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P a r t 3

ASH AND SLAG HANDLING

3.5. Applications of ash and slag from power coals

3.5.1.4. Fly ash in cement and concrete composition

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ABSTRACT

Fly ash is a by product of hard or brown coal combustion process. Owing to the size of spherical particles (similarly to cement), its chemical and mineral composition as well as the activity, fly ash is widely used in cement and concrete production.

Properly used fly ash has a positive effect both on properties of concrete mixture and concrete itself. It allows the production of high-quality concrete in economical and ecological way. The addition of fly ash to cement (or concrete) composition indicates the reduction of cement clinker content, thus, lower CO2 emission and preservation of non-renewable natural resources.

INTRODUCTION

For several decades fly ash has been globally used as a main component of cement and an additive to concrete. The wide usability of fly ash in building industry results from high fineness (similar to cement), chemical and phase composition close to the one of clay minerals as well as the hydraulic and/or pozzolanic activity [1-4].

Hereby paper attempts to combine the knowledge available in the specialist literature, domestic and foreign, with the practical experience of the applications of fly ash in cement and concrete. The subject of discussion was both siliceous fly ash and calcareous fly ash obtained in conventional furnaces meeting the requirements of cement [5] and fly ash [6] standard.

1. CLASSIFICATION OF FLY ASH

Cement standard PN-EN 197-1 [5] categorizes fly ash into two groups:

- siliceous fly ash denoted as V,
- calcareous fly ash denoted as W.

The first one (siliceous) has pozzolanic properties; the second one (calcareous) may additionally present hydraulic properties.

Loss on ignition of fly ash should fall into one of the following categories:

- Up to ≤ 5.0 % of ash mass,
- Up to ≤ 7.0 % of ash mass,
- Up to ≤ 9.0 % of ash mass.

1.1. Siliceous fly ash (V)

Siliceous fly ash consists mostly of reactive silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3). The remainder contains iron oxide (Fe_2O_3) and other compounds. The proportion of reactive silicon dioxide shall be at least 25,0 % by mass [5, 6]. Table 1 presents the exemplary chemical compositions of fly ash obtained by hard coal combustion [7].

Siliceous fly ash is a dust with very fine particles, generally spherical in shape and pozzolanic properties. i.e., in the presence of water, react chemically with calcium hydroxide to form compounds of hydrated silicates and calcium aluminates. The composition of the liquid phase arising in the paste from non-clinker minerals hydrolysis is just the calcium hydroxide solution with a high degree of saturation, reacting with the pozzolanic additive (fly ash) [2, 3, 8].

An impermanent siliceous-aluminium-potassium glass is a decisive agent determining pozzolanic properties of fly ash. It is formed as a result of separation of an inorganic substance in the carbon combustion process, its melting and solidification in the form of very fine, spherical particles, detected from the waste gases.

The high content of SiO_2 in the siliceous fly ashes and a large proportion of glass in the composition cause the contents of the active SiO_2, so the silica reacting under normal conditions with $Ca(OH)_2$ is relatively high and can exceed 25 % (Table 1). This affects a relatively high pozzolanic activity of siliceous fly ash [3,8].

The main crystalline phases encountered in fly ashes from coal combustion are: quartz, mullite, hematite, and magnetite.

Particle size distribution of siliceous fly ash usually varies, and their proper surface area ranges from 2500 to 4200 cm^2 / g acc. to Blaine [8, 9].

1.2. Calcareous fly ash (W)

Calcareous fly ash is a fine powder, having hydraulic and/or pozzolanic properties. It consists essentially of reactive calcium oxide (CaO), reactive silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3). The remainder contains iron oxide (Fe_2O_3) and other compounds.

The proportion of reactive calcium oxide shall not be less than 10,0 % by mass. Calcareous fly ash containing between 10,0 % and 15,0 % by mass of reactive calcium oxide shall contain not less than 25,0 % by mass of reactive silicon dioxide [5].

Adequately ground calcareous fly ash containing more than 15,0 % by mass of reactive calcium oxide, shall have a compressive strength of at least 10,0 MPa at 28 days when tested in accordance with EN 196-1 [5].

Calcareous fly ash has a different chemical composition and more complex as compared to phase composition of the siliceous fly ash (Table 2). Large differences in the phase composition of siliceous and calcareous fly ash, concern both, the type and the proportion of the crystalline and glassy phase (amorphous).

Table 1. **Chemical composition of siliceous fly ash**

Content, % by mass												
LOI	SO_3	Cl^-	CaO	SiO_2 react.	SiO_2	Al_2O_3	Fe_2O_3	$SiO_2+Al_2O_3+Fe_2O_3$	MgO	Na_2O	K_2O	Na_2O eq.
1,79	0,70	0,02	3,56	44,20	49,86	28,58	6,66	85,10	2,77	1,27	3,48	3,56
7,80	0,35	0,02	4,66	37,47	47,85	24,52	6,30	78,67	2,16	1,14	3,01	3,12
8,48	0,26	0,02	4,35	35,34	47,73	24,93	5,78	78,44	2,53	1,10	2,81	2,95
6,20	0,69	0,05	6,22	30,34	49,80	20,86	8,84	79,50	4,79	1,33	2,16	2,75
8,22	0,47	0,01	5,04	35,49	48,27	20,02	6,64	74,93	1,76	0,99	2,35	2,54
6,25	0,34	0,01	3,53	36,44	49,77	21,95	5,83	77,55	1,49	0,93	2,49	2,57
4,06	0,70	0,02	4,14	34,75	50,46	21,10	6,97	78,53	2,80	1,28	3,07	3,30
7,66	0,39	0,01	4,47	34,95	47,71	24,02	6,55	78,28	2,92	0,96	2,71	2,74
5,17	0,74	0,01	4,33	31,96	49,16	26,28	6,49	81,93	3,01	1,02	2,76	2,84
4,66	0,70	0,01	3,88	33,75	49,65	25,52	6,14	81,31	3,02	1,01	2,76	2,83
3,55	0,38	0,01	3,60	42,41	50,98	25,78	6,02	82,78	2,62	1,17	3,12	3,22

Table 2**. Phase composition of calcareous and siliceous fly ash [10]**

Calcareous fly ash		Siliceous fly ash
Bełchatów	Pątnów	
Crystalline minerals listed in descending order of content		
Quartz Gehlenite Anhydrite Hematite Anorthite Larnite Ye'elimite $C_4A_3\hat{S}$ $C_{12}A_7$ C_3A Free lime Mullite	Quartz Anhydrite Hematite Free lime Larnite Periclase Gehlenite Ye'elimite $C_4A_3\hat{S}$ $C_{12}A_7$ C_3A Anortite	Mullite Quartz Hematite Magnetite
Amorphous phase		
Alumina siliceous calcium glass	Alumina siliceous calcium glass	Alumina siliceous glass

2. FLY ASH AS A MAIN COMPONENT OF CEMENT

The use of mineral additives in cement production is now common action, with the two fundamental aspects: technological and ecological. The immediate effect of the use of mineral additives is, on the one hand, the possibility of secondary raw materials application of the steel and energy industry (reducing CO_2 emissions), on the other – provision to building practice of cements with the most desirable properties.

Siliceous fly ash V and calcareous W, conforming to the standard PN-EN 197-1:2012 [5], may be a component of cement of a common use:

- Fly ash Portland cement CEM II/A,B-V, CEM II/A,B-W.
- Composite Portland cement CEM II/A,B-M in combination with other additives: limestone LL (CEM II/A,B-M(V,LL), CEM II/A, B-M(W,LL); granulated blast furnace slag CEM II/A,B-M(V,S), CEM II/A,B-M(W-S) plus remaining. The combination of three additives with Portland clinker is also possible, provided the minimum content of the additive of 6 %.
- Pozzolanic cement CEM IV/A, B.

In addition, siliceous fly ash V is a component of:

- Composite cement CEM V/A, B.

Cements with the addition of siliceous fly ash V and calcareous fly ash W show a large number of favourable properties compared with Portland cement CEM I. These are the following: extended setting time, good workability of concrete mixture in time, low heat of hydration, high density of concrete, increased and high resistance to corrosion, high growth of strength in longer period, moreover, performing very good strength parameters after low -pressure heat treatment.

Table 3 presents the basic properties of cements with the addition of siliceous fly ash V commercially available in relation with the parameters of Portland cement CEM I 42,5R.

Europe annually produces over 70.0 million tons of calcareous fly ashes (ECOBA 2009). Such fly ash type has been successfully used in cement production in

Bosnia and Herzegovina. Some of the selected properties of cements manufactured in this country are shown in Table 4 [11, 12].

Composite Portland cement CEM II/B-M (V-W) 32,5 R produced in Poland, containing calcareous fly ash W and siliceous V performed the properties listed in table 5.

Table 3. **The properties of cements with siliceous fly ash V addition**.

Cement type	Water demand [%]	Setting time [min]		Compressive strength [MPa]	
		beginning	end	after 2 days	after 28 days
CEM I 42,5R	27,0	185	230	29,3	55,2
CEM II/B-M (V-LL) 32,5R	26,6	230	290	15,8	43,3
CEM II/B-V 32,5R	29,8	170	230	16,6	42,7
CEM II/B-V 32,5R	33,2	205	270	20,5	45,3
CEM II/A-V 42,5R	28,4	225	310	26,3	55,1
CEM V/A (S-V) 32,5R-LH	29,4	195	255	13,9	43,0
CEM V/A (S-V) 32,5R	33,0	235	325	16,8	52,9

Table 4. **Basic properties of cements with calcareous fly ash W.**

Property	Cement type	
	CEM II/B-W 42,5N	CEM IV/B (W) 32,5N
Beginning of setting time, min	210	120
Compressive strength in MPa:		
• after 2 days	20,0	
• after 7 days		25
• after 28 days	49,0	38

Table 5. **Compressive strength of cement CEM II/B-M (V-W) 32,5R compared to other cements manufactured industrially.**

Cement type	Compressive strength [MPa] after:				
	2 days	7 days	28 days	90 days	180 days
CEM II/B-M(V,W)	19,0	33,6	49,3	62,7	69,1

3. FLY ASH AS CONCRETE COMPONENT

Siliceous fly ash conforming to the requirements listed in the tables 6 and 7 [6] is the material commonly applied throughout Europe. It is an essential component of modern concrete.

The proper application of fly ash guarantees improved properties of concrete mixture (consistency, workability, density of concrete) and hardened concrete (reduced thermal hardening process, high strength in longer test periods, increased resistance to chemical corrosion).

Table 6. **Requirements set against fly ash – chemical composition [6]**

Component	Allowed content	
	Fly ash received from coal combustion only	Fly ash received from co-combustion only
Loss On Ignition		
• category A	≤ 5,0 %	
• category B	≤ 7,0 %	
• category C	≤ 9,0 %	
Chlorides	≤ 0,10 %	
SO_3	≤ 3,0 %	
CaO free	≤ 1,5 %[1)]	
CaO reactive	≤ 10,0 %	
SiO_2 reactive	Determination of the content is not necessary It is assumed that the requirement is met	≥ 25,0 %
Sum of oxides: SiO_2, Al_2O_3, Fe_2O_3		≥ 70,0 %
Content MgO		≤ 4,0 %
Sum of alkalis expressed in Na_2O_{eq}		≤ 5,0 %
Content of soluble phosphate compounds expressed in P_2O_5		≤ 100 mg/kg

1) Fly ash, in which the free CaO content is higher than 1.5% by mass may be accepted provided the soundness - Le Chatelier's test at ≤ 10 mm

Table 7. **Requirements set against fly ash – physical properties [6]**

Property		Requirement
Fineness, sieve residue with 0,045 mm of mesh sieve acc.to PN-EN 451-2 • category N • category S		 ≤ 40 % ≤ 12 %
Pozzolanic activity index:	after 28 days after 90 days	≥ 75 % ≥ 85 %
The soundness (test necessary when content of CaO_{free} varies between 1,0 % and 2,5%)		max. 10 mm
Consistent density		Maximum difference ± 200 kg/m^3 compared to the one declared by the producer
Initial setting time of paste containing 25% of fly ash and 75% of Portland cement CEM I		Not longer that 120 minutes compared to the setting time of applied Portland cement CEM I
Water demand (determined for fly ash of S category)		≤ 95% of water demand of Portland cement CEM I used in tests

Siliceous fly ash is also a desirable component of specialist concretes (concrete for massive constructions, hydro technical concrete, and underwater concrete) and a new generation of concrete (high performance and ultra high performance concrete, self-compactive concrete).

The separation of fly ash and obtaining the S category (fineness lower than 12 % and reduced water demand) gives also a wide range of opportunities. Such a fly ash type (category S) is not only a highly active additive to concrete, moreover, it allows for the reduction of water (w/c ratio) essential to reach the complex consistency of concrete mixture, leading to hardened concrete with high durability.

The combination of the use of fly ash with the latest generation of chemical admixtures (superplasticizers, air entraining admixtures) allows to obtain concrete with high content of fly ash with sufficient strength and durability (frost resistance). In this respect, there is a large area for future research and application studies, aimed especially at the durability of concrete.

Calcareous fly ash is not the standardized additive in Europe in contrary to the United States and Canada. In the United States, the requirements for this type of fly ash are covered by the standard ASTM C618 -12 [13], while in Canada the CAN/CSA-A23.5-98 [14]. Table 8 shows the basic requirements for calcareous fly ash set in these standards.

Table 8. **Requirements set against fly ash in the standards ASTM [13] and CAN-CSA [14]**

Property	ASTM C618		CAN/CSA –A23.5-98		
	Class F	Class C	Class F	Class CI	Class CH
Total content of CaO	≤ 10%	≥ 10%	≤ 8%	8 – 20%	≥ 20%
Loss on ignition, maximum, %	6*		12	6	
Fineness (sieve residue 45 μm), maximum, %	34				
Water demand, maximum, %	105%		------		
SO_3 content, maximum, %	5				
Oxides sum content (SiO_2, Al_2O_3, Fe_2O_3)	> 70%	> 50%	-	-	-
Activity index after 7 and 28 days	75%**		68%**		
Autoclave soundness, %	0,8				

**- it is allowed till 12% under the condition of suitability verification*

*** - can not be compared because of the different compositions of mortars fineness and density of fly ash can vary by up to 5% of the declared value*

American experience shows, that calcareous fly ash is more active in the initial stage of hardening (till 28 days) compared to siliceous fly ash (Class F). This may result from the type of hydraulic activity of the fly ash, which effects are previously visible than the pozzolanic activity of siliceous fly ash. Increased activity of calcareous fly ash, in particular, with higher content of calcium, when compared to siliceous fly ash, allows using it in the composition of concrete in bigger proportion [1, 2]. The introduction of calcareous fly ash is not as efficient, in terms of the reduction of thermal parameters of concrete hardening, as the use of siliceous fly ash. Further reduction of thermal parameters of concrete with the addition of calcareous fly ash is observed at its higher share in concrete composition (50 – 60 % relatively to cement mass). Calcareous fly ash, especially added in significant quantities, increases the tightness of the concrete (lower permeability of chloride ions) and prevents or mitigates the negative effects associated with alkaline reaction. Furthermore, it is necessary to consider increased content of SO_3 in cement composition and correlate it with the contents of sulphates in the cement.

SUMMARY

Fly ash, as a by-product of coal combustion, is an interesting mineral additive which should be widely applied in industrial practice, specially, in the production of cement and concrete. The use of fly ash in cement production is associated with continuous control of quality of applied fly ash and thus, the cement produced with their inclusion. The process of co-grinding of fly ash with cement clinker and with the setting time agent, performed very often in cement industry leads to their activation and the increase of their activity. Higher compressive strengths of fly ash cement in standard time are the outcome of such a process. Co-grinding creates great conditions for proper mixing (homogenization) of fly ash with cement.

Fly ash, siliceous and/or calcareous one, is a respected and valuable component of concrete, provided it is of a good quality and applied in accordance with current knowledge and guidelines contained in the reference documents (standards, guidelines, instructions).

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