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Д.В. Сокольский атындағы «Жанармай,
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ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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NEW METHOD FOR DISPOSAL OF GRANULATED PHOSPHORIC SLAG FROM HAZARDOUS GASES

Abstract. New wet method of decontamination of GPS from hazardous gases (PH_3, H_2S, HF, etc.) and their sources (Ca_3P_2, CaF_2 and CaS) is proposed, since dry methods for decontamination turn out to be inviable due to their difficulty and non-efficiency; thus, GPS in construction (and not only) is used without cleaning pursuant to the existing regulatory documents.

The wet method of decontamination of GPS from hazardous gases and their sources is developed based on the following comparative methods:

First – 2 kg GPS were dried at temperature of about 600°C at the drying furnace within 5 hours; then the air mixture was measured from the special hole for presence of gases.

Second – Dried slag after cooling was ground at the vibration mill to the specific surface of 500 m^2/kg with Na_2CO_3 additive or cement (5 % by weight) and FeO (3 %) and without such activating and neutralizing additives; then the qualitative content of gases was measured at the mill and in slag.

Third –2-kg composited sample of GPS was placed in the laboratory vibration mill and was added with water in ratio 1:6 (slag : water by weight). This mixture was ground with Na_2CO_3 additive or cement (5 % by weight) and FeO (3 %) and without them to the specific surface of 500 m^2/kg; then, the qualitative content of gases was measured at the mill and in slag.

It was determined that:

- maximum quantity of gas emission from GPS is observed during drying without decontaminating additives;
- in presence of decontaminating additives, gas emission from GPS is reduced by one step – due to neutralizing properties of additives;
- grinding of dried GPS assists in additional gas emission therefrom – with additive to a lesser extent, without additive – to a greater extent;
- in case of GPS grinding in water environment, gas emission is maximally reduced, and with additive – gases are fully neutralized.

It follows from what has been said that irrespective of the GPS treatment method, introduced additives are capable to neutralize gases; however, the wet method is more efficient in comparison with the dry one, since:

- the wet method does not require drying of GPS; particles are more easily broken to the necessary specific surface with less time;
- in the closed space like the vibration mill, in water environment, gases may not volatilize by any reasons and are fully neutralized with additives and activating agents;
- products of interaction of gases with neutralizing and activating additives become the activating components of ground GPS.

It is shown that during GPS grinding in water environment, the neutralizing and activating additives provide the chemical, physical-chemical and catalytic reactions in the system (totally they are about 20).

Studies of the phase composition, hydration degree of ground GPS and strength of consolidated slag stone produced from ecophosphoslag binding agent show the following:

- Na_2CO_3 has higher activating properties than cement-additive; thus, strength and hydration degree of consolidated ecophosphoslag binding agent with Na_2CO_3 additive are much higher – achieve correspondingly 79.3…83.5 MPa and 21.7…23.3 %, and with cement-additive – only 28.7…37.9 MPa and 16.8…20.4 %;

- Higher activating capability of Na_2CO_3 in comparison with cement-additive is explained by the fact that:

- sodium carbonate in the consolidating system creates the increased alkaline medium (pH>12); therefore, glass-slag is much dissolved; in its turn, assisting in increase in content of hydrate phases in slag stone;

- strengthening of slag stone is positively impacted also by ions Na^+ included into hydrated calcium silicates – C-S-H and CSH (I), resulting in generation of new expanded coordination centers, like MeO_6, assisting in increase and stability of the crystal latitude and hydrate phase, and this is also the positive factor impacting on increase in strength of slag stone.

It is defined that FeO does not only neutralizes hazardous gases and their sources, but activates ground GPS. Neutralizing and activating capability of FeO may be related to presence of electron-free orbitals at the 3d-sublevel of Fe^{2+} (Fe^{3+}), assisting to iron ions as acceptor with neutralizing and activating properties. It may be supposed that such properties shall be common for the compounds, including the elements of transition metals having electron-free orbitals at the 3d-sublevel.

It is detected that consolidated ecophosphoslag binding agent contains mainly two types of hydrated calcium silicates – amorphous tobermorite gel (C-S-H) and submicrocrystalline CSH (I).

Keywords. Granular phosphorus slag, hazardous gases and their sources, iron oxide, soda, cement, strength, degree of hydration.

Introduction. Among technogenic mineral formations (and there are more than 25 billion tons of them in Kazakhstan), granular phosphoric slag in terms of importance and technical and economic efficiency as a raw material in the construction industry and construction is ranked second after granulated blast-furnace slag, and they are interchangeable.

The field of production of building and silicate materials, products and structures based on these technogenic materials is very wide, since they are used in all sectors of the construction industry [1-9].

Unlike the blast-furnace slags the granular slags are ecologically clean mineral raw materials, granular phosphorus slag (hereinafter GFSH) contain hazardous gases (PH_3H_2S, HF, SiF_4 and others.) and minerals (Ca_3P_2 – highly poisonous, CaF_2 and CaS). Gases occur during production of phosphorus and its compounds from a mixture of phosphorite, quartz and coal, and minerals are initially present in the composition of $Ca_3(PO_4)_2$ in the form of impurities, which are constant sources of hazardous gases in slags according to the equation [10]:

$$Ca_3P_2 + 3H_2O + 3SiO_2 = 2PH_3 + 3\,(CaO \cdot SiO_2),$$

$$CaF_2 + H_2O + SiO_2 = 2HF + CaO \cdot SiO_2,$$

$$CaS + H_2O + SiO_2 = H_2S + CaO \cdot SiO_2$$

The presence of these hazardous ingredients in GFS was known from the very beginning (since 1965), but this was not given much importance. Therefore, until 1990 GFS without neutralization was used as independent binders, mineral additives in the production of Portland cement and components in the composition of slag Portland cement [1-9]. As a result of this, GOST 3476-74 [11] which is valid at the present time, was issued. A new standard GOST 31108-2016 [12] allowing the use of GFS without neutralization which has a major socio-ecological and economic danger to biogeocenosis was added.

With an acute cement deficit in Kazakhstan at the end of the 1980s, a decision at the level of the Government of the USSR and KazSSR was made to organize the production of cementless binders based on GFS [13,14]. That time the danger of using them without neutralizing gases was mentioned.

In this regard, Almaty NIIstromproekt, together with the IOCE of the Academy of Sciences of the Kazakh SSR and the NIIKP of the Ministry of Healthcare began to neutralize GFS from PH_3 and H_2S, offering their own formulation [15-17], as a result of which ST RK 2301-2013 was developed [18], where it is clearly stated that GFS should be neutralized from phosphorous and fluoride compounds by the introduction of neutralizing additives.

However, in practice, this regulatory document was not viable, because: the * PH_3 and H_2S neutralizing methods were very complicated and some processes were questionable. For example, GFS is simultaneously used for neutralization (since some additives neutralize some gases, others – the rest gases): calcium hypochlorite [Ca $(OCl)_2$] in an amount of 0.4% by weight, steelmaking slag (5%), caprolactam waste (2 %) and ferro-slag of chromium compounds (6%) [19], which should be used for drying (> 600°C) and grinding the phosphoric slag binders by dry mechanochemical method [20].

The disadvantages of the mechanochemical GFS neutralizing method include the multicomponentness of neutralizing additives, the dependence of the degree of purification on their chemical and mineralogical composition which is not always constant, the negative effect of some of them (for example, calcium hypochlorite, Cr^{6+} , etc.), partial removal harmful impurities with exhaust gases during GFS drying process.

There is also a patent [21] for a method for phosphorus slag purification from harmful gases using vanadium-containing converter slag.

Research methods.

Option 1. A certain amount (2 kg) of GFS was dried at a temperature of about 600°C in a drying oven. Five hours after drying from an opening, the air mixture was measured for the presence of gases.

Option 2. After cooling, the dried slag was ground in a vibratory mill to a specific surface of 500 m^2/ kg with and without Na_2CO_3or cement (5%) and FeO (3%), after which the qualitative gas content in the mill and slag was measured.

Option 3. We took 2 kg of GFS of the averaged sample and placed in a laboratory vibratory mill, and poured water in a ratio 1: 6 (slag: water by weight). This mixture was ground with the addition of Na_2CO_3 or cement (5%) and FeO (3%) and without them to a specific surface of 500 m^2/ kg, after which the qualitative content of gases in the mill and slag was measured.

Note: the quantitative gas content in the studied systems must be checked in two more independent accredited laboratories in order to minimize errors in these studies. The presence of gases in the slag was measured using an ALTAIR gas analyzer.

To define the effect of the type of activators on the strength and degree of hydration of the hardened ecophosphoslag binder, samples were prepared with a composition of 1: 0 (slag dough) 2x2x2 cm in size, solidified under steaming conditions at 90 ° C based on the 3 + 10 + 34 mode (rise + isotherm + descent) .

The phase composition of neoplasms – cementing agents was established using the X-ray and derivatographic units DRON-3M and MOM-1500.

Results and discussion. The results are shown in table 1, from which it can be seen that:

- maximum amount of gas evolution from GFS is observed when it is dried without neutralizing additives;
- in the presence of neutralizing additives, the output of gases from GFS decreases by one step - due to the neutralizing properties of the additives;
- grinding the dried GFS promotes an additional emission of gases from it - with addition to a lesser extent and without - to a greater extent;

Table 1 – Qualitative gas content in GFS depending on the method of its processing

Methods and numbers of treatment		GFS condition	Presence of neutralizing substances	Gas content*
Dry	1	Source in the form of granules	without additive	++++
			with additive	+++
	2	Ground	without additive	+++
			with additive	++
Wet	3	Combined with water	without additive	+
			with additive	-
*4 pluses - maximum gas content, 3 - below maximum, 2 - medium, 1 – small, minus - the absence of gases				

- during the GFS grinding in an aqueous medium without additives, the gas yield decreases as much as possible, and with the additive - the gases are completely neutralized.

It follows from what has been said that, regardless of the processing method of GFS, additives are able to neutralize gases, however, the wet method is significantly more effective than the dry one, because:

- with the wet method, the GFS drying is not required, the particles are easier to grind to the required specific surface with less time;
- in a confined space in the aquatic environment, gases cannot escape for any reason but are completely neutralized by additives and activators;
- the products of the interaction of gases with neutralizing and activating additives themselves become activating components of ground GFS.

GFS-based conglomerate initially consists of the following active components: slag, including harmful gases, phosphide, fluoride, sulfide: water, activator and detoxifying agents. Because of this, during the GFS grinding by wet method, the chemical, physico-chemical and catalytic reactions occur in the system. For example (some of them):

$$Na_2CO_3 + H_2S \rightarrow Na_2S + H_2CO_3$$

$$Ca\ (OH)_2 + 2(HF) \rightarrow CaF_2 + 2(H_2O)$$

$$3[Fe(OH)_3^2] + 3(PH_3) \rightarrow 3(FeO) + 9H_2O$$

$$8[F_2O_3] + Ca_3P_2 \rightarrow Ca_3(PO_4)_2 + 16FeO$$

$$Glass + Na_2CO_3 + H_2O \rightarrow xCaO\ (2Na) \cdot ySiO_2 \cdot zH_2O$$

$$Glass + Ca(OH)_2 \rightarrow xCaO \cdot ySiO_2 \cdot zH_2O$$

Table 2 shows the strength and degree of hydration of slag (cement) stone, which shows that:

- Na_2CO_3 has a higher activating property than cement and thus the strength and degree of hydration of hardened binder with Na_2CO_3 are considerably higher - they reach respectively 79.3 ... 83.5 MPa and 21.7 ... 23.3% and cement - only 28.7 ... 37.9 MPa and 16.8 ... 20.4%.

The increased activating ability of Na_2CO_3 compared with cement is due to the fact that:

- sodium carbonate in the hardening system creates an increased alkaline environment (pH>12), due to which glass slag dissolves in large quantities; this in turn contributes to an increase in the content of hydrated phases in the slag stone;
- slag stone hardening is positively affect also by the ions Na^+ included in the calcium hydrosilicate, resulting in the formation of new extended focal type MeO_6 conducive ascending and lattice stability of the hydrate phase, and this is also a positive effect on increasing slag rock strength in general.

Table 2 − Change in the strength and degree of hydration of hardened ecophosphate slag stone depending on the type of activator and the presence of a neutralizer

Activator,%	Neutralizer,%	Compressive strength, MPa	Hydration degree,%
Cement, 5	-	28,7	16,8
	FeO, 3	37,9	20,4
Na_2CO_3, 5	-	79,3	21,7
	FeO, 3	83,5	23,3

The reduced activating ability of cement compared with sodium carbonate is due to the lower reactivity of $Ca\ (OH)_2$ than Na_2CO_3.

An interesting fact: FeO − not only neutralizes hazardous gases and their sources, but also activates slag. This is probably due to the presence on the 3d sublevel $Fe^{2+}(Fe^{3+})$ of electron-free orbitals) which favors iron ions, like an acceptor with neutralizing and activating properties. If this proposition is correct, then we must assume that these properties should have transition metal ions from manganese to copper with electron-free orbitals in them.

Figure 1 shows the X-ray and thermograms of the original slag and hardened slag stone with the addition of soda and cement.

The GFS structure in the X-ray diffraction pattern (1) is not fixed due to its X-ray amorphous state, however:

- its vitreousness is clearly indicated on the thermogram (6), where two peaks appear: the end effect at 800°C, showing softening of the glass and exoeffect at 920°C, characteristic of crystallization of wollastonite;
- a halo is fixed on it, a characteristic attribute of glass.

On X-ray diffraction patterns of slag stone, regardless of the type of activator, the peaks typical for CSH (I) are recorded (d/n = 3,03; 2,28 and 1,83 Å). On the thermograms of slag stone with soda addition, endo effects appear at 160°C and at 140°C with the addition of cement, belonging to the tobermorite gel. In this case, the tobermorite gel which appeared in the slag stone with the addition of soda, is more stable as a result of the introduction of sodium ions in its structure - because of which the endoeffect is shifted towards an elevated temperature (160°C).

The formation of wollastonite during thermal reactions occurring in samples with activators occurs at low temperatures (800°C and 850°C) in comparison with its occurrence from the initial slag only. This is due to the additional appearance of wollastonite from calcium hydrosilicates, which have low resistance at high temperatures.

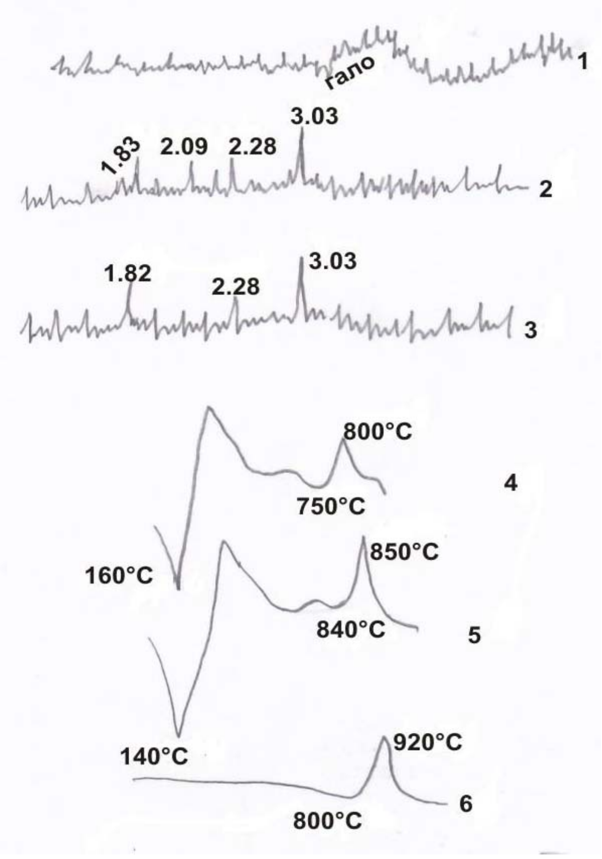

Figure 1 - X-ray diffraction patterns (1-3) and thermograms (4-6) of the initial GFS (1 and 6) and hardened binder with the addition of Na_2CO_3 (2 and 4) and cement (3 and 5)

Finally, it should be noted that both activators and neutralizers do not create independent compounds and do not remain in a free state (doses taken by us), but are included in the structure of calcium hydrosilicates.

Conclusions. It is known that dangerous gases (PH_3, H_2S, HF, etc.) are present in the shells of porous GFS and their sources (Ca_3P_2, CaF_2 and CaS), which makes it undesirable to use it in construction, including road, and in agriculture.

1. However, GFS, according to GOST 3476-74 and 31108-2016, is actively used without neutralization in the production of Portland cement and slag Portland cement, respectively, as a mineral additive and component, which is not acceptable.
2. Meanwhile, there is another regulatory document - ST RK 2301-2013, which clearly states that GFS should be neutralized from phosphorous and fluoride compounds by introducing neutralizing additives by the dry method in the production of cements.

However, this standard is not used in practice by cement producers and not only by them, since methods GFS neutralizing are very complex and some processes are doubtful.

3. In this regard, we proposed (started) a new GFS neutralization trend - the wet method, where hazardous gases and their sources are not only completely neutralized but also become activators, turning into new compounds.

4. It is shown that the hydrated phase of the slag stone consists of calcium hydrosilicates - tobermorite gel and CSH (I), the structure of which includes the components of activators and a neutralizer.

5. It has been suggested that the compound of transition metals of the manganese series to copper, where on the 3d sublevel there are electron-free orbitals capable of neutralizing the dangerous ingredients of GFS.

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ТҮЙІРШІКТЕЛГЕН ФОСФОР ҚОЖДАРЫН ҚАУІПТІ ГАЗДАРДАН ЗАЛАЛСЫЗДАНДЫРУДЫҢ ЖАҢА ТӘСІЛІ

Аннотация. ТФҚ-ны қауіпті газдардан (PH_3, H_2S, HF және т.б.) және олардың көздерінен (Ca_3P_2, CaF_2 және CaS) залалсыздандырудың жаңа дымқыл тәсілі ұсынылады, өйткені залалсыздандыру бойынша құрғақ тәсілдер олардың күрделілігіне және тиімсіздігіне байланысты өміршең емес болып шықты, осыған байланысты ТФҚ құрылыста (және тек онда ғана емес) қолданыстағы нормативтік құжаттарға сәйкес тазартусыз қолданылады.

Зиянды газдардан және олардың көздерінен ТФҚ-ны залалсыздандырудың дымқыл тәсілін әзірлеу кезінде келесі салыстырмалы әдістемелерді қолданамыз:

Біріншісі - 2 кг ТФҚ кептіру пешінде шамамен 600°С температурада 5 сағат бойы кептірілді, содан кейін арнайы тесіктен ауа қоспасын газдың болуына өлшеді.

Екіншісі - кептірілген қож суғаннан кейін дірілдиірменде Na_2CO_3 немесе цемент (салмағы бойынша 5%) және FeO (3 %) қоспасын қосып және осы белсендіретін және бейтараптандыратын қоспаларды қоспай 500 $м^2$/кг меншікті бетке дейін ұсақталды, содан кейін диірмен мен қождағы газдардың сапалық құрамын өлшеді.

Үшіншісі - 2 кг ТФҚ орташаланған сынамасын алып, зертханалық дірілдиірменге салды, содан кейін оған 1:6 ара қатынасында (қож:су салмағы бойынша) су құйылды. Бұл қоспаны Na_2CO_3 немесе цемент (салмағы бойынша 5%) және FeO (3 %) қоспасын қосып және оларды қоспай 500 $м^2$/кг меншікті бетіне дейін ұсақтады, содан кейін диірмен мен қождағы газдардың сапалық құрамын өлшенді.

Анықталғаны:

- ТФҚ-дан бөлінген газдардың ең көп мөлшері залалсыздандыратын қоспаларсыз кептіру кезінде байқалады;

- залалсыздандыратын қоспалар болған кезде ТФҚ-дан газдардың шығуы қоспалардың бейтараптандыратын қасиеттеріне байланысты бір сатыға азаяды;

- кептірілген ТФҚ-ны ұнтақтау газдардың одан қосымша шығуына ықпал етеді – қоспалармен аз дәрежеде, қоспаларсыз - көп дәрежеде;

- ТФҚ су ортасында ұнтақтаған кезде газдардың шығуы барынша азаяды, ал қоспамен – газдар толығымен бейтараптандырылады.

Жоғарыда айтылғаннан ТФҚ өңдеу тәсіліне қарамастан, енгізілетін қоспалар газды бейтараптандыруға қабілетті болғаны байқалады, алайда құрғақ әдіспен салыстырғанда дымқыл тәсіл тиімдірек көрінеді, өйткені:

- дымқыл тәсілді қолданған кезде ТФҚ кептіру талап етілмейді, бөлшектер аз уақытпен қажетті меншікті бетке дейін оңай ұнтақталады;

- дірілдиірмен болып табылатын жабық кеңістікте, су ортасында газдар қандай да бір себептер бойынша ұшып кете алмайды, және қоспалар мен белсендіргіштер арқылы толық бейтараптандырылады;

- газдардың бейтараптандырушы және белсендіруші қоспалармен өзара әрекеттесу өнімдері өздері ұнтақталған ТФҚ-ның белсендіруші компоненттеріне айналады.

ТФҚ-ны бейтараптандыратын және белсендіретін қоспалары бар су ортасында ұсақтау барысында жүйеде химиялық, физикалық-химиялық және каталитикалық реакциялар (жалпы алғанда олардың саны шамамен 20) орын алатыны көрсетілген.

Фазалық құрамды зерттеу, ұнтақталған ТФҚ гидратация дәрежесі және экофосфошлак тұтқышынан алынған қатайған қож тасының беріктігі төмендегілерді көрсетті:

– Na_2CO_3 цементтің-қоспаның неғұрлым жоғары белсендіргіш қасиеттеріне ие, сондықтан Na_2CO_3 қоспасы бар қатайған экофосфошлак тұтқырғыштың беріктігі мен гидратация дәрежесі айтарлықтай жоғары – тиісінше 79,3 ... 83,5 МПа және 21,7 ... 23,3% жетеді, ал цементпен-қоспамен - тек 28,7...37,9 МПа және 16,8...20,4 % жетеді;

– Цемент-қоспамен салыстырғанда Na_2CO_3 жоғары белсендіргіш қабілеті мыналарға негізделген:

- натрий карбонаты қатаятын жүйеде жоғары сілтілі ортаны (pH>12) құрады, соның арқасында шыны қож көп мөлшерде ериді; бұл өз кезегінде қожды тастағы гидраттық фазалардың мөлшерін арттыруға ықпал етеді;

- қож тасының нығыздалуына кристалды тор мен гидратты фазалардың өсуі мен орнықтылығына ықпал ететін MeO_6 типті жаңа кеңейтілген үйлестіру орталықтарының пайда болуы нәтижесінде кальций гидросиликаттарының – C-S-H және CSH (I) құрамына кіретін Na^+ иондары да оң әсер етеді, бұл да қож тасының беріктігінің жоғарылауына оң әсер етеді.

FeO қауіпті газдар мен олардың көздерін бейтараптандырып қана қоймай, сонымен қатар ұнтақталған ТФҚ-ны белсендіретіні анықталды. FeO бейтараптандыратын және белсендіретін қабілеті Fe^{2+} (Fe^{3+}) 3D-төменгі деңгейінде электрондардан бос орбитальдардың болуымен байланысты болуы мүмкін, бұл, акцептор ретінде, бейтараптандыратын және белсендіретін қасиеттері бар темір иондарына ықпал етеді. Мұндай қасиеттерге қосылыстар, соның ішінде 3D-төменгі деңгейде электрондардан бос орбитальдері бар ауыспалы металдар элементтерінің өздері де ие болуы тиіс деп болжауға болады.

Қатайған экофосфоқожды тұтқырда негізінен кальций гидросиликаттарының екі түрі – аморфты тоберморитті гель (C-S-H) және субмикрокристалды CSH (I) пайда болатыны анықталған.

Түйін сөздер: түйіршіктелген фосфор қожы, қауіпті газдар және олардың көздері, темірдің шала тотығы, сода, цемент, беріктік, гидратация дәрежесі.

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НОВЫЙ СПОСОБ ОБЕЗВРЕЖИВАНИЯ ГРАНУЛИРОВАННОГО ФОСФОРНОГО ШЛАКА ОТ ОПАСНЫХ ГАЗОВ

Аннотация. Предлагается новый мокрый способ обезвреживания ГФШ от опасных газов (PH_3, H_2S, HF и др.) и их источников (Ca_3P_2, CaF_2 и CaS), поскольку сухие способы по обезвреживанию оказались нежизнеспособными в виду их сложности и неэффективности, из-за чего ГФШ в строительстве (и не только) применяют без очистки согласно существующим нормативным документам.

При разработке мокрого способа обезвреживания ГФШ от вредных газов и их источников применяем следующие сравнительные методики:

Первая – 2 кг ГФШ подвергли сушке при температуре около 600°С в сушильной печи в течение 5 часов, после чего из специального отверстия измеряли воздушную смесь на предмет присутствия газов.

Вторая – высушенный шлак после остывания измельчали в вибромельнице до удельной поверхности 500 $м^2/кг$ с добавкой Na_2CO_3 или цемента (5 % по массе) и FeO (3 %) и без этих активизирующих и нейтрализующих добавок, после чего измеряли качественное содержание газов в мельнице и шлаке.

Третья – взяли 2 кг ГФШ усредненной пробы и поместили в лабораторную вибромельницу, а затем туда же налили воду в соотношении 1:6 (шлак: вода по весу). Измельчали эту смесь с добавкой Na_2CO_3 или цемента (5 % по массе) и FeO (3 %) и без них до удельной поверхности 500 $м^2/кг$, после чего измерили качественное содержание газов в мельнице и шлаке.

Установлено, что:

- максимальное количество выделения газов из ГФШ наблюдается при сушке без обезвреживающих добавок;

- в присутствии обезвреживающих добавок выход газов из ГФШ уменьшается на одну ступеньку – из-за нейтрализующих свойств добавок;
- размол высушенного ГФШ способствует дополниельному выходу газов из него – с добавкой в меньшей степени, без – в большей степени;
- при размалывании ГФШ в водной среде выход газов максимально уменьшается, а с добавкой – газы полностью нейтрализуются.

Из сказанного следует, что независимо от способа обработки ГФШ вводимые добавки способны нейтрализовать газы, однако мокрый способ эффективнее по сравнению с сухим, поскольку:

- при мокром способе сушка ГФШ не требуется, частицы легче размалываются до необходимой удельной поверхности с меньшим временем;
- в замкнутом пространстве, каким является вибромельница, в водной среде газы не могут улетучиваться по тем или иным причинам, а полностью нейтрализуются добавками и активизаторами;
- продукты взаимодействия газов с нейтрализующими и активизирующими добавками сами становятся активизирующими компонентами молотого ГФШ.

Показано, что в ходе измельчения ГФШ в водной среде с нейтрализующими и активизирующими добавками в системе происходят химические, физико-химические и каталитические реакции (в общей сложности их около 20).

Исследования фазового состава, степень гидратации молотого ГФШ и прочность затвердевшего шлакового камня, полученного из экофосфошлакового вяжущего, показали следующее:

- Na_2CO_3 обладает более повышенными активизирующими свойствами цемент-добавка, поэтому прочность и степень гидратации затвердевшего экофосфошлакового вяжущего с добавкой Na_2CO_3 существенно выше – достигают соответственно 79,3…83,5 МПа и 21,7…23,3 %, а с цементом-добавкой – только 28,7…37,9 МПа и 16,8…20,4 %;
- Повышенная активизирующая способность Na_2CO_3 по сравнению с цементом-добавкой обусловлена тем, что:
- карбонат натрия в твердеющей системе создает повышенную щелочную среду (pH>12), благодаря чему стеклошлак растворяется в большом количестве; это в свою очередь способствует увеличению содержания гидратных фаз в шлаковом камне;
- на упрочнение шлакового камня позитивно влияют также ионы Na^+, входящие в состав гидросиликатов кальция – C-S-H и CSH (I), в результате образования новых расширенных координационных центров, типа MeO_6, способствующих возрастанию и устойчивости кристаллической решетки и гидратных фаз, а это тоже положительно влияет на повышение прочности шлакового камня.

Определено, что FeO не только нейтрализует опасные газы и их источники, но и активизирует молотый ГФШ. Нейтрализующая и активизирующая способность FeO, возможно, связана с наличием на 3d-подуровне Fe^{2+} (Fe^{3+}) свободных от электронов орбиталей, что способствует ионам железа, как акцептор, с нейтрализующими и активизирующими свойствами. Можно предполагать, что такими свойствами должны обладать соединения, и в том числе, сами элементы переходных металлов, имеющих в 3d-подуровне пустующие от электронов орбитали.

Установлено, что в затвердевшем экофосфошлаковом вяжущем возникают в основном два вида гидросиликатов кальция – аморфный тобермоQитовый гель (C-S-H) и субмикрокристаллический CSH (I).

Ключевые слова: гранулированный фосфорный шлак, опасные газы и их источники, закись железа, сода, цемент, прочность, степень гидратации.

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