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IMPROVEMENT OF PHYSICAL AND MECHANICAL CHARACTERISTICS OF CLAY GYPSUM OF KHOJAKUL DEPOSIT OF KARAKALPAKSTAN MODIFIED WITH PHOSPHOGYPSUM

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ABSTRACT

The chemical and mineralogical properties of clay gypsum of the Khojakul deposit of Karakalpakstan, phosphogypsum of Almalyk chemical enterprise for the production of mineral fertilizers “Almalyk Maxam” Ltd., and slag waste of Almalyk mining and metallurgical combine have been investigated. The physical and mechanical characteristics of gypsum binder from alumina gypsum and developed compositions with modified phosphogypsum in different proportions have been determined. The positive influence on the increase of strength characteristics of binder compositions based on alumina gypsum containing modified phosphogypsum has been shown.

Keywords: clay gypsum, phosphogypsum, slag, binder, strength, waste, modifier, water-soluble, ion, dehydration, calcium sulfate, environment, petrography, crystal.

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INTRODUCTION

Gypsum binders today acquire increased demand due to their low energy intensity of production, uncomplicated production technology, and operation in the process of construction works. However, increasing rates and volumes of exploitation of gypsum binders naturally observed a decrease in their conditioned natural reserves [1, 2]. It is known that the quality of raw materials determines the main construction and technical properties of the final product. This, in turn, puts before the researchers an urgent task to expand the prospective raw material base of silicate building materials by processing substandard raw materials and utilizing wastes of various productions. The solution to this problem will contribute to the expansion of the raw material base of silicate materials on the one hand, as well as to the preservation and restoration of natural ecosystems, stabilization, and improvement of the environment [3-5]. Involvement in the production of “by-products” and wastes of industrial production will allow for rational use of natural mineral resources, increase the volume of production with lower production costs, and save energy resources [6-10]. In this regard, clay gypsum from the Khozhakul deposit of Karakalpakstan and phosphogypsum wastes from the production of phosphate fertilizers are of particular importance [11].

According to experts' calculations, the Almalyk Ammophos and Kokonbiokimyo enterprises in Uzbekistan annually collect more than 200 thousand tons of phosphogypsum, and tens of millions of tons of waste have accumulated in the dumps since the beginning of the enterprises' activity. It should be noted that the waste stored in the dumps pollutes the environment and groundwater in the region. On this basis, the issue of the production of gypsum materials from clay gypsum and modified by metallurgical slag, phosphogypsum, is considered very relevant [12-20]. From the published literature data, it is known that in the developed countries of Western Europe, PRC, and Japan, the use of technogenic raw materials, phosphogypsum, is becoming more and more significant; the processing of waste into useful products reaches maximum values. Numerous works of leading researchers of the world, such as P.P. Budnikov, P.F. Gordoshevsky, I.V. Kravchenko, K. Murakami, T. Yamaguchi, T.A. Atakuzieva, and N.A. Sirazhiddinov is devoted to the issue of phosphogypsum utilization [21-27].

In this regard, the aim and objective of the scientific work is to increase the strength of gypsum materials based on clay gypsum with the addition of modified phosphogypsum.

MATERIALS AND METHODS

Clay gypsum is a common sedimentary rock of chemical genesis and is a mechanical or mechanochemical mixture of gypsum, clay minerals, and some sand. As a result of the thermal treatment of clay, gypsum is obtained as a binder in many ways similar in properties to the binder based on semi-aqueous gypsum and, in particular, having a short setting time, a significant increase in strength when drying the material, and a low softening coefficient. Average density in the air-dry state of lumpy clay gypsum (1.4 - 1.6) t/m³ and loose - 1 t/m³. True density (2.3 - 2.51) t/m³ and bulk density (0.9 - 1.0) t/m³.

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The chemical composition and physical properties of clay gypsum are in Table 1.

It is known that in the process of production of phosphate fertilizers from natural phosphorite or apatite ores, the technology provides for its decomposition by sulfuric acid to obtain phosphoric acid.

This process produces a large amount of waste consisting of $CaSO_4$-$2H_2O$, which is bi-aqueous gypsum with impurities of sulphuric and phosphoric acid, as well as silica and other substances, and is identified as phosphogypsum. This waste is pumped into large dumps and stored in the open air. Phosphogypsum has a friable, finely divided structure. Even though the technological process provides for neutralization with calcium hydroxide, water-soluble phosphorus and fluorine ions remain in the end.

Table-1. Material compositions of the materials used.

Sample names	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	R_2O	SO_3	P_2O_5	SPT	amount
Clay gypsum	37.02	5.19	2.61	16.16	2.40	1.10	18.22	-	16.43	99.13
Phosphogypsum	10.33	0.52	0.13	33.34	0.44	0.08	45.41	1.45	7.74	99.44
Slag from AGMK	34.31	6.85	51.55	3.04	1.8	1.3	0.01	-	-	98.86

Chemical analysis of raw materials and experimental samples was carried out according to standard silicate-analytical methods, conditioned by GOST 4013-2019, as well as the accelerated method.

X-ray diffraction study of crystalline phases was carried out using a modern powder diffractometer LABX XRD-6100 (Shimadzu, Japan), controlled by a computer, in the range of angles 2θ = 10-80° using CuKα-radiation (Ni-filter, wavelength 1.5418 Å, X-ray tube operation mode: current - 30 mA, voltage - 30 kV). The detector rotation speed was kept constant at 4°/min with a step of 0.02° ($\omega/2\theta$-scan), and the scanning angle was varied in the range of 4-80°. The experimental conditions for all samples were kept constant during the acquisition of X-ray radiographs. For the analysis and identification of phases, the tables and references given in the papers, as well as the international American X-ray powder data file [28, 29], were used.

Differential thermal analysis (DTA) was used to investigate high-temperature phase transformations, thermal stability region, and changes in the characteristics of the studied raw materials and test samples. Experimental studies were carried out using a Labsys EVO Setaram instrument providing heating up to 800°C at a rate of 20°C/min. During the analysis, synchronous registration of the differential thermal curve with simultaneous recording of changes in linear dimensions and mass loss of samples was carried out. The interpretation of the obtained results was based on fundamental research in the field of thermal analysis [30].

RESULTS AND DISCUSSIONS

Differential thermal analysis (DTA) of clay-hypsum and phosphogypsum samples (Figure-1, Figure-2) showed the presence of pronounced double endothermic effects of dehydration of bi-hydrous gypsum ($CaSO_4$-$2H_2O$) in the temperature range of 120-200°C, accompanied by mass loss of the studied samples. The DTA curve clearly records the first endothermic peak at 128.94°C, which corresponds to the removal of crystallization water molecules, with the process starting at 107.88°C and ending at 145.43°C. The total thermal effect of dehydration is -210 J, and the enthalpy is 266.34 J/g, confirming the sequential nature of the phase transition. Additionally, a broad endothermic signal is observed in the temperature range of 98.74-164.07°C, indicating a gradual loss of water. The combined data of thermogravimetric analysis (TGA) and DTA confirm the thermal instability of hydrated phases and phase transformations characteristic of clay-hypsum and phosphogypsum.

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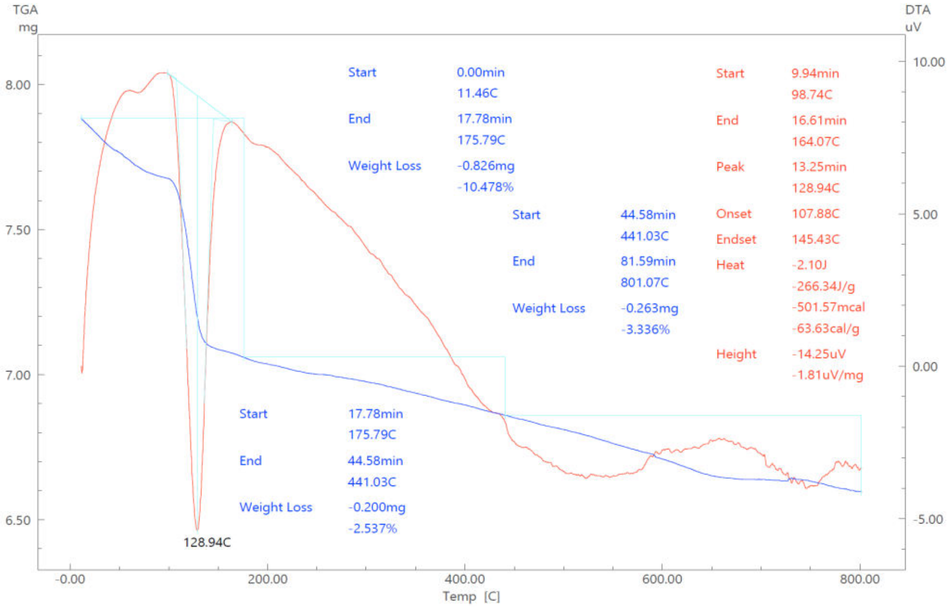

Figure-1. DTA of the clay gypsum sample.

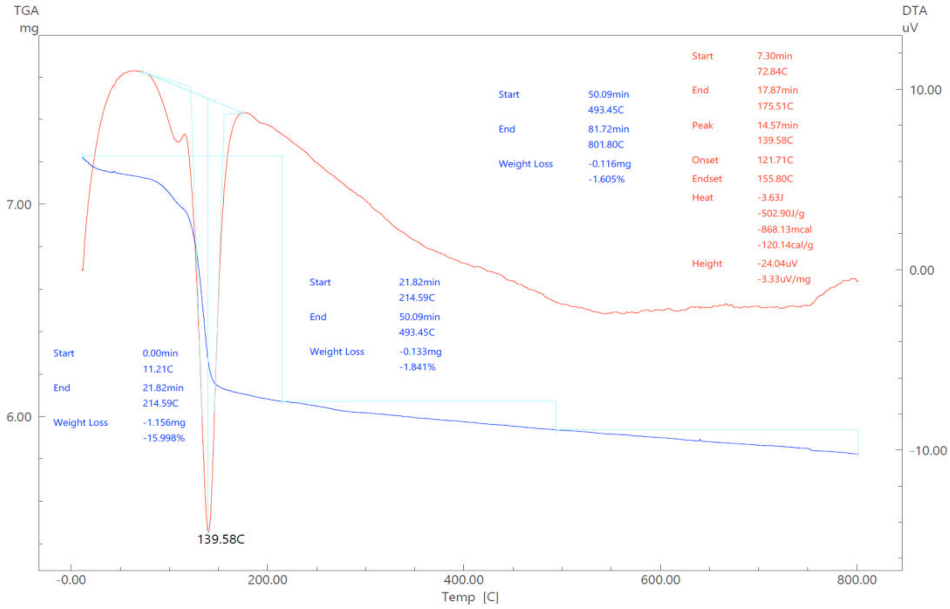

Figure-2. DTA of phosphogypsum sample.

X-ray phase analysis of clay-hypsum and phosphogypsum samples revealed the presence of diffraction reflexes at interplanar distances d = 0.740; 0.421; 0.303; 0.284; 0.266; 0.243; 0.188 and 0.153 nm, correlating with characteristic diffraction maxima of calcium sulfate dihydrate ($CaSO_4$-$2H_2O$). Additionally, reflexes at d = 0.375; 0.315; 0.247 nm corresponding to albite, as well as at d = 0.330 and 0.181 nm, identified as diffraction appearances of quartz, were recorded. The above crystal-phase components are confirmed in the X-ray diffraction patterns presented in (Figure-3 a, b).

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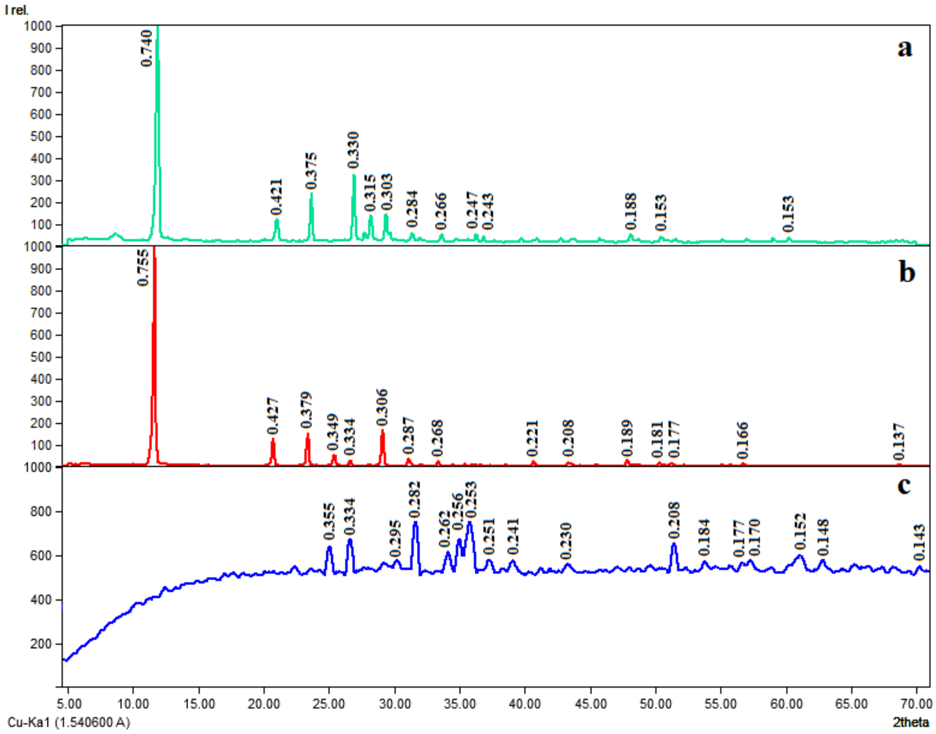
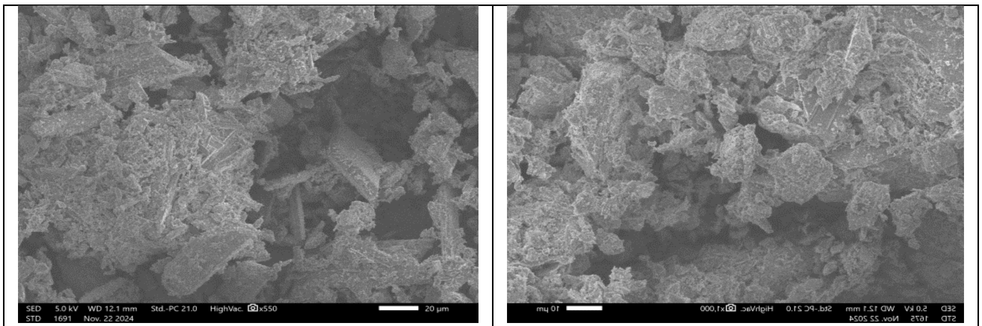


Figure-3. Radiographs of clay-hypsum (a), phosphogypsum (b), and AGMK slag (c).

X-ray phase analysis of a sample of slag from Almalyk mining and smelting plant revealed the predominant presence of diffraction maxima (Figure-3. c) corresponding to the mineral fayalite at interplanar distances d = 0.355; 0.282; 0.262; 0.256; 0.241; 0.230; 0.177; 0.152; 0.143 nm, as well as hematite at d = 0.251; 0.208; 0.184; 0.170; 0.148 nm, while diffraction lines related to wustite (d = 0.295; 0.253 nm) and quartz (d = 0.334 nm) were recorded in insignificant amounts.



(a) (b)

Figure-4. SEM image of raw samples (a) phosphogypsum, (b) clay gypsum.

Investigations show that the limited samples mainly contain crystals of bi-hydrous gypsum ranging in size from 0.15 to 0.3 mm measures. These include colorless, transparent gypsum crystals, soft mineral texture, and light refraction indices Ng=1.528 and Np= 1.525.

Figure-4 shows that in phosphogypsum Figure-4 (a) there are insignificant amounts of quartz impurities, and in the sample of clay gypsum Figure-4 (b) except for crystals of double-water gypsum, there are observed aggregated areas of clay compounds, characteristic of clay gypsum. The SEM analysis on the device JSM-IT210 confirms the results of chemical and X-ray phase analysis (Figure-5, Figure-6).

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Display name	Standard data	Quantification method	Result Type
Spc_017	Standardless	ZAF	Metal

Element	Line	Mass%	Atom%
C	K	4.61±0.04	7.69±0.07
O	K	56.41±0.17	70.59±0.21
Al	K	0.20±0.01	0.15±0.00
Si	K	0.72±0.01	0.51±0.01
P	K	0.57±0.01	0.37±0.01
S	K	15.70±0.04	9.80±0.02
Ca	K	21.79±0.06	10.89±0.03
Total		100.00	100.00
Spc_017			Fitting ratio 0.0124

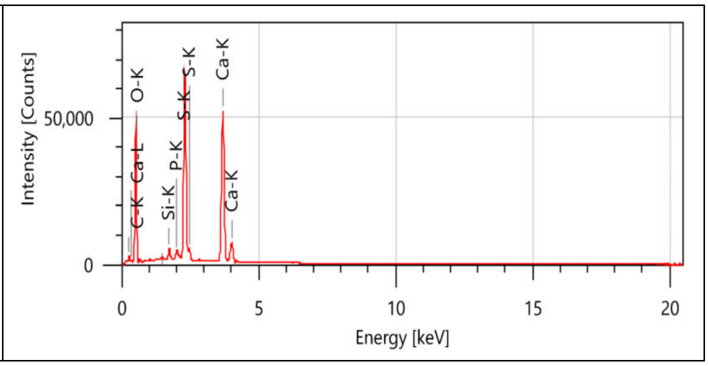

Figure-5. EMF image of raw phosphogypsum.

Display name	Standard data	Quantification method	Result Type
Spc_015	Standardless	ZAF	Metal

Element	Line	Mass%	Atom%
C	K	8.24±0.06	13.35±0.10
O	K	53.10±0.17	64.59±0.20
Mg	K	1.28±0.02	1.03±0.01
Al	K	2.58±0.02	1.86±0.01
Si	K	9.11±0.04	6.31±0.03
S	K	7.77±0.03	4.72±0.02
Cl	K	0.31±0.01	0.17±0.00
K	K	0.70±0.01	0.35±0.01
Ca	K	13.46±0.05	6.54±0.02
Ti	K	0.15±0.01	0.06±0.00
Fe	K	2.45±0.03	0.85±0.01
Zr	L	0.84±0.02	0.18±0.00
Total		100.00	100.00
Spc_015			Fitting ratio 0.0148

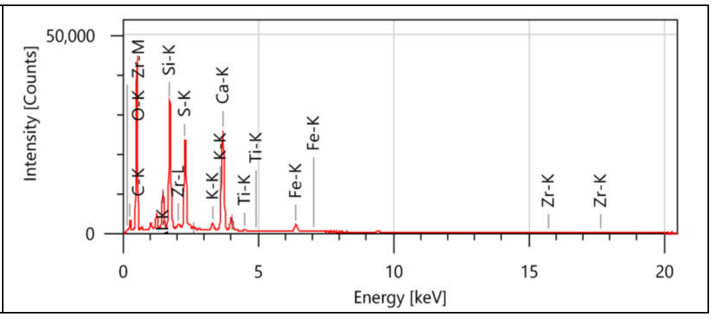

Figure-6. EMF image of raw clayey gypsum.

To test the physical and mechanical properties of gypsum binder degraded at 185-200°C based on clay gypsum (CG) and modified phosphogypsum (PG), we prepared several compositions with different additions of modified phosphogypsum (CGPG) in the composition of clay gypsum (Table-2). Since the physical and mechanical characteristics of phosphogypsum due to the presence of water-soluble P_2O_5 and clay gypsum due to the presence of a significant amount of clay minerals are not high, we have studied the characteristics of compositions of gypsum binder with the addition of modified phosphogypsum in the composition of clay gypsum (PG) in different ratios (Table-2). In this case, modified (by metallurgical slag) phosphogypsum plays the role of a formulator of the center of crystallization of $CaSO_4$-$2H_2O$ (bi-hydrous calcium sulfate) in the hydration of gypsum composition and positively affects its terms of the beginning and end of setting and strength properties.

Table-2. Physical and mechanical characteristics of clay-hypsum with different addition of modified phosphogypsum.

No	Name of samples	Compositions, wt.%		Setting time, min		Strength of samples, MPa	
		clay gypsum	phosphogypsum. modification.	commencement	end	bend	compression
1	CG	100	-	7	35	1.5	1.30
	PG. modif.	0	100	1.5	2.5	4.3	10.20
2	CGPG -1	95	5	4	19	2.5	5.55
3	CGPG -2	90	10	3	17	3.1	7.06
4	CGPG -3	85	15	2	16	4.4	10.42
5	CGPG -4	80	20	2	15	5.1	11.13
6	CGPG -5	75	25	2	13	5.3	12.46

The results of tests conducted [31, 32] according to GOST 125-2018, samples (Table-2) show that the setting time and strength of dehydrated clay gypsum show minimum values of flexural and compressive strength, while the strength of phosphogypsum modified with slag shows flexural strength of 4.3 MPa and compressive strength of 10.20 MPa. Even a 5% addition of slag-modified phosphogypsum increases the compressive strength of the binder composition up to 5.55 MPa, which corresponds to gypsum grade G5. In this case, according to GOST 125-2018, it corresponds to the normally hardening type "B.". Further increase of phosphogypsum addition up to 25% in the composition of composite gypsum binder increases its compressive strength characteristics up to 12.46 MPa, and the terms of the beginning and end of setting also meet the requirements of the standard.

CONCLUSIONS

Thus, the conducted studies show the real possibility of increasing the physical and mechanical properties of clay gypsum, Khojakul deposit modified phosphogypsum, which in turn contributes to their use in the relevant sectors of construction. In addition, the obtained results contribute to the expansion of the raw material base for the production of gypsum binders and have ecological significance.

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