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Industrial waste materials as raw materials for the production of low heat hydration cement

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ABSTRACT

It has long been known that certain industrial waste can be used as a raw material or additive in the production of cement. European standards define waste materials that can be used as additives in the production of cement, which are, in particular, fly ash from thermal power plants, granulated blast furnace slag, silica fume, etc. In Bosnia and Herzegovina, there are certain energy and industrial plants that produce such waste materials, which are mostly deposited on open landfills. Such disposal of waste results in contamination of water, soil, and air. Therefore, the aim of this paper was to conduct a preliminary examination of the possibilities of increasing use of industrial materials (fly ash from TPP Kakanj and granulated blast furnace slag of ironworks ArcelorMittal Zenica). The basic parameter that is followed in the work is the heat hydration of cement with different percentages of the addition of industrial waste materials.

1. Introduction

1.1. General information about cement

Construction cannot be imagined without the key inorganic mineral binder - cement, which is used to prepare mortars and concrete, the leading building materials. Thus, cement production can be a measure of both the economic situation and the development of individual countries. Annual cement production in the world has reached an incredible figure of 4.18 billion tons in 2016. In order to have an image of the increase in the annual world production of cement, it is sufficient to know that in 1990, "only" 1.1 billion tons of cement were produced, which means that for 26 years, in the period of 1990-2016, cement production increased almost fourfold. By 2030, cement production is expected to reach 4.8 billion tons of cement per year (Bušatlić and Bušatlić, 2018).

Cement is a hydraulic mineral binder that mixed with water solidifies, both in the air and in the water. The cement production process consists of two stages. The first stage is sintering of limestone and clay in a mass ratio of 3:1, at a temperature of about 1450 °C, when Portland cement clinker is obtained. After that, during the second stage, the obtained Portland cement clinker is milled and mixed with raw gypsum and possibly with other additives that improve its physical and mechanical properties.

1.2. Industrial waste materials as additives to cement

As additives in the cement production, natural and artificial pozzolans are used. Natural pozzolans are volcanic tufts, aluminate and high silicon, amorphous SiO_2 such as diatomite, and trass. Artificial pozzolans are blast furnace slag, fly ash from thermal power plants, silica fume etc. Pozzolans in the cement production are

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used as the correction components of the raw material mixture for the cement production, and as additives to the milled cement clinker when their properties of latent hydraulic binders are used (Bušatlić, 2013).

Inorganic particles, present in fuel gases produced by combustion of coal in thermal power plants, are separated in electrostatic filters, resulting in a waste material known as fly ash. The fly ash, due to sudden cooling, retains the amorphous structure and as such has the pozzolanic properties. As a substitute for clinker, fly ash can be used up to 60 % by mass.

The characteristics of fly ash depend on the type of coal that burns and the combustion regime. Generally, the fly ash with a greater silica content is pozzolan, and if it prevails in calcium then it has latent hydraulic properties. Fly ash has been used as a mineral additive for cement since the 1930s and it can be used as a substitute material in cement for the purpose of environmental protection (Bušatlić, 2013).

Many research have shown that, when fly ash is used, in addition to economic advantages, cement-based composites with high strength and durability are obtained. Cement based concrete containing fly ash materials has a lower initial compressive strength.

Granulated blast furnace slag (GBS) is produced from molten blast furnace slag, which is obtained simultaneously with the iron as a byproduct (Lizarazo-Marriaga et al., 2011). By rapid cooling with water and air glassy granulated material with latent hydraulic properties is formed (Yoshitaka, 2015). It is used for cement, concrete, mortar and aggregates (grained stone of a certain size, e.g. sand, gravel). The above mentioned blast furnace slag that is obtained as a byproduct in iron production can replace up to 80 % of clinker in cement production. The molten slag is similar to the natural liquid lava. If it suddenly hardens, granulated blast furnace slag (GBS) becomes inorganic, glassy material. Glassy nature is responsible for its cement properties. The four basic components represented as oxides are CaO, SiO_2, Al_2O_3 and MgO. In addition, TiO_2 and MnO are also present and affect latent-hydraulic properties (Bušatlić, 2013).

1.3. Cement production and its influence on the environment

The process of cement production is highly energy intensive, and it is estimated that the energy makes up about 40-50 % of the production cost. This provides sufficient opportunities to reduce energy consumption, considering that many cement companies in developing countries consume more energy than the costs show for the developed countries. The theoretical consumption of heat energy for the production of one tonne of clinker is 1,700-1,800 MJ. The most modern cement production plants, which in addition to the rotary kiln have a multiphase cyclone pre-heater and a pre-calcinator, consume 3,000-3,300 MJ/tonne clinker of heat energy, while the outdated plants have consumed 6,000-6,500 MJ/tonne in a wet process (Bušatlić and Bušatlić, 2018).

Cement production is associated with the release of large amount of greenhouse gases, primarily CO_2. Countries that produce the largest quantities of cement, such as India and China, are blamed for increasing cement-related pollution. Cement production accounts for 5 % of the World's total CO_2 emissions in the atmosphere caused by human activity (Bušatlić and Bušatlić, 2018).

The concept of "green cement" was developed as a replacement for a current cement production methods. Green cement uses less natural raw materials, energy and water and appears as a substitute for Portland cement. Green cement is a cement that is produced with the lowest consumption of natural raw materials and fossil fuels, with the maximum use of industrial waste materials as a material for cement production and alternative fuels instead of fossil fuels. Research is ongoing on the development of innovative methods of green cement production in order to reduce and even eliminate emissions of gases that enhance the greenhouse effect and other toxic pollutants (Bušatlić and Bušatlić, 2018).

The basic ingredients of the Portland cement clinker are CaO (C), SiO_2 (S), Al_2O_3 (A) and Fe_2O_3 (F). The above mentioned compounds in cement do not appear as free, but they are always in the form of different complex compounds. In addition, some other ingredients are included in the composition of the cement (admixtures): Na_2O, K_2O, SO_2 (due to the presence of gypsum) as well as free CaO. These ingredients are generally harmful, but they are difficult to avoid because they usually incorporate basic raw materials that are never completely clean (Bušatlić, 2013).

At the sintering temperature, there are a number of chemical reactions from which the most important ones are those that lead to the formation of so called mineral clinker. Regarding the mineral composition of Portland cement, the following ratios are present:

- C_3S (alitte) 45 - 60 %
- C_2S (belitte) 20 - 30 %
- C_3A - 12 %
- C_4AF 10 - 20 %.

As can be seen, silicate minerals account for about 75 % of the total mass and their properties mostly determine the technical characteristics of Portland cement. However, other mineral components are also significant. For example, tricalcium aluminate (C_3A) is often a cause of sulphate corrosion of cement, and because of that in the cement which should be resistant to sulphate activity, the content of this mineral is limited to a maximum of 5 %. Mineral C_3S, on the other hand, has a very high heat of hydration, and thus so called low heat hydration cements tend to have the content of this component at the lowest possible level (Bušatlić, 2013).

1.4. Hydration of cement

Mixing cement with water results in a hydration reaction between cement constituents and water, i.e. hydration of cement. Hydration reactions of individual constituents affect one another and as a result a new chemical equilibrium in the liquid phase is established (Petrovski and Bušatlić, 2006).

All of this has a significant effect on the formation of hydration products. The hydration process of cement minerals is exothermic. The total heat of the cement hydration is equal to the sum of the heat developed during the hydration of certain clinker minerals (Merdić et al., 2012). The heat of hydration is not released at once, but gradually over a longer period of time. Low thermal conductivity of concrete prevents the radiation of heat from the interior of the concrete mass into the atmosphere, especially for large concrete structures such as dams, tunnels, bridges, massive foundations, piers, etc (Bušatlić and Karić, 2018). A large amount of heat released during hydration causes certain strain and formation of cavity and cracks in the cement composite which leads to reduced durability of the structure. With the formation of cavities and cracks, the path to the entry of chemical aggressive water into the concrete mass opens, which leads to the destruction of the entire structure even more rapidly, and which can be completed by demolition of the entire object.

Controlled heat of the cement hydration, which can be adjusted to mineral composition of cement, influences the formation of the hydration products and the density of the cement paste. The too low heat of the cement hydration results in very slow formation of hydration products (Karić, 2017).

Since cement is the only active thermal factor, i.e. the only component of the concrete that produces (releases) heat, by determining the heat of the cement hydration the amount of heat developed when the concrete is hardened, i.e. the temperatures to be reached during that process can be perceived.

Therefore, when constructing concrete structures of large masses, it is of crucial importance to know the characteristics of cement in terms of the heat of hydration or heat that these cements develop in the process of their hydration. Incorporating cement with unknown thermal properties can lead to the demolition of the entire building, due to the disturbed compactness of concrete under the influence of high heating of concrete masses and resulting cavities, cracks, and corrosive water penetrations.

2. Experimental part

At the beginning of the experiment, the chemical analysis of the starting materials was made. In the second part of the study it is examined the heat of hydration of ordinary Portland cement and cement with the addition of fly ash and addition of granulated blast furnace slag.

For the preparation of cement samples the following raw materials were used: cement clinker (produced in CF Kakanj), gypsum stone (Bistrica near Gornji Vakuf), fly ash (TPP Kakanj), and granulated blast furnace slag (ArcelorMittal Zenica).

2.1. Chemical analysis of the starting materials

In Table 1 are shown the results of the chemical analysis of the raw materials used for the preparation of cement samples examined by X-ray fluorescence method (XRF).

In the fly ash from the Thermal power plant Kakanj the highest mass percentage has SiO_2. However, according to BAS EN 197-1 it belongs to calcium ash (CaO content > 10 mass %), whereas according to the American standard ASTM C 618 it is classified as fly ash of class C, i.e. fly ash with high calcium content (CaO content between 5 and 40 mas %) generated by coal burning of lower quality.

Granulated blast furnace slag (ArcelorMittal Zenica) in its composition has the highest percentage of SiO_2 (41.86 %), and CaO (37.01 %).

2.2. Determination of hydration heat

The hydration heat of cement samples was determined according to the standard BAS EN 196-8, which describes the dissolution method for determining the heat of cement hydration using a calorimeter for dissolution (Figure 2).

The hydration heat was determined after 7 days of hydration, and is expressed in Joules per gram of cement.

Samples for determination of hydration heat were prepared by grinding in a laboratory ball mill to a specific surface area of about 3,000 cm^2/g (Figure 1).

Table 1
Chemical composition of materials

Material	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)	Total (%)
Clinker	20.35	6.72	3.74	64.80	1.00	1.07	0.08	0.45	98.21
Gypsum	4.53	1.66	1.20	31.40	2.60	38.45			79.84
Fly ash	46.82	17.57	7.88	17.70	2.21	1.25	0.25	1.62	95.30
GBS	41.86	8.29	1.30	37.01	5.24	1.34			95.04

Figure 1. Laboratory ball mill

After grinding, the samples were sieved through a sieve of 1 mm. According to the standard BAS EN 196-8, the method for determining the heat of cement hydration consists of measuring the dissolution heat in a mixture of acids of unhydrated cement and cement hydrated under conditions prescribed by standard for a period of 7 days. The acidic mixture is obtained by adding 2.760 g of 40 % hydrofluoric acid to each 100.0 g of (2.00 ± 0.01) mol/l nitric acid, or 2.60 ml of hydrofluoric acid per 100.0 ml of nitric acid. The norm prescribed hydration conditions are:

- water/cement ratio 0.40,
- use of pure cement paste,
- curing the samples during the hydration process (until full 7 days after the preparation of the cement paste) at a constant temperature of (20 ± 0,2) °C.

Hydration heat Hi is obtained from the difference between the hydration heat of the nonhydrated cement, Qa, and the hydration heat of hydrated cement, Qi.

The calorimeter which is used for determination of the hydration heat consists of a dissolution vessel, a thermometer, a funnel, and a mixer (Figure 2).

Figure 2. Calorimeter

Four samples of cement were prepared for this examination. In the table 2 the cement mark and composition of the tested cement samples are shown, as well as specific masses and specific surface areas. As it can be seen from the table, the first reference cement sample (C) consisted only of clinker and gypsum.

To the second sample (CFA), 50 % of the fly ash was added to the cement in the grinding stage, while to the third sample (CBS) was also added, at the grinding stage, 50 % of the granulated blast furnace slag. To the fourth sample addition was made in the same way, 25 % of the fly ash and 25 % of the granulated blast furnace slag.

In the table 3 the heat of cement hydration (H_i) for all tested cement samples is given, and figure 3 shows the reliability diagram of cement hydration heat from cement content.

Table 2
Designations and composition of the cement samples

Cement mark	Cement mark according to BAS-EN 197-1	Mass content of individual components, (%)				Specific mass (g/cm^3)	Specific surface area (cm^2/g)
		Clinker	Gypsum	Fly ash	Granulated blast furnace slag		
C	CEM I	96	4	-	-	3.12	2,970
CFA	CEM IV/B-W	46	4	50	-	2.89	3,010
CBS	CEM III/A	46	4	-	50	2.85	2,950
CFABS	CEM V/A	46	4	25	25	2.87	3,090

Table 3
The hydration heat of cement samples

Cement mark	Hydration heat (J/g)
C	308.280
CFA	205.813
CBS	182.457
CFABS	204.736

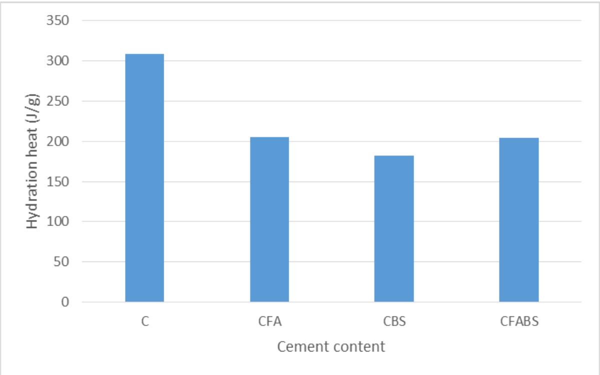

Figure 3. The reliability diagram of cement hydration heat from cement content

3. Discussion of results

Low heat hydration cements, according to the standard BAS EN 197-1, are cements that have hydration heat less than 270 J/g and their mark is LH (low heat), while cements of very low heat of hydration, according to this standard, are cements that have the hydration heat less than 220 J/g of and their mark is VLH (very low heat).

Based on the obtained results and in accordance with the above mentioned standard, the C cement sample, consisting of 96 % clinker and 4 % gypsum, cannot be used as low heat hydration cement.

Hydration heat of the other three cement samples, CFA, CBS, and CFABS, which besides clinker and gypsum consist of industrial waste materials, is less than 220 J/g, and these are cements of very low heat of hydration.

4. Conclusion

Based on the conducted examination, it can be concluded that the industrial waste materials, the fly ash from the Thermal power plant Kakanj and granulated blast furnace slag (ArcelorMittal Zenica), can be used for the production of low and very low heat hydration cement, which are used for the construction of large concrete structures such as dams, bridges, tunnels, massive foundations, piers, etc.

This way, a certain amount of these industrial waste materials can be used, instead of being deposited on a daily basis on the landfill, thus reducing soil pollution in and around the landfill, air pollution during transportation and disposal of the mentioned industrial waste materials, as well as the pollution of underground waters below and around the landfill.

By using the examined industrial waste materials, the use of cement clinker would be reduced, and in that way the emission of harmful gases (CO_2, SO_2, NOx) and the dust generated during the production of clinker would also be reduced.

Also, this would save a certain amount of energy consumed for the production of clinker, and thus the emission of harmful gases generated during the energy production would be reduced.

The subject of further research may be the examination of mechanical properties for the tested cement samples, such as flexural and compressive strength, as well as standard consistency, setting time, cement resistance to sulphate corrosion, etc.

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Korišćenje industrijskog otpada kao sirovine za dobijanje cementa niske toplote hidratacije

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I Z V O D

Odavno je poznata činjenica da određeni industrijski otpad može da se koristi kao sirovina ili aditiv u proizvodnji cementa. Evropskim standardima su definisani otpadni materijali koji se mogu koristiti kao adtivi u proizvodnji cementa, među kojima se nalaze leteći pepeo iz termoelektrana, granulisana visokopećna šljaka, silikatna prašina i drugi. U Bosni i Hercegovini postoje energetska i industrijska postrojenja koja dobijaju takav otpadni materijal koji se uglavnom odlaže na otvorenim deponijama. Odlaganje otpada na taj način dovodi do zagađenja vode, zemljišta i vazduha. Stoga, cilj ovog rada je bio da se izvrši preliminarno ispitivanje mogućnosti povećanja upotrebe industrijskog otpada (leteći pepeo iz Termoelektrane „Kakanj“ i granulisana visokopećna šljaka iz kompanije za proizvodnju čelika ArcelorMittal iz Zenice). Osnovni parametar koji je ispitivan u radu je toplota hidratacije cementa koji sadrži industrijski otpad kao dodatak u različitim procentima.