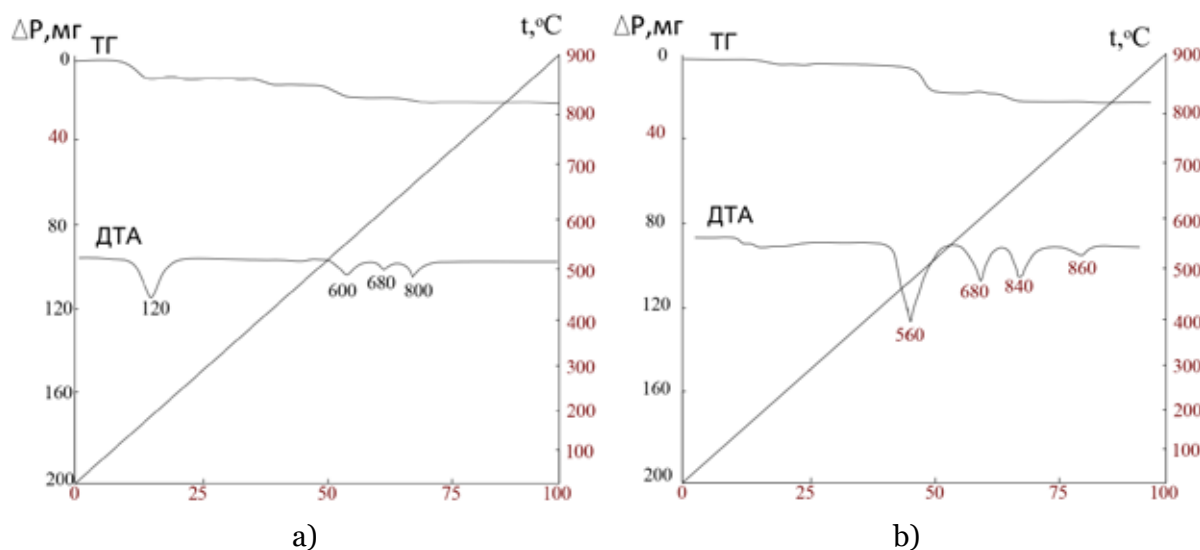


With an increase in the temperature of gypsum heat treatment from 500 to 600 °C and the transition to the lime-pozzolan type of hardening, when the chemical activity of the clay component increases as a result of dehydration, the role of calcium hydroxide in creating strength increases.

Measurements of the kinetics of structure formation in concentrated suspensions with the addition of $\text{Ca}(\text{OH})_2$ (1–20%) show that its

presence in the system begins to manifest itself after 24 hours. At the same time, the strength increases as the $\text{Ca}(\text{OH})_2$ content in the mixture increases, passing through the maximum at the higher concentrations, the higher the activity of the clay part of the ganch, which is determined by its firing temperature. For compositions based on ganch 550 and 700 °C, maximum strength is achieved in mixtures with 5–10% $\text{Ca}(\text{OH})_2$ (Picture 3).

Picture 3. Diffractograms and derivatograms of initial samples of natural gypsum and clay-gypsum mixtures



Calcium hydroxide added to gypsum binders also affects the kinetics of hydration of its gypsum component. As a result of the interaction with water of anhydrite, which is part of gypsum, burned at 550 °C and above, a dihydrate is formed. For a composition with gypsum 550 °C, the appearance of dihydrate in the solid phase is unambiguously fixed 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 releasing a solid phase, increases to several days. When hydrating burnt gypsum at 1000 °C, this process proceeds even more slowly.

The role of calcium hydroxide introduced into high-temperature gypsum binders (550–700 °C) is not limited to its participation in the formation of new hydrate phases, it also affects the kinetics of hydration of anhydrite.

Conclusions:

Thus, gypsum binders obtained by firing at a temperature of 550–700 °C from natural gypsum, with the addition of $\text{Ca}(\text{OH})_2$, they acquire properties of increased moisture 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 concentration of gypsum and an increased content of clay.

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