ҚАЗАҚСТАН РЕСПУБЛИКАСЫ ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В. Сокольский атындағы «Жанармай, катализ және электрохимия институты» АҚ

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК РЕСПУБЛИКИ КАЗАХСТАН АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского»

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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Етегдіпд Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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PHYSICAL AND CHEMICAL PROCESSES OCCURRING IN THE GRANULATED PHOSPHORUS SLAG DUMPS

Abstract. One of the most dangerous man-made mineral formations located in the territory of Kazakhstan is disposal areas for granulated phosphorus slag, since its shells contain initially the dangerous gases such as PH_3 , H_2S , HF, etc. Permanent sources of such gases are also Ca_3P_2 (intrinsically poisonous gas), CaS and CaF_2 . In the structures of phosphorous ash disposal areas, the chemical and physical-chemical processes contain initially gases, which may be in different modifications. For example:

- Phosphene (PH₃) in the form: $PH_3 \rightarrow P_2O_5 \rightarrow HPO_3 \rightarrow H_3PO_4$;
- Hydrogen sulfide (H₂S): $H_2S \rightarrow H_2SO_3 \rightarrow H_2SO_4$;
- Hydrogen fluoride and silicon tetrafluoride: $HF \rightarrow SiF_4 \rightarrow H_2SiF_6 \rightarrow H_2SiO_3$;
- Carbon oxide (CO): $CO \rightarrow CO_2 \rightarrow COCl_2$.

Such chemical processes intensify greatly the anthropogenic effect of phosphorous ash disposal areas on the environment – biogeocoenosis.

In addition to the processes related to gas components, in the phosphorous ash disposal areas, the hydration processes occur as a result of interaction of slag with water. Thereat, sub-microcrystalline CSH(I) and calcium are generated. Depth of slag hydration reaches $1...3~\mu m$. Such processes form a thin layer on the surface of slag particles resulting in linking of separate grains into a whole. Therefore, the surface of phosphorous ash disposal areas has the certain strength with cracks, through which water, air, snow, etc. are penetrating into the disposal area.

It is evident that granulated phosphorus slag in the form of disposal areas has very adverse impact on the biogeocoenosis, causing the pressing need for their disposal; moreover, such slags are valuable raw material for the construction industry and agriculture only after their decontamination from dangerous gases.

Keywords. Granular phosphorus slag, dumps, hazardous gases, chemical reactions.

Introduction. One of the most dangerous technogenic mineral formations located on the territory of Kazakhstan is the granular phosphorus slag dumps (hereinafter referred to as GPS or GPD), (figure 1), formed as by-products in the production of phosphorus and its compounds [1].

Near Shymkent and Taraz there dumps have more than 20 million tons of granular phosphorus slag where chemical and physicochemical processes constantly occur, due to which hazardous gases derivatives in the dump structures such as phosphine (PH₃), hydrogen fluoride (HF), hydrogen sulfide (H₂S) and others, previously occurring during the sublimation of elemental phosphorus from phosphorite [2.3], are formed.

In addition, under certain conditions, phosphide (poisonous in itself), calcium sulfide and fluoride, which are part of the slag can serve as these gases sources, which while interacting with water, form a hydration phase of type CSH (I), generating a crust of certain strength with cracks on the surface of the dumps [4-6].



Figure 1 – The dump of granular phosphorus slag near the city of Taraz

Consequently, slag dumps are the same hazardous objects as emissions of the same gases during production processes. At the same time, emissions are controlled, and phosphate slag dumps are uncontrolled, constant, and therefore their danger is significantly higher.

The utilized phosphate slag dumps through the neutralization of granular phosphorus slag, which is environmentally friendly can be an excellent raw material used for construction and agriculture.

The phosphorus and GPS generation technology is the following: in electric furnaces at temperatures of $1450 \dots 1500^{\circ}$ C in mixtures consisting of phosphorite ($3\text{CaO} \cdot \text{P}_2\text{O}_5$) of the Karatau deposit, quartz sand (SiO₂) and carbon (C), the reaction occurs according to the following formula:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3 (CaO \cdot SiO_2) + 2P \uparrow + 5CO \uparrow$$
 (1)

From this formula it follows that P and CO are released as gases, and $CaO \cdot SiO_2$ – as a melt, at rapid cooling the GPS is generated.

In addition, as a result of complex physical and chemical processes, dangerous gas-dust-like impurities arise - in the form of phosphine (PH_3) , fluoride (HF) and hydrogen sulfide (H_2S) , slag (and other) dust that are released into the atmosphere, in production and other premises concentrated in the GPS shells located in dumps [7.8].

Emission of harmful dust and gas substances into the atmosphere and their presence in production facilities are well studied [7.8]. For example, at slag production and bucket discharge sites, the content of PH $_3$ reaches 0.3 ... 3.5 g / m 3 , and HF – 1.25 ... 6.9 mg / m 3 [8]. At four phosphorus production plants (before 1990) in Shymkent and Zhambul, the emission of harmful gas-dust-like substances into the atmosphere reached 150 billion m 3 , the content of phosphine, hydrogen fluoride and hydrogen sulfide, dust up to 200 thousand tons per year (currently, "Kazphosphate" LLP pay special attention to labor protection and safety) . There is no such close attention to phosphate slag dumps.

The above mentioned gases are very dangerous and toxic (table 1).

Substance Hazard Maximum permissible concentration (mg/m³) MPCwa **MPC**_{MS} **MPC**_{AD} 0,008 H_2S 10 0,008 HF 0,02 0,005 2 SiF₄ 0,5 0,02 0,005 2 PH₃ 0,5 0,1 0,1 CO 4 20 0,3 0,1 Dust

Table 1 – MPC (in mg/m³⁾ gas toxic substances occurring in the composition of phosphorus slag dumps [9]

Studies have shown that higher MPC may cause various human diseases (peptic ulcer, chronic gastritis, cirrhosis of the liver, musculoskeletal disorders) and animals' skull bones and teeth destruction. They are especially dangerous for river and marine animals [7.8].

^{*}WA - working area, MS - maximum single, AD - average daily

There are known developments of non-fired and composite binders and concrete on the basis of electrothermophosphorus slags from the Novo-Zhambul phosphoric plant, Kazfosfat LLP with high strength and durability, also physicochemical processes of the products of hydration and structure formation of these binders have been studied [10-12].

An analysis of the literature data shows [7.8] that in the phosphorus industry, particular attention is paid to emissions and production facilities, and phosphorus slag dumps are almost absent. Meanwhile, these dumps have a significant uncontrolled anthropogenic impact on biogeocenosis, i.e. the environment. Therefore, the study of physical and chemical processes associated with GFSD is quite urgent – this is what this work is devoted to.

Research Methodology. The object of the study was granular phosphorus slag from dumps located on the territory of Kazphosphate LLP (Taraz).

The chemical and phase GPS compositions were identified using a DRON-3M X-ray machine (Russia), derivatographic unit Q-1500 D (MOM, Hungary), infrared spectrophotometer Specord M 80, a MIN-8 polarizing microscope, and traditional chemical analysis.

The determination of hazardous gases was done using the ALTAIR PRO gas analyzer (single-channel explosion-proof portable). Sample preparation with a specific surface of 500 m²/ kg was carried out for physicochemical analyzes at a laboratory vibratory mill with a capacity of 2 kg. In this case, the released gases were measured through holes with a diameter of 2 mm.

The experimental results. The dumps of granular phosphorus slag (GFSD) in Shymkent and Taraz occupy about 1730 hectares of fertile land with the enclosing territory allocated based on the sanitary standards. In addition, chemical enterprises engaged in the production of phosphorus-containing products are located near the rivers Sairam (Shymkent) and Assa (Taraz), which due to location reasons raises many negative issues.

The GFSD storage period has already reached about 30 ... 50 years. The total amount is more than 20 million tons (moreover, the Shymkent GFSD is constantly decreasing, due to the fact that it is constantly used in road construction - without any permits, Taraz plant is growing due to the existing new Zhambul phosphorus plant).

The chemical composition (rounded) GFS, %: SiO_2 - 41 ... 44; CaO - 44 ... 48; Al_2O_3 - 3.2 ... 3.6; Fe_2O_3 - 0.5 ... 0.6; MgO - 2.5 ... 3.2; P_2O_5 - 1.07 ... 2.5; SO_3 - 0.5 ... 0.8; F - 1.2 ... 2.0; calcium phosphide (Ca_3P_2) - 0.2 ... 0.3; calcium fluoride (CaF_2) - 4.0 ... 4.5; calcium sulfide (CaS) - 0.2 ... 0.3.

Such a chemical composition of GFS is obtained as a result of physicochemical processes occurring at a temperature of about 1450°C in electrothermal furnaces in mixtures consisting of phosphate [Ca₃(PO₄)₂] from the Karatau deposit, quartz sand (SiO₂) and carbon (C) based on the following formula (1).

When molten slag comes into contact ($t = 1450 \dots 1500^{\circ}$ C) with water vapor and in case of water granulation the chemical pyrohydroline reactions occur (schematically) [13] as follows:

$$CaF_{2} + H_{2}O + SiO_{2} = 2HF + CaO \cdot SiO_{2},$$

$$Ca_{3}P_{2} + 3H_{2}O + 3SiO_{2} = 2PH_{3} + 3 (CaOSiO_{2}),$$

$$CaS + H_{2}O + SiO_{2} = H_{2}S + CaO \cdot SiO_{2}.$$
(2)

Elemental phosphorus, interacting with atmospheric oxygen, forms phosphoric anhydrite based on the following formula:

$$4P + 5O_2 \rightarrow 2P_2O_5 \tag{3}$$

With rapid water cooling, the melt does not have time to crystallize and by retaining some of the internal energy, passes into the vitreous state. This state gives GFS a certain astringent property which increased when grinded and activated by various additives. The average GFS density is about 1100 ... 1200 kg/m³, its soft shell material is easily destroyed by external influences.

The formation of the halo in the X-ray diffraction pattern and the diffusivity of the main maxima of the absorption bands of the IRS confirm its amorphism. The endoeffect in its thermogram at 800 $^{\circ}$ C shows softening of the glass, and the exoeffect at 920 $^{\circ}$ C – the crystallization of pseudo-(CaO $^{\circ}$ SiO₂) (figure 2). From this physical analysis it can be seen that GFS is an excellent material for use in silicate and building materials and products, including road construction and agriculture. However, only if it is neutralized from hazardous impurity gases.

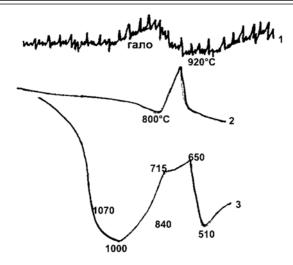


Figure 2 - X-ray diffraction pattern (1), thermogram (2) and a fragment of the infrared spectrum (3) of the GFS

It should be emphasized that the components of the GFS are not inactive but actively interact with the environmental ingredients and themselves, by significantly increasing its anthropogenic impact on biogeocenosis. Gas-dust emissions of the existing phosphorus plant settling on the surface of GFSD will make their negative contribution.

In GFSD structures the main interdependent parallel physical and chemical processes may occur as follows:

- chemicals associated with harmful gases;
- physical and chemical, associated with the hydration of slag and its dust.
- a) Chemical reactions associated with gases in GFS shells, for example, with PH₃:

$$PH_3+H_2O \rightarrow PH4++OH$$
,
 $PH4++H_2O \rightarrow PH_4OH+H$,

or

$$PH4++H_2O \to PH_3+H_3O^+,$$

 $PH4++OH^- \to PH_3+H_2O^+,$
 $2PH_3+4O_2 \to P_2O_5+3H_2O,$
 $P_2O_5+H_2O \to 2HPO_3,$
 $HPO_3+H_2O \to H_3PO_4$ (4)

Therefore, depending on the environment, a phosphine in the ecosystem can exist in the form of compounds as follows: $PH_3 \rightarrow P_2O_5 \rightarrow NRA_3 \rightarrow H_3PO_4$.

The same chemical reactions occur with H_2S , $HF + SiF_4$ and CO, respectively, with the formation (schematically):

$$H_2S \rightarrow H_2SO_3 \rightarrow H_2SO_4;$$

$$HF \rightarrow HF_2; SiF_4 \rightarrow H_2SiO_3 \rightarrow H_2SiF_6$$

$$CO \rightarrow CO_2 \rightarrow COCl_2$$
(5)

Furthermore:

- calcium phosphide is poisonous gas it may under certain conditions be a constant source of formation of a new portion of PH3;
 - calcium sulfide turns into H₂S based on the following formula:

CaS + 2H₂O
$$\xrightarrow{100C}$$
 Ca(OH)₂+ H₂S \uparrow (under conditions of phosphoric slag binders steaming);
CaS + CO₂+ H₂O \rightarrow CaCO₃+ H₂S \uparrow ; (6)

calcium fluoride - during autoclaving of phosphoric slag binders it can give HF based on the following formula:

$$CaF_2 + H_2SO_4 \xrightarrow{130.200^{\circ}C} CaSO_4 + 2HF \uparrow$$

$$= 50 = 50$$
(7)

As can be seen from the table 2 the content of Ca₃P₂, CaF₂ and CaS in the composition of GFSD in the amount of 20 million tons of solids: 69.3; 2700 and 69.3 respectively, t.

| Name of gas-forming substances | Chemical formula | Content of gas-forming substances | |
|--------------------------------|------------------|-----------------------------------|------|
| | | % | t |
| Calcium phosphide | Ca_3P_2 | 0,3 | 69,3 |
| Calcium fluoride | CaF ₂ | 4.0 | 2700 |

Table 2 – The total content of gas-forming substances in GFSD, the amount of which is 20 million tons

b) Physical and chemical processes associated with slag hydration:

Sulfide calcium

A neoplasm is formed on the surface of the slag grains as a result of interaction with water. A physicochemical study showed (figure 3) that this neoplasm consists of a gel- and crystalline CSH (I) and calcite. As can be seen from this figure, peaks appear on the radiograph at d/n = 3.03; 2.84 and 1.82 Å, typical for crystalline CSH (I). Five effects are recorded on the thermogram – three endo and two – exoeffects.

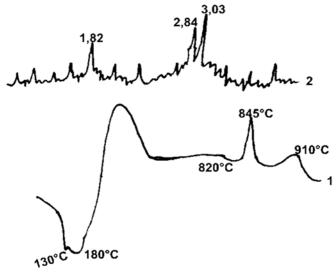


Figure 3 – X-ray diffraction pattern (2) and thermogram (1) of GFSD grains

The endoeffect at 130 °C indicates the presence of gel-like phases in the neoplasm and the endoeffect at 180 °C is apparently a submicrocrystalline part of the hydrosilicate phases.

These processes proceed according to the following schemes:

$$C_2SH_2 \xrightarrow{120-180^{\circ}C} C_xS_vH_z + CH.$$

The endoeffect at 820°C shows the calcite decarbonization according to the scheme:

$$CaCO_3 \xrightarrow{180^{\circ}C} CaO + CO_2,$$
 (8)

69.3

which confirms carbonization of previously formed hydrosilicate phases that arose during the surface interaction of slag grains with water.

The exoeffect at 840°C indicates the transition of CSH (I) at elevated temperature to wollastonite by the reaction:

$$CSH \xrightarrow{845 \,{}^{\circ}C} \beta - CS. \tag{9}$$

The exoeffect at 910 °C confirms crystallization of the initial glassy slag with the formation of β -CaO-SiO₂.

Petrographic studies show that the gel-like silicate mass has light refraction in the range n = 1.51 ... 1.53; CSH (I) - n = 1.54 ... 1.56, and CaCO₃ $- n_0 = 1,658$; $n_s = 1.485$. In this case, CSH (I) has a fibrous structure, and calcite crystals are formed as a rhombohedron and a prism. The depth of hydration of the slag grains is 0.1 ... 0.3 microns.

Thus, in dumps, granular phosphorus slag is hydrated in the presence of water, which leads to its transformation into stone with a certain strength, as a result of which individual grains are crosslinked into a single whole, which is denser than slag, therefore it envelops the slag grains in a dense layer, which prevents further hydration of the slag itself. However, this dense layer in the form of a crust occurs with cracks through which water, gas, snow, etc. penetrate into the dump.

Phosphate slag dumps are a constant source of pollution of the region's ecosystem. In fact, as long as these phosphorus slag dumps exist nearby, there can be no improvement of the environmental situation in the southern region of Kazakhstan.

In preventing environmental pollution caused by phosphorus slag and waste disposal facilities, there are four main options:

- cover them with a thick layer of earth or with a special polymer or concrete mixture;
- liquidate by laying them in mine and other man-made spaces;
- use as fertilizer for agricultural farming and material for land reclamation purposes;
- produce various building materials on their basis.

It is possible, of course, to leave everything as it is. However, this is counterproductive, as discussed above.

Let's briefly consider all the pros and cons of implementing the above in terms of environmental and economic efficiency.

- 1. The closure of phosphate slag dumps with a total area of 50 hectares with a thick layer of land is unproductive, because:
- removal of this land causes additional anthropogenic environmental pollution and the alienation and desolation of lands;
 - huge financial, human and technical costs;
- earth filling of phosphate storage facilities with a height of 50 m each is not so simple based on the technical capabilities of existing machines and mechanisms;
- the main low productivity of this venture is that this work will need to be repeated periodically, since the thickness of the backfill may decrease due to erosion reason;
- when closing the dumps with concrete mix it can be considered that the environmental problem will be solved, however, such work will be more expensive than backfilling option (for example, the cost of 1 ton of land is 2500 tg, cement 14500 ... 15000 tg) therefore, from an economic point of view such an event is extremely ineffective;
- closing the dumps with a special polymer mixture is the most promising among others, however, the life of the polymer film is relatively short (1-1.5 years), such an expensive mixture will need to be exported, since it is not produced in Kazakhstan, in addition, under certain conditions (for example, in its interaction with acids toxic substances) it creates an environmental problem.
- 2. Even more inefficient in environmental and economic terms is the liquidation of phosphate slag dumps by laying down mine and other man-made spaces. For example, the cost of one 60-ton wagon reaches 320 thousand tenge. For 20 million tons of phosphorus slag, 333,333 wagons are needed. It is easy to calculate the transportation of slag dumps by wagons will amount to 106 billion tenge. But in addition to transportation, there are other operations such as loading and unloading, filling, etc. These are additional costs their cost is equal to 20-30 % of the transportation cost.
- 3. If slag dumps are used as fertilizer for agricultural farming and as material for land reclamation, then, first of all, a technological line cleaning gaseous substances, especially phosphine, hydrogen fluoride and hydrogen sulfide will be needed. In addition, the technical and economic efficiency of slag dumps as fertilizer used for land reclamation shall be defined since there are conflicting data on this [14].
- 4. What if to produce various effective building materials on the basis of slag dumps? However, we note the following: with some certainty, it can be argued that there is simply no alternative to processing these dumps into building and silicate materials. In our opinion, this direction is the most promising and environmentally and economically effective, since in this case the problem associated with the slag dumps utilization is solved comprehensively.

The specificity and nature of the phosphate dumps in which the prehistory of their occurrence is associated with the production of phosphate-containing products, determines the increased degree of their anthropogenic impact on the ecosystem, namely, as already mentioned on biogeocenosis.

Summary. 1. In the phosphorus industry, environmental, technological and sanitary safety usually means the measures and technical requirements related to the emission of harmful substances into the atmosphere and hydrosphere, as well as their level of concentration in production facilities without giving the required attention to the granular phosphorus slag dumps.

Meanwhile, the granular phosphorus slag dumps in the amount of 20 million tons have a significant anthropogenic impact on biogeocenosis, i.e. the environment, since hazardous gas-dusty ingredients are accumulated in its structures.

- 2. Chemical and physico-chemical processes constantly occur in the structures of dumps, as a result of which:
 - phosphine (PH₃) can be in the form: PH₃ \leftrightarrow P₂O₅ \leftrightarrow HPO₃ \leftrightarrow H₃PO₄;
 - hydrogen sulfide $(H_2S) H_2S \leftrightarrow H_2SO_3 \leftrightarrow H_2SO_4$;
 - hydrogen fluoride and silicon tetrafluoride HF \leftrightarrow SiF₄ \leftrightarrow H₂SiF₆ \leftrightarrow H₂SiO₃;
 - carbon monoxide (CO) CO \rightarrow CO₂ \rightarrow COCl₂;
 - slag \rightarrow CSH (I).
- 3. The potential amount of 20 million tons of phosphate and calcium sulfide sludge can reach 69.3 tons, and calcium fluoride up to 2700 tons, which under certain conditions can be sources of the above-mentioned dangerous gases.
- 4. Finding granular phosphorus slag in the form of dumps is extremely dangerous for biogeocenosis and the urgent need for their disposal suggests itself, especially since these slags are valuable raw materials for the construction industry and agriculture.

Confirmations. Scientific results were obtained within the framework of TsELSIM LLP work.

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ТІЙІРШІКТЕЛГЕН ФОСФОР ҚОЖДАРЫ ҮЙІНДІЛЕРІНДЕ БОЛАТЫН ФИЗИКАЛЫҚ-ХИМИЯЛЫҚ ПРОЦЕСТЕР

Аннотация. Қазақстан аумағындағы ең қауіпті техногендік минералдық түзілімдердің бірі — түйіршіктелген фосфор қожының үйінділері, өйткені оның қабықтарында бастапқыда PH_3 , H_2S , HF және т.б. сияқты қауіпті газдар бар. Бұл газдардың тұрақты көздері — Ca_3P_2 (өзімен өзі улы газ), CaS және CaF_2 де. Фосфор қожы үйінділерінің құрылымдарында үнемі химиялық және физикалық-химиялық процестер орын алып тұрады, нәтижесінде бастапқыда болатын газдар әртүрлі модификацияларда болуы мүмкін. Мысалы:

- Фосфин (PH₃) PH₃→P₂O₅→HPO₃→H₃PO₄ түрінде;
- Күкірт сутегі (H_2S): $H_2S \rightarrow H_2SO_3 \rightarrow H_2SO_4$ түрінде;
- Фторлы сутегі және кремний тетрафториді: $HF \rightarrow SiF_4 \rightarrow H_2SiF_6 \rightarrow H_2SiO_3$;
- Көміртегі оксиді (СО): СО→СО₂→СОСІ₂.

Мұндай химиялық процестер фосфор қожы үйінділерінің қоршаған ортаға антропогендік әсерін – биогеоценозды айтарлықтай күшейтеді.

Газды құрамдастарға байланысты процестерден басқа, фосфор қожы үйінділерінде қождың сумен өзара әрекеттесуі нәтижесінде гидратациялық процестер орын алады. Бұл ретте субмикрокристалды СSH(I) және кальций түзіледі. Қождың гидратация тереңдігі 1...3 мкм-ге жетеді. Осы процестердің нәтижесінде кож бөлшектерінің бетінде жұқа қабат пайда болады, соның салдарынан жекелеген түйіршіктердің біртұтас болып бірігуі орын алады. Сондықтан фосфор қожы үйінділерінің беті үйіндінің ішіне су, ауа, қар және т.б. кіретін жарықтармен белгілі бір беріктікке ие.

Түйіршіктелген фосфор қождарының үйінділер түрінде болуы биогеоценозға өте теріс әсер ететіні белгілі, осыған байланысты оларды кәдеге жаратудың аса үлкен қажеттілігі туындайды, әсіресе, бұл қождар, оларды қауіпті газдардан зарарсыздандырғаннан кейін ғана құрылыс индустриясы мен ауыл шаруашылығы үшін бағалы шикізат болып саналады.

Түйін сөздер. Түйіршіктелген фосфор қожы, үйінділер, қауіпті газдар, химиялық реакциялар.

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ФИЗИКО-ХИМИЧЕСКИЕ ПРОЦЕССЫ, ПРОИСХОДЯЩИЕ В ОТВАЛАХ ГРАНУЛИРОВАННЫХ ФОСФОРНЫХ ШЛАКОВ

Аннотация. Одним из наиболее опасных техногенных минеральных образований, находящихся на территории Казахстана, являются отвалы гранулированного фосфорного шлака, поскольку в его скорлупах изначально присутствуют такие опасные газы как PH_3 , H_2S , HF и др. Постоянными источниками этих газов являются также Ca_3P_2 (сам по себе ядовитый газ), CaS и CaF_2 . В структурах фосфошлакоотвалов постоянно происходят химические и физико-химические процессы, в результате которых изначально присутствующие газы могут находиться в различных модификациях. Например:

- Фосфин (PH₃) в виде: $PH_3 \rightarrow P_2O_5 \rightarrow HPO_3 \rightarrow H_3PO_4$;
- Сероводород (H_2S): $H_2S \rightarrow H_2SO_3 \rightarrow H_2SO_4$;
- Фтористый водород и тетрафторид кремния: $HF \rightarrow SiF_4 \rightarrow H_2SiF_6 \rightarrow H_2SiO_3$;
- Оксид углерода (CO):CO \rightarrow CO₂ \rightarrow COCl₂.

Такие химические процессы существенно усиливают антропогенное влияние фосфошлакоотвалов на окружающую среду – биогеоценоз.

Кроме процессов, связанных с газовыми составляющими, в фосфошлакоотвалах происходят гидратационные процессы в результате взаимодействия самого шлака с водой. При этом образуются субмикрокристаллические CSH(I) и кальций. Глубина гидратации шлака достигает 1...3 мкм. В результате этих процессов на поверхности частиц шлака возникает тонкий слой, вследствие чего происходит сшивание отдельных зерен в единое целое. Поэтому поверхность фосфошлакоотвалов обладает определенной прочностью с трещинами, через которые внутрь отвала проникают вода, воздух, снег и др.

Очевидно, что нахождение гранулированных фосфорных шлаков в виде отвалов чрезвычайно негативно влияет на биогеоценоз, в связи с этим возникает настоятельная необходимость их утилизации, тем более эти шлаки являются ценным сырьем для строительной индустрии и сельского хозяйства, только после их обезвреживания от опасных газов.

Ключевые слова. Гранулированный фосфорный шлак, отвалы, опасные газы, химические реакции.

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REFERENCES

- [1] Sadykov P. About storages of technogenic raw materials and their impact on the environment // Journal: Regional Bulletin of the East (UKGU), No. 3, 2002. S.13-16.
- [2] Sadykov P.I., Estemesov Z.A. Silicate-forming processes occurring during hardening of an eco-slag binder // In Journal: Complex Use of Mineral Raw Materials, No. 5, 2002. P.78-80.
- [3] Sadykov P.I., Estemesov Z.A. Physico-chemical silicate-forming processes occurring in phosphorus slag dumps // Journal: Hydrometeorology and Ecology, No. 3, 2002. P.148-151.

[4] Estemesov Z.A., Barvinov A.V., Sarsenbaev N.B. Hidden problems associated with the use of granular phosphorus slag in cement // Sat .: High technology and innovation, part 6, Belgorod, 2019. P.29.

- [5] Kurakbaeva R.Kh., Dorfman Y.A, Polimbetova G.S., Shokorova L.A., Kuatbaev K.K., Kozlovsky V.A. Mechanochemical oxidation of bound and free oxygen of trace amounts of calcium phosphide in electrothermophosphorus slag // Journal of Applied Chemistry, vol. 3, 1992. S. 487-497.
- [6] Dorfman Ya.A., Kurakbaeva R.Kh., Polimbetova G.S. Catalytic neutralization of electrothermophosphorus slag // Journal of Applied Chemistry, Edition10, 1992. P. 2179-2183.
- [7] Kurakbaev R.H., Dorfman Ya.A., Polimbetova, etc. Preparation of binders from electrothermal phosphorus slag // Izvestiya of the Academy of Sciences of KazSSR, chemical series. 1991, No 2. P. 18-23.
- [8] Sh. Moldabekov. Purification of phosphorus, fluorine and sulfur-containing gases produced by phosphorus and its compounds: Abstract. Thesis of Dr. of Technical Sciences. Moscow: 1984. 36 p. [Russian].
- [9] Turgaeva K.S. Hygienic working conditions in the production of cast slag crushed stone at the Zhambul phosphorus plant / In the book: The use of slag obtained through electrothermal processing of phosphorus ores from the Karatau deposit of the Kazakh SSR for the manufacture of building materials and products. Alma-Ata: NIIStromproekt, 1975. p. 143. 146. [Russian].
 - [10] Chemical encyclopedic dictionary. Moscow: SE, 1983. p.791.
- [11] Sarsenbayev N.B., Sarsenbayev V.K., Aubakirova T.S., Aimenov J.T., Abdiramanova K.S. Phase composition and structure-formation of the low-clinkered floral cements // Eurasian Chemico-Technological Journal. 2014. V. 16. Edition 4. P. 333-338.
- [12] Aymenov Zh.T., Sarsenbayev B.K., Sarsenbayev N.B., Aldiyarov Zh.A. Use of solar energy for heliothermal treatment of concretes on the basis of alkali cements // The 15th Asian Regional Conference of Soil Mechanics and Geotechnical Engineering, Japan, 2015.
- [13] Aymenov A.Zh., Sarsenbayev N.B., Khudyakova T.M., Sarsenbayev B.K., Kopzhassarov B.T. Influence of addition of polymetallic ores' tailings on properties of composite cements. SCOPUS Scientific Journal. Eurasian Chemico-Technological Journal 2016. p. 153-160.
- [14] Poluboyartsev A.G., Patrushev D.A., Yumanova L.V., Bogacheva G.N., Amelin E.S., Torsis E.T. The interaction of molten phosphorus slag with water, water vapor and air / In the book: Slag phosphorus industry. Chelyabinsk, 1970, S. 41-44. [USSR].
- [15] Castred Yu.K. Phosphate wastes land reclamation // In the book: Solid waste generation, collection, processing and disposal. Translated from English by E.G. Teterina and A.S. Syutnikova. Moscow: Stroyizdat, 1979. S. 473-480. [USA].

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