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ORIGINAL ARTICLE

Air void system in concrete containing circulating fluidized bed combustion fly ash

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Abstract The increased use of advanced coal-burning technologies for power generation, such as circulating fluidized bed combustion (CFBC), results in new waste products. The potential for using CFBC fly ash in air-entrained concrete was investigated in order to assess the influence of CFBC fly ash on the microstructure of air voids in hardened concrete. A special specimen surface preparation technique for contrasting the image and enabling measurements of air voids size and distribution using an automated image analysis procedure was used. The microstructure of air voids was evaluated on the basis of the total air content, the spacing factor, and the specific surface of air voids. It was found that a satisfactory air void system in concrete could be produced when using CFBC fly ash for partial replacement of cement. The air-void system was characterized by a decreased specific surface of voids and an increased spacing factor.

Keywords CFBC fly ash · Image analysis · Microstructure · Air-entrained concrete

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1 Introduction

In recent years a variety of so called ''clean'' combustion technologies have been developed for power generation. One such technology, that has gained common acceptance, is the combustion of different kinds of coal in circulating fluidized bed combustion (CFBC) boilers [1]. Solid residues from CFBC boilers contain components from three general groups [2]: fuel ash with unburned coal, desulphurisation products (almost exclusively anhydrite), and products of ground limestone sorbent decomposition. Therefore, and also because of rather low combustion temperatures (approximately 850°C), such by-products distinctly differ in their physical, chemical and phase compositions from ashes produced in conventional pulverized coal combustion boilers, which commonly are used as a concrete additive.

Common industrial standards for the use of fly ash as a concrete additive, such as ASTM C 618-05 [3] or EN 450-1 [4], do not include fly ash from fluidized bed combustion. Although CFBC fly ash did not meet the requirements imposed by these standards, especially with respect to SO_3 content, free CaO and unburned carbon content, some tests did reveal the potential of such waste products as cement additives [5, 6] or concrete additives [7]. It is known [8] that a 20–30% replacement of cement by standard fly ash could require up to four times the quantity of air entraining agents to entrain the same volume of air. It depends on the chemical and physical properties of fly ash, e.g. the increased content of unburned carbon in fly ash is known to influence the efficiency of air-entraining agents used in concrete. It was shown in [9] that air entraining agents could be adsorbed by unburned carbon in fly ash, thus the volume of the entrained air is significantly reduced. No data are available for air void systems in concrete modified with CFBC fly ash addition. Since the proper air void structure is considered to be a critical factor for freeze-thaw resistance of concrete, such data could be very important for potential outdoor applications.

The objective of this investigation was to study the influence of two types of fly ash, coming from fluidized bed combustion boilers in selected power plants in Poland, on the air-entrainment of a concrete mix and on the air-void system in hardened concrete. Tests were carried out on several concrete mixes designed with a constant water to binder ratio and with substitution of a part of the cement by CFBC fly ash.

2 Experimental

2.1 Materials and specimens

The basic materials included ordinary Portland cement CEM I 32.5 R (the chemical composition is given in Table 1), crushed basalt aggregates with grain sizes of 2–8 and 8–16 mm, sand with a maximum grain size of 2 mm (the grain size distribution is given in Fig. 1), and ordinary tap water. Chemical admixtures used included a high range water reducer, based on a polycarboxylatether and an air-entraining agent, based on a natural resin. The following additives were also used:

– CFBC fly ash from stone coal combustion in a power plant in Warszawa, Poland, designated as ‘‘FLW’’,
– CFBC fly ash from stone coal combustion in a power plant in Katowice, Poland, designated as ‘‘FLK’’.

Both types of CFBC fly ash were subjected to mechanical homogenization in order to avoid particle clustering. The chemical properties of CFBC fly ash, determined using standard European procedures, are given in Table 1. A high content of sulfuric anhydride, SO_3, a high loss on ignition and an increased content of free CaO should be noted. Since some loss on ignition can be attributed to the presence of calcium carbonates in CFBC fly ash, an estimation of unburned carbon content was obtained using the TGA-DTA method in a helium/air atmosphere (Fig. 2a, b).

Table 1 Chemical composition of CEM I 32.5 R and CFBC fly ash (‘‘FLW’’ and ‘‘FLK’’) as well as basic requirements of EN 450-1:2005 for fly ash for concrete

Test parameters	Contents			Requirements of EN 450-1:2005 for fly ash for concrete
	CEM	FLW	FLK	
SiO_2, (% by mass)	20.38	34.36	47.46	The sum of contents $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70$
Al_2O_3, (% by mass)	5.4	20.82	23.29	
Fe_2O_3, (% by mass)	2.82	6.29	7.53	
CaO, (% by mass]	63.04	12.22	7.48	*
SO_3, (% by mass)	2.5	6.58	3.56	$\leq$3.0
Cl^-, (% by mass)	0.02	0.12	0.08	$\leq$0.10
CaO free, (% by mass)	0.84	1.79	0.35	$\leq$1.0 or $\leq$ 2.5 and **
MgO, (% by mass)	1.74	4.02	3.10	$\leq$4.0
Loss on ignition, (% by mass)	1.66	11.77	3.30	$\leq$5: Category A 2–7: Category B 4–9: Category C
Unburned carbon content by TGA-DTA, (% by mass)	–	3.9	0.3	–

* The content of reactive calcium oxide $\leq$10.0%

** Additional requirements for soundness: the expansion in accordance with EN 196-3 not greater than 10 mm

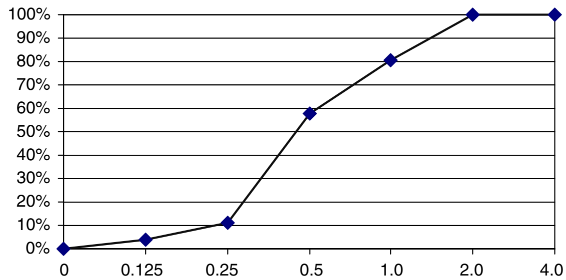

Fig. 1 The grain size (mm) distribution of the sand

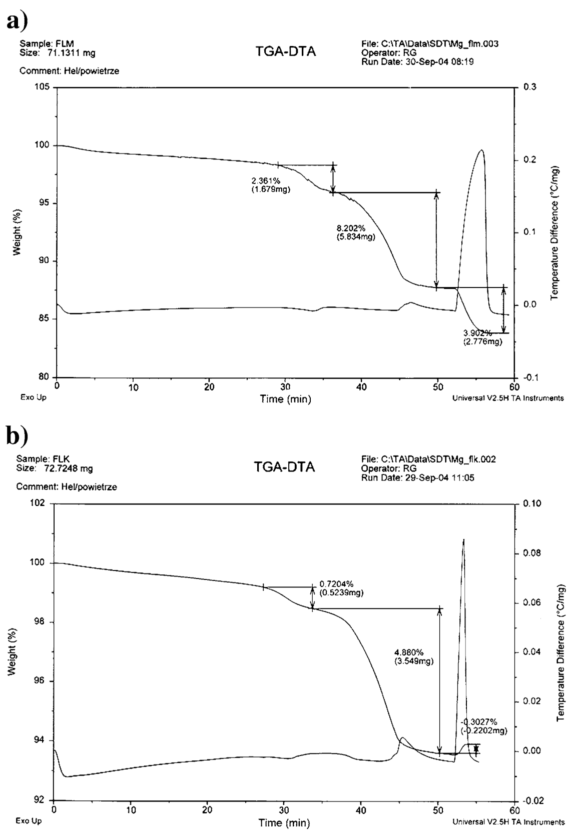

Fig. 2 The TGA-DTA analysis of CFBC fly ash in a helium/air atmosphere: (**a**) FLW fly ash, (**b**) FLK fly ash

Concrete mixes were designed with a constant water to binder ratio of 0.42, a constant slump of 80 ± 20 mm and a constant air-void content of 6 ± 1%. To achieve the target slump and the target air-void content different amounts of admixtures were used in various mixes. The CFBC fly ash was used as 20, 30 or 40% replacement of the cement by weight. A reference concrete mix without any additives (designated as ''CEM I'') was also designed. The experimentally established amounts of high-range water reducer and air-entraining admixture required to achieve the target slump and air content values fell within the range of 0.6–1.2 and 0.1–0.8% by weight of the binder, respectively. The proportions of the concrete mixes are given in Table 2. The air contents were measured using the pressure method according to EN 12350–7:2001. The mixing procedure consisted of three steps. At first dry constituents with 1/3 part of water were mixed for 1 min, next the air entraining agent mixed with 1/3 part of water was added (time of mixing about 1 min), finally the last part of water with the water reducer was added and all constituents were mixed for another 1 min. Specimens were cast in the cubical moulds (100 × 100 × 100 mm) used for compressive strength testing. The fresh mixes were consolidated by vibration (5–7 s on a vibrating table). After 24 h in moulds at RH > 90% and at the temperature 18–20°C specimens were demoulded and cured in high humidity conditions (RH > 90%) at the temperature of 18–20°C until the age of 28 days.

2.2 Test procedures

For determination of air-entrainment efficiency the nonstandarized foam index test was used (a critical examination of the foam index test was presented in [10]). The procedure was as follows: 7 g of Portland cement, 3 g of CFBC fly ash and 25 ml of the deionised water were placed in a 300 ml cylindrical glass jar. The capped jar was shaken for 1 min to completely wet the cement and ash. Next a 10% aqueous solution of AEA was added, one drop (0.02 ml) at time, from a pipette gun. After of each drop the jar was shaken for approximately 15 s and then the surface of liquid was observed. The amount of the 10% AEA solution added to achieve the stable foam at the surface for at least 45 s was regarded as the foam index. For lower AEA additions the foam on the liquid surface was unstable and would quickly brake. A reference foam index value was also measured using only Portland cement without CFBC fly ash.

For quantitative measurements of air voids in plane sections a special preparation technique of concrete specimens was used. A rectangular specimen of about 20 mm thick was cut from a moulded

Table 2 Concrete mix proportions

Mix	Type of additive	Cement Content (kg/m^3)	Additive	Sand	Basalt 2–8 mm	Basalt 8–16 mm	Water	HRWR l/m^3	AEA l/m^3
CEM I	None	339	0	640	650	678	151	2.03	0.34
FLW20	FLW	274	69	648	657	686	152	2.74	1.37
FLW30		242	104	652	662	691	154	3.45	2.07
FLW40		209	139	657	667	696	155	4.18	2.78
FLK20	FLK	279	70	658	668	697	155	2.79	1.39
FLK30		246	105	663	673	702	156	3.51	2.11
FLK40		211	141	665	675	704	157	4.23	2.82

HRWR—High range water reducer, AEA—Air entraining admixture

cube specimen. Surface polishing with SiC polishing powders was carried out until the surface was essentially free from defects, and the edges of the air voids were sharp as observed in a stereomicroscope. The next step was colouring of the surface using a blue, water resistant marker, and then filling the air voids with zinc paste. Any surplus of such paste was removed using a sharp blade. Finally, the surface was cleaned using paraffin oil. At this stage, the quality of surface preparation, especially the precision of filling air-voids with zinc paste was monitored using a stereomicroscope. In case of poor quality of the surface the entire treatment was repeated. A very careful preparation of specimens was found to be very important to assure precision of subsequent measurements.

Air void parameters in hardened concrete were determined using a computer-driven image analysis system. The automated linear traverse system for determination of air-void parameters in concrete was developed following the concepts described in [11]. Algorithms for measurement of the structural parameters were prepared using the special programming language built into the image analysis software [12], which enabled the application of morphological filtering and various complex image-processing operations from the core of the system. The measurement of the length and the number of chords corresponded to the application of the linear traverse air void analysis method.

The automatic measurement procedure, performed according to the computer program described in [13], was designed to comply with the requirements imposed by the European Standard EN 480-11 [14]. Results of measurement were available as a set of standard parameters for air-void structure characterization:

- Spacing factor $\bar{L}$ (mm),
- Specific surface α (1/mm),
- Air content A (%),
- Content of air voids with diameter less than 0.3 mm A_{300} (%).

3 Test results and analysis

During the preparation of the concrete mixes it was found that increasing the content of CFBC fly ash caused a considerable decrease in the air volume of the mix. In order to obtain the target air content, an increasing amount of air entraining admixture was used, as shown in Table 2. It should be noted that the dosage of air entraining admixture was increased proportionally to the content of CFBC fly ash. No difference in the required dosage of air entraining admixture for the two types of CFBC fly ash was noted.

Results of the quantitative description of the air void system using the four standard parameters are shown in Table 3. The three parameters A, A_{300} and α were determined experimentally using the linear traverse method, and the spacing factor was calculated using the standard formula given in [14]. The influence of the content and type of CFBC fly ash on the total content of air voids in the hardened concrete is presented in Fig. 3. The two lines represent two series of concrete specimens, prepared with different contents of CFBC fly ash, denoted FLK and FLW. In order to achieve the same content of air voids in the

Table 3 Air-void structure parameters in hardened concrete specimens

Mix	Type of additive	Percentage of cement replacement	Paste content by volume (%)	Air-void structure parameters			
				$\bar{L}$(mm)	A_{300} (%)	α(1/mm)	A (%)
CEM I	none	0	26.6	0.13	2.22	33.2	6.25
FLW20	FLW	20%	27.2	0.13	2.58	32.3	6.67
FLW30		30%	27.5	0.17	2.90	27.6	5.33
FLW40		40%	27.7	0.23	1.66	20.8	5.26
FLK20	FLK	20%	27.2	0.13	3.66	32.5	6.25
FLK30		30%	27.5	0.14	2.92	27.1	7.08
FLK40		40%	27.7	0.18	2.09	24.1	6.03

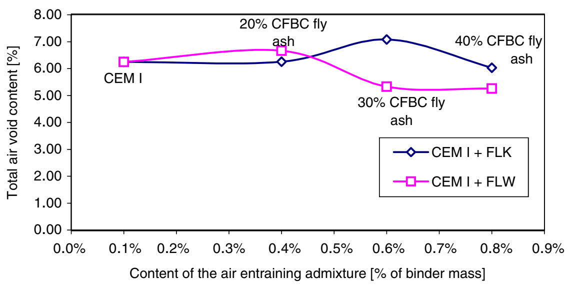

Fig. 3 Air void content in hardened concrete as a function of amount of air entraining admixture; the content of CFBC fly ash is indicated

concretes with 40% addition of CFBC fly ash, the amount of the air-entraining admixture was increased eight times in comparison to the reference mix made with pure cement. The compressive strength of concrete at the age 7 and 28 days was within the range 44.9–47.5 and 49.7–56.4 MPa (average values), respectively. Thus the differences in strength induced by partial cement replacement and increased dosage of admixtures were not greater than 12%.

The determination of α enables the estimation of the size of the air voids in concrete, irrespective of the total volume of air voids. The data in Table 2 indicate a clear decrease of the specific surface of the air void system due to an increase in CFBC fly ash content. Thus, the formation of air voids with larger diameter was encouraged for increasing cement replacement (Fig. 4a, b). The spacing factor—a parameter related to the maximum distance from any point in the cement paste to the periphery of the nearest air void—was also found to increase with increasing CFBC fly ash content. In spite of a constant total air void content within the range 5–7%, the air void structure actually achieved was different due to addition of CFBC fly ash. The use of CFBC fly ash of higher LOI (unburned carbon content) resulted in a larger spacing factor of the air voids; at 40% cement replacement the spacing factor was found to be greater than 0.20 mm, which is commonly assumed as the limiting value for ensuring high frost resistance of concrete. The results of the foam index test (Fig. 5) were used to explain the observed effects. As it is shown the amount of the air entraining admixture necessary for bubble stability was significantly increased for CFBC fly ash additions. At equal contents of CFBC fly ash the adsorption of AEA was about twice higher for FLW than for FLK. Thus the adsorption was significantly increased for increasing content of unburned carbon in CFBC fly ash. Such test results could contribute to a better understanding of the observed increase of air voids diameters for an increased replacement of cement. It seems that an increased adsorption of the AEA on cementitious materials is a key factor to influence the air volume and the air void distribution in concrete containing CFBC fly ash. Such a hypothetical explanation could be further elaborated on the basis of measurements of surface tension of admixtures in water and cement with an addition of CFBC fly ash. Using such a test method for a variety of air entraining admixtures it was shown in [15] that the phenomenon of creation of larger air voids by these admixtures could be related to the surface-tension-reduction capability of the cementitious mixture. Since the air void formation is physically attributed to surface tension of the phase in the paste/liquid stage, the larger air void sizes in hardened concrete suggest a more marked reduction of the surface tension in cementitious mixtures containing CFBC fly ash.

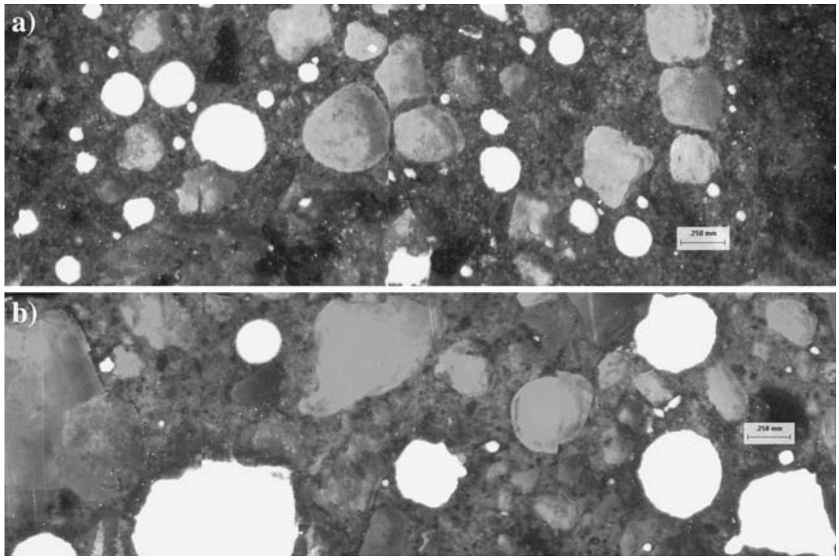

Fig. 4 View of air voids (white) in a flat section of concrete with different content of CFBC fly ash addition: (**a**) 20% of FLK (**b**) 40% of FLW

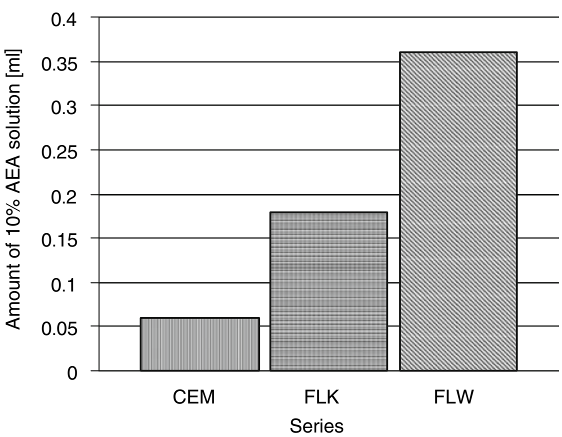

Fig. 5 The amount of the 10% water solution of the air-entraining admixture necessary to achieve the bubble stability

4 Conclusions

A special specimen surface preparation technique for contrasting the image and an image acquisition and analysis procedure enabled an automated determination of the air void structure parameters in concrete. The tests carried out resulted in the following conclusions:

A proper air entrainment of concrete made with the addition of CFBC fly ash was possible, although it required a significantly increased amount of air entraining admixture. The air void system in CFBC fly ash concrete was characterized by larger diameter voids than those found in concrete without CFBC fly ash. Increasing the CFBC fly ash content up to 40% induced an increase of the spacing factor by 0.05–0.10 mm and a decrease of the specific surface by 9–12 mm^{-1}; such effects were enhanced with increasing loss on ignition (unburned carbon content) of CFBC fly ash.

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