

POLYMER MODIFIED CEMENT BRICKS BASED ON FLY ASH

Raman Aliti, Gordana Ruseska, Slobodan Bogoevski, Perica Paunović, Goran Načevski, Anita Grozdanov

*Faculty of Technology and metallurgy, University Ss Cyril and Methodius in Skopje, Rugjer Boskovic
16, 1000 Skopje*

Abstract

Fly ash is a pouzzollanic material generated asan industrial waste from the fero-nickel production process as well as from coal-burning thermal power plants. Though a significant fraction of coal fly ash is used as a cement and concrete additive in the world, only a very small portion of the million tons of generated fly ash is re-utilized in Macedonia.

Polymer modified cement bricks based on fly ash were produced in this work. Two types of polymer modified structures with two types of fly ash obtained from FENI and Oslomej have been tested. Test-samples were prepared with 20% of fly ash content in conventional Portland cement. The obtained sample were tested with simulation of aging test in water, acid media (0,25M HCl) and alkali media (0,25 M NaOH). Besides the absorbtion %, morphological changes and porosity of the studied bricks were also followed. Mechanical behavior was followed by the compression test.

Introduction

Industrial waste Fly ash (FA) particles are usually generated as an industrial by-product from the fero-nickel production process as well as from coal-burning thermal power plants and it is recognized as an environmental problem (hot spot). Due to the increased environmental concern, a significant effort on the FA utilization has been undertaken all over the world. Fly ash based cements and mortars have started to be regarded as green cements or alternative low-cost binders to Portland cements for some construction purposes. However, even though application of this type of new materials is wide spread around the world, concrete structures are still rare. There are several challenges, including technical, supply-chain, quality control and cost [1,2].

Fly ash is suitable for use as a geopolymer source material because it consists mostly of glassy, hollow and spherical particles. Fly ash-based geopolymer cement and concrete were studied extensively, and they were well known for their properties, which were better than those of normal concrete due to their lower creep, lower shrinkage, better fire and acid resistance, and resistance to sulfate attack [3,4]. Al Bakri *et al.* reported the study for the production and properties of fly ash-based geopolymer lightweight concrete using foaming agent [4]. Huajun Zhu *et al.* have tested the durability of alkali-activated fly ash concrete and chloride penetration in pastes and mortars [5]. Kumaret *al.* studied the effect of mechanically activated fly ash on the

properties of geopolymer cement [6]. Komljenović *et al.* have studied mechanical and microstructural properties of alkali-activated fly ash geopolymer [7]. They found that compressive strength increases when the finest of fly ash increases. The highest value for the compressive strength was obtained using a solution of sodium silicates as an activator ($n = 1.5$; 10% Na₂O). Sodium silicate was the most suitable as alkaline activator because it included dissolved and partially polymerized silicon which was incorporated into the reaction products and

significantly improved mortar characteristics [7].

Obada Kayalihas developed and patented production process of high performance bricks from 100 % fly ash. He has reported the results of the mechanical properties and advantages gained by this type of bricks over conventional clay bricks [8].

In this work, an attempt was made to produce and to compare the properties of the fly ash based cement bricks by using two different types of fly ash waste particles obtained from Macedonian metallurgical and coal power-plant industry.

Experimental

Two types of polymer modified cement bricks structures with two types of Fly ash obtained from FENI and Oslomej were tested. Test-samples with fly ash content of 20% in conventional Portland cement were prepared by allowing the mix to harden spontaneously at a temperature of 20 °C. Two different mortars were studied: first one with PVC granules embedded inside of the mortar mixture, and the second one with PVC film coatings on the surface of the fly-ash based bricks. The obtained samples were tested with simulation of aging test in water, acid media (0,25M HCl) and alkali

media (0,25 M NaOH). Besides the absorption %, morphological changes have been followed as well. Analysis were realized with Carl ZEISS Jena microscope. Mechanical behavior was followed by the compression test. Compressive strength test was performed according to ASTM C 109/C 109 M by using Universal Compression Testing Machine (a minimum of three samples were tested to evaluate the compressive strength). Porosity was determined according to ASTM C642 and it was calculated using the equation 1.

$$\text{Porosity} = [(M_w - M_d) / (M_w - M_s)] \times 100 \quad \text{eq. (1)}$$

where: M_w – mass of the specimen after immersion in water [g], M_d – mass of the specimen after drying in the oven [g], M_s – mass of the specimen suspended in the water [g].

The water absorption was determined according to ASTM C642 and it was calculated by the equation 2. Water absorption was followed after 24h and after 72 hours in deionized water.

$$\text{Water absorption} = [(M_s - M_d) / M_d] \times 100 \quad \text{eq.(2)}$$

Where: M_s - mass of surface dried sample [g], M_d – mass of oven-dried sample [g].

Results and discussion

Chemical composition of both types of Fly ash used in the preparation of the polymer modified cement bricks was analyzed and the obtained data are shown in Table 1. The differences in the composition of the studied fly ashes fluctuated by ± 10 to 15 % regarding the main oxides SiO_2 , Al_2O_3 ,

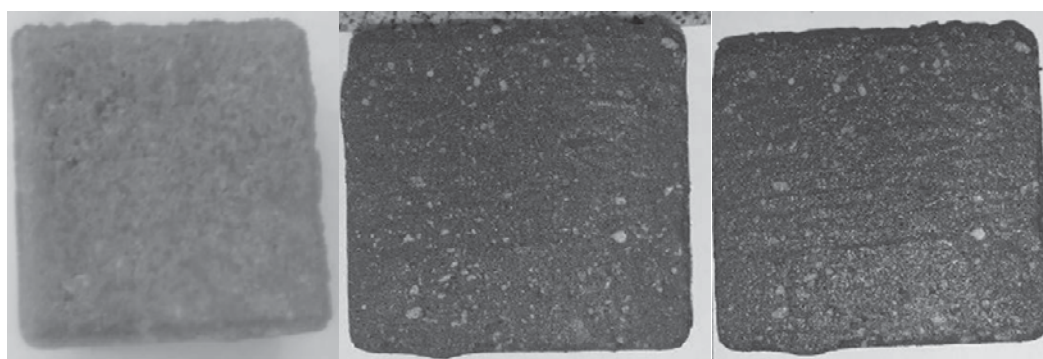
MgO and Fe_2O_3 . As it was expected, in the fly ash supplied from Oslomej dominant fractions were SiO_2 and Al_2O_3 oxides, while in the fly ash obtained from FENI, besides SiO_2 , the oxides of Fe_2O_3 and MgO were in higher portions, also.

Table 1: Chemical composition of Fly Ash samples

Elements	FA-Oslomej [%]	FA-FENI [%]
SiO_2	50	37,5
Al_2O_3	30	1,8
Fe_2O_3	13	22,5
MgO	1,5	14,5
CaO	3,0	2,3
TiO_2	1,0	/
Cr_2O_3	/	1,0

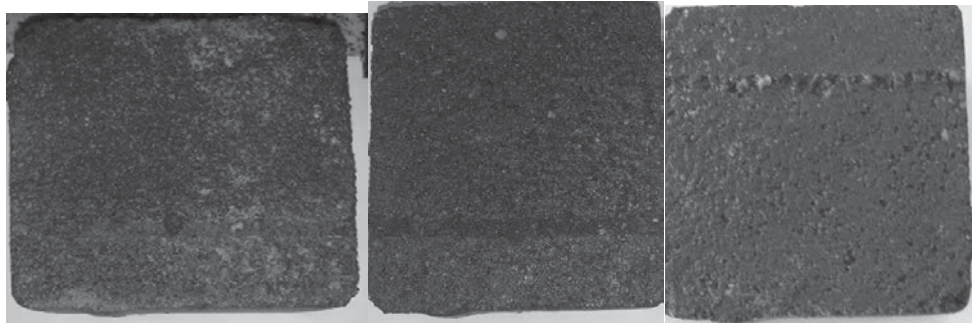
Chemical composition of the FA used in the polymer modified cement bricks is closely related to the corrosion behavior of the obtained bricks. It was shown that better corrosion resistance was demonstrated by the bricks with the FA obtained as a by-product from the ferro-nickel production process. Also, higher corrosion stability

was shown for the polymer modified samples where the bricks were coated with PVC film, compared to the bricks with embedded polymer PVC granules. Surface changes were registered by topographical analysis of the tested samples and representative ones are shown in Figure 1 and Figure 2.



a) Starting **b)** after 24 h in 0,25 M HCl **c)** after 24h in 0,25 M NaOH

Figure 1. Surface changes due to the surface corrosion of the FA-Oslomej based cement bricks



a) Starting b) after 24 h in 0,25 M HCl c) after 24h in 0,25 M NaOH

Figure 2. Surface changes due to the surface corrosion of the FA-FENI based cement bricks

Compressive strength as an essential characteristic for all construction elements based on FA based cements mainly depends on the content of fly ash particles as well as on curing time and curing temperature. It was found that the compressive strength increases when the fly ash content increases, from 11,3 MPa for 5 % FA-Oslomej content to 30,86 MPa for 20 % FA-Oslomej content, or from 13,5 MPa for 5 % FA-FENI content to 32,67 MPa for 20

% FA-FENI content. Comparison of the studied samples with two various fly ash waste shows that higher compression strength exhibited for the bricks with fly ash obtained from FENI, while the comparison of two different polymer modified cement bricks confirmed that the FA-based cement bricks with PVC polymer coating shows higher values for the compressive strength. The obtained results are shown in Table 2.

Table 2. Compressive strength of the FA-based cement bricks

Fly ash cement bricks	F [MPa] with embedded polymer granules	F [MPa] with polymer coating
Bricks with FA-OSLOMEJ	16,62	30,86
Bricks with FA-FENI	20,64	32,67

The obtained data for the higher compressive strength of the fly ash cement bricks with FA-FENI were due to the lower content of open pores in the studied samples.

Due to the different type of the fly ash used in both cement bricks as well as to various type of polymer presence in the studied FA-based cement bricks, some differences in

the type and degree of porosity of the studied samples were registered. The obtained data are shown in the Table 3. The porosity (in both samples and two modes of incorporation) is of the same kind, which indicates that the pores are interconnected and allows free transport or accumulation of the fluid all throughout the volume of the material.

Table 3. Porosity testing in fly ash based cement bricks

Porosity type	Bricks with FA-Oslomej		Bricks with FA-FENI	
	Embedded PVC	PVC coating	Embedded PVC	PVC coating
Open	7,73	18,04	4,70	13,35
Closed	14,46	11,76	21,04	15,01
Total	22,19	29,80	25,74	28,36

Characteristic pores formed in the produced FA-based cement bricks were followed by optical microscopy and they are shown in Figure 3 for bricks with FA-Oslomej (width ~ 0,5mm) and in Figure 4 for bricks with FA-FENI (width ~ 0,8mm). Difference at the samples with different way of

application of the polymer derived from the fact that in its insertion, in the stage of formation, partial filling and blocking the micropores occurs. From there actually originated difference in values for porosity at second sample.

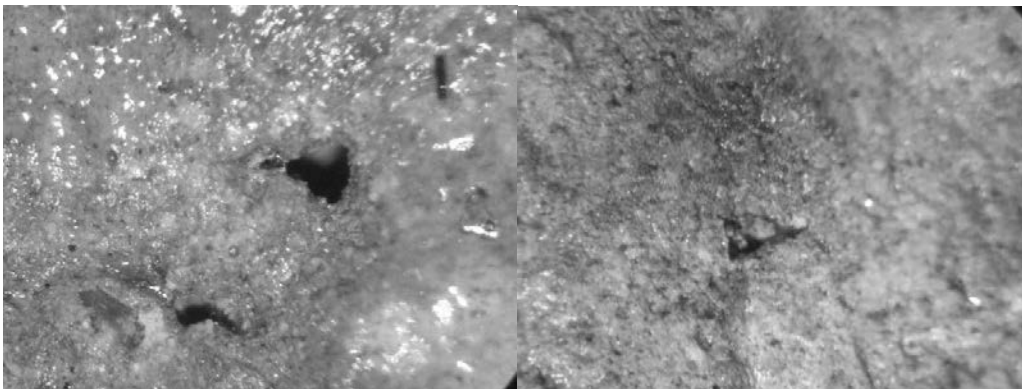


Figure 3. Characteristic pores formed in the bricks from FA-Oslomej

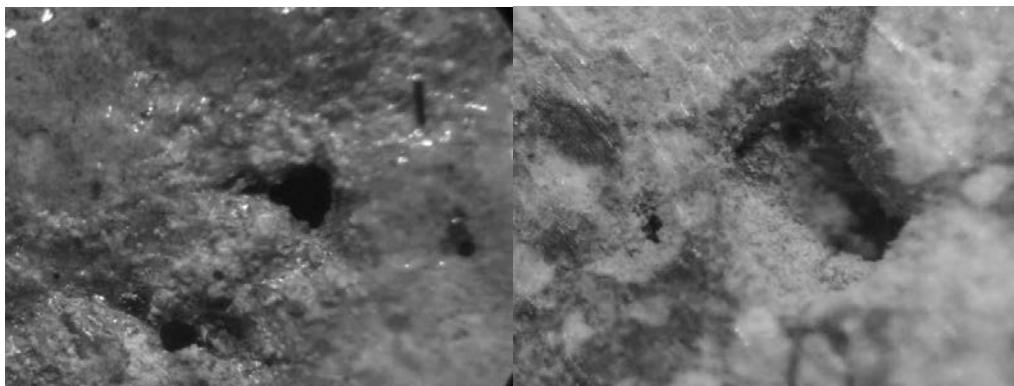


Figure 4. Characteristic pores formed in the bricks from FA-FENI

At the same time, the volume distributed polymer significantly adversely affect the formation of chemical bonds in the cement mass, due to its distribution on the surface of the filler particles and cement. This fact affects the value of the intensity of pressure, which decreases at the sample with volume distribution.

If the sample is applied to the surface after the formation and stabilization shows increased strength of pressure, forming a coating for the exterior of the sample, with the pores filled with a polymer, which causes hardening of the total volume.

The surface layer is not completely filled, therefore, open porosity in the whole

volume of the sample remains available for the fluid (in the case of the experiment - the water).

The narrow margin of almost all parameters of ash samples from different origin, comes probably from different adhesion bonds between the particles of ash and cement particles.

Water absorption data are shown in Table 4. Higher water absorption was measured for the both samples with polymer coating, due to the higher total porosity of the samples (open and trapped voids) in the fly ash based cement bricks.

Table 4. Water absorption data for FA-based cement bricks

Fly ash cement bricks	Water absorption [%] (With embedded polymer)	Water absorption [%] (With polymer coating)
Bricks with FA-OSLOMEJ	3,65	9,45
Bricks with FA-FENI	2,50	6,78

After 24 h in deionized water higher values for water absorption were measured for bricks based on fly ash from FENI (6,33%), while after 72 h in deionized water higher values were obtained for the bricks based on FA supplied from the coal mine Oslomej (6,62%). The obtained data were similar for both types of FA-based cement bricks and they were in the range of 5,93 to 6,62%.

Durability of the FA-based cement bricks was studied by following the stability and

mass changes of the bricks during the freezing and defrosting cycles taking place in the aqueous environment (no disintegration of the samples took place). No visible defects or deformation could be observed after 10 cycles in range 3h at -15°C to 3h at 17°C. From the obtained results it is obvious that the fly ash based cement materials possess an excellent frost resistance.

Conclusions

Two different types of polymer modified cement bricks based on two types of fly ash were produced and tested. Comparison of the studied samples with two various fly ashes waste show that higher compression strength exhibited the bricks with fly ash obtained from FENI, while the comparison of two different polymer modified cement bricks confirmed that the FA-based cement bricks with PVC polymer coating exhibited better compressive strength. Higher water absorption was measured for the both samples with polymer coating due to the higher total porosity of the samples (open and trapped voids) in the fly ash based cement bricks. Porosity testing suggested that there was now remarkable changes between porosity degree in the bricks with the two studied fly ashes. The test results confirmed that the obtained fly ash based cement materials possess an excellent frost resistance

Acknowledgment

This research was performed within the Project “Environment protection of industrial waste through valorisation of metallurgical dust and slags in new environmental friendly polymer mortars and concretes” founded by Ministry of environment and physical planning of R. Macedonia (2012-2014).

References

- [1] Palomo A, Grutzeck MW, Blanco MT. Alkali-activated fly ashes: a cement for the future, *Cem Concr Res* 1999;29(8):1323–9.
- [2] Puertas F, Martinez-Ramirez S, Alonso S, Vazquez T. Alkali-activated fly ash/slag cement strength behaviour and hydration products., *Cem Concr Res* 2000;30(10):1625–32.
- [3] Hardjito, D.; Wallah, S.E.; Sumajouw, D.M.J.; Rangan, B.V. On the development of fly ash based geopolymer concrete. *ACI Mater. J.* **2004**, *101*, 467–472.
- [4] Mohd Mustafa Al Bakri Abdullah, Kamarudin Hussin, Mohamed Bnhussain, Khairul Nizar Ismail, Zarina Yahya and Rafiza Abdul Razak, Fly Ash-based Geopolymer lightweight Concrete Using Foaming Agent, *Int. J. Mol. Sci.*, 2012, *13*, 7186-7198
- [5] Huajun Z, Zuhua Z., Yingcan Z., Liang T., Durability of alkali-activated fly ash Concrete, Chloride penetration in pastes and mortars., *Construction and Building Mater.* , 2004; *65*, 51-59
- [6] Kumar, S.; Kumar, R.; Alex, T.C.; Bandopadhyay, A.; Mehrotra, S.P. Effect of Mechanically activated fly ash on the properties of geopolymer cement. In *Proceedings of the 4th World Congress on Geopolymer*, Saint-Quentin, France, 30 June–2 July 2005; pp. 113–116.
- [7] Komljenović M, Bascarević Z, Bradic V, Mechanical and microstructural properties of alkali-activated fly ash geopolymer. *J. Hazardous Mater.*, (2010), *181*: 35-42.
- [8] Obada Kayali, 2005 World of Coal Ash (WOCA), April 11-15, 2005, Lexington, Kentucky, USA