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**ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ**

БАЯНДАМАЛАРЫ

ДОКЛАДЫ

**НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН**

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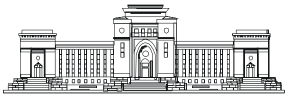

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ENVIRONMENTAL DISPOSAL OF LARGE-TONNAGE INDUSTRIAL WASTE FOR THE PRODUCTION OF FIRE EXTINGUISHING POWDERS

Abstract. The given research presents the classification of fire extinguishing and explosion suppression compositions. Phosphogypsum is a large-scale waste from the production of orthophosphoric acid, obtained by extraction from phosphorite with sulfuric acid. The presence in phosphogypsum of pollutants in the form of phosphorus and fluorine compounds, during the preparation of which sludge wastes are emitted into the air, adversely affecting not only the human body, but also the environment. As a result of studies conducted on the study of multi-purpose industrial wastes, including phosphogypsum and its use as flame retardants, the study of reactive, physicochemical, thermal and fire-resistant properties, it is shown for the first time that it is useful as a localization and extinguishing of combustible solid combustible materials and the use of phosphogypsum in fire extinguishing powder formulations.

Keywords: Fire extinguishing powders, explosion-suppressing composition, large-scale industrial waste, powder efficacy, gypsum, phosphogypsum.

Introduction. Currently, in the Republic of Kazakhstan, over 19 billion tons of solid household and industrial wastes have been accumulated. Municipal solid waste is only partially recycled, which leads to the deterioration of the sanitary conditions and epidemiological situation in large cities. Thus, disposal of household industrial waste demands substantive action.

In Zhambyl region, located in the south of Kazakhstan, Kazphosphate LLP is recognized as the largest environmental polluter. More than 90% of industrial pollution are phosphate production wastes, such as cast and granulated electrothermophosphoric slag, phosphogypsum.

At present, the rational and integrated use of industrial waste from various sectors of the economy in the construction industry comprises less than 20% of its annual production. For example, in the manufacture of building materials for various purposes from phosphate and metallurgy production wastes, an insignificant part of molten slag and phosphogypsum is used. Mining and chemical industries produce hundreds of tons of mineral raw materials annually, from which by-products and industrial wastes that are suitable for obtaining building materials make up about 10% of the rock mass. Significant amounts of these materials can be used as additives in the manufacture of concrete, reinforced concrete, bricks and porous aggregates. The use of multi-ton waste phosphoric acid remains insufficiently explored.

Industrial waste can substantially reduce the consumption of materials for the production of building materials and products, as well as improve quality and reduce production costs in road construction, taking into account areas of man-made waste or deposits of local natural materials

Foreign and domestic experience confirms that the most promising is the use of ash, fuel slags and slags of metallurgical industries as aggregates in the preparation of concrete, cements, and porous aggregates.

It should be noted that when using ash and slag in concrete instead of cement, heat conductivity and shrinkage deformations of concrete decrease, whereas its water permeability, sulfate resistance and other indicators, such as frost- and water resistance, increase.

Chemical and processing industries waste is used for production of composite additives for concrete, by which various properties of the mixture are regulated. These additives reduce cement costs and increase the strength of the concrete; regulate the process of setting, hardening and heat generation; reduce the duration of heat and moisture treatment; increase frost- and water resistance, density, resistance in different corrosive environments.

The use of additives in the preparation of concrete mixtures significantly improves the quality and efficiency of concrete and reinforced concrete structures, reduces the energy intensity and complexity of technological processes. The use of concrete and reinforced concrete in the construction industry accelerates the pace of reconstruction and leads to the accumulation of substandard products and waste [1].

In the construction industry, one of the main ways to meet the needs for improving the range and quality of manufactured building materials is the processing of waste from the mining, metallurgical, energy and chemical industries, associated products from the extraction and enrichment of mineral raw materials, waste from processing of natural materials, secondary resources.

According to the Environmental Code of the Republic of Kazakhstan [2, Chapters 6 and 32], environmental protection is defined as a system of state and public measures aimed at preserving and restoring the environment, preventing the negative impact of economic and other activities on the environment and eliminating its consequences. However, to solve environmental problems in our country, it is not enough to have a system of authorized state bodies of environmental safety. This requires the overall fostering ecological culture among our citizens, the formation of responsibility toward future generations.

A significant part of industrial waste in South Kazakhstan has been produced by the former Shymkent phosphorus plant, where, until 1995, above 3 million tons had accumulated; by the former Shymkent lead plant (more than 4 million tons of sludge); from the coal mining industry at the Lenger field (about 6 million tons of waste).

The emerging problems of dumping and storage of wastes from various industries in the Republic of Kazakhstan require the adoption of a government program for their disposal and the creation of a regulatory framework, the strengthening of measures to protect the environment and the subsoil of the earth. In manufacturing plants that produce and dump industrial waste, incentives should be generated for waste management and recycling. Therefore, to improve the ecological situation in the region, it is necessary to neutralize, recycle or dispose of industrial waste without harming the environment.

Compositions based on gypsum, as well as products made from them, are widely used as flame retardant materials. The heat-shielding, sound-insulating properties and fire resistance of gypsum materials surpass cement-based materials, and they are unparalleled in construction in terms of decorative, comfortable, and environmental performance.

At the same time, the depletion of the reserves of natural gypsum stone and their uneven distribution in the territory of Kazakhstan forced us to look at industrial waste in the form of phosphogypsum and fluorogips. The largest tonnage waste currently is phosphogypsum - a by-product obtained in the production of orthophosphoric acid and mineral fertilizers. Phosphogypsum is obtained in the form of sludge waste with humidity up to 50%.

However, the presence in phosphogypsum of pollutants in the form of phosphorus and fluorine compounds, during the preparation of which sludge wastes are emitted into the air, adversely affecting not only the human body, but also the environment.

At the same time, in view of the content in the phosphogypsum composition of undesirable impurities, the processing of phosphogypsum into flame retardant binders requires significant costs associated with its preparation for the production of flame-retardant gypsum compounds. Analysis of the existing methods of preparing phosphogypsum for the production of flame-retardant gypsum compositions showed that, to date, four methods are used to remove impurities:

1. Washing of phosphogypsum with water;
2. Washing in combination with neutralization and sedimentation of impurities in aqueous suspension;
3. The method of thermal decomposition of impurities;
4. Introduction of neutralizing, mineralizing and crystallization regulating additives before and after calcination.

The first and second methods are associated with the formation of significant m³ of contaminated water (2-5 m³ per 1 ton of phosphogypsum), and the high costs of their removal and purification.

The third method, due to its energy consumption, was also not widely used, since it is based on the burning of phosphogypsum before the formation of soluble anhydrite, with its further hydration and re-burning to hemihydrate.

The fourth method of removing impurities has not yet been widely used, since for the implementation of this method requires scarce additives and, most importantly, they do not provide the constant properties of flame-retardant gypsum compounds.

In this regard, in order to prepare phosphogypsum for the production of flame retardant gypsum compounds, it is proposed to carry out the mechanochemical activation of phosphogypsum together with dolomitic lime using the universal disintegrator-activator technology (UDA-technology) [3].

Disintegrator is a high-speed impact grinder, which, with conventional grinding, initiates mechanochemical processes that increase the reactivity of materials, including mineral ones.

The rationale for this proposal can serve as the results of the following works. Y. Hint [3], Boldyrev V.V. [4] and a number of other researchers, analyzing the processes taking place in mineral materials during their machining with the UDA-technology, concluded that during such processing shear stresses and crystal destruction occur, usually accompanied by an increase in temperature and pressure, breaking of chemical bonds on newly formed surfaces and the formation, as a result, of centers with increased activity.

The authors of [5] found that the processes of drying and grinding can proceed directly in the grinder of a shock-reflective action without the supply of a high-temperature drying agent from the outside. Their studies showed that by grinding a polymer material with an initial moisture content of 15 ... 20%, a product with a final moisture content of 0.02% or less is obtained at the outlet of the shredder. This is because in such grinders the drying process is intensified by increasing the mass transfer surface, the turbulence of the air flow, the presence of internal heat sources arising in the gas and solid phases during the grinding process [4].

The authors of [6] on various systems showed the passage of the following mechanochemical reactions in substances that are jointly processed in a disintegrator:

1. Recovery of metals from oxides (removal from ZnO to 20% O2);
2. Decomposition of carbonates;
3. Reactions in the solid phase.

Based on the above, it is assumed that when disintegrating the phosphogypsum together with dolomitic CaMg (CO3) 2 limestone (Satka, chemical composition: CaO - 30.41%; MgO - 21.86%; CO2 - 47.73%), in addition to the removal of chemically bound water and the decomposition of carbonates, it is possible for a chemical reaction of fluorine to be bound by the reaction:

$$Mg + F2 = MgF2 \quad (1)$$

either by reaction:

$$Ca + F2 = CaF2 \quad (2)$$

At different stages of the technological process, during the preparation of mixtures, harmful substances affecting the environment are formed. Their types are listed in Table 1 [7].

Table 1-Types of environmental impact in the process of mixtures preparation

Impact types	Technological processes and operations
Dust release	*Preparatory operations* Unloading of raw materials, its storage, crushing, drying, and mixing
Weathering inert materials from storage depots	Excessive reserves of sand, crushed stone, technical salt
Soil and water pollution	*Fire (oxidative) processes* Leakage of fuel, oil, bitumen and untimely elimination
Air pollution by toxic substances	Work of the drying drum, oil burners Non-observance of the regulations for the maintenance of cyclones, scrubbers, dust precipitation chambers, other cleaning devices
Dust release	The presence of open bitumen storage, open ground
Soil pollution by solid waste	Solid waste generation and irregular export for recycling and disposal

According to the Moscow Automobile and Road Construction State Technical University (MADI-TU), the amount of harmful substances emitted into the atmosphere per 1 ton of asphalt-concrete mixture is as follows (kg/t): 15.04 of inorganic dust, 0.14 of hydrocarbons, 0.01 of sulfur dioxide, 0.0005 of carbon monoxide, 0.0004 of phenol, and 0.000045 of nitrogen oxides.

Table 2 provides information on the use of phosphate production wastes, where molten and granulated electrothermophosphoric slag is used in the production of ready-mixed concrete instead of building sand and natural crushed stone, with the production of ready-mixed concrete.

Table 2- The volume of formation and accumulation of waste products of yellow phosphorus, mineral fertilizers and coal mining

Name of industrial waste	The accumulated waste and the annual release, thousand tons	Occupied area of industrial waste accumulation, ha	Volume of accumulated waste utilization, thousand tons
Phosphogypsum produced by the plant of mineral fertilizers "Kazphosphate" LLP	4.3 annually	34.8	1.1
Granulated electrothermophosphoric slag produced by "Kazphosphate" LLP	2.45 annually	1.2	-
Cast granulated slag of Taraz Metallurgical Plant	accumulated 8,000	44.3	3.4
Internal overburden of coal from the Lenger field	accumulated 6,000	53.6	-

The main measures to reduce the environmental impact at enterprises of processing raw materials and obtaining energy resources are:

(i) Rational and comprehensive use of material and energy resources in the application of not only the targeted raw materials, but also secondary materials.

(ii) Prevention of production waste generation and minimum refund of off-test products for processing.

(iii) Recycling of waste products in the form of ferrous and non-ferrous slag, plastics and recycled operating materials, as well as in the production of yellow phosphorus and mineral fertilizers, much of which is emitted in the form of solid and liquid waste.

Phosphogypsum and its physic-chemical properties. Phosphogypsum is a large-scale waste from the production of orthophosphoric acid, obtained by extraction from phosphorite with sulfuric acid. About 430 thousand tons of phosphogypsum are produced annually. In the Republic of Kazakhstan, extraction orthophosphoric acid is used as a raw material for the production of phosphate, concentrated simple and complex fertilizers, such as amorphous, double superphosphate, notophs, nitrophos, etc. [8, p. 32-38], [9, p. 27-30].

Today, the main way to dispose phosphogypsum in the Republic of Kazakhstan is storage in dumps, which has a negative impact on the environment. The appearance of phosphogypsum formed during the production of extraction phosphoric acid is shown in Figure 1.

Figure 1 - The appearance of phosphogypsum

As a result of leaching of harmful substances by atmospheric precipitation and their dusting in dry weather, the air, groundwater and surface water, the soil and vegetation layer are polluted [10].

The average granulometric composition of phosphogypsum is shown in Table 3.

Table 3-The average granulometric composition of phosphogypsum.

Size of fractions, mm	2-5	1-2	1-0.5	0.1-0.5	less than 0.1
Content, in %	0.3	21.8	63.6	10.1	4.2

The angle of repose of phosphogypsum obtained in the Taraz branch of Kazphosphate LLP, is determined using a plexiglass box and is within 330.

The bulk density of phosphogypsum varies between 1300 kg / m^3 depending on the size of the product.

In the production of phosphoric acid, about 6 tons of washed phosphogypsum with a specific surface area of 0.18 to 0.25 m^2/t per 1 ton of finished product is formed, the humidity of which is about 40%. In terms of dry matter, phosphogypsum contains on average (in %): 36.2 of SO3, 39.8 of CaO, about 1 of P2O5, 0.1 of Fe2O3, 0.03 of MgO3, 0.03 of K, and 0.1 of Na.

The average chemical composition of phosphogypsum obtained in the Taraz branch of Kazphosphate LLP contains (%): P2O5 total - 0.74, P2O5 water - 0.21, MgO – traces, N2O - 0.3789, Al2O3 - 0.087, F - 0.081, insoluble residue – 19.67, Fe2O3 - 0.093, CaO - 31.80, SO42 - 54.5. Table 12 shows the chemical composition of phosphogypsum.

The phosphogypsum general view enlarged 100 times and its chemical composition was established using a JSM-5610 LVc scanning electron microscope with the EDXJED-2201 chemical analysis system (JEOL, Japan) and is shown in Figure 2 [8, p. 32-38, 5, p. 27-30].

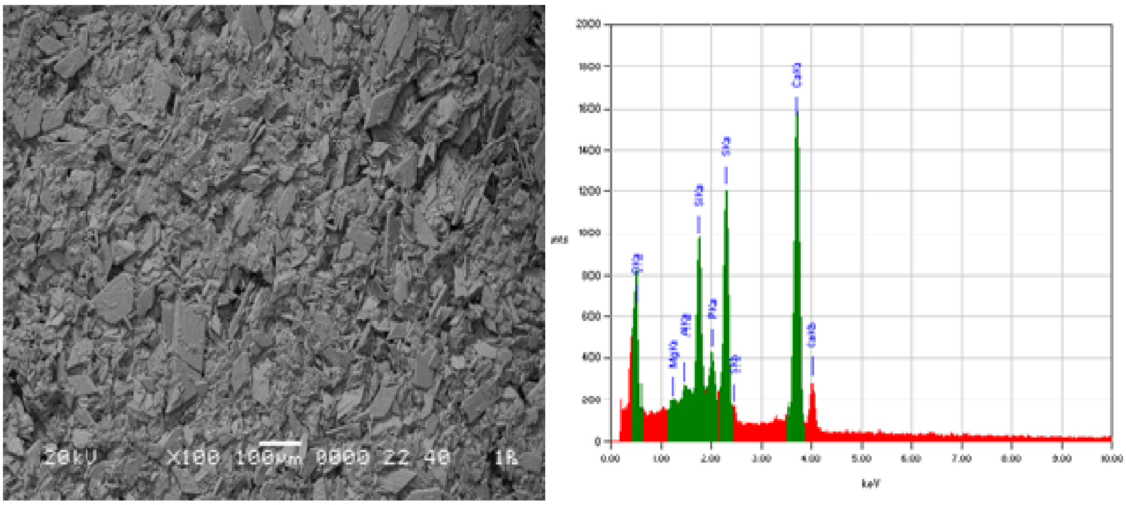

Figure 2 - General view of phosphogypsum enlarged 100 times

Hydrodynamic-active polymer compositions for increasing the efficiency of fire extinguishing using three types of gypsum: phosphogypsum, slag gypsum and class A gypsum have been applied in the author's work [11], showed that the normal density of the test is achieved with a "gypsum-water" ratio of 7:3.

The time intervals characterizing the beginning and end of the setting of gypsum from the moment it was mixed in water and in aqueous solutions of polyethylene oxide were determined on the Vicat device, the mass of the movable part of which together with the needle is (120 ± 1) g. At the same time, the beginning of the setting of gypsum was taken of its solution, when the needle does not begin to reach the bottom of the container into which it is poured, and the gypsum stone is considered formed (end of setting) if the needle enters the test specimen by no more than 0.5 mm.

Table 4- The chemical composition of phosphogypsum

Element	(keV)mass%	Error%	At%	Compound mass%	K
OK *	0,525	46,53	0,59	65,20	28,8456
Mg K *	1,253	0,72	0,13	0,66	0,5028
Al K *	1,486	0,59	0,11	0,49	0,5135
Si K	1,739	8,08	0,10	6,45	8,6563
PK	2,013	3,49	0,12	2,53	4,7441
SK	2,307	14,09	0,09	9,85	19,0820
Ca K	3,690	26,49	0,15	14,82	37,6557
Total		100,00		100,00	
O*0,000	46,45	0,00	0,00	0,00	0,0000
Mg K*1,253	0,72	0,21	1,99MgO	1,19	0,7066
Al K *1,486	0,59	0,21	0,74Al_2O_3	1,12	0,7217
Si K 1,739	8,09	0,21	19,38SiO_2	17,31	12,1655
PK 2,013	3,50	0,28	3,80P_2O_5	8,02	6,6674
SK 2,307	14,11	0,23	29,59SO_3	35,24	26,8177
Ca K 3,690	26,53	0,20	44,51CaO	37,12	52,9212
Total	100,00	100,00	100,00		

The determination of the tensile strength of the formed gypsum stone was carried out according to the following scheme. Initially, three specimens in the form of cubes with dimensions of 7.07x7.07x7.07 cm were made from the studied gypsum with various closing liquids.

For the manufacture of samples took a sample of gypsum, equal to 1.2 kg. Gypsum for 30 sec. poured into a cup of water or polymer solution, taken in an amount that corresponds to the normal density of the dough, and stirred for 1 minute. until a homogeneous mass, which is then poured into metal molds, lightly lubricated with engine oil. All forms are filled at the same time. Samples were removed from the forms after 1 hour and tested after 1.5 hours from the start of mixing. The edges of the specimen adjacent to the press plates should be parallel and not deviate from the plane by more than 0.5 mm. Samples with defects were not tested [14-16].

The load when tested on the press should increase evenly at a speed of 2-3 kg / cm^2 per second until the sample is destroyed. The compressive strength of an individual sample was calculated in kg/cm^2, as the quotient of dividing the breaking load in kg by the size of the working edge of the sample in cm^2. The compressive strength of the tested gypsum stone was calculated as the arithmetic average of the test results of three samples.

Conclusion

As a result the classification of fire extinguishing and explosion suppression compositions was investigated. The presence in phosphogypsum of pollutants in the form of phosphorus and fluorine compounds, during the preparation of wastes are emitted into the air, adversely affecting not only the human body, but also the environment. The study of reactive, physicochemical, thermal and fire-resistant properties, it is shown that it is useful as localization and extinguishing of combustible solid combustible materials and the use of phosphogypsum in fire extinguishing powder formulations.

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ӨРТ СӨНДІРЕТІН ҰНТАҚТАРДЫ ӨНДІРУГЕ АРНАЛҒАН ІРІ ӨНЕРКӘСІПТІК ҚАЛДЫҚТАРДЫ ЭКОЛОГИЯЛЫҚ ЖАҒЫНАН ҚАЙТА ӨҢДЕУ

Аннотация. Бұл зерттеуде өрт сөндіру және жарылысты басатын қоспалардың классификациясы берілген. Фосфогипс – фосфориттен күкірт қышқылы арқылы экстракциялау жолымен алынатын ортофосфор қышқылының кеңауқымды қалдықтары болып табылады. Фосфор мен фтор түріндегі ластаушы заттардың фосфогипсіде болуы, оларды дайындау кезінде пайда болатын лай қалдықтары ауаға еніп адам ағзасына ғана емес, қоршаған ортаға да кері әсерін тигізеді. Көпмақсатты өндіріс қалдықтарын, оның ішінде фосфогипсті және оның антипирен ретінде пайдалануын зерттеу, олардың реактивтік, физика-химиялық, термиялық және отқа төзімді қасиеттерін зерттеу бойынша жүргізілген зерттеулер нәтижесінде алғаш рет оның қатты жанғыш материалдарды оқшаулау және сөндіру барысында пайдалы екендігі және фосфогипстің өрт сөндіру ұнтақтарының құрамында пайдалану мүмкіндігі көрсетілген.

Түйін сөздер: өрт сөндіру ұнтақтары, жарылғыштықты басатын құрам, ірі тоннажды өнеркәсіптік қалдықтар, ұнтақтың тиімділігі, гипс, фосфогипс.

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ЭКОЛОГИЧНАЯ УТИЛИЗАЦИЯ МНОГОТОННАЖНЫХ ОТХОДОВ ПРОМЫШЛЕННОСТИ ДЛЯ ПРОИЗВОДСТВА ОГНЕТУШАЩИХ ПОРОШКОВ

Аннотация. В данном исследовании представлена классификация огнетушащих и взрывоподавляющих составов. Фосфогипс представляет собой крупномасштабные отходы производства ортофосфорной кислоты, полученные экстракцией из фосфорита серной кислотой. Наличие в фосфогипсе загрязняющих веществ в виде соединений фосфора и фтора, при приготовлении которых иловые отходы выбрасываются в воздух, отрицательно влияет не только на организм человека, но и на окружающую среду. В результате исследований, проведенных по изучению многоцелевых промышленных отходов, включая фосфогипс и его использование в качестве антипиренов, по изучению реактивных, физико-химических, термических и огнестойких свойств, впервые показано, что он полезен как локализация и тушение горючих твердых горючих материалов и использование фосфогипса в огнетушащих порошковых составах.

Ключевые слова: огнетушащие порошки, взрывоподавляющая композиция, многотонажные промышленные отходы, эффективность порошка, гипс, фосфогипс.

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