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Problems of the Utilization of Industrial Waste Produced by the Phosphoric Industry of the Republic of Kazakhstan

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Abstract: The study shows classifies phosphoric industry waste of the Republic of Kazakhstan regarding their applications in order to identify the reserves of complex processing of waste as raw material. The results of a comparative evaluation of the physico-chemical and structural properties of the phosphoric industry waste are presented. Assessment of waste regarding such technical characteristics as alkali-lime index (Mo) and activity (SiO_2/Al_2O_3) ratio (Ma) has performed which has shown that all tested waste possess binding properties and can be used for constructional materials production. The modelling methods of composite materials compositions, based on given waste are described. The system CaO-SiO_2-Al_2O_3 diagram is introduced as a technical model for determining of the optimal composition of the main oxides, contained in the binding material. It is shown that the presence in raw components of main oxides (CaO, Al_2O_3, SiO_2, Fe_2O_3) which determines processes of the hydration and hardening of constructional materials is the mandatory for the modelling of composition. On the basis of generalisation of theoretical propositions of constructional materials science and research experience in the field of synthesis of chemically unfired binding systems, a method of complex processing of phosphoric industry waste to produce desired products, the constructional materials in particular is proposed.

Key words: Physico-chemical, raw material, phosphoric industry, constructional materials, theoretical propositions

INTRODUCTION

World experience shows that the construction is one of the most material-intensive industries with a wide assortment of used binders and mortars which may include a variety of technogenic waste, industrial waste such as granulated blast slag, steel slag (Lin, 2011; Martinez *et al*., 2010; Huang and Lin, 2010).

The most important raw material resource for constructional complex is enormous amount of phosphoric industry waste, (phosphogypsum, phosphorus slag) (Lin, 2011; Martinez *et al*., 2010; Huang and Lin, 2010; Chernisheva *et al*., 2010; Yang *et al*., 2009).

One of the current trends of building materials are research to develop effective new composites based on industrial waste has a low cost and meet the modern requirements of durability and operational reliability (Kaptyushina and Bondarenko, 2011; Mirsaev *et al*., 2010). At the moment Kazakhstan has accumulated millions of tons of wastes of phosphoric industry which occupy large areas and affect the ecological and economic state of society.

The researchers of this research carried out gathering information on the volume of the accumulation and processing of phosphoric industry waste of Zhambyl region has allowed to identify the emerging waste market and possible volumes of their involvement in economic turnover as a raw material or binders and composite building materials (Turgumbayeva *et al*., 2012a, b; Lapshina *et al*., 2012). Using industrial waste provide the construction industry and a source of cheap raw materials already prepared. At the same time recycling frees large areas of land and reduces the degree of environmental pollution.

MATERIALS AND METHODS

Experimental: Industrial waste disposal methods are based on the study of physico-chemical properties and structure, allowing to determine the principal

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opportunity (or impossibility) of their use in a particular production (Kaptyushina and Bondarenko, 2011).

The study includes determination of the chemical and mineralogical composition of the samples, taken from Kazphosphate LLC stacks. Coordinates of all sampling points are defined by portable satellite navigator GPSGarminOregon. The waste sampling data was processed by vector mapping of sampling points coordinates using software MapInfo 9.0.

Quantitative chemical analysis of samples performed, using standard spectral, spectrophotometric, potentiometric, complexometric, gravimetric, titrimetric, atomic absorption analysis methods.

Differential Thermal Analysis (DTA) of samples was performed, using derivatograph Q-1000/D (Hungary). Recording is performed in the air within the temperature range of 20-1000°C, the heating mode is dynamic (dT/dt = 10 deg/min), reference substance is calcined Al_2O_3, sample weight is 500 mg.

The study of mineralogical composition is based on examination of diffraction patterns of X-ray analysis of powder samples, using the method of equal sample weights and artificial mixtures and automated diffractometers XPertPro (Netherlands) and DRON-4 (Russia) with CuK_α-radiation (β-filter). The processing of diffraction patterns was performed using ASTM powder diffraction file data and diffraction patterns of pure minerals.

The study of radioactivity for all considered waste was conducted according to "Methods of measuring radionuclide activity" using Progress-BG scintillation gamma spectrometer. Measurements took place in the Department of Radiology and Radiation Hygiene of Scientific and Practical Centre (SPC) "Sanitary-Epidemiological Examination and Monitoring".

RESULTS AND DISCUSSION

Table 1 presents the averaged results of chemical analysis of nine different samples of phosphoric industry waste of Zhambyl region. Generalised results of overall average laboratory tests of the waste chemical composition showed that the deviation limits (minimum and maximum content of components) are within the long-term study values that lead to the conclusion about relative stability of the chemical composition of technogenic phosphoric industry waste of Zhambyl region.

Table 1 indicates that in all waste types, chosen as potential materials for further study and production of constructional composites, the main components are calcium and silicon oxides, aluminium and iron oxides are presented too. The presence of these oxides characterizes hydration properties of raw materials used for the production of binding constructional materials and plays an important role in the constructional mixtures (portland cement, aluminous cement, glass, fine ceramics, etc) production process.

A preliminary assessment of suitability of materials as raw materials for the composite constructional materials production was performed by comparison of alkali-lime index (M_o) and SiO_2/Al_2O_3 ratio (M_a):

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

$$M_a = Al_2O_3/SiO_2$$

When $M_o>1$ raw materials are considered to be basic components, when $M_0<1$-to acidic components. Calculation of raw charges of different raw materials regarding their alkali-lime index allows determining methods of utilising of different industrial waste without long-term and costly experiments.

Alkali-lime index and SiO_2/Al_2O_3 ratio, characterising the hydraulic properties of used raw components were determined based on of the averaged chemical composition (Table 1).

If the alkali-lime index of the materials does not exceed 1 and during their hydration process the formation of a large amount of monoaluminate, ferrites and calcium sulphates is not expected, the binding properties of these materials during their hydraulic hardening process can be

Table 1: The averaged chemical composition of phosphoric industry waste of Zhambyl region

	Weight content of components (%)								
Name of waste	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	CO_2	P_2O_5	SO_3	Percentage of other impurities
Granulated slag, NDPP	41.44	35.89	8.26	1.3	5.15	<0.1	1.49	0.89	-
Dolomite (overburden of Karatau)	0.13	29.16	21.77	<0.1	3.21	45.87	0.06	<0.1	-
Lime-stone (overburden of Karatau)	0.94	42.62	10.48	<0.1	2.86	42.88	0.12	<0.1	-
Molten slag, Khimprom	41.66	39.86	8.87	<0.1	4.29	<0.1	1.15	0.75	-
Phosphogypsum, stack of chemical fertilizers plant	13.33	26.59	0.48	0.45	0.80	<0.1	1.03	42.71	5.94
Phosphate chert, Koksu	61.1	5.04	2.41	9.18	4.79	3.63	5.76	<0.1	4.25
Phosphate argillite, Koksu	75.18	4.48	2.02	3.70	3.19	1.21	5.39	<0.1	1.43
Phosphated dolomite (slabby), Koksu	10.05	24.11	19.35	1.53	2.39	40.12	0.80	<0.1	<0.1
Phosphated chalcedony, Zhanatas	76.36	5.04	1.61	1.83	2.60	1.60	7.65	<0.1	2.1

Table 2: Alkali-lime index M_o and SiO_2/Al_2O_3 ratio M_a calculation results

Name of waste	Alkali-lime index M_o	SiO_2/Al_2O_3 ratio M_a
Granulated slag, NDPP	1.04	0.04
Dolomite (overburden of Karatau)	221.44	0.77
Lime-stone (overburden of Karatau)	51.06	0.11
Molten slag, Khimprom	1.17	0.01
Phosphogypsum (mature), stack of chemical fertilizers plant	1.97	0.04
Phosphate chert, Koksu deposit	0.11	0.15
Phosphate argillite, Koksu deposit	0.09	0.05
Phosphated dolomite (slabby), Koksu deposit	3.61	0.15
Phosphated chalcedony, Zhanatas deposit	0.09	0.03

neglected. When the alkali-lime index is up to 1.6 and sufficient amount of calcium compounds during hydraulic hardening is formed, the binding properties of these materials shall be taken into account. Silicate materials with alkali-lime index over 1.6 exhibit hydraulic activity which is higher as the M_o value increases (Table 2).

Obtained alkali-lime index M_o values (Table 2) indicate the possibility of using these waste for binding materials production. During selection of these wastes as raw materials for the constructional materials production, their compliance with regulations on the radionuclides content was examined. As the total specific activity of radionuclides for each type of waste does not exceed 370 Bq/kg which corresponds to the requirements of SanPiN 2.6.1.2523-09, the sanitary and epidemiological examination report confirmed the possibility of using these waste as a mineral raw material for all kinds of constructional materials without any restrictions.

During the preliminary assessment of the suitability of the phosphoric industry waste for the constructional materials production, the satisfactory gross chemical composition and the minimum contaminants content along with their chemical and mineralogical homogeneity should be ensured.

For all considered waste, the mineral composition study was conducted which analysis results are presented in Table 3.

Thus, the analysis of physical-chemical and technological properties of the phosphoric industry waste allows to recommend them as raw materials for the development of composite constructional materials composition.

Based on certain chemical and phase composition of existed phosphoric industry waste resources of Zhambyl region, researchers developed a hypothesis about the possibility of utilising the industrial waste for production of unfired binding material. It is proposed to use $CaO-SiO_2-Al_2O_3$ diagram (Rankin diagram) (Kaptyushina and Bondarenko, 2011) as a technical model for determining of the optimal composition of the main oxides, containing in binding materials. $CaO-SiO_2-Al_2O_3$ system plays an important role in the portland cement, aluminous cement, fireclay and high-alumina refractories, glass, fine ceramics production processes.

Table 3: The results X-ray diffraction analysis of phosphoric industry waste of Zhambyl region

The object of analysis	Mineralogical composition of waste: Mineral	Content (%)
Granulated slag, NDPP	Quartz SiO_2	65.9
	Halo	100
Dolomite (overburden of Karatau)	Dolomite $CaMg(CO_3)_2$	100.0
Lime-stone (overburden of 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
Molten slag (Khimprom plant)	Quartz SiO_2	44
	Rankinite $Ca_3Si_2O_7$	13.7
	Apatite, blue $(Ca_5(PO_4)_3F$	11.7
	Laihunite $(Fe_{1.57}Mg_{.03})(SiO_4)$	10.6
Phosphogypsum mature, stack (Chemical Fertilizers plant)	Gypsum $CaSO_4{\bullet}2H_2O$	100
Phosphate chert, (Koksu deposit)	Quartz SiO_2	64.9
	Hydroxylapatite $Ca_5(PO_4)_3(OH)$	12.7
	Dolomite $CaMg(CO_3)_2$	11.0
	Calcite $Ca(CO_3)$	5.9
	Mica (muscovite) $Kal_2(AlSi_3O_{10})(OH)_2$	5.5
Phosphate argillite, (Koksu deposit)	Quartz SiO_2	81.0
	Hydroxylapatite $Ca_5(PO_4)_3(OH)$	- 19.0
Phosphated dolomite (slabby) (Koksu deposit)	Quartz SiO_2	2.9
	Dolomite $CaMg(CO_3)_2$	97.1
Phosphated chalcedony, (Zhanatas deposit)	Quartz SiO_2	68.7
	Hydroxylapatite $Ca_5(PO_4)_3(OH)$	- 13.4
	Dolomite $CaMg(CO_3)_2$	11.6
	Calcite $Ca(CO_3)$	6.3

Figure 1 shows a composition triangle of this system with highlighted areas that correspond to compositions of different technical products, used in technology. Analysis of the location of different constructional materials and raw components regarding their chemical and mineralogical composition on $CaO-SiO_2-Al_2O_3$ system indicates that the studied phosphoric industry waste are in close proximity to the border of portland cement which is taken for a reference. For new constructional composites production it is proposed to reduce the initial composition of raw materials (waste) oxides to the composition of the oxides (CaO, Al_2O_3, SiO_2, Fe_2O_3) of portland cement as a binder with high physical and mechanical properties.

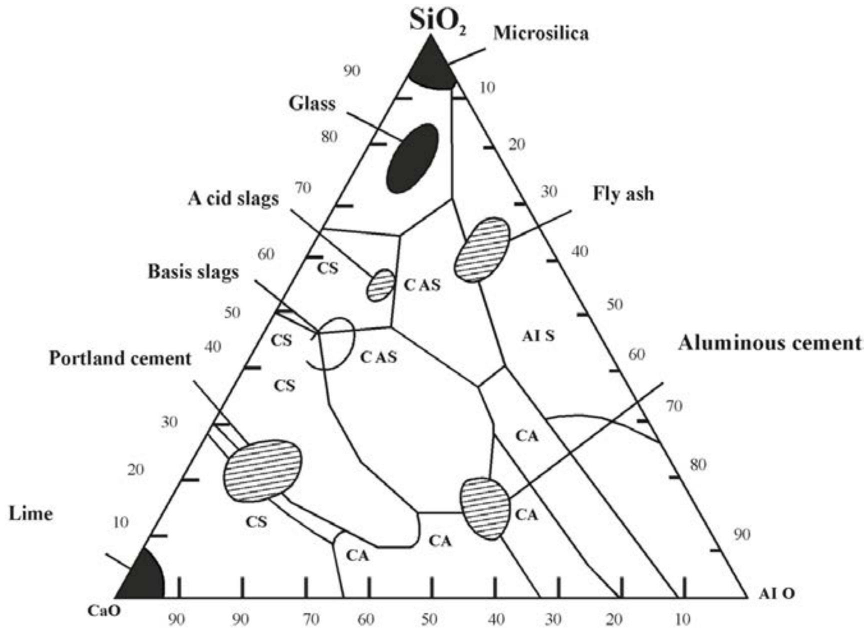

Fig. 1: Technical Products Areas of $CaO-Al_2O_3-SiO_2$ system

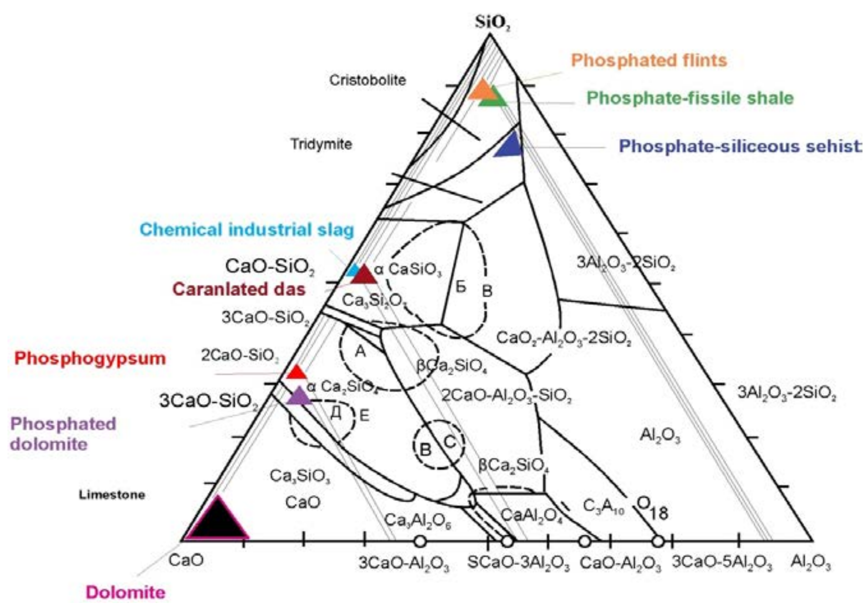

Fig. 2: Diagram of $CaO-SiO_2-Al_2O_3$ system condition

Location areas of phosphoric industry waste on the of $CaO-SiO_2-Al_2O_3$ phase diagram are determined by the limits of minimum and maximum oxides content values. Using Table 1 data, the amount of basic oxides CaO, SiO_2, Al_2O_3, Fe_2O_3 of studied raw materials is reduced to 100% and based on the obtained results, each oxide fractions are calculated separately (Table 4).

The results of comparison of boundary values of the phosphoric industry wastes based on the obtained data with the location areas of minerals on Rankine diagram indicate that location areas of chemical and mineralogical compositions are practically identical (Fig. 2).

When on the Rankin diagram in the $CaO-SiO_2-Al_2O_3$ system (Fig. 2) designate some area (E) which borders the

Table 4: Minimum and maximum values of the basic oxides content of the phosphoric industry waste of Zhambyl region, reduced to 100%

Baasic oxide	Max. content (%)	Summition (%)	Min. content (%)	Summition (%)
Granulated slag, NDPP				
Basic oxide	Maximum content (%)	Σ = 89.01 = 100%	Minimum content (%)	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
Dolomite (overburden of Karatau)				
Basic oxide	Maximum content (%)	Σ = 34.03 = 100%	Minimum content (%)	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
Lime-stone (overburden of Karatau)				
Basic oxide	Maximum content (%)	Σ = 48.51 = 100%	Minimum content (%)	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
Molten slag, Khimprom				
Basic oxide	Maximum content (%)	Σ = 89.71 = 100%	Minimum content (%)	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
Phosphogypsum (mature), stack of chemical fertilizers plant				
Basic oxide	Maximum content (%)	Σ = 43.99 = 100%	Minimum content (%)	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
Phosphate chert, Koksu deposit				
Basic oxide	Maximum content (%)	Σ = 82.40 = 100%	Minimum content (%)	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
Phosphate argillite, Koksu deposit				
Basic oxide	Maximum content (%)	Σ = 87.52 = 100%	Minimum content (%)	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
Phosphated dolomite (slabby), Koksu deposit				
Basic oxide	Maximum content (%)	Σ = 40.79 = 100%	Minimum content (%)	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
Phosphated chalcedony, Zhanatas deposit				
Basic oxide	Maximum content (%)	Σ = 87.46 = 100%	Minimum content (%)	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

physical and chemical characteristics of the raw components (A-C) shell be reduced to with most close corresponding to its typical composition and generalised specific features, it is possible to obtain a new composite constructional material.

The most significant area of $CaO-SiO_2-Al_2O_3$ system is the portland cement area (E) which mechanical and technical characteristics currently are the best out of all binding materials and which production is highly power consuming.

For maximum approximation of the chemical composition and properties of the components areas (A-C) to the chemical composition of the portland cement area (E), the optimisation program calculation, using Microsoft Office Excel was performed (Table 5).

Table 5 presents the calculation results, using Microsoft Office Excel of three new constructional composites which quantitative composition of oxides of raw components (wt. %) is the most approximate to the quantitative composition of the oxides of portland cement.

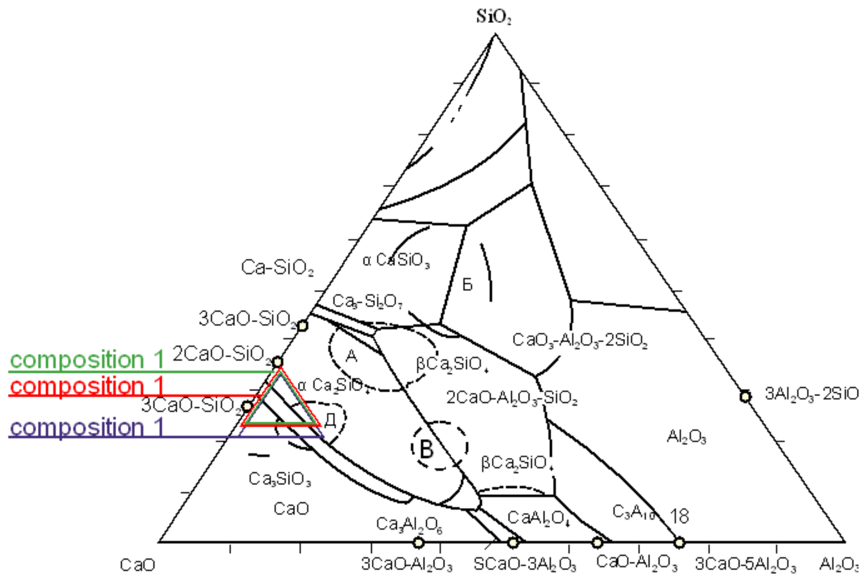

Fig. 3: Diagram of $CaO-SiO_2-Al_2O_3$ system condition

Table 5: Results of calculation of the charge composition of new constructional composites of phosphoric industry waste of Zhambyl region

Charge components	Charge composition (%)	Total charge composition (%)
Composite 1		
Phosphate cherts WT.	7.11	95.32
Phosphogypsum	50.49	
Lime-stone	37.71	
Composite 2		
Phosphate cherts	6.23	95.77
Phosphogypsum	55.09	
Lime-stone	34.45	
Composite 3		
Phosphate cherts	10.77	95.24
Phosphogypsum	30.91	
Lime-stone	53.56	

The portland cement as the activator in amount of 5% of the components mixture total weight is added into each composite. Thus, a systematic approach for the design of a multi-component composition of mineral binder, resulted in the complex structured composite materials (compounds 1-3), consisting of mineral materials (waste) with different properties and attaining new properties as the result of their combination (Fig. 3).

Based on performed studies, the systematisation of phosphoric industry waste regarding their applications in construction in order to identify additional reserves of their complex management by incorporating in closed and processing cycles as part of the specialised complexes was conducted.

CONCLUSION

Based on generalisation of theoretical propositions of constructional materials science and research experience in the field of synthesis of chemically unfired binding systems, a method of complex utilising of the industry waste for their maximum implication into production of constructional materials is introduced. In compliance with the requirements of the effective regulatory documents, the system for assessment of the industrial waste properties and characteristics was developed, allowing identifying industrial by-products in order to determine their potential construction industry processing methods. Using ternary systems in the industry to predict the solid phase formation in compositions with different chemical and mineralogical composition allowed offering the use of the basis of the ternary system $CaO-SiO_2-Al_2O_3$ as a technical model for the design of a raw mixture of constructional materials. Using this model, the rational composition of multicomponent mineral binder, based on the chemical and mineralogical composition of the raw mixture for complex utilising of phosphoric industry by-products of Zhambyl region is determined.

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