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INVESTIGATION AND DEVELOPMENT OF THE TECHNOLOGY FOR INTEGRATED PROCESSING OF WASTES FROM PHOSPHOROUS INDUSTRY

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ABSTRACT

The article presents a classification of the wastes from the phosphorus industry in Zhambyl Region of Republic of Kazakhstan. The wastes are classified according to their application as construction materials. The comparative assessment results of physical, chemical and structural properties of phosphorus industry wastes are presented. Process characteristics as alkali-lime factor and reactivity factor are also taken account of. It is shown that all studied waste types have binding properties and can be utilized as construction materials. Methods of material composition modeling on the ground of the wastes are described. The diagram $CaO – SiO_2 – Al_2O_3$ diagram is suggested to be used to determine the optimum composition of the basic oxides forming the binding materials. It is shown that the pre-requisite for generating binding materials is the presence of basic oxides (CaO, Al_2O_3, SiO_2, Fe_2O_3) in the recyclables since those oxides stipulate the hydration and maturing of the construction materials.

A method of integrated management is proposed for the wastes of the phosphorus industry resulting in the production of construction materials.

Keywords: man-made waste, phosphorous industry, physico-chemical properties, mineral binders, construction composites, lime factor, activity modulus.

INTRODUCTION

The work is devoted to the development of innovative methods for obtaining construction and road composites with maximum involvement of large-tonnage wastes of the phosphorous industry of Zhambyl region (“mature” phosphogypsum, phosphoric slag, and overburden rocks).

There are more than 30 million tons of accumulated phosphorus wastes at present in the southern part of Republic of Kazakhstan. They occupy vast territories and affect the ecological and economic state of the region.

The world experience shows that construction is one of the most material-intensive industries [1, 2] using a wide range of applied astringent and construction mixtures. They can include a variety of man-made industrial waste [3 - 8], for example, blast-furnace granulated slag, steel-smelting slag. The phosphorous industry large-tonnage waste (phosphogypsum, phosphoric slag) is a major raw material reserve of the construction complex.

The main advantage of recycling large-tonnage anthropogenic wastes refer to the production of materials on their basis of properties and characteristics similar to those of the natural raw products and the expansion of the raw material base for the production of binding and road-building materials. The use of industrial waste can provide the construction industry with a source of cheap and already prepared raw materials. In addition, large areas of land occupied by dumps are set free, which in turn decreases the degree of environmental pollution at these sites.

The authors of this work [9, 10] collected and analyzed information on the accumulation and processing of industrial wastes from the phosphorous industry in Zhambyl region. This provided the identification of the emerging waste market and the possibility of wastes involvement in the economic circulation as raw materials for obtaining binding and composite construction materials.

EXPERIMENTAL

Anthropogenic wastes of the phosphorus industry (granulated phosphoric slag of Novozhambul Phosphorous Plant, mature phosphogypsum of the Mineral Fertilizers Plant, overburden rocks from Koksu deposit) in the dumps of LLP "Kazphosphate" were subjected to research. Samples were selected from the dumps during the autumn-summer period of 2014 - 2016.

Methods

The methods of utilization of industrial wastes are based on the study of their physicochemical properties and structure, allowing to determine the principle possibility (or impossibility) of their application to a particular production. Therefore, the experimental studies, presented in this paper, included the determination of the toxicological properties, the chemical and mineralogical composition of the anthropogenic waste samples.

The coordinates of the sampling points were determined using a portable GPSGarminOregon satellite navigator, while the interpretation of the sampling data was carried out using the MapInfo 9.0 software by building vector maps on the ground of the sampling points coordinates.

The quantitative chemical analysis of the samples was performed using spectral, spectrophotometric, potentiometric, complexometric, gravimetric, titrimetric, atomic absorption methods of analysis.

The differential thermal analysis (DTA) of the samples was performed using Q-1000/D (Hungary) derivatograph. The shooting took place in the air in the temperature range of 20°C - 1000°C applying a dynamic heating mode (dT/dt = 10 $\frac{dgree}{mnt}$). The reference substance was burnt Al_2O_3, while the sample weight was 500 mg.

The mineralogical composition was studied using X-ray diffraction analysis performed on an automated diffractometers XPertPro (Netherlands) and DRON-4 (Russia) with $Cu_{K\alpha}$– radiation (β-filter) by diffraction of powder patterns using the method of equal weights and artificial mixtures. The interpretation of the diffractograms was carried on the ground of data from the ASTM Powder diffraction files and pure minerals diffractograms.

A radioactivity study of all samples was also carried out. It was performed using "Progress-BG" scintillation gamma spectrometer. The measurements were carried out at the Department of Radiation Hygiene and Radiology of SPC "Sanitary-epidemiological examination and monitoring" division.

RESULTS AND DISCUSSION

Table 1 presents the generalized results of the average statistical laboratory studies of the phosphorous industry waste samples studied. It is evident that the limits of deviations (the minimum and the maximum content of the components) correspond to those of long-term studies. This provides the conclusion that the wastes chemical composition is relatively stable.

Table 1 shows also that calcium and silicon oxides are the main components of all wastes selected as potential materials for further research and construction composites. Aluminium and iron oxides are also present. As follows from the provisions of building materials science [11], the presence of these four oxides characterizes the hydration properties of the raw materials used as binding one in construction, and plays an important role in the manufacturing technology of mortars (portlandcement, aluminous cement, glass, fine ceramics, etc.) [4].

The preliminary evaluation of the man-made raw materials used in the production of composite construction materials is carried out by comparing the lime factor (Mo) and the activity modulus (Ma). The lime factor Mo is defined by $(CaO+MgO)/(SiO_2+Al_2O_3)$, while the activity modulus Ma – by Al_2O_3/SiO_2. Mo characterizes the hydraulic properties of the raw materials used. The latter are found basic in case Mo > 1 components, while they are acidic if M0 < 1. Raw materials of a lime factor

Table 1. The average chemical composition of waste products of the phosphorous industry of Zhambyl region.

Names of wastes	The average content of components, mass %								
	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	CO_2	P_2O_5	SO_3	Ignition loss
Granulated slag, NZhPhP	41,44	35,89	8,26	1,3	5,15	<0,1	1,49	0,89	-
Dolomith, overburden rocks of Karatau	0,13	29,16	21,77	<0,1	3,21	45,87	0,06	<0,1	-
Limestone, overburden rocks of Karatau	0,94	42,62	10,48	<0,1	2,86	42,88	0,12	<0,1	-
Phosphogypsum, pile dumps of MFP	13,33	26,59	0,48	0,45	0,80	<0,1	1,03	42,71	5,94
Phosphate siliceous schist of Koksu deposit	61,1	5,04	2,41	9,18	4,79	3,63	5,76	<0,1	4,25
Phosphate siliceous schist of Koksu deposit	75,18	4,48	2,02	3,70	3,19	1,21	5,39	<0,1	1,43

Table 2. Waste products radioactivity study results of the phosphorous industry of Zhambyl region.

Name of a sample	Sampling point	Volume activity, Bq/kg			
		Th - 232	Ra - 226	K - 40	Effective volume activity, Bq/kg
Granulated slag	NZhPhP dump	27±10	163±23	124±49	209±28
Phosphogypsum	pile dumps of MFP	12±8	75,2±16	103±35	100±37
Dolomith	overburden rocks of Karatau	7±3,0	16,2±9	127±37	37±17
Limestone	overburden rocks of Karatau	16,9±10,0	11,0±8,0	66,0±27	39±12,0
Phosphate siliceous schist	Koksu deposit	18±9,0	30,0±7,3	79±29	60,7±14,0
Phosphate siliceous schist	Koksu deposit	11,0±5,0	22±8,0	93±25	45±11

greater than 1.0 have high hydraulic activity and stronger binding properties accordingly. The results of lime factor calculation are of importance for the production of mineral knitting materials.

The compliance of the wastes studied with the standards for the content of radionuclides is also investigated (Table 2). The sanitary-epidemiological conclusion derived confirms the possibility of using these wastes as mineral raw materials for the production of all types of construction materials without restrictions. The total radionuclides specific activity of each waste type studied does not exceed 370 Bq/kg, i.e the requirements of SanPiN 2.6.1.2523-09 are met.

Based on the chemical and phase composition analysis of the phosphate industry wastes in Zhambyl region the authors of refs. [12, 13] have suggested the possibility of obtaining composite non-burning binders from these industrial wastes.

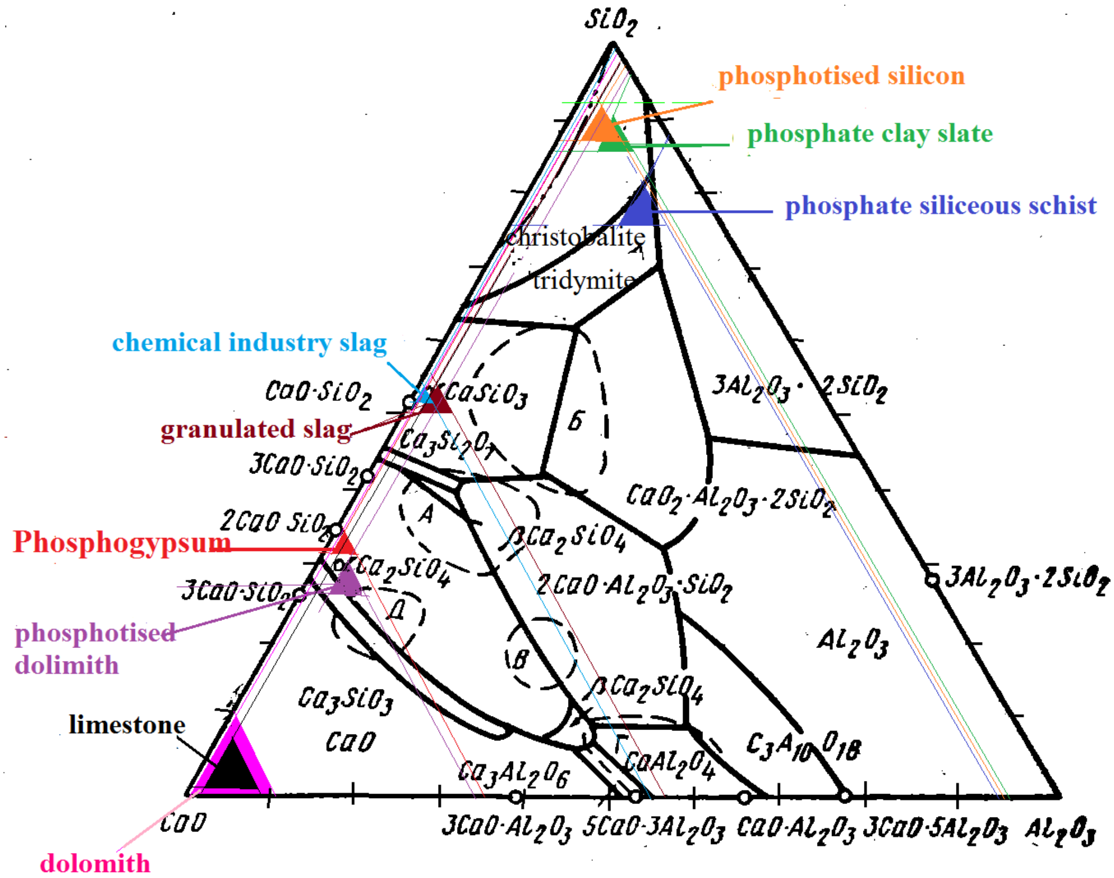

Fig. 1. Areas of technical products and wastes in system CaO - Al_2O_3 -SiO_2.

In order to determine the optimal main oxides composition required for binding materials, it is suggested to use the diagram of the system CaO – SiO_2 – Al_2O_3 (Rankin diagram) as a technical model. The system pointed out plays an important role in the technology of production of portlandcement, aluminous cement, chamotte and high-alumina refractories, glass, fine ceramics [14], since it gives an idea of the quantitative composition of CaO, SiO_2, Al_2O_3, having main impact on the processes of hydration and hardening of binding construction materials.

Fig. 1 shows the three-component system diagram, where the areas corresponding to the compositions of the various technical products are identified. In particular, the “D” area corresponds to portlandcement, which nowadays has the best physical, mechanical and technical characteristics of all binders. The Rankin’s triangle outlines also the chemical and mineralogical composition of the phosphorus industry wastes studied.

The present investigation focuses on mathematical modeling of the construction composites containing the optimum ratio of the chemical oxides provided by the raw materials under study – phosphogypsum, granulated phosphorus slag, limestone, phosphate-clay slate, phosphate-siliceous schist. During the design, the initial content of the main four oxides CaO, SiO_2, Al_2O_3, Fe_2O_3 included in the composites aimed at is referred to their content in portland cement as a binder of high physico-mechanical characteristics. Other oxides are not considered because they have insignificant effect on the physico-mechanical characteristics of the binding materials formed and the hydration processes followed. Aiming to obtain new composite building materials on the Rankin diagram, the portland cement area (D) is selected. Its boundaries are modified to include the physico-chemical characteristics of the raw components that most closely correspond to its typical composition and generalized characteristic features. The calculations required are carried out using the Microsoft Office Excel optimization method. The designed composites

Table 3. The results of charge mixture calculation of new construction composites from the waste of the phosphorous industry of Zhambyl region.

Composite 1	Phosphate clay slate	Phosphogypsum	Limestone	Portlandcement
CaO	5,04	64,53	92,06	67,85
Al_2O_3	4,07	0,78	0,22	5,38
Si_2O	87,11	33,16	2,00	23,41
Fe_2O_3	3,78	1,71	5,74	3,35
Charge mixture potential composition, mass %	7,11	50,49	37,71	4,77
Composite 2	Phosphate siliceous schist	Phosphogypsum	Limestone	Portlandcement
CaO	6,74	64,53	92,06	67,85
Al_2O_3	11,61	0,78	0,22	5,38
Si_2O	74,68	33,16	2,00	23,41
Fe_2O_3	5,98	1,71	5,74	3,35
Charge mixture potential composition, mass %	6,23	55,09	34,45	4,79
Composite 3	Granulated slag	Phosphogypsum	Limestone	Portlandcement
CaO	42,84	64,53	92,06	67,85
Al_2O_3	1,53	0,78	0,22	23,41
Si_2O	49,41	33,16	2,00	5,38
Fe_2O_3	6,45	1,71	5,74	3,35
Charge mixture potential composition, mass %	10,77	30,91	53,56	4,76

composition is determined on the ground of the sum of all components contents. It has to be close to one (the sum should be close to 100 mass %). Thus three new construction composites are designed (Table 3):

- Composite 1: phosphate clay slate – phosphogypsum – limestone;
- Composite 2: phosphate siliceous schist – phosphogypsum – limestone;
- Composite 3: granulated phosphorous slag – phosphogypsum – limestone.

Portland cement is added as an activator to each composite in an amount of 5 % of the total mass of the mixture. The system approach used to design a multicomponent mineral binder composition provides to obtain composites of a complex structure containing mineral materials (wastes) of various properties.

Based on the studies carried out, a technological scheme is advanced (Fig. 2). It provides the simultane-

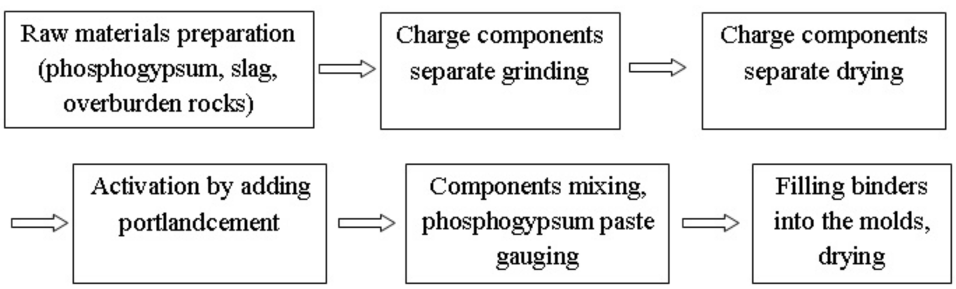

Fig. 2. Technological scheme for obtaining an unburned mineral binder.

ous production of an unburned multicomponent phosphogypsum binder and construction products (gypsum blocks, gypsum partitions, etc.). In accordance with this scheme the initial components of the charge are ground to a certain size (separate grinding), then the components are dried separately. The heat treatment of phosphogypsum proceeds at 2000°C until the transition of calcium sulfate dihydrate into hemihydrate. The remaining components are then dried at 1050°C. Then all components of the charge are mixed with the addition of the calculated amount of portlandcement (activator). A predetermined amount of water is added and gauged into the phosphogypsum paste. After thorough mixing the paste is filled into molds of building blocks. The latter are dried in air without access of moisture.

The crushed samples of composites 1, 2, 3 referring to the phosphogypsum binders obtained are additionally analyzed. Their physico-mechanical characteristics and strength are identified by standard methods. Standard samples presenting test-beams of 40 mm x40 mm x160 mm are used to determine the compressive strength and bending. The test results obtained show that composites 1, 2 and 3 meet the requirements of the standard for slowly hardening gypsum binders of grade G-4 and can be used as binders in the construction and road construction industry.

The hardening of the phosphogypsum binder (composites 1, 2, 3) is determined by X-ray phase and thermal analysis.

CONCLUSIONS

On the basis of generalization of the building materials science and investigations in the field of synthesis of unburned binding systems, a method for the integrated use of industrial wastes is advanced with the aim of maximizing their involvement in the production of building materials. In accordance with the requirements of the modern regulatory documentation, a system for assessing the properties and characteristics of the industrial wastes is developed. It provides to identify secondary industrial products of potential application in the construction industry. A technical model for the design of construction material raw mixtures on the ground of the three-component system $CaO - SiO_2 - Al_2O_3$ is developed. A rational composition of a multicomponent mineral binder based on the chemical and mineralogical composition of the initial raw mixtures is identified using this model. Thus an integrated use of the secondary products of Zhambyl region phosphorous industry is achieved.

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REFERENCES

1. L.I. Dvorkin, Stroitelnyie materialy iz otkhodov promyshlennosti, Rostov-na-Donu: Feniks, 2007, 368, (in Russian).
2. L.I. Dvorkin, Stroitelniye mineralniye vyazhuschie materialy, Moskow, Infra-Ingineria, 2011, 554, (in Russian).
3. E.A. Karpovich, S.V. Vakal, A.E. Zolotarev, Otrabotka promyshlennogo variant technologiy pereabotki phosphogipsa na gipsovoe vyazhuschee, Material of XVI international scientific conference "Ecologia I zdoroviye zheloveka. Okhrana vozdushnogo I vodnogo basseinov. Utilizatsia otkhodov", Kharkov, UKNTC "Electrostal", 2008, 2, 234-238, (in Russian).
4. R.N. Mirsayev, I.I. Akhmadullina, V.V. Babkov, I.V. Nedoseko, A.R. Gaitova, V.V. Kuzmin, Gipsoshlakovye kompositsii iz otkhodov promyshlennosti v stroitlnykh technologiyakh, Stroitelniye materialy, 2010, 7, 4-6, (in Russian).
5. A.G. Kapruyshina, G.V. Bondarenko, Proektirovanie sostava kompositsionnogo bezobzhigovogo vyazhuschego na baze tekhnogennykh otkhodov Cherepovetskogo promyshlennogo uzla I issledovanie ego tchnicheskikh kharakteristic, Khimicheskaya promyshlennost segodniya, 2011, 11, 37-41, (in Russian).
6. N.V. Chernysheva, S.V. Sverguzova, G.I. Tarasova, Poluchenie gipsovogo vyazhuschego iz fosfogipsa Tunisa, Stroitelniye materialy, 2010, 7, 28-30, (in Russian).

7. Huang Yun, Zongshou Lin, Issledovanie vyazhuschego na osnove fosfogipsa, staleplavilnogog shlaka, domennogo granulirovannogo shlaka I izvestniyaka. Investigation on phosphogypsum steel slag sgranulated blast-furnace slag slimestone cement, Constr. and Build. Mater., 2010, 6, 24, 1296-1301.
8. Huang Yun, Zongshou Lin, Vyazhuscheye na osnove fosfogipsa, molotogo domennogo granulirovannogo shlaka I portlandcementa, A binder of phosphogypsum-ground granulated blast furnace slag-ordinary portland cement, J. Wuhan Univ. Technol. Mater. Sci. Ed., 2011, 3, 26, 548-551.
9. Kh.Kh. Turgumbayeva, T.I. Beisekova, I.Z. Lapshina, R.KH. Turgumbayeva, A.Zh. Abildayeva, M.S. Ikanova, Sistemniyi analiz utilisatsii oykhodov fosfornoi promyshlennosti na primere TOO "Kazkhosophate", Khimicheskiy jurnal Kazakhstana, 2012, 4,198-204, (in Russian).
10. Kh.Kh. Turgumbayeva, T.I. Beisekova, I.Z. Lapshina, S.V. Vakal, I.N. Kerimbayeva, M.Zh. Shanbayev, Formirovanie mestnoi syrievoi bazy na osnove technogennykh otkhodov Zhambylskogo regiona , Khimicheskiy jurnal Kazakhstana, 2013, 2, 151-157, (in Russian).
11. L.I. Dvorkin, O.L. Dvorkin, Stroiyelnoye materialovedenie, Moskow, Infra-Ingineria, 2013, 832, (in Russian).
12. Kh.Kh. Turgumbayeva, T.I. Beisekova, I.Z. Lapshina, A.Zh. Abildayeva, Innovatsionniy potentsial okhodov TOO "Kazphosphate", Promyshlennost Kazakhstana, 2012, 4, 28-30, (in Russian).
13. Kh.Kh. Turgumbayeva, I.Z. Lapshina, T.I. Beisekova, Zh.U. Abdualieva, Formirovanie svoistv minerlanykh bezobzhigovykh vyazhuschikh, Khimicheski jurnal Kazakhstana, 2016, 2, 100-107, (in Russian).
14. V.S. Gorshkov, V.G. Saveliyev, N.F. Fedorov, Phizicheskaya himiya silikatov I drugikh nugoplavkikh soedineniy, Moskow, Vysshaya shkola, 1988, 400, (in Russian).