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LOW-BURNED GYPSUM BINDERS BASED ON GYPSUM MINERALS OF USTURTA DEPOSITS

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

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

SADYKOVA A. M.
Karakalpak State University named after Berdakh, Nukus

MINAZHOV A. N.
Karakalpak State University named after Berdakh, Nukus

ZHUGINISOV B. B.
Karakalpak State University named after Berdakh, Nukus

ABSTRACT:

The article presents the results of a study of the effect of heat treatment on the physicochemical and technological properties of gypsum minerals from the Ustyurt deposits. The results of diffraction patterns, differential thermal analyzes of gypsum minerals are presented. The possibility of obtaining low-calcined gypsum binders based on gypsum minerals from the Ustyurt deposits is shown, their physicochemical and physicomechanical properties are studied.

KEYWORDS: Gypsum binders, dihydrate gypsum, semi-aqueous gypsum, soluble gypsum, insoluble gypsum, anhydrite, Ustyurt.

INTRODUCTION:

At the present stage of economic and social development of the Republic of Uzbekistan, the issue of the integrated use of local raw materials, the development of environmentally friendly, energy and resource-saving highly efficient technologies for the production of composite and building materials is gaining great importance. The creation of building materials with optimal mechanical properties based on mineral binders is also one of the important tasks of modern applied colloidal chemistry and its section - physicochemical mechanics of dispersed systems. There is every reason to assert that the physicochemistry of dispersed systems and surface phenomena is the scientific basis of technological processes occurring in heterogeneous systems, including the processes of creating a variety of binders [1-2].

It is known that gypsum binders are the most effective in technical and economic terms, especially in terms of the specific consumption of raw materials, fuel, electricity and labor per unit of product. The reserves of the original natural raw materials, as well as by-product gypsum-containing materials for the production of gypsum binders, are also unlimited. For the production of gypsum and anhydrite binders, natural dihydrate gypsum, anhydride, clay gypsum, as well as gypsum-containing waste from the chemical industry - phosphogypsum, borogypsum, etc. are used as raw materials.

Natural dihydrate gypsum is a rock of sedimentary origin, composed mainly of large or small crystals of calcium sulfate $CaSO_4 \cdot 2H_2O$. By the appearance and structure of the rock, gypsum, transparent crystalline gypsum, gypsum spar, fine-fiber gypsum with a silky sheen (selenite) and granular gypsum are distinguished. The purest variety of granular gypsum, resembling marble in appearance, is sometimes called alabaster. The average density of gypsum stone depends on the amount and type of impurities and is 2,2 – 2,4 g/cm^3.

Natural anhydride is a rock of sedimentary origin, consisting mainly of a mineral - anhydrous calcium sulfate $CaSO_4$. Anhydride deposits are usually underlain by a layer of gypsum dihydrate. Anhydride is a rock that is stronger and more dense than gypsum dihydrate. Its true density reaches 2,9-3,1 g/cm^3, pure white anhydride, but depending on impurities, it, like gypsum, has different shades. In nature, anhydride is less common than gypsum dihydrate [4].

MATERIAL AND METHODS:

Gypsum stones of the studied deposits of Ustyurt belong to the rock of sedimentary origin, the content of dihydrate calcium sulfate in them varies from 60 to 98%. For the study, samples were taken from two deposits: Urge (sample no. 1) and Raushan (sample no. 2) of Ustyurt, and their complete silicate analysis was carried out.

The work used X-ray phase, structural-mechanical, DTA thermographic, chemical and other research methods. X-ray diffraction patterns were taken on a DRON-05 diffractometer. Cu_2 was studied, the voltage and current of the X-ray tube were 30 kV and 12 mA, respectively. The shooting speed is 2 deg/min. DTA was carried out on the Q-Derivatograph system F. Paulik, N. Paulik and L. Erdeya.

RESULTS AND DISCUSSIONS:

The results of complete silicate analyzes of samples of gypsum minerals from the Ustyurt deposits are presented in Table 1.

Table 1. Chemical composition of gypsum minerals from Ustyurt deposits

Oxides		Field	
		Urge	Raushan
Mass content in % on air dry matter	SiO_2	1,37	4,85
	TiO_2	<0,01	0,035
	Al_2O_3	<0,10	0,53
	Fe_2O_3	0,17	0,31
	MgO	0,65	0,70
	MnO	<0,01	<0,01
	CaO	31,66	31,40
	Na_2O	0,07	0,18
	K_2O	0,03	0,36
	P_2O_5	0,053	0,048
	$SO_{3,\text{gen.}}$	44,7	44,90
	$SO_{3,\text{sukfate}}$	44,52	41,52
	L.O.I.	21,86	20,06
	H_2O,320 °C	20,1	16,89
	CO_2	1,76	3,14

As can be seen from its data, gypsum mineral - sample No. 1 is a mineral selenite, which is crystalline, transparent, practically free of impurities, the content of CaO, SO_3, H_2O in it is close to theoretical, 98% consists of calcium sulfate dihydrate. This gypsum mineral belongs to the highest grade gypsum rock; on its basis, it is possible to obtain a gypsum binder and products with increased physical and mechanical properties for the porcelain-faience, ceramic and medical industries.

Sample No. 2 contains a large amount of clay impurities, mainly in the form of silica material, is characterized by a low content of CaO, SO_3. The total amount of dihydrate calcium sulfate salt ($CaSO_4$ H_2O) in it is -87%. This mineral belongs to the second grade gypsum rock, on its basis it is possible to obtain gypsum and building materials with increased

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physical and mechanical properties for the construction industry [7].

Gypsum binders are air binders, which, according to the conditions of heat treatment, as well as the speed of setting and hardening, are divided into two groups: low-fired and high-fired. Low-calcined binders quickly set and harden, they consist mainly of semi-aqueous gypsum obtained by heat treatment of gypsum stone at a temperature of 383-453 K; these include construction (alabaster), molding, high-strength (technical) and medical gypsum, as well as gypsum binders made of gypsum-containing materials.

High-calcined binders slowly set and harden, they consist mainly of anhydrous calcium sulfate, obtained by roasting at a temperature of 873-1173 K; these include anhydrite binder (anhydrite cement), high-fired gypsum (estrich-gypsum) and finishing gypsum cement [5-6].

Ustyurt selenite is a mineral that has no analogue in Uzbekistan. In terms of composition, it is close to the theoretical one, which can be used to obtain binders with high physical and mechanical properties [8].

On the basis of the Ustyurt gypsum minerals, we obtained a low-calcined gypsum binder - stucco gypsum by dehydration of dihydrate gypsum to β-hemihydrate at temperatures of 150-160 °C. For this, a weighed portion of the dihydrate in an open dish was placed in a thermostated drying oven, stirred at each definite time and kept until a constant mass corresponding to the β-hemihydrate was obtained. In this case, the dehydration reaction of gypsum dihydrate $CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 0{,}5H_2O + 1{,}5H_2O$ proceeds by absorbing heat in 588 J/g of hemihydrate, 19,3 kJ/mol of water or 85,27 kJ/mol of steam.

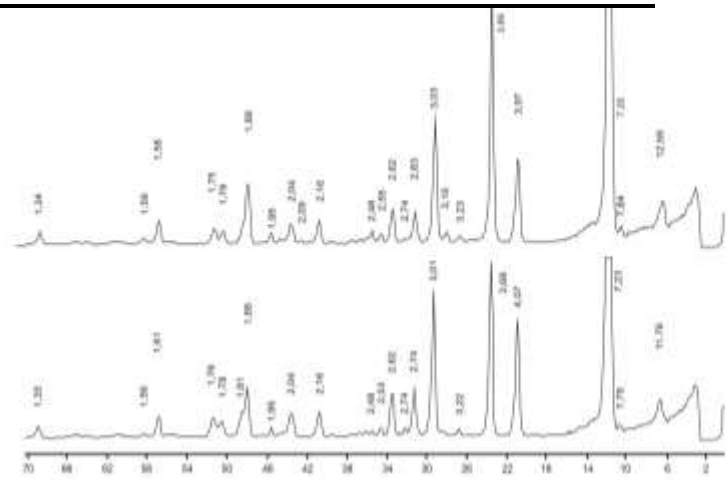

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Fig. 1. Diffraction patterns of gypsum minerals from deposits: 1-Urge; 2-Raushan;

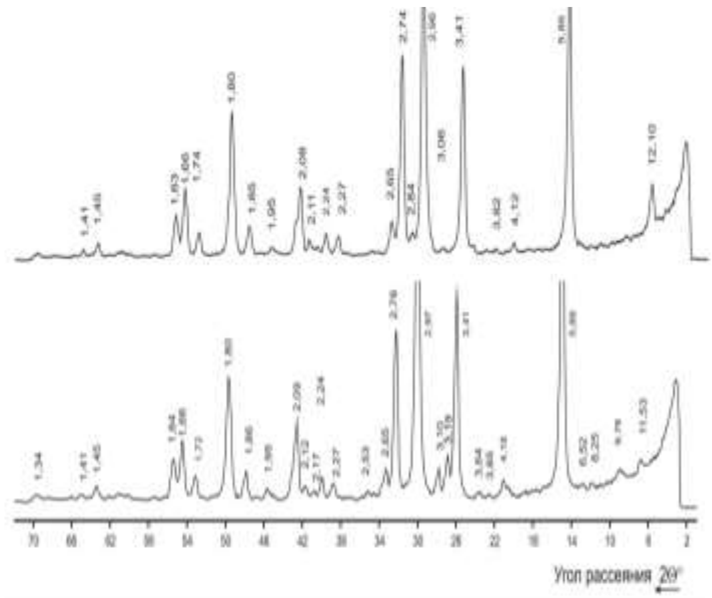

Fig. 2. Diffraction patterns of calcium sulfate modifications obtained by heat treatment at 160 °C (0,5 hour): 1-Urge; 2-Raushan;

Dehydration of the studied gypsum dihydrate to hemihydrate is accompanied by complete rearrangement of the crystal lattice. X-ray phase analysis shows reflexes: 5,85; 3,1; 2,96; 2,74; 2,27; 2,08; 1,85; 1,80; 1,74; 1,66 Å, which is typical for the product of dehydration of gypsum dihydrate β-hemihydrate $CaSO_4 \cdot 0{,}5H_2O$ (Fig. 2) [3].

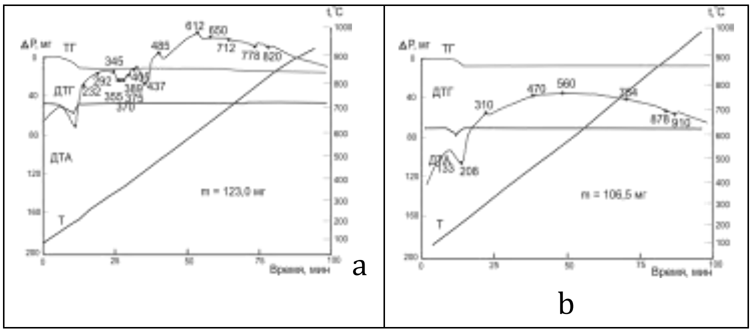

Fig. 3. Differential thermal analysis of gypsum stone of Ustryuta, deposits:
a - Urge, b - Raushan.

At temperatures above 220 °C, α-dehydrated hemihydrate transforms into α-soluble anhydrite, and at 320° -360 °C, β-dehydrated hemihydrate transforms into β-soluble anhydrite. Soluble anhydrite III $CaSO_4$ was investigated by X-ray, spectroscopic, thermal analysis, electron microscopic analysis; its porous structure was studied by mercury porosimetry, and the specific surface area of anhydrite was established.

The water demand of soluble anhydrites is 25-30 % higher than that of hemihydrates; their dispersions set faster and their strength is lower. α - and β - soluble anhydrites have identical X-ray patterns and very close refractive indices. The increased activity of soluble anhydrites is due to their greater dispersion.

The physicochemical and physicomechanical properties of gypsum binders obtained on the basis of gypsum minerals from the Ustyurt deposit have been studied. The true density of the hemihydrate ranges from 2,62-2,66 g/cm^3, its solubility is 8,07 g/l, in terms of $CaSO_4$. The specific heat of the β-hemihydrate corresponds to 0,84 kJd/(kg °C). The hemihydrate consists of the smallest aggregates of poorly expressed crystals. Indicators of its light refraction: Ng = 1,557 and Np = 1,551.

Calculation of the specific surface area Ssp. according to the data of sorption-desorption isotherms of water vapors showed that it changes extremely depending on the temperature of heat treatment - sharply increasing (60-80 times) during dehydration of gypsum dihydrate to hemihydrate and soluble anhydrite, and increasing only 4 times during dehydration to insoluble anhydrite.

$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 0{,}5H_2O \rightarrow CaSO_4$, sol. at 300 °C $\rightarrow CaSO_4$, at 700 °C

$S_{spec.}$, m^2/g: 3,5 250 180 13,6

Gypsum binders - semi-aqueous calcium sulfate, soluble and insoluble anhydrites, in the presence of water under normal conditions are converted into dihydrate calcium sulfate. In practical terms, the hydration, setting and hardening of these binders is influenced by many factors, such as the water-gypsum ratio (W/G), microfillers, temperature and humidity conditions, etc. (Table 2).

Table 2. Influence of the water-gypsum ratio (W/G) on the plastic strength of gypsum binders based on gypsum minerals from Ustyurt, Pm, kgf/cm^2

Field	W/G	Measurement time, min.					
		1	5	15	30	60	120
Urge (sample No. 1)	0,50	0,30	4,1	190	193	188	197
Raushan (sample No. 2)	0,50	1,18	14,4	118	128	140	142
Urge (sample No. 1)	0,60	0	0,90	91,7	137	122	125
Raushan (sample No. 2)	0,60	0,10	20,4	78,8	76,9	79,4	75,1

The properties of gypsum binders depend on the type of raw material, the method and mode of processing parameters. When natural gypsum is heated with steam under pressure up to 2-3 atm, followed by drying at a temperature of 160-180 °C, semi-aqueous gypsum of the α-modification is obtained. In this case, larger crystals are formed, which determine a lower water demand for gypsum (40-45 % of water), which makes it possible to obtain a gypsum stone with high density and strength. Such gypsum began to be called high-strength, its strength can reach 150-400 kg/cm^2. However, this type of binder has not found wide application due to its insufficient plasticity and water resistance, which necessitates the introduction of plasticizing additives. The introduction of plasticizing additives and fillers into the binder can give it the missing properties and obtain high-quality materials based on it [8].

The study of the physicochemical and mechanical properties, as well as the grade of gypsum binders based on gypsum minerals of the Ustyurt plateau, was carried out in accordance with GOST 23789-04. The test results are shown in Table 3.

Table 3. Physicochemical and mechanical properties of gypsum binders based on gypsum minerals from the Ustyurt deposits

№	Indicator name	Gypsum binder based on sample No. 1 of the Urge deposit	Gypsum binder based on sample No. 2 from the Raushan deposit
1	Fineness of grinding, sieve residue 0.2, %	2	13
2	Normal density W/G, %	52	58
3	Setting time start, min. end, min.	5 14	6 17
4	Compressive strength after 2 hours, kgf/cm^2	115	64
5	Tensile strength. bending, kgf/cm^2	50	39
6	Binder grade	G-10	G-6
7	The content of metal - impurities, mg	2	2
8	Volumetric expansion, %	0,2	0,4
9	Impurities insoluble in hydrochloric acid, %	0,5	30

Analysis of the data in Table 3 shows that on the basis of sample No. 1 (Urge deposit), gypsum binder G-10 BSh was obtained, i.e. gypsum binder of thin floor, grade G-10, normally hardening, and on the basis of sample No. 2 (Raushan deposit) gypsum binder G - 6 BP, i.e. gypsum binder brand G - 6, normally hardening.

CONCLUSIONS:

Laboratory studies confirm the possibility of using gypsum stone corresponding to the composition of sample No. 1 (Urge deposit) to obtain a gypsum binder with increased physical and mechanical properties by steaming, and gypsum stone corresponding to the composition of sample No. 2 (Raushan deposit) - a gypsum binder by boiling in gypsum boilers.

The study of the physicochemical and physicomechanical properties of gypsum binders obtained on the basis of gypsum minerals of minerals from the Ustyurt deposits shows the possibility of their use for the production of low-calcined gypsum binders - stucco, high-strength gypsum, estrich-gypsum and anhydrite cement.

REFERENCES:

1) Volzhensky A.V. Mineral binders. M., Stroyizdat, 1986.- 464 p.
2) Butt Yu.M., Sychev M.M., Timashev V.V. Chemical technology of binders. M., Higher School, 1980. - 472 p.
3) Mikheev V.I. Radiometric determinant of minerals // State. scientific and technical ed. lit. On geology and protection of mineral resources. – M. 1957. – P. 527.
4) Directory. Gypsum materials and products (production and use) / ed. prof., dr. tech. Sciences A.V. Ferronskaya. - M.: Publishing house AVS, 2004.- 485 p.
5) Turemuratov Sh.N. “Mineral resources of Karakalpakstan for the production of binders and building materials // Materials of the republican scientific and practical conference.” Physiologically active compounds based on plant resources and the technology of inorganic substances", Nukus, 2008. - P. 3-9.
6) Asamatdinov O., Turemuratov Sh.N. Regulation of gypsum properties by

additives // Uzbek chemical journal, 2006, No. 3, - P. 15-19.

7) Abilova A.Zh., Turemuratov Sh.N., Khamraev S.S. Chemical and physicochemical characteristics of gypsum minerals of the Ustyurt deposit // Bulletin of the journal NUUz. - 2014. -№1. - P. 51-56.
8) Abilova A.J., Turemuratov Sh.N., Uralbaeva G.B. Gypsum binders based on Karakalpakstan field // Austrian Journal of Technical and Natural Science. No. 3-4, 2018, - P. 38-42.