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UTILIZATION OF INDUSTRIAL WASTE PRODUCED BY THE PHOSPHORIC INDUSTRY

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ABSTRACT

The article presents the results of systematization of technogenic waste of phosphoric industry in Zhambyl region, amounts of their accumulation in the dumps and possible ways of processing as a secondary raw material are identified. A physic-chemical and structural properties of the waste were studied and a comparative evaluation of the content of basic oxides and their mineralogical composition were presented. Preliminary assessment of the waste was held by technological characteristics such as modulus of basicity (Mo) and module activity (Ma), which showed that all of the waste in varying degrees, have astringent properties. The results show a possibility of using man-made waste of phosphoric industry to produce mineral binders and building composites. The methods of modeling formulations of composite materials based on technogenic waste of Zhambyl region. It is shown that in the main technological process industrial wastes undergoes a high temperature treatment with the formation of mineral. It is offered to consider their phase and chemical compositions in the system $CaO – SiO_2 – Al_2O_3$. Diagram of the system $CaO – SiO_2 – Al_2O$ can be used as a technical model to determine the optimal composition of the basic oxides binder based on man-made materials. Indicated that a necessary condition of modeling compositions is the presence of basic oxides in raw ingredients. With the help of technical model represented by the basis of the ternary system, rational composition of multicomponent mineral binder is set. On the basis of summarizing the theoretical propositions of building materials and research experience in the field of synthesis without roasting binding systems a method of comprehensive utilization of industrial wastes in the production of building materials is proposed.

Key words: Industrial waste, Phosphoric industry, Zhambyl region.

INTRODUCTION

One of the most important directions of construction material engineering is the study on the development of new effective composites based on industrial materials, which are characterized by low cost and ability to meet up-to-date requirements of durability and

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serviceability[1]. The most important raw material reserves of construction sector are large-tonnage secondary products (industrial waste) of the phosphoric industry, which integrated use will enable to form rational structures of new composite materials as a result of physical and chemical interactions.

Set of technologies of certain industries located in the Zhambyl industrial region and connected not only by means of main production cycles, but also by strategic issues concerning the effective use of accumulated industrial waste, determine a search for new trends to reduce its volume with simultaneous resolution of cost-effective use of resources[2].

Industrial waste treatment system in accordance with the laws of the Republic of Kazakhstan requires not only the accounting of accumulation volume of the industrial waste in dumps, but also its classification according to its type. Acquisition of data on the volume of storage and utilization of industrial waste, produced by the phosphoric industry in Zhambyl region, revealed the emerging waste market and possible volumes of its involvement in economic circulation as raw materials.

Creation and study of structure formation of new types of mixed binders, construction materials and structures based on them, the management of these processes, resources and energy, to reduce the cost of construction products through the integrated use of the regional base of local raw material sources, made reference to the use of phosphoric products industry Zhambyl region.

EXPERIMENTAL

Main objectives of research

The content of the following compounds in phosphogypsum is determined during the study: SO_3, SiO_2, CaO, MgO, Fe_2O_3, P_2O_5, Al_2O_3, F, Na_2O, as well as moisture content and losses on ignition (LOI)[3-5]. Besides the determination of the total content of SO_3 и P_2O_5, also their content in aqueous extract is determined.

Materials and methods

The chemical composition of phosphogypsum is determined using the standard procedures of physical and chemical and quantitative chemical analysis, such as spectral, photometric, absorption, gravimetric and chelalatometric methods. The following certified instruments are used: KFK-2 photoelectric concentration colorimeter, KFK-3-0 photoelectric colorimeter, EV-74 laboratory ionometer, FLAPHO-4 flame photometer, VLR-200 analytical balance, AAS-3 atomic absorption spectrophotometer. Calibration and certification data for the instruments, used in the study, are attached.

X-ray phase analysis of phosphogypsum is done using automated XPertPro (Netherlands) and DRON-4 (Russia) diffraction meters using Cu_K line (β-filter) in X-ray powder diffraction patterns and the method of equal weights and artificial mixtures. The diffraction patterns are interpreted using the A*STM* Powder diffraction file data and the diffraction patterns of minerals free of impurities (gypsum, quartz, calcium phosphates). The diffraction patterns were obtained at the following conditions: U = 35kV; I = 20 mA; scale: 2000 imp; time constant: 2c; scan mode: theta-2theta; detector: 2 grad/min.

Thermographic analysis of phosphogypsum sample is done using Q-1000/D derivatograph (Hungary). Scanning is done in air at temperature range 20-1000^{o}C in dynamic heating mode (dT/dt = 10 grad/min), reference substance is incinerated Al_2O_3, sample weight – 500 mg. Measuring instrument sensitivity is set the same for all samples: TG = 100 мг = 500 μV, ДТА = 250 μV, ДТG = 500 μV, T = 500 μV. The method is based on the recording of changes in thermal/chemical and physical parameters of a substance when it is heated. Identification of minerals in powder samples is done using the morphology of their thermal curves and numerical values of the intensities of endo- and exothermal effects. The results of analysis are compared with data in atlases of the thermal curves of rocks and minerals[4-6].

Procedures for analysing physical and mechanical properties of phosphogypsum[8,9]

BET surface area of phosphogypsum samples is determined using the BET method depending on the adsorption of nitrogen at isothermal state and the temperature of liquid nitrogen (-196^{0}C). The analysis is conducted using AccuSorb Micrometrics sorptometer (USA). To remove surface impurities samples are held in vacuum at 220^{0}C for 3-4 hours. Calculations to determine BET surface area (SW, m^2/g) are done using PC software by plotting (on horizontal/vertical coordinates) the dependence of relative pressure P_2/Ps versus P/V_a (P_s – P), where V_a – volume of gas (nitrogen) adsorbed at pressure P; P_s – pressure of saturated gas at the temperature of the experiment (-196^{0}C); P_2 – remaining pressure after the adsorption of nitrogen.

The granulometric distribution of phosphogypsum is determined using the sieve and dropper methods to calculate the percentages of various particle fractions of phosphogypsum.

To determine the sizes and distribution of phosphogypsum particles the suspension sedimentation analysis is used. It is based on determining experimentally the sedimentation rate of particles in a dispersed phase in a dispersion medium with the further determination of particle size distribution and dispersion rate[7-10]. BT-500 torsion balance, set of sieves, calibrated droppers are used in the study.

A particle in a viscous medium falls down under the action of gravitational force, which is equal to its apparent weight P:

$$P = \frac{4}{3}\pi r^3 (D - d)\, g$$

where *r* is particle's radius

D, d-Density of the particle and the medium correspondingly

g-Gravitational acceleration.

A falling down particle is decelerated by frictional force, the value of which is determined according to Stokes' law:

$$P = 6\pi\, \eta r u$$

where η is medium's viscosity;

u is the velocity of the particle, equal to h/t;

h is the height from which the particle falls down and

t is the time of falling down to the bottom.

Steady falling down begins from the moment of time when the gravitational force becomes equal to the frictional force. Making equal the right-hand members of equations (1) and (2) one may find the radius of the particle *r*:

$$\frac{4}{3}\pi r^3 (D - d)\, g = 6\, \pi \eta r u \text{ где } u = \frac{h}{\tau} \quad \frac{4}{3}\pi r^3 (D - d)\, g = 6\, \pi \eta r u$$

$$r = K \sqrt{\frac{h}{\tau}}$$

Knowing time t_1 one may calculate the size of the smallest particle among fallen down particles using equation (3). Plotting $Q_0 = f(r)$ we get an integral distribution curve with y-coordinates showing the percentage of particles. To obtain the differential curve one relates the difference of two values of Q_0 to the difference of the two respective radii. With function Q/r = f (r) the differential curve of phosphogypsum distribution may be plotted.

Physical and mechanical properties of phosphogypsum: Density (true), bulk weight, porosity, water content, angle of repose[11].

To determine true density the pycnometer method is used. It is based on measuring the weight of a liquid-filled pycnometer when a part of this liquid is replaced by a weighed quantity of certain substance. A glass 50-mL pycnometer and analytical balance VLR-200 are used as basic instruments for determining true density. Density δ is determined using the formula:

$$\delta = \frac{A - B}{(C + A) - (D + B)}$$

Where δδ is density in g/cm^3

A – Mass of pycnometer with the weighed quantity, g

B – Mass of empty pycnometer, g

C – Mass of pycnometer with water, g

D – Mass of pycnometer with water and the weighed quantity, g.

To determine bulk weight a volumetric glass with known volume A and weight P_o is used. The glass is fully filled with the studied substance with specific weight. The substance in the glass is shaken by tapping its bottom on table, excessive amount of the substance above the rim is removed by a ruler or glass stick, after that the weight of the glass with phosphogypsum (P_1) is determined using AX-200 analytical balance.

Bulk weight is determined using the formula:

$$\Delta = \frac{P_1 - P_o}{A}$$

where is bulk weight in g/cm^3

P_0 – Weight of empty glass, g

P_1 – Weight of glass filled with phosphogypsum, g

A – Volume of glass, cm^3.

Porosity of phosphogypsum F is determined using the formula:

$$F = \Delta = \frac{\delta - \Delta}{\delta} * 100\%$$

where F is porosity in %;

δ – Density, g/cm^3;

– Bulk specific weight, g/cm^3.

Angle of repose is maximum possible angle between free surface of powder material and horizontal surface without dynamic impact. To measure it a metallic cylinder without bottom is placed on a horizontal surface and filled with phosphogypsum. The cylinder is then slowly removed, and the height and diameter of the formed cone are measured.

RESULTS AND DISCUSSION

Since in the basic industrial process, the processing waste are treated at high-temperature resulting in formation of minerals, it is possible to consider their phase and chemical compositions in the system $CaO – SiO_2 – Al_2O_3$, and the diagram of this system can be used as a technical model to determine the optimum composition of basic oxides of the developed binder based on the industrial raw materials[12]. To solve the problem of designing the optimum composite non-baked binder, one significant area is assumed in the system $CaO – SiO_2 – Al_2O_3$. The physical and chemical characteristics of the raw components matching the typical binder composition and generalized by the similar properties of the binders shall be brought to the boundaries of such significant area[13].

At this stage, based on the analysis of scientific research on the optimum structures of non-baked binders with improved performance characteristics, taking into account the existing raw base of industrial waste with a certain phase composition, regarding the waste properties and chemical composition, we have put forward a hypothesis about the possibility of obtaining a composite non-baked binder designed in the system $CaO – SiO_2 – Al_2O_3$ from the industrial waste.

Analysis of the industrial waste location areas in Zhambyl region (Fig. 1) in relation to the location areas of the known materials (glass, Portland cement, aluminous cement, etc.) with a match (or non-match) of chemical and mineralogical composition in the system $CaO – SiO_2 – Al_2O_3$ allows to determine the group boundaries, which the studied waste is closest to, and, accordingly, which group it could potentially belong to.

To create new types of composite mineral non-baked binders, an option is suggested when the values are on the boundary of the Portland cement properties range (a pattern).

In order to implement the creation of the composite non-baked binder based on the system $CaO – SiO_2 – Al_2O_3$, taken as the technical model (Fig. 1), the presence of oxides CaO, SiO_2, Al_2O_3, Fe_2O_3 in the raw components is the necessary condition.

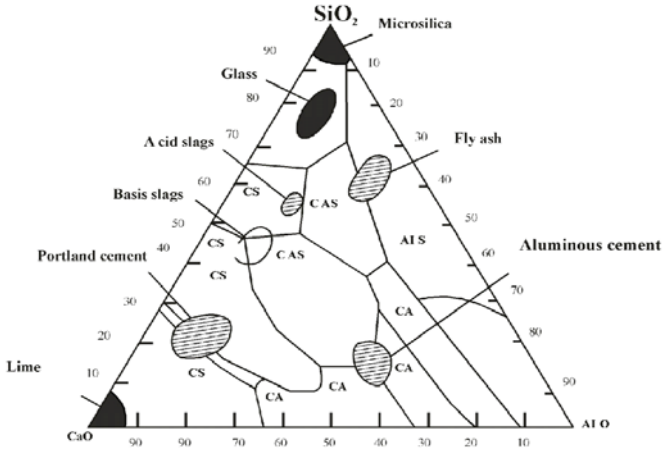

Fig. 1: Technical products areas of CaO - Al_2O_3 -SiO_2 system

The location areas of phosphoric industry after products in Zhambyl region on the CaO – SiO_2 – Al_2O_3 phase diagram are determined by the minimum and maximum limit values.

According to Table 3, the sum of basic oxides CaO, SiO_2, Al_2O_3 in the raw materials is brought to 100%, and the fractions of each element are calculated separately based on the result. The results are given in Table 1.

The location areas of phosphoric industry after products in Zhambyl region on the CaO – SiO_2 – Al_2O_3 phase diagram are determined by the minimum and maximum limit values.

Table 1: Minimum and maximum values for the content of basic oxides brought to 100% in the industrial waste of Zhambyl region phosphoric industry

1. NDFZ granulated slag				
Basic oxide	**Maximum percentage (%)**	**Σ = 89.01 = 100%**	**Minimum percentage (%)**	**Σ = 78.72 = 100%**
CaO	37.67	42.33	34.12	43.35
Al_2O_3	1.70	1.91	0.90	1.15
SiO_2	44.19	49.65	38.70	49.17
Fe_2O_3	5.45	6.13	5.00	6.36

Cont…

2. Dolomite (Karatau overburden)				
Basic oxide	**Maximum percentage (%)**	**Σ = 34.03 = 100%**	**Minimum percentage (%)**	**Σ = 31.25 = 100%**
CaO	30.20	88.75	28.10	89.92
Al_2O_3	0.15	0.44	0.05	0.16
SiO_2	0.17	0.50	0.09	0.29
Fe_2O_3	3.51	10.31	3.01	9.64
3. Limestone (Karatau overburden)				
Basic oxide	**Maximum percentage (%)**	**Σ = 48.51 = 100%**	**Minimum percentage (%)**	**Σ = 44.09 = 100%**
CaO	44.20	91.12	41.00	93.00
Al_2O_3	0.15	0.31	0.05	0.12
SiO_2	1.17	2.40	0.70	1.59
Fe_2O_3	2.99	6.17	2.34	5.31
4. Himprom molten slag				
Basic oxide	**Maximum percentage (%)**	**Σ = 89.71 = 100%**	**Minimum percentage (%)**	**Σ = 82.24 = 100%**
CaO	41.70	46.49	38.00	46.21
Al_2O_3	0.15	0.17	0.05	0.06
SiO_2	43.10	48.05	40.10	48.76
Fe_2O_3	4.76	5.31	4.09	4.98
5. Phosphogypsum (mature), mineral fertilizers plant				
Basic oxide	**Maximum percentage (%)**	**Σ = 43.99 = 100%**	**Minimum percentage (%)**	**Σ = 36.20 = 100%**
CaO	27.32	62.11	24.23	66.94
Al_2O_3	0.50	1.14	0.15	0.42
SiO_2	15.16	34.47	11.42	31.55
Fe_2O_3	1.01	2.30	0.4	1.11

Cont…

6. Phosphate-siliceous schist, Koksu deposit				
Basic oxide	**Maximum percentage (%)**	**Σ = 82.40 = 100%**	**Minimum percentage (%)**	**Σ = 79.51 = 100%**
CaO	5.90	7.16	5.01	6.31
Al_2O_3	9.80	11.90	9.00	11.32
SiO_2	61.60	74.76	60.90	76.59
Fe_2O_3	5.10	6.18	4.60	5.78
7. Phosphate-fissile shale, Koksu deposit				
Basic oxide	**Maximum percentage (%)**	**Σ = 87.52 = 100%**	**Minimum percentage (%)**	**Σ = 85.62 = 100%**
CaO	4.51	5.16	4.21	4.92
Al_2O_3	3.75	4.28	3.31	3.86
SiO_2	75.81	86.62	75.01	87.61
Fe_2O_3	3.45	3.94	3.09	3.61
8. Phosphated dolomite (slabby), Koksu deposit				
Basic oxide	**Maximum percentage (%)**	**Σ = 40.79 = 100%**	**Minimum percentage (%)**	**Σ = 36.98 = 100%**
CaO	24.98	61.24	23.90	64.63
Al_2O_3	1.89	4.63	1.10	2.97
SiO_2	10.99	26.95	9.98	26.99
Fe_2O_3	2.93	7.18	2.00	5.41
9. Phosphated flints, Zhanatas deposit				
Basic oxide	**Maximum percentage (%)**	**Σ = 87.46 = 100%**	**Minimum percentage (%)**	**Σ = 85.11 = 100%**
CaO	5.79	6.62	4.91	5.77
Al_2O_3	2.00	2.29	1.74	2.05
SiO_2	76.89	87.91	76.12	89.44
Fe_2O_3	2.78	3.18	2.34	2.75

Cont…

10. Slag Achpolymetall				
Basic oxide	**Maximum percentage (%)**	**Σ = 76,38 = 100%**	**Minimum percentage (%)**	**Σ = 71,93 = 100%**
CaO	26,3	34,4	24,5	34,1
Al_2O_3	5,95	7,79	5,05	7,02
SiO_2	29,03	38,0	28,97	40,3
Fe_2O_3	15,1	19,8	13,41	18,6

According to Table 3, the sum of basic oxides CaO, SiO_2, Al_2O_3 in the raw materials is brought to 100%, and the fractions of each element are calculated separately based on the result. The results are given in Table 1.

At imposing the limit values of after products of Zhambyl region phosphoric industry, according to the obtained values (Fig. 2) in the minerals area of Rankine diagram, revised according to E. Osborn, it may be noted that the areas of chemical and mineralogical compositions location match[15].

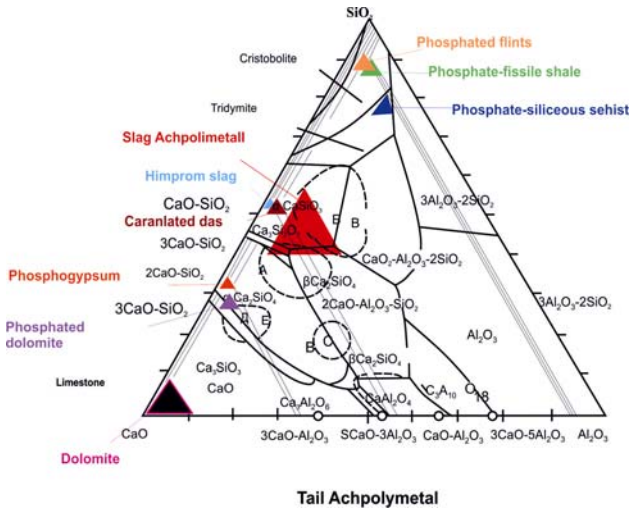

Fig. 2: The state diagram of system CaO – SiO_2 – Al_2O_3 with application of components of the designed building composites

It should be noted that the proposed methodology can be used not only to solve problems of designing of the optimal composition of the raw mixture of bender, but other composite building materials based on an integrated appreach to the use of.

In this case, the issue can be raised concerning the active impact of approximation of industrial waste properties to the particular material properties, i.e., to the set range of recommended properties. For this purpose, on the diagram of ternary system $CaO – SiO_2 – Al_2O_3$, we give the compositions of Zhambyl region industrial waste with the necessary properties, and due to the integrated use (mixing) in the mathematically-based ratios we approximate the quantitative chemical composition to the center of the set range of the recommended properties for a particular material.

Thus, to make a new effective material, the following is required: calculate the content of basic oxides CaO, Al_2O_3, SiO_2 of the industrial after products in the mass fractions from 100% and bring the fractional chemical composition to the typical composition of the basic oxides of a particular building material in the system $CaO – SiO_2 – Al_2O_3$.

The given reasoning allows to assume the following. It is possible to get a new composite building material if some significant area (E) is assumed in the Rankine diagram in the system $CaO – SiO_2 – Al_2O_3$ (Fig. 2), the physical and chemical characteristics of the raw materials (A, B, C) are brought to the boundaries of such area and most closely match the typical composition and generalized characteristic properties of the significant area (E).

The Portland cement area (E) is the most significant area in $CaO – SiO_2 – Al_2O_3$ system, and as for today, it has the best physical, mechanical and technical characteristics of all binders, but Portland cement requires large power consumption at its production.

The basic condition to bring the chemical composition and the components (A, B, C) area properties to the chemical composition of the Portland cement (E) area as close as possible, has been accomplished by calculation in Microsoft Office Excel program (Table 2).

Table 2: Results of calculation of the new building composites compositions

Composition 1		**Phosphate-fissile schist**	**Phospho-gypsum**	**Limestone**	**Portland cement**	
CaO		5.18	64.56	91.62	67.52	67.52
Si_2O		86.87	32.4	2.02	23.3	23.29
Al_2O_3		4.28	1.1	0.21	5.618	0.939
Fe_2O_3		3.67	1.94	6.15	3.56	3.56
	0.95319	0.071125169	0.50492378	0.37714138	4.67896716	

Cont…

Composition 2		**Phosphate-siliceous schist**	**Phospho-gypsum**	**Limestone**	**Portland cement**	
CaO		6.3	64.56	91.62	67.52	67.52
Si_2O		76.27	32.4	2.02	23.3	23.29
Al_2O_3		11.45	1.1	0.21	5.618	1.392
Fe_2O_3		5.98	1.94	6.15	3.56	3.56
	0.957721	0.062335407	0.55092319	0.34446332	4.22590803	
Composition 3		**Granulated slag**	**Phospho-gypsum**	**Limestone**	**Portland cement**	
CaO		42.8	64.6	91.62	67.52	67.52
Si_2O		49.5	23.3	32.4	23.3	23.29
Al_2O_3		1.6	1.1	0.3	5.618	1.392
Fe_2O_3		6.1	1.9	6.1	3.56	3.56
	0.9524	0.1077	0.3091	0.5356	4.4639	

At calculation of the binder components composition, a factor has been taken into account that in the hydration processes of hydraulic binders, the ferrous oxide (Fe_2O_3) acts for the better.

In the high temperature cement chemistry, at studying the physical and chemial processes in the system $CaO – SiO_2 – Al_2O_3$, it has been shown that, as the final result, the new growths C_2F, CF, appearing across $CaO – Fe_2O_3$ boundary, actively influence on the material structure formation and properties[14-16].

The systematic approach at designing the multi-component mineral binder (MMB) allowed to obtain a composite material with the complex structure consisting of mineral materials with very different properties and gaining as a result of their combination a set of new properties, not inherent in the source materials. In this case, the synergistic effect is manifested (Fig. 3).

The analysis of location of different building materials and raw components in the system $CaO – SiO_2 – Al_2O_3$ by the chemical and mineralogical composition has allowed us to determine that the investigated industrial after products are the closest to the Portland cement boundary. Systematization of industrial waste was made according to the areas of its

practical use in construction engineering in order to identify additional reserves of its integrated utilization by means of its incorporation into closed and technological cycles as a part of specific complexes.

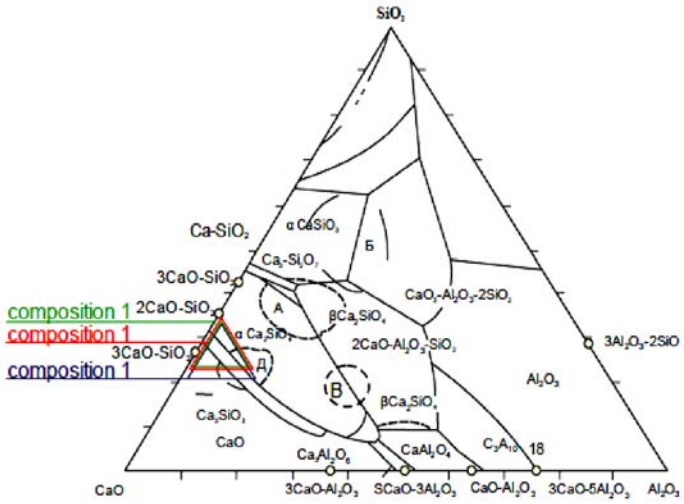

Fig. 3: Diagram of $CaO-SiO_2-Al_2O_3$ system condition

Utilization methods are based on physicochemical analyses of properties and structure of waste, enabling to define the fundamental possibility (or impossibility) of its use in a particular production[17]. According to this provision, one has identified the reserves for extending the field of application of accumulated industrial waste, produced by the phosphoric industry, and conducted laboratory studies of chemical (Table 1), physical and special (specific) properties of waste using standard physicochemical and chemical quantitative analysis in accordance with methods[18].

Table 1 shows average results of chemical analysis of nine different waste samples produced by the phosphoric industry in Zhambyl region. Summarized results of average laboratory studies of chemical content of waste showed that boundary variances (minimum and maximum content of components) lie in values specific to long-term research; on the basis of these data it is possible to make a conclusion on the relative stability of the chemical content of industrial waste produced by the phosphoric industry in Zhambyl region.

As Table 1 shows, all wastes that have been selected as potential materials for further study and obtainment of construction composites, have main components such as calcium and silicon oxides, most wastes contain aluminum and iron oxides. Presence of

these oxides describes hydration properties of raw components used for production of binding materials in construction engineering, and also plays an important role in the synthesis of building mixes (portland cement, aluminous cement, glass, fine ceramics, etc.).

When choosing this waste as a raw material for the production of building materials its compliance with regulations on the content of radionuclides has been verified. Sanitation and epidemiological conclusions confirmed the possibility of using this waste as mineral raw materials for all kinds of building materials without any limitations, as the total specific activity of radionuclides for each type of waste did not exceed 370 Bq/kg, corresponding to the requirements of Sanitary Regulations & Norms 2.6.1.2523-09.

In a preliminary assessment of the availability of the industrial raw materials for the production of building materials it was necessary to assure oneself of a satisfactory gross chemical content and the minimum content of harmful impurities, as well as of their chemical and mineralogical homogeneity.

At this stage it is important to take into account temperatures at which the formation of industrial waste occurs, and what kinds of crystalline phases are formed. Physical properties and conditions of phase formations in the main technological process describe the reactivity of the industrial waste, as well as enable one to define conditions under, which it is possible to activate their properties. Mineralogical content analysis was prepared for all kinds of waste; the results are shown in Table 2.

X-ray diffraction analysis on a semi-quantitative basis is made on diffraction patterns of powder samples using the method of equal batches and artificial mixtures. Quantitative relationships of crystalline phases were determined. Interpretation of diffraction patterns was made by means of ASTM Powder diffraction file and diffraction patterns of pure minerals. Calculation of content was carried out for the main phases. Possible impurities, identification of which may not be clear due to small amounts and the presence of only 1-2 diffraction reflections or poor crystallinity are specified in Table 3.

For comparative data processing Table 4 shows the content of basic oxides, which greatly influence structural formation of binding systems of building materials.

The presence of CaO (C), SiO_2 (S), Al_2O_3 (A) oxides at a predetermined ratio determines hydration properties of raw materials used for the manufacture of binders in construction engineering. The presence of minerals in waste, which have a hydraulic activity (C_3S, C_2S, C_2F et al.), and their hydrates thereof, determines the possibility to obtain from them binding components after pre-drying, grinding and introduction of activizers.

Table 3: The results of chemical analysis of the industrial waste samples in LLP "Kazphosphate", July 2015

Probe #	Title	Content of components (%)													
		SiO_2	CO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	F	Ппп	H_2O	Σ
1	Granulated slag NDFZ	41.44	< 0.1	5.15	1.3	35.89	8.26	0.94	0.83	1.49	0.89	4.05	-	-	100.24
2	Dolomite (overburden Karatau)	0.13	45.67	3.21	< 0.1	29.16	21.77	< 0.05	< 0.05	0.06	< 0.1	< 0.05	-	-	100.00
3	Limestone (overburden Karatau)	0.94	42.86	2.86	< 0.1	42.62	10.48	< 0.05	< 0.05	0.12	< 0.1	< 0.05	-	-	99.88
4	Cast slag of chemical industry	41.66	< 0.1	4.29	< 0.1	39.86	8.87	0.94	0.63	1.15	0.75	2.5	-	-	100.65
5	Stale Phosphogypsum, heap, fertilizer mneral plant	13.33	-	0.80	0.45	26.59	0.48	0.10	0.12	1.03	42.71	0.35	5.94	8.08	99.95
6	Phosphate-siliceous shales «Koksu» bed	61.10	3.63	4.79	9.18	5.04	2.41	2.86	0.36	5.76	-	-	4.25	-	99.08
7	Phosphate shales, « Koksu » bed	75.18	1.21	3.19	3.70	4.48	2.02	2.20	0.36	5.39	-	-	1.43	-	99.07
8	Phosphated dolomite (slabby), « Koksu » bed	10.5	40.12	2.39	1.53	24.11	19.35	0.47	0.25	0.8	-	-	<0.1	-	99.52
9	Phosphated flints, «Zhanatas» bed	76.36	1.60	2.60	1.83	5.04	1.61	0.29	0.30	7.65	-	-	2.1	-	99.46

Table 4: The results of X-ray diffraction analysis of industrial waste samples in LLP "Kazphosphate"

Probe #	Test object	Mineralogical content of industrial waste	
		Mineral	**Content (%)**
1	Granulated slag NDFZ (Novodzhambulsk phosphorus plant)	Quartz	65.9 %
		Halo	100%
2	Dolomite (overburden Karatau)	Dolomite $CaMg(CO_3)_2$	100.0%
3	Limestone (overburden Karatau)	Calcite $Ca(CO_3)$	100%
		Calcite $Ca(CO_3)$	9.5%
		Calcite $Ca(CO_3)$	7.9
		Calcite $Ca(CO_3)$	7.5
		Calcite $Ca(CO_3)$	7.4
		Calcite $Ca(CO_3)$	5.4
		Dolomite $CaMg(CO_3)_2$	5.2
4	Slag cast (Plant "Khimprom" Taraz)	Quartz SiO_2 - 44.0%	44
		Rankinite $Ca_3Si_2O_7$	13.7
		Apatite, blue. $(Ca_5(PO_4)_3F$	11.7
		(JI) Laihunite $(Fe_{1.57}Mg_{.03})(SiO_4)$	10.6
5	Stale Phosphogypsum, heap, fertilizer mineral plant	Hydrous sulphate of lime $CaSO_4 \cdot 2H_2O$	100
6	Phosphate-siliceous shales «Koksu» bed	Quartz SiO_2	64.9
		Hydroxyapatite $Ca_5(PO_4)_3(OH)$	12.7
		Dolomite $CaMg(CO_3)_2$	11.0
		Calcite $Ca(CO_3)$	5.9
		Glist (muscovite) $KAl_2(AlSi_3O_{10})(OH)_2$	5.5
7	Phosphate shales, « Koksu » bed	Quartz SiO_2	81.0
		Hydroxyapatite $Ca_5(PO_4)_3(OH)$	19.0
8	Phosphated dolomite (slabby), « Koksu » bed	Quartz SiO_2	2.9
		Dolomite $CaMg(CO_3)_2$	97.1
9	Phosphated flints, «Zhanatas» bed	Quartz SiO_2 - 68,7	68.7
		Hydroxyapatite $Ca_5(PO_4)_3(OH)$	13.4
		Dolomite $CaMg(CO_3)_2$	11.6
		Calcite $Ca(CO_3)$	6.3

Table 5: Chemical content of major oxides of industrial waste in LLP "Kazphosphate"

Probe #	Test object	CaO	SiO_2	Al_2O_3	Fe_2O_3
		Weight content (%)			
1	Granulated slag NDFZ (Novodzhambulsk phosphorus plant)	42.8	49.5	1.6	6.1
2	Dolomite (overburden Karatau)	89.5	0.4	0.3	9.8
3	Limestone (overburden Karatau)	91.6	2.0	0.3	6.1
4	Slag cast (Plant "Khimprom" Taraz)	46.4	48.5	0.1	5.0
5	Stale phosphogypsum, heap, Fertilizer mineral plant	64.6	32.4	1.1	1.9
6	Phosphate-siliceous shales «Koksu» bed	6.30	76.27	11.45	5.98
7	Phosphate shales, « Koksu » bed	5.18	86.87	4.28	3.67
8	Phosphated dolomite (slabby), « Koksu » bed	62.58	27.26	3.95	6.21
9	Phosphated flints, « Zhanatas » bed	5.88	88.97	2.12	3.03

Preliminary assessment of the materials, as raw materials for the production of composite building materials, was made by comparing such important technological characteristics as basicity (Mo) and activity (Ma) modules.

$$M_o = (CaO + MgO)/(SiO_2 + Al_2O_3)$$

$$M_a = Al_2O_3/SiO_2$$

When Mo > 1, then raw components are referred to the principal, when M0 <1 - raw components are referred to acidic components[17-19].

Burdening calculation of different kinds of raw materials based on basicity coefficient enables to identify ways of using a variety of industrial by-products without longstanding and costly experiments. Basicity (Mo) and activity (Ma) modules (the first group of modules), which describe the hydraulic properties of the raw components, were determined on the basis of the average chemical content (Table 1).

If the basicity coefficient of materials does not exceed 1, and in the process of their hydration the formation of a large amount of monoaluminates, ferrites and sulfates of calcium is not expected, so the binding properties of these materials in the process of hydraulic hardening can be neglected. When the basicity coefficient is up to 1.6, and if it is

possible to form a sufficient amount of calcium compounds in the process of hydraulic hardening, one should consider binding properties of these materials. Silicate materials with the basicity coefficient exceeding 1.6 have hydraulic activity and as higher as higher are the above values of.

Table 6: The results of calculations of the Basicity module M_0 and the activity module M_a

Probe #	Title	Basicity module M_0	Activity module M_a
1	Granulated slag NDFZ (Novodzhambulsk phosphorus plant)	1.04	0.04
2	Dolomite (overburden Karatau)	221.44	0.77
3	Limestone (overburden Karatau)	51.06	0.11
4	Slag cast (Plant "Khimprom" Taraz)	1.17	0.01
5	Stale Phosphogypsum, heap, Fertilizer mineral plant	1.97	0.04
6	Phosphate-siliceous shales «Koksu» bed	0.11	0.15
7	Phosphate shales, « Koksu » bed	0.09	0.05
8	Phosphated dolomite (slabby), « Koksu » bed	3.61	0.15
9	Phosphated flints, «Zhanatas» bed	0.09	0.03

The resulting characteristics of the basicity module M_0 (Table 4) indicate the possibility of using this waste to obtain binding materials.

The analysis of physicochemical and technological properties of waste produced by the phosphoric industry enables to recommend it as raw components in the development of integrated content of composite materials.

CONCLUSION

On the basis of summarizing the theoretical propositions of building materials and research experience in the field of synthesis without roasting binding systems a method of comprehensive utilization of industrial wastes in the production of building materials is proposed. In accordance with the requirements of current regulatory documentation a system has been developed to evaluate the properties and characteristics of industrial waste making possible the identification of industrial by-products and the further investigation of their potential for reprocessing and use in construction industry. Using the diagrams of ternary

systems for prediction of the solid phase formations in combinations with different chemical and mineralogical compositions allowed us to offer using the basis of the ternary system $CaO – SiO_2 – Al_2O_3$ as the technical model for designing the new composites of building materials. Using a technical model of the three-component system $CaO – SiO_2 – Al_2O_3$, the composition and properties of the mineral raw-material by-products of the phosphor-producing industry in Zhambyl region have been established. It should be noted that the proposed methodology can be used not only to solve the problems of designing the optimum composition for the binder raw mixture, but also for other composite building materials based on the integrated approach for the use of industrial waste from different industrial regions of the country.

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