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RESEARCH FOR IMPROVING ENVIRONMENTAL ISSUES AND HEALTH AND SAFETY

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ABSTRACT

Information is provided on the waste of mining and manufacturing enterprises formed during the extraction, preparation and processing of raw materials for the target products. In particular, off-balance, substandard P_2O_5 content, phosphate-siliceous and carbonate - siliceous phosphate ores of the Karatau basin. Materials on phosphogypsum related to the technological costs of obtaining extraction phosphoric acid (EPA) by the method of leaching sulfuric acid phosphorus by the dehydrate method are presented. The concepts of chemistry occurring in the electro thermal, in the presence of a coolant and a flux, as well as chemical, with the use of H2SO4, methods of extracting phosphorus from phosphorus-containing raw materials are given. The data of differential thermal analysis of phosphogypsum is shown. The mineralogical and chemical compositions of phosphogypsum, the main technogenic waste of the process of the dihydrate method of obtaining EPA, which in the process of storage in dump dumps can lead to a violation of the ecological equilibrium state of industrial regions in the form of dust-gaseous substances, are presented.

Keywords: industrial waste, ecology, off-balance ores, phosphogypsum, chemical composition, mineral fertilizers, phosphorites fines, utilization of phosphogypsum.

INTRODUCTION

At the present stage of the development of society, the issues of ecology and improving human well-being are of paramount importance not only in the Republic of Kazakhstan, but also abroad. This situation is compounded by the fact that the waste of the chemical, metallurgical, petrochemical, mining, energy and construction industries of the state economy is not fully utilized or processed into target products, disrupting the ecological balance in industrial regions.

The world around us feels the invisible and direct impact on the environment of gaseous, liquid and solid substances, which are the costs of production.

All the above-mentioned branches of the economy are also closely connected with the agro-industrial complex, including vegetable and fruit growing, poultry farming, animal husbandry and crop production, which affect the environment and the safety of life.

For example, if you take the chemical industry, including the production of mineral phosphoric salts, fertilizers, acids, complex compounds and a single product, from extraction of raw materials to obtain the target product formed millions of tons of industrial waste solid materials in the form of off-balance ores, screening in detail in the substandard grading, dust emissions, slag, phosphogypsum and other materials, which occupies large areas of agricultural land and pasture.

Technogenic waste should be considered harmful in the broad sense of the word, since all of them are the result of mechanical, physico-chemical or chemical changes in the original biocompatible natural complexes. In a narrow sense, waste that has a sharply negative impact directly on humans, animals and plant organisms and on their habitat should be considered harmful.

Currently, man-made waste should be distinguished from hazardous, toxic and super toxic emissions. The depth of man-made interference in nature has reached such an enormous scale that it is becoming increasingly difficult to control their annual intake and predict the environmental impact of hundreds of thousands of new synthetic compounds and materials. All this violates the sanitary and hygienic working conditions of the service personnel of the enterprise for the production of extraction phosphoric acid and products based on it. Therefore, the utilization and use of off-balance-sheet phosphorites ores and phosphogypsum requires careful treatment of material resources, by reducing the amount of waste and secondary materials, industrial waste storage areas in production regions, and is an urgent problem. The introduction of new industrial and innovative technologies, improving the quality of raw materials and products on their basis, the reduction of material and energy resources through rational and integrated use, allow you to create a reliable mechanism for the functioning of the various sectors of the economy and to solve ecological problems of industrial regions of our country.

EXPERIMENTAL PART

The total global amount of orthophosphoric acid (H_3PO_4) produced during the processing of phosphate raw materials is about 20 million tons / year, from which 90% is obtained by hydrochemical and 10% by thermochemical methods [1,2].

As a phosphorus - containing raw material, apatites and phosphorites of various deposits are used in the production of phosphoric acid and their processing is carried out by two main methods-thermochemical and chemical.

The thermochemical method of processing raw materials is carried out in two stages.

At the first stage, elemental phosphorus is obtained in closed-type ore-thermal furnaces during the

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processing of raw material resources with the use of metallurgical coke and electric energy as a fluxing additive reducing agent.

Depending on the physical and chemical properties of the raw material, about 13-15 MW of electricity is consumed per 1 ton of phosphorus, 11-13 tons of phosphorite, 2-3 tons of quartzite, 2-3 tons of coke. At the second stage, phosphorus is burned in the tower by oxidizing it with air oxygen to phosphorus pentoxide (P_2O_5) hydrolysis with water or weak phosphoric acid, converting it to concentrated phosphoric acid in the hydration towers.

The chemical method is less energy-intensive and is carried out by extracting phosphorus into phosphoric acid from natural finely ground apatites and phosphorites with strong acids and mainly sulfuric acid[1, 10].

We will briefly discuss these methods.

The thermochemical method of phosphoric acid production is based on the $4Ca_5 (PO_4)$ reaction) $3F + 10 C + 21 SiO_2 = 6 P_2 + 20 CaSiO_3 + 10 CO + SiF_4$ and is carried out in special ore-thermal furnaces at a temperature of about 1600^0C. As phosphorus-containing raw materials, phosphorites of various deposits are used, as a reducing agent metallurgical coke and as flux additive quartzites. The required temperature of about 1600^0C is achieved through the use of electrical energy [4]. The resulting phosphorus gas is condensed and sent to a warehouse, where it is stored under water in containers. Then the phosphorus is oxidized with air oxygen and the resulting P_2O_5 is dissolved in an aqueous or weak acid solution. In this case, orthophosphoric acid is formed.

$P_2O_5 + 3 H_2O = 2 H_3PO_4$

The advantage of this method is the simplicity of the hardware design and the possibility of obtaining pure orthophosphoric acid, which practically does not contain impurities. The main disadvantages of the process are:

- significant consumption of material and energy resources of electricity;
- the need to use two chemically opposite processes-reduction of P+5 → PO and oxidation PO → P+5;
- the formation of a significant amount of solid waste in the form of slag up to 11-13 t/t P_4 and ferrophosphorus about 200 kg/t P_4, as well as liquid and gaseous phosphorous products that violate the ecological balance;
- complexity of hardware and technological design of electro thermal and hydro chemical methods [2-4, 9-11].

The chemical method of production of H_3PO_4 is based on an effective process of sulfuric acid extraction of apatite's and phosphorites by reactions:

$Ca_5(PO_4)_2OH + 5 H_2SO_4 = 3 H_3PO_4 + 5 CaSO_4 + H_2O$ или
$Ca_5(PO_4)_3F + 5H_2SO_4 = 3H_3PO_4 + 5 CaSO_4 + HF$,

which proceed without complications. The main difficulties are associated with the significant presence of impurities of valuable components that need to be extracted from the initial phosphorous-containing raw materials or from the resulting "tailings" of the extraction process, called phosphogypsum [2].

The main component of waste gases, along with phosphorus, carbon oxides, sulfur, etc. in the thermochemical method, it is volatilized in the form of SiF_4, and in the hydrochemical method in the form of hydrogen fluoride (t°c = 19.5°C). Fluorine is widely used in various sectors of the economy, nuclear power, in the production of polymer materials, freons, glass and ceramics. In the production of H_3PO_4, silicon tetrafluoride and hydrogen fluoride are extracted from the waste gases by 10% lime milk by alkaline absorption or in absorption columns. The absorption of HF by lime milk does not cause complications:

$Ca(OH)_2 + 2 HF = CaF_2 + H_2O$,

Tetrafluoride, along with the crystalline precipitate of calcium hexafluorosilicate, forms an amorphous silicon hydrate:

$2 Ca(OH)_2 + 3 SiF_4 = 2CaSiF_6$

Both methods of phosphoric acid production involve the formation of solid, liquid and gaseous waste.

Solid and liquid waste from the production of phosphorus and phosphoric acid can include phosphoric slags, phosphogypsum, ferrophosphorus, cottrel dust, waste water, phosphoric acids and its aqueous suspensions, gaseous compounds of phosphorus, carbon disulfide [3,4]. All these man-made wastes cause irreparable damage to the fauna and flora of the environment, as well as to humanity and living organisms. This is due to the fact that fine compounds of gaseous emissions, deposited on plants and trees, waste water, fall on the surface of the earth's soil layer, and then into the composition of plants and grasses. They feed on birds, large and small cattle, the meat of which we eat. The meat may contain various heavy metals and toxicological compounds.

In the chemical processing of phosphorites, by sulfuric acid extraction, phosphoric acid is obtained. In the technological process, significant amounts of poorly soluble calcium sulfate are formed, which is a phosphogypsum that accumulates a certain part of the target products-fluorine and phosphorus. The annual production of phosphogypsum worldwide is about 160 million tons, of which 40 million tons (25%) are produced in the United States. The total volume of phosphogypsum formation until 2006 is estimated at about 6 billion tons, of which 2.2 billion tons (37%) in the United States [5].

Phosphogypsum waste not only in Kazakhstan, but also in Russia amounts to tens of millions of tons and accumulates faster than it is disposed of, the volume of their processing reaches no more than 3%, so its processing is more relevant. They have a number of methods for processing phosphogypsum, including its condensed, production of binders, building mixes, building blocks, etc. [6]. These processes road in the

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implementation and solution of problems connected with extraction of valuable components or mixtures for the liming of soils [7].

In real conditions, production is limited to the construction of sludge storage facilities, sedimentation ponds and dumps, to which the phosphogypsum pulp is fed by hydraulic transport or in a wet state by road transport [11, 12]. When solving this problem, a number of problems arise:

- reverse intake of naturally dehydrated and dried sediment which is very difficult;
- the abrasive action of the sludge causes corrosion and destruction of pumps and pipelines;
- phosphogypsum storage depots are environmentally hazardous facilities.

RESULTS AND DISCUSSIONS

The analysis of literary sources shows that during the formation of the phosphorus sub-branch of the chemical industry of the Republic of Kazakhstan, in the 60-90s of the last century, millions of tons of off-balance waste, in terms of P_2O_5 content, of the mining complex of LLP «Kazphosphate» have accumulated in dumps.

The main industrial resources of the Karatauphosphorite basin were concentrated in five main mines: Zhanatas, Kok-Dzhon, Tiesay, Aksai, Chulaktau, which are characterized by a large extent and the presence of productive layers, according to estimates, amount to 1.2 billion tons. (about 80%). Deposits of the Karatauphosphorite basin are characterized by a complex structure and the main types of phosphate raw materials of the Karatau basin are subdivided into the following varieties, where the P_2O_5 content in the ore is (in%):

- rich phosphorite-28-30 directed for extraction;
- ordinary carbonate and siliceous-carbonate-22-26, which are extracted after flotation enrichment;
- ordinary siliceous and carbonate - siliceous-21-25 and poor (off-balance) - 18-21 are sent for electro thermal processing;
- phosphatized silicones-2-6, used as a fluxing additive in electro thermal phosphorus treatment.

According to the qualitative characteristics of phosphorus-containing ores and rocks of the Karatau basin are divided into (in %):

- balance sheet of phosphate ore - 60;
- off-balance sheet phosphorite ores-13;
- phosphate-siliceous rocks-8;
- phosphatized flints -19 [9,10,13,14].

For example, 22 million tons of phosphate-siliceous shale (PSS) has been stockpiled in the «Tsentralny» open pit of the Zhanatas deposit alone, and the process of upgrading the open pits of the Zhanatas mine to the design depth is possible to obtain about 20 million tons. The data of the analysis of the chemical composition and the normative technical documentation used during the research are shown in tables 1 and 2 of phosphogypsum from the old and new dump storage [6, 9]. P_2O_5 more than 13% of insoluble residue (H_2O) about 49%, MgO more than 1.4%, more than 5 million phosphate-shale ores accumulated in dumps of the Aksai deposit with a P_2O_5 content of more than 16%, H_2O more than 30% and MgO more than 4.5% ..
To enrich these ores to a P2O5 content of more than 20% to produce a concentrate when fed for chemical or thermal processing, significant material and energy resources are required.

Off-balance-sheet ores in their mineralogical composition mainly consist of phosphorite, dolomite, quartz and calcite, as well as a significant amount of pyrite, siderite, etc. [10,11,14,15].

Microscopic analysis revealed that the off-balance phosphorites of the Karatau basin mainly consist of phosphorite, silica, carbonates, aluminum, iron hydroxides, as well as inclusions of other minerals pyrite, fluorite in small amounts. Phosphorite is represented in the form of fluorine, apatite, the bulk of which is concentrated in grains and oolites, in most cases they are colorless and transparent optically and uniaxial and with a very low birefringence index Ng-1,630 and Np-1,627.

Studies of the chemical composition of off-balance phosphorites have shown that they belong to phosphate-siliceous and carbonate-siliceous shales, it is established that the average chemical composition of off-balance phosphorites includes (in %) P_2O_5 up to 19, n. o. up to 36, CaO up to 32; MgO up to 3.6; Fe_2O_3 -2.6; Al_2O_3 up to 4, CO_2 up to 3.0; SO_2 up to 0.3; K_2O up to 0.4.

The composition of phosphogypsum mainly includes gypsum, quartz and basanite.
For the research, representative samples of samples shown in Figure-1 a and b from the old and new dump storage facilities of the mineral fertilizers plant, where the production of extraction phosphoric acid is carried out by the dehydrate method, were selected.

(a) (b)

Figure-1. General view of phosphogypsum sample samples A from the old dump and B from the new dump dump.

The chemical composition of phosphogypsum from the old and new dump is presented in Tables 1 and 2.

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Table-1. Chemical composition of phosphogypsum from the old dump.

No Apx.	Name of the defined characteristics, units of measurement	ThenormforND	Actual * values based on test results	NDontestmethods
1	Massfractionofboron,%	-	0,009	-
2	Massfractionofpotassium,%	-	0,13	GOST 5382-91
3	Massfractionofcalcium,%	-	17,55	GOST 4013-82
4	Massfractionofmagnesium,%	-	0,028	GOST 5382-91
5	Massfractionofmanganese,%	-	0,0029	GOST 5382-91
6	Massfractionofarsenic,%	-	0,0025	GOST 23581.9-79
7	Massfractionofphosphorus,%	-	0,35	GOST 5382-91
8	Massfractionoffluorine, %	-	0,5	GOST 5382-91
9	Mass fraction of phosphorus oxide, %	-	0,80	GOST 5382-91
10	Mass fraction of potassium oxide,%	-	1,79	GOST 5382-91
11	Mass fraction of magnesium oxide,%	-	0,10	GOST 5382-91
12	Insolubleresidue (n. o.),%	-		GOST 5382-91

Table-2. Chemical composition of phosphogypsum from the new dump dump.

No Apx.	Name of the defined characteristics, units of measurement	Thenormfor ND	Actual * values based on test results	NDontestmethods
1	Massfractionofboron, %	-	0,008	-
2	Massfractionofpotassium, %	-	0,14	GOST 5382-91
3	Massfractionofcalcium, %	-	19,42	GOST 4013-82
4	Massfractionofmagnesium, %	-	0,036	GOST 5382-91
5	Massfractionofmanganese, %	-	0,003	GOST 5382-91
6	Massfractionofarsenic, %	-	0,004	GOST 23581.9-79
7	Massfractionofphosphorus, %	-	0,30	GOST 5382-91
8	Massfractionoffluorine, %	-	0,60	GOST 5382-91
9	Mass fraction of phosphorus oxide, %	-	0,69	GOST 5382-91
10	Mass fraction of potassium oxide, %	-	0,61	GOST 5382-91
11	Mass fraction of magnesium oxide, %	-	0,13	GOST 5382-91
12	Insolubleresidue (n. o.), %	-		GOST 5382-91

In order to determine the effective technology for processing phosphogypsum, its differential-thermal analysis of the selected samples was carried out, shown in Figures 2 and 3.

Figure 2-Thermal analysis of phosphogypsum from an old dump dump Figure 3-Thermal analysis of phosphogypsum from the new dump site

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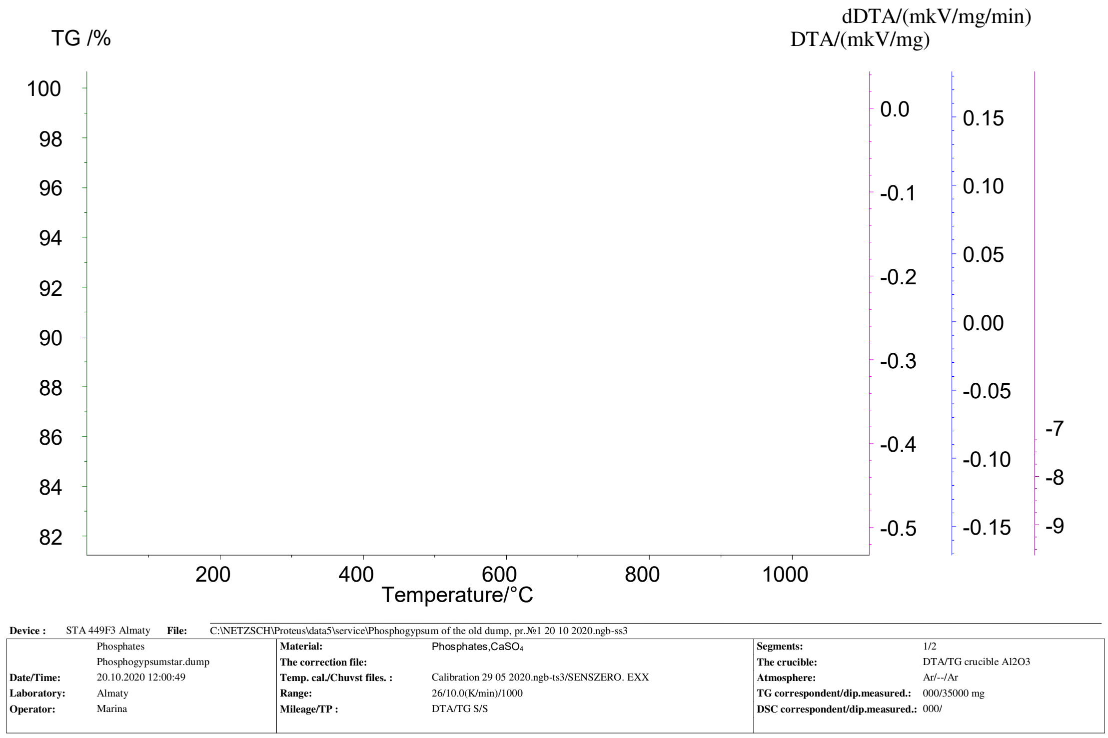

Figure-2. Differential-thermal analysis of the selected samples for processing phosphogypsum.

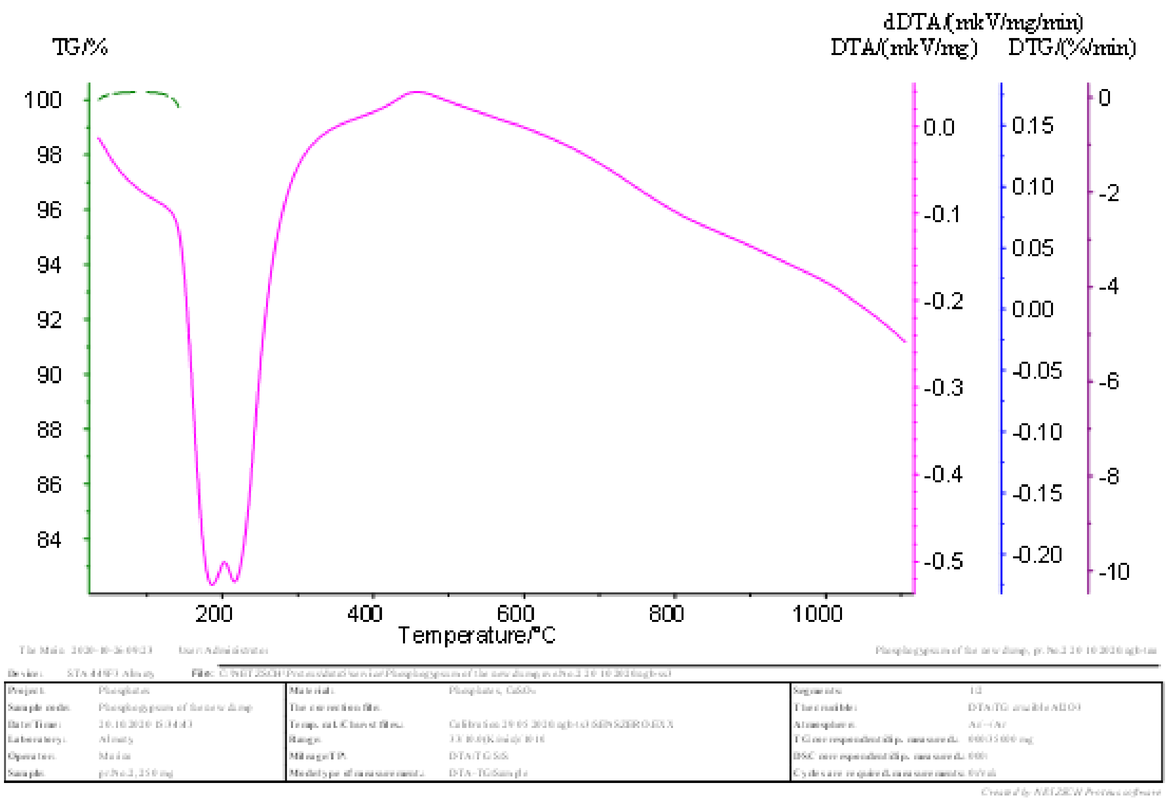

Figure-3. The result of thermal analysis.

Thermal analyses of the phosphogypsum of the old and new dump sites were carried out using the STA 449 F3 Jupiter synchronous thermal analysis device. The total volume of the incoming gas was kept within 80

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ml/min. The results obtained with the STA 449 F3 Jupiter were processed using the NETZSCH Proteus software. Differential-thermal analysis was carried out in the National Scientific Laboratory of Collective use in the priority direction "Technologies for the hydrocarbon and mining and metallurgical sectors and related service industries" of the OA "Institute of Metallurgy and Enrichment" in Almaty. An analysis of Tables 1 and 2 and Figures 2 and 3 shows that there are no large differences in both the chemical composition and the thermograms.On the basis of this, it is possible to jointly process the accumulated waste, mixed with off-balance ores and rocks, in a certain ratio to obtain an average raw material product and apply it in several areas of the economy sectors: road construction, construction industry. This does not require large financial costs, in comparison with the extraction of valuable components from them. The next direction of utilization of phosphogypsum and off-balance ores and rocks is the production of a new range of tukosmesh, while solving environmental issues. Utilization of phosphogypsum mixed with off-balance phosphorites for highway construction will dramatically reduce the use of natural resources and preserve flora and fauna in areas of natural resource extraction with simultaneous environmental and economic issues.

CONCLUSIONS

The studies showed that the phosphorus and phosphate acid due to the formation of large volumes of solid, liquid and gaseous wastes that violate the ecological balance in the industrial region of the country and Border States.

During the extraction and preparation of phosphorites of the Karatau basin, up to 60% of balance ores, off-balance ores, about 13%, phosphate-siliceous rocks up to 8%, phosphatized flints about 19% are formed, which require a certain method of disposal or processing.

The mineralogical and chemical compositions of off-balance phosphorites, which are mainly related to phosphate - siliceous and carbonate-siliceous phosphate rocks, depending on the deposits, have been studied.

The similarity of the phosphogypses of the old and new dump dumps is established, both in chemical composition and in the differential thermal characteristics of endothermic and exothermic processes occurring when heated in the temperature range 0 -1100 ^{0}C.Therefore, it is possible to offer a planning of the use of phosphogypsum in various sectors of the economy, as the construction of roads, backfilling deep gullies and holes in the highway and construction industry requires significant financial and material resources.

Based on the research results, it is also preferable to use phosphogypsum for obtaining a new type of fertilizer - fertilizer mixtures, which, in comparison with other processing methods, do not require significant heat and energy consumption.

The use of a mixture of phosphogypsum and off-balance ores in the production of a new type of mineral fertilizer mixtures, or for filling deep hollows and pits encountered in the construction of roads, as well as in the construction industry will significantly improve the environmental situation of industrial regions and the safety of living organisms and people.

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