ENGINEERING TRANSACTIONS • *Engng. Trans.* • **63**, 2, 191–201, 2015
Polish Academy of Sciences • Institute of Fundamental Technological Research (IPPT PAN)
National Engineering School of Metz (ENIM) • Poznan University of Technology

The Influence of Fly Ash Type on Properties of Cements Composites

Katarzyna SYNOWIEC

Silesian University of Technology
Faculty of Civil Engineering
Akademicka 5, 44-100 Gliwice, Poland
e-mail: katarzyna.synowiec@polsl.pl

This paper presents the results of tests carried out on mortars prepared with fly ash – slag cements. Two types of fly ash were used – siliceous (V) and calcareous (W). The influence of fly ash type on properties of mortars was evaluated on the base of results of following tests: compressive strength, consistency and its stability in time and chloride ions permeability and carbonation depth. It was claimed that mortars made with cements containing calcareous fly ash (W) are characterized by higher compressive strength (at each age). Moreover, negative impact of calcareous fly ash (W) on rheological properties of mortars was observed. Durability tests revealed favourable effect of calcareous fly ash on resistance of mortars to corrosive agents attack – lower chloride ions permeability and carbonation depth in comparison to siliceous fly ash – slag cement mortars.

Key words: cement, fly ash, ground granulated blast furnace slag, multicomponent cement.

1. Introduction

The use of multicomponent cements contributes to reduction of CO_2 emission from cement industry by limitation of Portland cement clinker content in cement composition in favour of mineral additives. As non-clinker main constituents of cement the most often used are ground granulated blast furnace slag, siliceous fly ash and limestone [5, 6, 8]. Calcareous fly ash despite its great availability in Poland and Europe (respectively over 5 and over 70 mln tons annually) is not commonly used in cement industry [3, 4]. Valid standard PN-EN 197-1:2012 [9] defines 27 types of common used cements although it restricts the content of the particular components and the possibility of their simultaneous use. Calcareous fly ash combined with ground granulated blast furnace slag might be used in composition of Portland composite cements CEM II/A, B-M. In case of composite cements CEM V besides ground granulated blast furnace slag only siliceous fly ash is possible to be used. Therefore, an interesting question nowadays is the performance of cements made with previously unusual combination and proportion of the cement main constituents, for example fly ash – slag cements containing calcareous fly ash and with low content of Portland cement clinker [5, 6].

Granulated blast furnace slag is generated by rapid cooling of fluid slag, which is a by-product of iron making in a blast furnace. It is characterized by latent hydraulic properties, while properly crumbled and activated by reaction with water binds, and reaction products are the same phases like in case of ordinary Portland cement hardening process [2, 7, 9].

Fly ashes are obtained by mechanical or electrostatic precipitation of dust-like particles from flue gases from furnaces fired with pulverized coal while combustion hard coal siliceous fly ashes with pozzolanic properties are formed. Calcareous fly ashes, on the other hand, are formed in consequence of brown coal combustion process. They reveal pozzolanic properties as well as hydraulic activity [1–4, 9].

Properties and effects of the use of fly ashes are well recognized [1, 3, 4]. Literature quite extensively describes the differences between siliceous and calcareous fly ash, particularly focusing on the physicochemical properties, reactivity of the ashes and the course of hydration process. Calcareous fly ash reacts quicker, especially in the initial period, although it reveals higher water demand in comparison to siliceous fly ash. A possible way to reduce unfavourable effects of the use of fly ashes is to incorporate into the clinker – fly ash system, a third main constituent, such as granulated blast furnace slag or limestone [1, 3–6].

The aim of this study is to examine and compare the effects of concomitant use of granulated blast furnace slag with fly ash (siliceous and calcareous) in cement composites.

2. Characteristics of the components and scope of research

Tested cements were prepared in laboratory with the use, in appropriate proportions, (Table 3) of ordinary Portland cement CEM I 52,5 R, ground granulated blast furnace slag (S) and siliceous fly ash (V) or calcareous fly ash (W). Cements were obtained by homogenizing the components. The chemical composition of the tested cements components is shown in Table 1, while the physical properties in Table 2.

Calcareous fly ash was used in two forms: raw – supplied form (W) and ground – mechanically activated (W+). As a result of grinding the morphology of calcareous fly ash particles has changed (Figs. 1a and 1b). Grains of raw fly ash (Fig. 1a) have an evolute surface area with a lot of open pores after grinding

Table 1. Chemical composition of components of tested cements.

Component	Content [% mass]									
	LOI	SiO_2	Al_2O	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl^-
CEM I 52,5R	2.80	20.05	5.35	2.61	63.42	1.46	2.81	0.18	0.86	0.071
Granulated blast furnace slag (S)	–	37.63	6.84	1.48	45.63	5.33	0.08	0.55	0.56	0.053
Calcareous fly ash (W)	2.67	45.17	20.79	4.58	20.60	1.49	2.96	0.23	0.19	0.001
Siliceous fly ash (V)	1.95	53.25	25.05	6.65	3.86	2.78	0.42	1.11	3.25	0.008

Table 2. Physical properties of components of tested cements.

Property	CEM I 52,5 R	Granulated blast furnace slag (S)	Siliceous fly ash (V)	Calcareous fly ash	
				raw (W)	ground (W+)
Density [g/cm^3]	3.07	2.93	2.22	2.55	2.71
Fineness [m^2/kg]	440.0	420.0	280.0	190.0	470.0

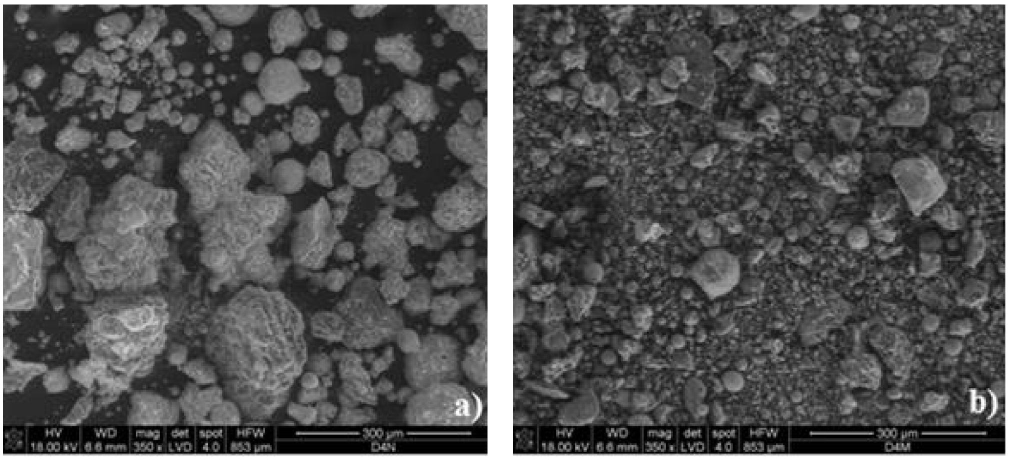

FIG. 1. Morphology of calcareous fly ash particles: a) raw (W), b) ground (W+).

fly ash grains crumbled considerably and the specific surface area increased more than two-fold (Fig. 1b, Table 2).

Tested cements were prepared in three versions – Table 3. In the first version (Table 3, designation PW1–PW3) raw calcareous fly ash (W) was used. In the second version (Table 3, designation PW1+–PW3+) cements contained activated form of calcareous fly ash (W+). In the third version (Table 3, designation PV–PV3) siliceous fly ash V was applied.

Table 3. Tested cements composition.

Component [% mass]	Cement designation								
	PW1	PW2	PW3	PW1+	PW2+	PW3+	PV1	PV2	PV3
CEM I 52,5R	20	20	20	20	20	20	20	20	20
Ground granulated blast furnace slag (S)	60	50	40	60	50	40	60	50	40
Calcareous fly ash (W)	20	30	40						
Calcareous fly ash (W+)				20	30	40			
Siliceous fly ash (V)							20	30	40

The clinker-component (cement CEM I 52,5 R) content was set at the level of 20% in all tested cements. The content of fly ash in the tested cements composition varied in the range of 20–40%, and granulated blast furnace slag in the range of 40–60% (Table 3, Fig. 2). Gypsum, as a regulator of setting time, was used in such a quantity as to obtain stable content of SO_3 in all tested cements equal to 2.81%.

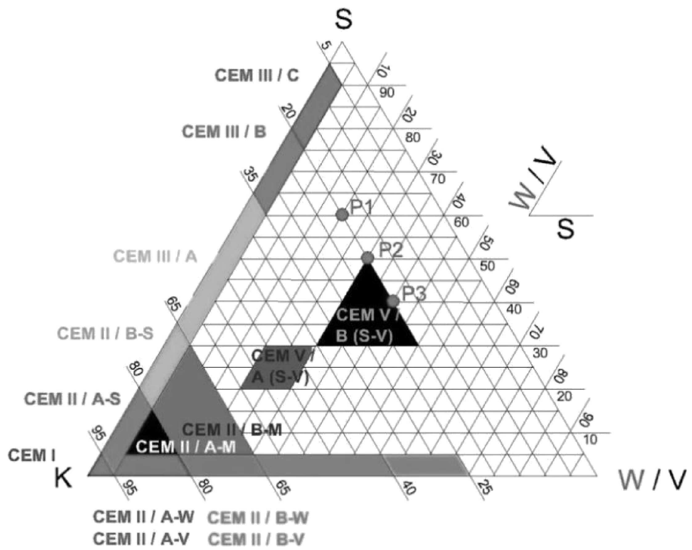

FIG. 2. Composition system of tested cements.

The conducted research allowed to determine the following properties of cements

- density and fineness acc. Blaine method,
- water demand for standard consistency and initial setting time (acc. PN-EN 196-3 [11]),
- compressive strength (acc. PN-EN 196-1 [10]),

- consistency of mortars (acc. PN-EN 1015-3 [12]) and its stability in time,
- chloride ions permeability (acc. ASTM 1202-05 [13]),
- carbonation depth (acc. prEN 12390-12:2010 [14]).

3. Results and discussion

Physical properties of cement were tested acc. PN-EN 196-3 "Methods of testing cement – Part 3: Determination of setting times and soundness" [11]. Cement paste was prepared by mechanically mixing of 500 g of cement and relevant quantity of water to obtain standard consistency. Water demand of cement paste is evaluated on the basis of the depth of penetration of the plunger into the center of prepared paste placed in mould in Vicat's apparatus. When the consistency of paste is set as normal, then mould with a paste is placed underwater in Vicat's apparatus equipped with needle. After suitable time, needle is released to penetrate the paste. Procedure should be repeated up to the moment when penetration depth range established level. Setting time is the time elapsed between zero time and the time at which the depth of penetration range established level, measured to the nearest minute.

Results of physical properties of cement tests are presented in Table 4. While the content of fly ash in tested cements increases (regardless of the type and form of fly ash) initial setting time prolongation was observed. Moreover, in the case of cements containing calcareous fly ash (PW, PW+) a slight increase of water demand in function of fly ash content in the composition of the cement was noticed. The opposite tendency reveals cements containing siliceous fly ash silica (PV).

Table 4. Physical properties of tested cements.

Property	Cement designation								
	PW1	PW2	PW3	PW1+	PW2+	PW3+	PV1	PV2	PV3
Density [g/cm^3]	2.85	2.85	2.8	2.88	2.86	2.83	2.77	2.68	2.6
Fineness acc. Blaine [cm^2/g]	3710	3760	3650	4050	4210	4260	3650	3840	3440
Water demand for standard consistency [%]	30	32	33	31	32	33	28	27	27
Initial setting time [min]	450	505	535	465	500	520	435	470	485

The compressive strength is an important criterion for assessing the quality and properties of the cement. Compressive strength was measured acc. standard PN-EN 196-1 "Methods of testing cement – Part 1: Determination of strength" [10] on 40×40×160 mm cement mortar beams. Standard mortar was prepared with 450 g of cement, 225 g of water and 1350 g of standard sand by mechanical mixing for appropriate time and compacting in special mould. Than the mould with fresh mortar was placed in a moist atmosphere for 24 h and, after demoulding, specimens were stored under water until strength testing date. At the required age, the specimens were taken from wet storage, broken in flexure, and each half tested for strength in compression.

The results of compressive strength test are presented in Fig. 3. Tested cements are characterized by low early compressive strength (after 2 and 7 days) and a significant increase in strength in the later period (Fig. 3). The increase of raw calcareous fly ash content in tested cements results in reduction of the compressive strength detected in each tested age. It should be pointed that mortar made of cement containing 40% calcareous fly ash (PW3) due to the encountered difficulties in proper compaction of mortar, was formed at a water/cement ratio $w/c = 0.60$.

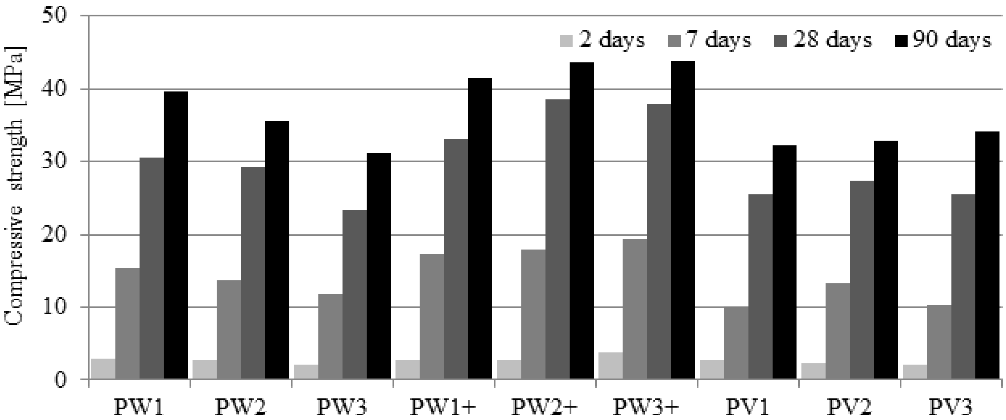

Fig. 3. The compressive strength of cement mortars.

When the component of cement was ground (activated) calcareous fly ash, mortars were concentrated in a proper manner, and with the increase of fly ash content in tested cements increase of strength was observed. It should be assumed that this was caused by the considerable crumbling of grains and the increase in activity due to activation process (by grinding). Compressive strength of mortars with cement containing siliceous fly ash is maintained at a similar level in each tested age, irrespective of fly ash content in cement.

Among all tested cements only those containing ground (activated) calcareous fly ash (PW+) meet the requirements for strength class 32.5 N (acc. PN-EN 197-1 [9]). Slower increase of strength in the early cure ages determinates the need for designation of the compressive strength at later dates. After 90 days of curing a significant increase in strength (Fig. 3) is still observed for all tested cements.

Consistency of mortars was determined by the flow table method acc. to standard PN-EN 1015-3 "Methods of test for mortar for masonry: Determination of consistence of fresh mortar (by flow table)" [12]. Consistency is therefore expressed as the value of the propagation of the mortar. At first standard mortar with 450 g of ordinary Portland cement, 225 g water and 1350 g standard sand should be prepared and after mixing process its spread should be measured. Tested cement mortar consistency is required to spread the same level as standard mortar (±10 mm) thus appropriate water dosage should be determined. Moreover consistency stability in time was tested up to 90 minutes with taking a measure every 30 minutes (starting from zero time).

Results of consistency test are shown in Fig. 4. Obtaining an initial consistency at the level of standard mortar made of cement CEM I 52,5 R ($w/c = 0.50$) was possible by regulating the appropriate amount of added water (w/c ratio). The lowest water demand revealed cements containing siliceous fly ash (PV) moreover, it was observed that higher content of siliceous fly ash in cement composition results in reduction of water demand.

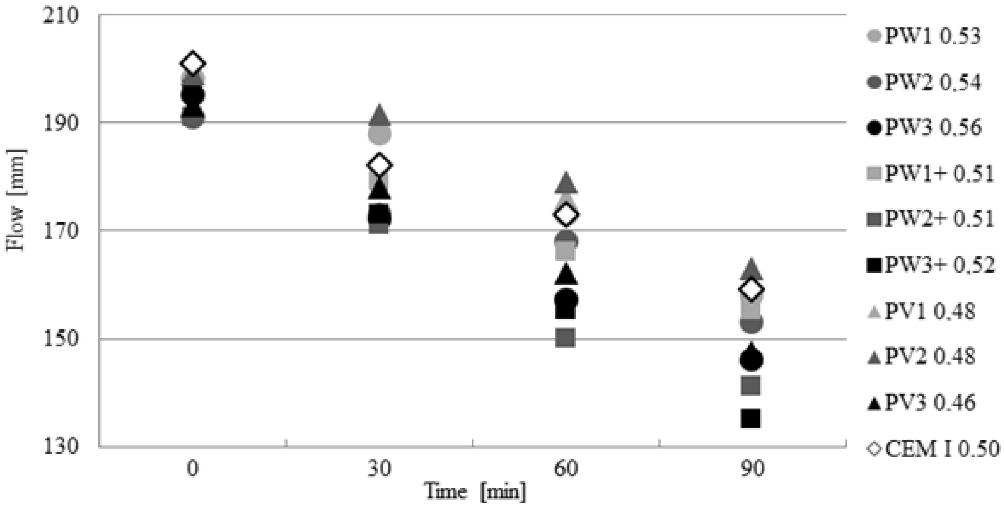

FIG. 4. Consistency of mortars in time.

In case of cements containing calcareous fly ash the opposite trend was observed, particularly evident in the case of cements with raw fly ash (PW). Mortars prepared with cements with calcareous fly ash were characterized by a higher rate of loss of plasticity over time compared to the standard mortar with Portland cement CEM I 52,5 R and cements PV. In addition, after 60 and 90 minutes of testing, cements containing ground calcareous fly ash (PW+), were characterized by significantly lower flowability than cements (PW) containing raw fly ash (Fig. 4).

Durability of cement composites, in parallel to compressive strength, is the main criterion for assessing their quality. The measure of durability is resistance to aggressive agents attack. Potential corrosion resistance of tested cements was evaluated on the basis of the chloride ions permeability test and measurement of the depth of carbonation. The tests were performed after 28 and 90 days of curing.

Mortars resistance to the action of chloride ions was assessed acc. ASTM C 1202-05 “Standard Test Method for Electrical Indication of Concrete’s Ability to Resist Chloride Ion Penetration” [13] on the basis of the rated amount of electric charge passing through the cylindrical sample placed between the electrodes. Cylindrical samples of diameter of 100 mm and height of 50 mm of standard mortar were prepared. At the required age, the specimens were taken from wet storage and before testing, the samples were vacuum saturated with water and placed between NaCl and NaOH solutions – electrodes connected to the device named PROOVE’it, which remained at constant voltage of 60±0.1 V for 6 h. The results of performed tests are shown in Fig. 5.

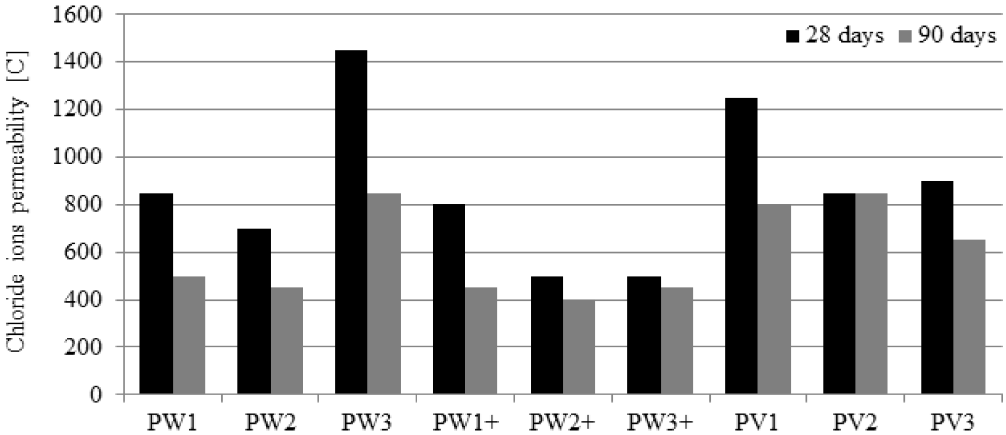

FIG. 5. Chloride ions permeability through mortars.

Tested cements, after 28 days of curing, were characterized by low (less than 2000 C) and very low (less than 1000 C) chloride ions permeability. For comparison, mortar made of ordinary Portland cement CEM I 52,5 R was characterized by high chloride ions permeability (passing charge > 6000 C). All tested cements have met the criterion of low permeability after 90 days of curing. The increase in corrosion resistance in longer terms might be an effect of chemical activity of the ashes. Pozzolanic reaction products tightened cement matrix, which became less porous, and therefore more resistant to aggressive liquids agents attack [3, 4].

The depth of carbonation was determined on standard mortar beam samples (40×40×160 mm) acc. prEN 12390-12 “Testing hardened concrete – Part 12:

Determination of the potential carbonation resistance of concrete. Accelerated carbonation method" [14]. At the required age, the specimens were taken from wet storage and next they were kept for 14 days under air – dry conditions. Afterwards samples were broken in flexure and one of the halves was placed in a chamber were the CO_2 concentration was 4±0.5%. Time of exposure to carbon dioxide was 56 days. The second half stayed under the air – dry conditions as a reference sample. Subsequently samples were broken once again, and the fresh fracture surface was sprayed with a 1% solution of phenolphthalein, the measurement of carbonation depth followed after 60 min of spraying phenolphthalein. The results are presented in Fig. 6.

a) b)

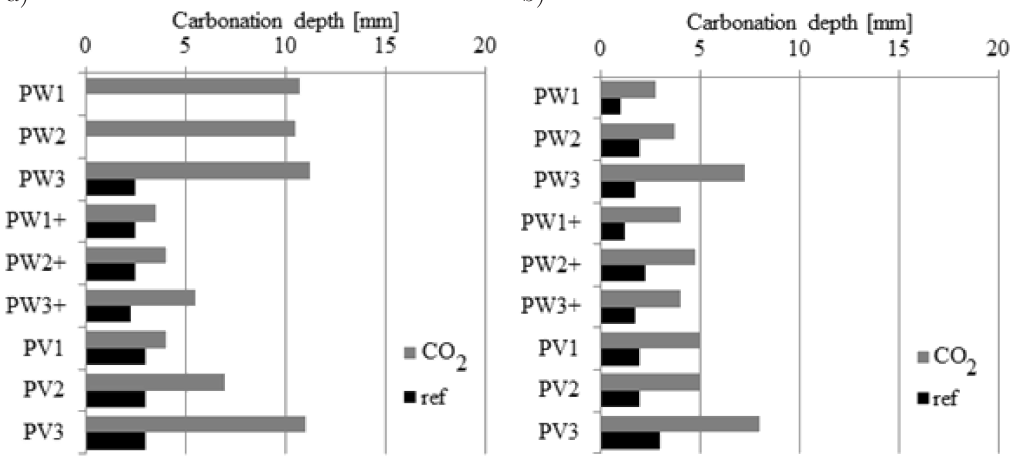

FIG. 6. Carbonation depth in mortars: a) after 28 days, b) after 90 days.

The depth of carbonation depends on the cement composition and the age of cement mortar, and as a result on the permeability of the cement matrix. It was observed that when fly ash content in cement composition increases, front of carbonation reaches deeper. After 28 days of curing the lowest resistance to carbonation was revealed in mortars made of cement containing raw calcareous fly ash (PW), on the other hand the highest resistance was observed in mortars made of PW+ cements – Fig. 6a. After 90 days of curing depth of carbonation was at a similar level (about 5 mm) for all of tested mortars (Fig. 6b). Parallel tested mortar prepared of Portland cement CEM I 52,5 R has not shown any signs of carbonation in any tested terms.

4. SUMMARY

Based on the analysis of the investigated research it was found that mortars prepared with cements containing calcareous fly ash have higher compressive strength at each tested term than cements containing siliceous fly ash. Mechanically activated (by grinding) fly ash was characterized by higher activity what gives the opportunity to produce low clinker content (20%) fly ash – slag cement in strength class 32.5 N. Unfavourable effects of using the calcareous fly ash in cement composition are water demand increase and deterioration of the rheological properties of pastes and mortars. It was also found that mortars made of fly ash – slag cement are characterized by greater resistance to aggressive liquid media (very low permeability of chloride ions), but much lower resistance to carbonation in comparison to ordinary Portland cement CEM I. Moreover, it was claimed that in longer terms tested mortars were characterized by tighter cement matrix, especially when calcareous fly ash was the component of cement.

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Received July 27, 2014; accepted January 3, 2015.