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THE EFFECT OF GRANULATED FLY ASHES WITH PHOSPHOGYPSUM ON THE HARDENING OF CEMENT MORTAR

WŁYW GRANULOWANYCH POPIOŁÓW LOTNYCH Z FOSFOGIPSEM NA PROCES TWARDNIENIA ZAPRAWY CEMENTOWEJ

A b s t r a c t

The results of research on the use of granulated fly ashes with phosphogypsum in the production of cement and their impact on the hardening of cement mortar are presented in this paper. The materials used for the production of granules were fly ash from power plants and a twenty-percent proportion of phosphogypsum waste from the production of phosphoric acid. The granules were tested in terms of their use for the production of cement. It has been shown that, in accordance with the Polish Standard PN-EN 197-1: 2012, cement with 20% of shredded granules meets the requirements of strength for class 32.5. Cement mortar was made and the properties were compared with typical mortar prepared from ash with gypsum. It was found that the tested cement mortar have a longer setting time. However, both types of mortar had similar compressive strengths and flexural strengths after hardening for twenty-eight days.

Keywords: fly ash, phosphogypsum, granulation, cement, mortar

S t r e s z c z e n i e

W pracy przedstawiono wyniki badań wykorzystania granulowanych popiołów lotnych wraz z fosfogipsem do produkcji cementu oraz ich wpływu na proces twardnienia zaprawy. Materiałem do produkcji granulatu były elektrowniane popioły lotne z 20% udziałem odpadowych fosfogipsów powstających przy produkcji kwasu fosforowego. Wykonano testy wytrzymałościowe granulatu w aspekcie jego wykorzystania do produkcji cementu. Stwierdzono, że zgodnie z polską normą cement z 20% udziałem granulatu zawierającego fosfogipsy spełnia wymagania wytrzymałościowe cementu dla klasy 32,5. Wytworzono zaprawę cementową oraz określono właściwości w porównaniu do typowej zaprawy z cementu popiołowo-gipsowego. Stwierdzono, że testową zaprawę charakteryzuje dłuższy czas wiązania i twardnienia. Jednakże oba rodzaje zaprawy uzyskały porównywalną wytrzymałość na zginanie i ściskanie po 28 dniach twardnienia.

Słowa kluczowe: popioły lotne, fosfogipsy, granulowanie, cement, zaprawa

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1. Introduction

Due to its dustiness, the fly ash resulting from coal-based energy production is problematic to transport and store [17]. The addition of a binder such as Silment (a fine hydraulic binder with a large share of active silica) to the ash at a proportion of 10% reduces its dustiness and allows its use in the upper section and substructure of high-quality road construction [24]. Among other benefits, more efficient dust reduction assists the granulation process in which pellets are formed with a higher density, stability, and more constant size distribution as compared to the granular material [12]. In order to increase the mechanical strength of the granules is added the binder to the agglomeration process [16].

In the nineteen-eighties in Police Factory technology for the granulation of ash with phosphogypsum waste in drum granulators was implemented. This made it possible to limit the dusting and leaching of water-soluble components [9]. A study of the granulation of ash from fluidised bed boilers from the Czechowice Dziedzice power plant was made using a vibrating gutter granulator and this obtained satisfactory strength parameters without the addition of binding agents. A much greater effectiveness of vibrating granulation compared to the typical preparation of grains in a disc granulator was also confirmed [6].

To granulation of coal mules on an industrial scale, implemented quick action mixers and drum granulators, where a traditional lime binder was replaced with calcareous fly ash and bottom ash – they are by-products of coal combustion in a fluidized bed boilers [6]. The obtained aggregate has high mechanical strength to weather conditions, transport and storage. It meets the requirements applicable to materials used in the construction of roads, highways and hydro-technical structures [20]. In the described technology the fuel-pellet as a stand-alone product or as a blending fuel component is produced [10].

Numerous studies have confirmed the possibility of using calcareous fly ash in the next-generation concrete, while preserving the required technological parameters of concrete mixtures with regard to their workability above all [7]. The compactability and mechanical properties of concrete made with cement and calcareous fly ash were adequate and fulfilled the established standards [2, 8]. Cements with the addition of granulated and crushed blast furnace slag, as well as siliceous fly ash, similarly used to the geoengineering works.

Phosphogypsum may be supplementary to alumina and calcareous cement, which is used as an alternative to Portland cement. The results confirmed that cement with a 10% content of phosphogypsum is of a high-quality [14]. Phosphogypsum from apatite processing was also tested – this is a mineral from the group of phosphates sourced from Kola Cape in Russia. Phosphogypsum is neutralized with lime with the addition of 5% clay and 5% of milled glass, it is then calcined at 900°C. Anhydrite cement was obtained; its strength after twenty-eight days of hardening was 55 MPa [13].

The lime-fly ash-phosphogypsum binder has a much higher strength (80–90%) than the lime-fly ash which is widely used as a road base material in China. When the content of phosphogypsum is 18–23%, the highest twenty-eight day strength is achieved [22]. The purified phosphogypsum can be used as an additive in place of mineral gypsum in the manufacture of ordinary Portland cement [18].

The aim of this paper is to present the results of industrial granulation tests of fly ashes with phosphogypsum and to determine the possibility of using the granules obtained for the production of cement.

2. Materials

Phosphogypsum from Gdansk Phosphate Fertilizer Plant “Fosfory”, which is part of the Azoty Group ‘Pulawy’ S.A., was used. Phosphogypsum is a waste product arising in the manufacture of phosphoric acid. Chemical analysis of the waste showed that it contained 93.4% gypsum by dry weight and other typical impurities of minerals (silicon oxide, aluminum oxide, iron oxide, phosphorus oxide) as well fluorides and chlorides (Table 1).

Table 1

Chemical composition of phosphogypsum

Component	Content of component (calculated on dry weight) [%]
Gypsum ($CaSO_4$)	93.4
Fluorides (CaF_2)	2.6
Phosphorus oxide (P_2O_5)	1.8
Silicon oxide (SiO_2)	1.2
Aluminum oxide (Al_2O_3)	0.7
Iron oxide (Fe_2O_3)	0.2
Chlorides ($CaCl_2$)	0.1

Studies of these wastes made in the years 1997 and 2007 by Borylo et al. [4] have shown elevated concentrations of radioactive radionuclides from phosphate rock. The concentration of uranium isotopes 238U in samples of phosphogypsum ranged from 8.0 ± 0.5 $Bq \cdot kg^{-1}$ and 48.1 ± 1.0 $Bq \cdot kg^{-1}$, while the concentration of isotopes of polonium 210Po was 613 ± 13 $Bq \cdot kg^{-1}$ and 695 ± 9 $Bq \cdot kg^{-1}$. The radioactivity of 234U / 238U in samples of phosphogypsum was close to unity (0.90 ± 0.06 and 1.03 ± 0.03) [4]. The high levels of polonium isotopes in the waste are as a result of the migration of these nuclides into a fraction of phosphogypsum in the production process, whereas the content of uranium isotopes are small, since it is bound to the fraction of phosphoric acid.

Isotopes of polonium and uranium emit alpha radiation, which, compared to beta or gamma radiation, are within a range that is less penetrating and is basically harmless when in contact with human skin. Alpha radiation may pose a risk to human health in such instances where the isotopes fall into the interior of the body, for example, as a result of the inhalation of air. Therefore, it is recommended that there should be effective ventilation in rooms built with building materials containing additives of fly ash or phosphogypsum [21].

According to the council of ministers regulation in Poland dated 03/12/2002, materials used for the construction of buildings should be restricted with regard to their content of radioisotopes. Their concentration was determined by two factors that have values f1 ≤ 1.2 and f2 ≤ 240 Bq·kg^{-1} [5].

The produced granules contained a 20% share of phosphogypsum waste, that after grinding added to the clinker. On the mass of cement mortar, there were only 4% pure waste of phosphogypsum. Based on a calculations stated that the concentration of uranium isotopes in the cement with the addition of phosphogypsum was a maximum of 1.96 Bq·kg^{-1}, and isotopes of polonium was up to 28.16 Bq·kg^{-1}. Therefore, their radioactive impact is much lower than the permissible amounting to 240 Bq·kg^{-1}. The addition of a 4% share of phosphogypsum to the cement does not therefore constitute a danger to human health when this material is used in construction.

The moisture levels of phosphogypsum ranged from 24.3% to 28.2%. The hydrated material was heat treated. A rotary dryer was used with a length of 8.0m and a drum diameter of 0.8 m can output approx. 700 kg·h^{-1}. After the process of drying, the resulting value of the moisture content was approx. 5.0% – this is sufficient for its use as a binder for the granulation of fly ashes.

Fly ash for the research came from electrostatic filters in fluidised bed boilers that burn hard coal in the Łagisza plant in Będzin. The average chemical composition of fly ash of ten samples taken from individual deliveries are shown in Table 2.

Table 2

Chemical composition of fly ash from fluidized bed boilers

Component	Content of component (calculated on dry weight) [%]
Silicon oxide (SiO_2)	49.3
Aluminum oxide (Al_2O_3)	24.8
Iron oxide (Fe_2O_3)	9.1
Calcium oxide (CaO)	3.8
Magnesium oxide (MgO)	2.7
Phosphorus oxide (P_2O_5)	1.8
Sulfur compounds (SO_3)	1.0
Nitric oxide (Na_2O)	0.9
Potassium oxide (K_2O)	0.7

3. Methods

3.1. Granulation of fly ash with phosphogypsum

The merger for pelleting was homogenized in a mixer for 5 minutes, adding the ash phosphogypsum of approx. 20% by weight. Water to humidification used by a spray nozzle with a diameter of 1.4 mm. The process of granulation occurred at an angle adjusted to of 50° and a plate speed of 30 rpm. The maximum diameter of the granules was approx. 20 mm and the average size was 5–15 mm. The finished products were seasoned for at least forty-eight hours. Next, the following research tests on these granules were performed:
– compressive strength,
– strength of gravitational dump,
– bulk density,
– moisture content,
– abrasion resistance.

Strength of the granules was evaluated on the basis of compressive strength test and through use of the gravitational dump test. The compressive strength conducted in axial test, by measuring the maximum contact pressure of stamp using the testing machine Zwick 100. The granules were placed on a flat surface between the heads of the testing device and compressed until the point of failure. The strength of gravitational dump was evaluated by the percentage weight defeat after three dumps of samples from a height of 1.0 meter onto a steel plate with a thickness of 20 mm, and after sieving the samples through a sieve with a mesh diameter of 6.5 mm.

On the basis of previous studies [3], the minimum rate of contact pressure breaking the granules should be above 1.0 MPa. In the test the required minimum strength for transport or storage should be at least 80% [3].

The abrasion resistance test was performed according to ASAE S269.4 [1] and involved mixing the granules at a speed of 50 min^{-1} for 60 seconds in a horizontally placed drum with a diameter of 0.25 m equipped with longitudinal baffles. Afterwards manually sieved samples through a sieve with a mesh diameter of 3.15 mm, and calculated the percentage wastage of granules after the test run.

3.2. Manufacture of cement with granules

Tests of cement with granules were carried out on an industrial scale. Cement mixture comprises 80% by weight of clinker and 20% of crumbled granules. Three-chambered cement mill used for shredding of, with a length of 11.0 m and a diameter of 2.0 m. Clinker, together with the granulate, was served to the dispenser of the mill using a feed rotary table. The output of the mill was 15 tons/h and produced approx. 80 tons of cement.

4. Results

The results of tests conducted on the physical and mechanical properties of granules made from fly ash with phosphogypsum shown in Table 3.

Table 3

Results of the test of granules made from fly ash with phosphogypsum

Trial No.	Compressive strength [MPa]	Strength of dump [%]	Bulk density [$kg \cdot m^{-3}$]	Moisture content [Wt. %]	Abrasion resistance [%]
1	3.8	76.3	762	14.0	7.6
2	3.9	78.4	795	13.8	8.0
3	3.9	77.3	800	14.2	7.7
4	4.0	82.5	775	13.3	7.8
5	4.1	81.3	783	14.2	7.2
6	4.2	83.9	790	15.0	7.6
7	4.3	79.5	834	14.8	7.5
8	4.5	82.3	823	14.0	7.8
9	4.6	83.4	841	14.6	6.9
10	4.7	85.2	842	14.0	7.7
Average	**4.2**	**81.0**	**805**	**14.2**	**7.6**

Based on our results, it was found that the average compressive strength of 4.2 MPa is much higher than the required 1.0 MPa. However, the resulting average value of the strength of gravitational dump was, at 81%, only slightly above the minimum of 80%. It should be noted that the granules were tested after a short storage time, but with continued seasoning, we prolonged the beneficial effect to further increase the strength of gravitational dump. The results confirmed that we can produce durable granules from fly ashes with the addition of phosphogypsum – this has the added benefit that it can be transported dust-free, unloaded and stored for further use.

Table 4 shows the results of tests carried out in accordance with the Polish Standard PN-EN 196-1:2006 ‘Methods of testing cement’. There were evaluated of the properties of tested cement, and for comparison, the properties of the typical cement with 16% fly ash and 4% addition of gypsum.

The results show that the cement mix containing granules had a longer setting and hardening time compared to the mixture containing ash and gypsum. The resulting mortar had comparable compressive strengths and flexural strengths after three, seven and twenty-eight days of hardening.

Table 4

Properties of two types of mixture and cement

Type of mixture	Specific surface area [$cm^2 \cdot g^{-1}$]	Setting time [min]		Mortar – strength [MPa]					
		initial	final	flexural [days]			compressive [days]		
				3	7	28	3	7	28
Clinker (80%) + ash (16%) + gypsum (4%)	3010	110	160	4.3	6.2	7.5	19.1	28.7	37.6
Clinker (80%) + granules (20%)	2990	180	260	4.1	6.2	7.3	19.2	27.6	38.7

Similar results to those above were obtained by Miletic et al. [15]. Cement in an industrial test line produced with the addition of phosphogypsum of 15% and samples were collected of Portland cement with natural gypsum of 15% from serial production. The chemical, physical and mechanical properties of both types of cement used for grout were determined. It was found that they met the basic quality requirements. Cement grout with phosphogypsum was characterised by its slow hardening.

The study by Kavas et al. [11] revealed specific peculiarities of the setting and hardening of Portland-fly ash cement. For a cement mixture of clinker 80.5% + fly ash 15% + gypsum 4.5%, setting time was 186 min (initial) and 270 min (final). It is much more than of typical mixture and very similar than tested one. Xinghua Fu et al. [23] tested blended cement with 20% fly ash and 8% gypsum content; the setting time was 162 min to 272 min from initial to final you need to insert the appropriate noun here in order to be grammatically correct. The strength of the cement mortar after twenty-eight days was 6.8 MPa (flexural) and 35.0 MPa (compressive). We found high values of strength, but similar setting time to tested cement.

Based on the results of the study, it was found that the properties of the cement with the addition of granules meet the requirements of Polish Standard PN-EN 197-1:2012 –'Composition, specifications and conformity criteria for common cements' for cement strength class 32.5. This cement is widely used in all types of construction work: as mortars, masonry and plastering, prefabricated articles and basements of supporting structures.

5. Conclusions

On the basis of the research, the following conclusions were drawn:

1. There is the possibility to obtain granules from fly ash and phosphogypsum with adequate strength for dust-free transportation, storage and dosage in the construction industry;

2. The addition of granules effect on drawing out of setting time, and the hardening as well;
3. The compressive strength and flexural strength of mortar with the addition of phosphogypsum are comparable to mortars of ash and gypsum where both cement mixtures meets the requirements of strength class 32.5;
4. The waste phosphogypsum contained in the granules can replace natural gypsum commonly used in the cement industry.

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