BULLETIN OF THE POLISH ACADEMY OF SCIENCES
TECHNICAL SCIENCES
Vol. 56, No. 1, 2008

The influence of CFBC fly ash addition on phase composition of air-entrained concrete

M.A. GLINICKI* and M. ZIELIŃSKI

Institute of Fundamental Technological Research, Polish Academy of Sciences,
21 Świętokrzyska St., 00-049 Warszawa, Poland

Abstract. The phase composition of the cement paste phase of concrete containing fly ash from circulating fluidized bed combustion (CFBC) was studied. The motivation was to broaden the knowledge concerning the microstructure and the durability of concrete containing new by-products from the power industry. Several air-entrained concrete mixes were designed with constant water to binder ratio and with substitution of a part of the cement by CFBC fly ash (20%, 30% or 40% by weight). X-ray diffraction tests and thermal analysis (DTG, DTA and TG) were performed on cement paste specimens taken from concrete either stored in water at 18°C or subjected to aggressive freeze-thaw cyclic action. The evaluation of the phase composition as a function of CFBC fly ash content revealed significant changes in portlandite content and only slight changes in the content of ettringite. The cyclic freeze-thaw exposure did not have any significant influence on the phase composition of concrete with and without the CFBC fly ash.

Key words: air-entrained concrete, fluidized bed fly ash, freeze-thaw durability, waste management.

1. Introduction

Fluidized bed combustion is becoming a common technology for clean power production in several European countries and in India, Japan, and the USA. The use of an advanced part of this technology, circulating fluidized bed combustion (CFBC) of coal for power generation, is also rapidly growing in Poland. This is mainly due to the possibility of reducing SO_2 and NO_x contents in the flue gas as well as economically burning various fuels, while meeting strict emission control regulations [1, 2]. Such a coal combustion process is associated with the production of two types of by-products, i.e. CFBC bottom ash and CFBC fly ash, which differ in their particle size distribution, the content of unburned carbon and the chemical composition. Common components are, however, unreacted and reacted sorbent used for desulfurization, and unreacted coal/char. CFBC fly ash captured by electrostatic precipitators and having a particle size distribution within the range of approximately 1–300 μm, usually contributes a major part of the ash production, up to 70%. Mainly due to the presence of sorbent material and the lower combustion temperature (400–800°C less than the temperature in conventional boilers), the solid residue coming from coal combustion in fluidized bed boilers differs in its physical, chemical and mineralogical properties from the fly ash commonly used as a mineral additive in the concrete industry according to standards EN 450-1 [3] or ASTM C 618 [4]. Moreover, according to the European standard definition, fly ash is a fine powder of mainly spherical, glassy particles derived from burning the pulverized coal, with or without co-combustion materials. In case of CFBC fly ash, grains are non-spherical and the glassy phase is not present, so that CFBC fly ash is beyond its scope.

Several attempts to use fly ash from fluidized bed combustion as cement or concrete additive have been reported [5–10]. Brandstetr et al. [5] reviewed the composition, utilization, standardization and performance requirements of atmospheric and pressurized fluidized bed combustion (AFBC and PFBC) fly ash. Sebok et al [6] found that the compressive strength of specimens containing fluidized bed combustion products depends on the mixing ratio of the compounds and the composition of binder. Test results indicated that the compressive strength after 2 years of hardening had a tendency to increase with increases of calcite and ettringite content in the specimens and to decrease with increasing contents of portlandite and gypsum. Construction applications have been identified as one of the major uses for CFBC ashes in [7]. It was concluded that typical CFBC ash couldn't be used as a cement replacement in concrete due to its unacceptably high sulfur content. However, laboratory investigations [8–9] revealed some possibility of using fluidized bed combustion fly ash as a complex addition to cement, where it played simultaneously the role of both a sulphate setting time controlling agent and a highly active pozzolanic additive. Some preliminary results indicating a potential for using CFBC fly ash in concrete were reported in [10]. The compressive strength of concrete was found to increase as a result of partial replacement of cement by CFBC fly ash at the age of 7 days and this strength gain was stable under laboratory conditions, amounting to up to 39% after two years. However, the addition of CFBC fly ash resulted in a major decrease in slump of the concrete mix at a constant water to binder ratio.

Research significance. Premature deterioration of concrete can be caused by many factors, including the role of potentially expansive minerals – deterioration is sometimes

*e-mail: mglinic@ippt.gov.pl

attributed to cracking related to their growth. The importance of ettringite formation and growth in promoting concrete deterioration is still controversial and not accepted by all workers [11]. Primary ettringite, which grows when concrete is still plastic is not considered harmful, but ettringite that forms long after concrete has hardened (late ettringite) may produce damaging expansive pressures [12]. Deterioration by ettringite expansion was clearly evidenced by the experiments reported in [13]. Late ettringite formation is especially enhanced by the availability of sulfur, because ettringite's other components, calcium, aluminum, and water are abundant in Portland cement concrete. The phenomenon is called a composition induced internal sulfate attack and is referred to in the classical literature as "oversulfation" [14]. Because of a high sulfur content in CFBC fly ash the phenomenon needs to be investigated, especially in air entrained concrete: the air voids adequate to provide a high freeze-thaw durability might become ineffective due to ettringite growth as evidenced in [15]. Free calcium oxide, if present in larger amounts than acceptable, causes an expansion of the hardened cement paste due to its conversion to calcium hydroxide; the expansive force generated by the CaO→ $Ca(OH)_2$ conversion may reach 150 MPa [16]. Because of an increased free lime content in CFBC fly ash the formation of calcium hydroxide should also be studied.

The objective of this investigation was to study the phase composition of cement paste in concrete modified with the addition of CFBC fly ash. Since frost aggression is a major durability concern for outdoor engineering structures in many countries, including Central European countries, it is important to address the issue of the stability of the phase composition of concrete exposed to frost. There is a strong sustainability-driven need to provide a basis for the development of an effective technology for the utilization of CFBC by-products in the concrete industry.

2. Experimental program

2.1. Materials and mix proportions. The following materials were used:

- aggregates: low absorbability crushed basalt aggregates of 2–8 and 8–16mm fractions, and pit sand with a maximum grain size of 2 mm
- cement: Portland cement CEM I 32.5 R
- mineral additive: fly ash from hard coal combustion in a CFBC boiler – with a density of 2550 kg/m^3,
- chemical admixtures: superplasticizer – based on a polycarboxylatether; and an air entraining admixture based on a natural resin,
- water.

Fly ash from circulating fluidized bed combustion was treated using so-called mechanical activation procedure by impacts. This treatment was intended mainly to enhance homogenization of the material and to break down agglomerated particles; no chemical treatment was applied [10]. Chemical composition of the CFBC fly ash determined using European standard methods [17, 18], as well as the basic requirements for fly ash for concrete [3] are presented in Table 1.

Table 1
Chemical composition of CFBC fly ash and basic requirements for fly ash for concrete

Test parameters	Content	Requirements of EN 450-1:2005 for fly ash for concrete
SiO_2, [% by mass]	34.36	the sum of contents $SiO_2 + Al_2O_3 + (Fe_2O_3 \geq 70$
Al_2O_3, [% by mass]	20.82	
CaO, [% by mass]	**12.22**	*)
SO_3, [% by mass]	**6.58**	$\leq$3.0
Cl^-, [% by mass]	0.12	$\leq$0.10
CaO free, [% by mass]	**1.79**	$\leq$1.0 $\leq$2.5 and **)
MgO, [% by mass]	4.02	$\leq$4.0
Loss on ignition, [% by mass]	**11.77**	$\leq$5: Category A 2–7: Category B 4–9: Category C

*) the content of reactive calcium oxide $\leq$10.0%

**) additional requirements for soundness: the expansion not greater than 10 mm

A high content of sulfuric anhydride SO_3, a high loss on ignition and an increased content of free CaO can be noted. Selected properties of CFBC fly ash are regularly tested at the power plant, as required by legal regulations. On the basis of such test results the scatter in the contents of CaO, SO_3 and LOI over a number of years of power generation in the power plant was within the limits of 12–20%, 6–10% and 6–12%, respectively.

Concrete mixes were designed with a constant water to binder ratio of 0.44 and a slump of 100 to 150 mm, which was regulated by the proper adjustment of superplasticizer content. The CFBC fly ash was used as a partial replacement of cement at the rate of 20%, 30% and 40%. A reference concrete mix without mineral additives was also prepared. Superplasticizers and air-entraining admixtures were used in different amounts ranging from 0.6% to 1.2% and from 0.1% to 0.8% of the binder weight, respectively. The target air-content in the mix was 5$\pm$1%. The concrete mix proportions and concrete mix properties are given in Table 2 and Table 3, respectively. A significant demand for increasing the content of air-entraining agent, and also the content of superplasticizer for increasing CFBC fly ash contents should be noted. The basic reason for that is the irregular, non-spherical shape of CFBC fly ash grains and an increased content of unburned carbon [19].

Concrete mixes were produced in a laboratory mixer. Specimens were cast in 100 mm cubical moulds and consolidated by vibration. After 24 hours in the moulds at RH $>$ 90% and at a temperature of 18–20°C, the specimens were demoulded and cured for 7 days in water at a temperature of 18–20°C, and subsequently in high humidity conditions at RH $>$ 90% at a temperature of 18–20°C until the age of 28 days.

Table 2
Concrete mix proportions

Mix designation	Cement replacement by weight	Cement	CFBC fly ash	Sand	Basalt 2–8 mm	Basalt 8–16 mm	Water	HRWR	AEA
		Content [kg/m^3]						[dm^3/m^3]	[dm^3/m^3]
CEM	0	340	0	643	652	681	142	1.70	0.34
FLW20	20%	271	68	640	649	678	141	2.03	1.36
FLW30	30%	236	101	637	646	674	140	2.70	2.02
FLW40	40%	202	135	637	646	674	140	3.37	2.70

HRWR – superplasticizer, AEA – air-entraining admixture

Table 3
Fresh mix properties

Mix designation	Cement replacement by weight	Total content of cementitious materials [kg/dm^3]	Slump [mm]	Air content [%]	Density [kg/m^3]
CEM	0	340	140	5.6	2.47
FLW20	20%	339	100	6.3	2.45
FLW30	30%	337	120	6.6	2.46
FLW40	40%	337	150	6.7	2.44

2.2. Freeze-thaw treatment. The hardened concrete specimens were divided into two series "A" and "B" (5 cubes in each series). Series "A" specimens were subjected to the cyclic freezing and thawing (F/T) according to the Polish Standard procedure [20]. The number of applied freeze-thaw cycles was 160. At the same time the reference specimens (series B) were stored in water at the temperature 18°C±2°C. The freeze-thaw procedure employed consists of rapid freezing of specimens in air at the temperature of minus 18 (±2)°C for a minimum of 4 hours and thawing in water at the temperature of 18 (±2)°C for a minimum of 2 h, maximum of 4 h, (3 cycles per day). The F/T treatment was performed using an Elbanton automatic climatic chamber with an internal temperature monitoring system. An example of the temperature-time history for two temperature-measuring devices placed inside the chamber is presented in Fig. 1.

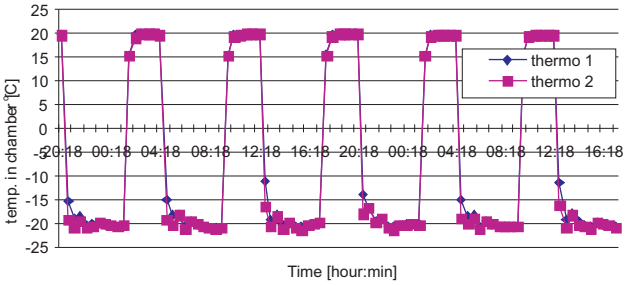

Fig. 1. An example of temperature-time history for 2 temperature-measuring devices placed inside the climatic chamber

2.3. Test methods. The assessment of the effects of cyclic freezing and thawing of concrete according to this method differs from the ASTM C 666 standard procedure: the compressive strength loss and the change in the mass of specimens are assessed, instead of measuring the changes of the dynamic modulus of elasticity and length. Standard specifications for concrete in outdoor engineering structures define the frost resistance to be adequate if the applied number of F/T cycles does not induce a loss of specimen mass of more than 5% or a loss of compressive strength of no more than 20% in relation to the compressive strength of reference specimens stored in water. The compressive strength of concrete cube specimens was determined according to a common standard procedure EN 12390-3.

The phase compositions of the input materials (cement CEM I and CFBC fly ash) were determined using X-ray diffraction analysis and thermal analysis. The phase composition of hardened cement paste in concrete was investigated using the pieces of specimens crushed in compression. Samples of crushed material were collected and designed as follows:

– concrete specimens subjected to 160 cycles of freezing and thawing:
  CEMA, FLW20A, FLW30A, FLW40A,
– reference concrete specimens stored in water at 18°C:
  CEMB, FLW20B, FLW30B and FLW40B.

Following the rules given in the instructions [21], the differential thermal analysis and the X-ray diffraction analysis were performed on cement paste separated from specimens of concrete series A and B. The concrete piece, after drying at 40°C to a constant weight, was mechanically crushed in a crushing machine, and the aggregate grains were removed. Next, the crushed material was sieved through the 0.063 mm sieve and placed into a desiccator to be kept in an environment free of H_2O and CO_2. The relatively low temperature of the drying process was used to avoid decomposition of certain phases at higher temperatures.

The thermal analysis was performed using MOM instrument at the following test conditions: the furnace atmosphere: air; the heat up rate: 10°C/min; the temperature range: 20–1000°C; the reference substance: aluminum oxide. The X-ray diffraction analysis was performed by means of a TUR M-62 X-Ray diffractometer at the following measurement conditions: the 2θ range: 6-66; the type of ray and filter: CuKα/ monochromator; the voltage and the current intensity of the RTG lamp: 40 kV and 20 mA; the counter type: BDS-7; the scanning speed: 1 cm/min; the counter rate: 0.5°/min.

3. Test results

3.1. Phase composition of basic materials. The estimation of the quality of the cement and CFBC fly ash was carried out on the basis of the results of the qualitative X-ray diffraction analysis, with simultaneous measurement of the absolute intensity of selected reflections of components. Although the Rietveld refinement technique is known, there is no sufficient data base available to apply and the assumed simplified approach according to the instruction [16] is considered adequate for characterization of the materials used. For quantitative determination of calcium hydroxide, calcium carbonate, ignition loss and the content of water bound in mono- and/or multihydrate calcium sulphates, the differential thermal analysis method (DTG, DTA and TG) was applied. The quantity of these components was calculated on the basis of data obtained from DTA, DTG and TG curves according to the instructions [17].

The phase composition of the cement and CFBC fly ash are presented in Tables 4 to 6. The XRD results for cement fall within the range expected for standard CEM I cement. Additionally certain products of the premature hydration and carbonation of cement were observed, such as calcium hydroxide and calcium carbonate. The amount of those components determined using the thermal analysis method was in the acceptable range established for cement CEM I.

The XRD results revealed the following phases in CFBC fly ash: quartz, anhydrite, calcite and calcium oxide. The cumulative weight loss determined in the TGA test was at 12.5%. The loss on ignition due to the presence of carbon was assessed at 8.5% (the loss of weight in the temperature range 360–780°C) and the maximum possible amount of calcite was estimated as 7.0% as an average of two measurements.

Table 4
Results of the X-ray diffraction analysis of cement CEM I 32.5 R and CFBC fly ash

Cement CEM I 32.5 R		CFBC fly ash	
Phase name and reflection according to JCPDS card number and interplanar distance d, Å	Absolute intensity of the reflection I_b, conventional units	Phase and reflection according to JCPDS card number and interplanar distance d, Å	Absolute intensity of the reflection I_b, conventional units
– Alite (13-272)		Quartz (5-0490)	
d = 2.776	658	d = 4.257	280
– Alite + belite (13-272 and 9-351)		d = 3.342	829
d = 2.744	560	d = 1.817	151
– C_3A (8-5)		d = 1.5418	132
d = 2.700	283	Calcite (5-0586)	
– C_4AF (11-124)		d = 3.035	261
d = 2.63	178	d = 2.285	149
– CaO (4-0777)			
d = 2.405	69	Anhydrite (6-0226)	
– MgO (4-0829)		d = 3.49	792
d = 2.106	83	d = 2.849	316
– Alite (13-272)		d = 2.328	181
d = 1.768	430		
– Gypsum (6-0046)			
d = 7.56	158	Calcium oxide (4-0777)	
– Bassanite (24-1068)		d = 2.406	133
d = 6.01	136		

Table 5
Results of thermal analysis of cement CEM I 32.5 R

Test parameters	Test results	Requirements
Calcium hydroxide content [%]	1.2	$\leq$ 2.0 [23]
Calcium carbonate content [%]	2.7	$\leq$ 3.0 [23]
Loss on ignition [%]	2.1	$<$ 5.0 [17]

Table 6
Thermal analysis results of the CFBC fly ash

Temperature range, °C	Decrease of mass, %
20–360	0.9
360–780	8.5
780–1000	3.1
20–1000	12.5

3.2. Composition of hardened cement paste separated from concrete. An example of the X-ray diffraction pattern of hardened cement paste separated from concrete subjected to freeze-thaw cycles is presented in Fig. 2. Results of qualitative XRD analysis with simultaneous measurements of the absolute intensity of selected reflections are presented in Table 7 for hardened cement paste, from both concrete series A and B.

The XRD patterns revealed the following major phases in the cement paste specimens A and B series: non-hydrated cement grains, mainly in form of alite and belite, products of the cement hydration in the form of portlandite, ettringite, and products of the carbonation of the hydrated cement in the form of calcite. Moreover, some relicts of aggregates and CFBC fly ash in the form of quartz were found.

The use of DTA according to the instructions [22] enabled an estimation of the content of such components of the cement paste as: water bound in the products of hydration (HI) and hydrolysis (HII) of cement, and calcium hydroxide (portlandite). The results obtained are presented in Table 8.

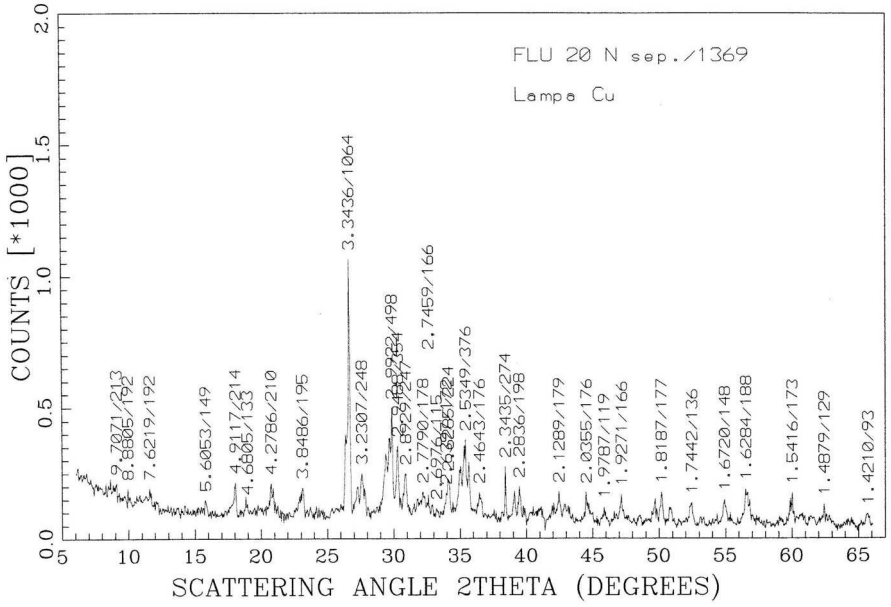

Fig. 2. An example of XRD pattern of cement paste separated from concrete subjected to 160 F/T cycles (20% CFBC fly ash concrete specimen)

Table 7
Phase peak intensities of cement paste separated from concrete specimens: Series A (after 160 F/T cycles) and B (water storage at 18°C)

Reflections according to JCPDS (card number and interplanar distance d, Å)	Absolute intensity of chosen reflect I_b, conventional units, content of FBC fly ash %, series name:							
	CEM		FLW20		FLW30		FLW40	
	B	A	B	A	B	A	B	A
Ettringite (9-0414) d:								
9.73	228	213	258	213	220	240	246	282
5.61	138	119	187	149	162	149	170	147
Portlandite (4-0733) d:								
4.90	290	305	268	214	175	151	141	124
2.63	355	443	304	224	157	159	140	131
Alite (13-0272) d:								
2.78	161	171	257	178	284	205	186	165
1.76	195	161	144	136	157	126	182	103
Calcite (5-0586) d:								
3.04	335	397	387	376	425	412	392	410
Quartz (5-0490) d:								
4.27	276	422	401	210	293	277	381	268
3.35	953	1064	1223	1064	849	1329	1506	1455

Table 8
Selected components of the cement paste separated from concrete series A and B (Series A – after 160 F/T cycles, series B – water storage at 18°C)

Series	Chosen components of cement paste, % mass			
	Bound water			Calcium hydroxide
	HI	HII	Σ	
CEMB	9.6	1.3	10.9	5.3
CEMA	10.4	1.3	11.7	5.3
FLW20B	13.0	0.3	13.3	1.2
FLW20A	10.4	0.4	10.8	1.6
FLW30B	10.6	0.3	10.9	1.2
FLW30A	10.1	0.3	10.4	1.2
FLW40B	11.7	traces	11.7	traces
FLW40A	12.6	0.1	12.7	0.4

3.3. The compressive strength of concrete. The examination of specimens subjected to 160 freeze-thaw cycles revealed neither damage nor visible cracks on the concrete surface. The results of compressive strength tests on concrete specimens subjected to freezing and thawing and on reference specimens stored in water are presented in Fig. 3. The compressive strength of concretes of all series subjected to 160 F/T cycles did not change significantly in comparison to the reference specimens (the drop of strength was only about 2–6%). The strength of the reference specimens was about 43–57 MPa and the strength of specimens subjected to freezing and thawing was about 42–55 MPa.

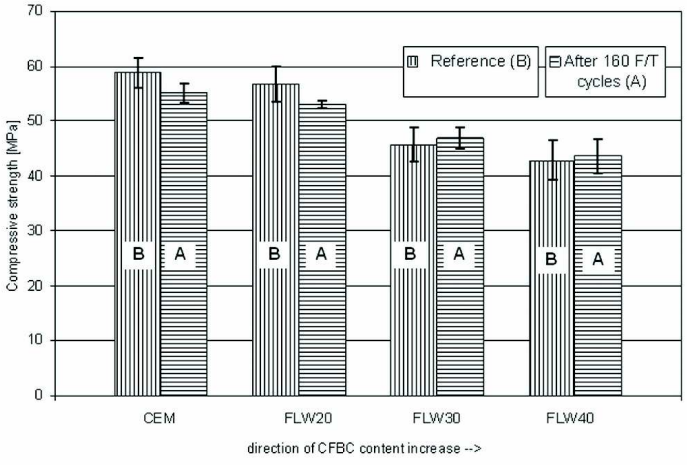

Fig. 3. The compressive strength of concrete specimens subjected to 160 F/T cycles (A) and reference specimens stored in water (B); the average values of 5 specimens and the standard deviation range

4. Analysis of results

The analysis of the DTG, DTA and TG results was performed on the basis of the quantitative assessment of water bound in the products of cement hydration (HI), and calcium hydroxide (portlandite) content. The changes in content of these components were assessed in comparison to the reference sample separated from concrete without CFBC fly ash and matured in water (CEM, series B). The content of components in this reference specimen was assumed as 100%. Results of the evaluation of the phase composition of cement pastes in relation to bonded water (HI) and calcium hydroxide (CH), determined as WsHI and WsCH respectively, were expressed as a % of the reference concrete value and called "ratio of cement paste changes". Results of this comparison are shown in Table 9.

Table 9
Ratios of the cement paste changes of specimens separated from concrete with different amount of CFBC fly ash – series A and B (Series A – after 160 F/T cycles, series B – water storage at 18°C)

Symbol	Series	Ratio of cement paste changes, (Ws), % relative			
		CEM	FLW20	FLW30	FLW40
WsHI	B	100	135	110	122
	A	108	108	105	131
WsCH	B	100	23	23	2
	A	100	30	23	8

The influence of CFBC fly ash addition and cyclic freezing and thawing on selected phase components of the cement paste was as follows:

- for concrete without CFBC fly ash addition: an increase of the bound water in hydration products of cement was observed – WsHI = 108%,
- for concrete with 20% of CFBC fly ash: a distinct decrease of the calcium hydroxide amount was observed (WsCH). Irrespectively of the conditioning environment (i.e. both in series A and B) an increase of the bound water in the hydration products of cement was observed.
- for concrete with 30% of CFBC fly ash: a further decrease of the calcium hydroxide content was observed,
- for concrete with 40% of CFBC fly ash: irrespectively of conditioning environment (water or freeze-thaw cycles) a further decrease of the calcium hydroxide down to WsCH = 2% and 8% was observed. Moreover, an increase of the bound water in hydration products was observed.

Specimens with the same content of CFBC fly ash showed very similar tendencies in the quantitative changes of selected phase components irrespective of the conditioning environment. The most essential changes were observed for concretes with different contents of CFBC fly ash: as shown in Table 9 the content of calcium hydroxide as a function of CFBC fly ash content decreased monotonically, down to almost zero at 40% CFBC fly ash. This phenomenon may be explained by the pozzolanic reaction as well as by a decrease of the total calcium oxide content in concrete with CFBC fly ash addition.

The influence of the CFBC fly ash addition as well as freeze-thaw exposure on the phase composition of the cement pastes separated from concretes was also investigated on the basis of the X-ray diffraction patterns. The XRD analysis consisted of assessing the total intensity of the diagnostic reflection of ettringite, calcium hydroxide and alite. Using the assumption that the total intensity of diagnostic reflection of a chosen phase is connected with the amount of that phase in the material, the relative changes in phase composition were estimated. The intensity of reflections was determined in relation to the diffraction pattern of specimens separated from

concrete without CFBC fly ash, which matured in water conditions; for comparison the intensity was assumed to be 100%. Results of this relative assessment are presented in Table 10.

Table 10
The total intensity of chosen diagnostic reflections of cement paste components separated from concrete specimens with different CFBC fly ash addition – series A and B (Series A – after 160 F/T cycles, series B – water storage)

Series	Global intensity of diagnostic reflections of chosen components of the cement paste, in conventional units		
	Ettringite d = 9.75 and 5.61 Å	Portlandite d = 4.90 and 2.63 Å	Alite d = 2.78 and 1.76 Å
CEMB	366 (100%)	645 (100%)	460 (100%)
CEMA	332 (91%)	748 (116%)	332 (72%)
FLW20B	445 (124%)	572 (87%)	401 (87%)
FLW20A	362 (99%)	438 (68%)	314 (68%)
FLW30B	382 (104%)	332 (51%)	441 (97%)
FLW30A	389 (106%)	310 (48%)	331 (72%)
FLW40B	416 (114%)	280 (43%)	368 (80%)
FLW40A	429 (117%)	255 (40%)	268 (58%)

The relative evaluation of the total intensity of chosen diagnostic reflections revealed the following observations:

- a slight increase of the total intensity of ettringite reflection in samples with CFBC fly ash addition,
- a steady decrease of the total intensity of portlandite reflection related to the content of CFBC fly ash added to concrete (increase of the CFBC fly ash decreased the total intensity of portlandite diagnostic reflections),
- a decrease of the total intensity of alite reflection related to increasing content of CFBC fly ash addition; a similar effect as in a case of portlandite (more CFBC fly ash leads to less alite).

It should be remembered that these results were obtained for concrete mixes of the same workability (determined by the slump) and for the same air content. To achieve this it was necessary to adjust adequately the content of superplasticizer and air-entraining agent.

5. Conclusions

The investigation on air-entrained concrete resulted in the following conclusions:

- The phase composition of cement paste separated from concrete without and with CFBC fly ash addition did not vary qualitatively; however changes in phase proportions were observed.
- The changes in the phase composition were mainly connected with the CFBC fly ash content. The influence of the CFBC fly ash was very significant in the case of the portlandite phase. The use of this additive at 40% replacement caused complete reduction of this phase.
- The steady decrease of the alite phase observed in case of cement pastes including CFBC fly ash was connected with the decrease of pure cement content in those specimens.
- The addition of the CFBC fly ash caused only slight changes in the content of ettringite, assessed on the basis of the X-ray diffraction analysis. No evidence of late ettringite formation was obtained in spite of an increased content of sulphates in CFBC fly ash.
- The phase composition of the hardened cement paste was not affected by the cyclic freeze-thaw exposure irrespective of the content of CFBC fly ash in concrete.

Further studies on strength and durability of concrete are needed for rational use of CFBC fly ash as a concrete additive.

Acknowledgements. The authors extend thanks to Dr. Róża Krzywobłocka-Laurów for help in the performance of tests and the interpretation of results. The investigation was financially supported by public funds for scientific research available for the period 2006–2008 (Polish Ministry of Science and Higher Education : Research-Development Project no R04 013 01).

REFERENCES

[1] P. Basu, "Combustion of coal in circulating fluidized-bed boilers: a review", *Chemical Engineering Science* 54, 5547–5557 (1999).
[2] W. Nowak, "Clean coal fluidized-bed technology in Poland", *Applied Energy* 74, 405–413 (2003).
[3] EN 450-1:2005, *Fly Ash for Concrete. Definition, Specifications and Conformity Criteria.*
[4] ASTM C 618-03, *Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*.
[5] J. Brandstetr, J. Havlica, and I. Odler, "Properties and use of solid residue from fluidized bed coal combustion", in: S. Chandra (ed.), *Waste Materials Used in Concrete Manufacturing*, 1–47, Noyes Publications Press, New Jersey, 1997.
[6] T. Sebok, J. Simonik, and K. Kulisek, "The compressive strength of samples containing fly ash with high content of calcium sulphate and calcium oxide", *Cem. Concr. Res.* 31 (7), 1101–1107 (2001).
[7] R.E. Conn, K. Sellakumar, and A.E. Bland, "Utilization of CFB fly ash for construction applications", *Proc. 15th Int. Conf. on Fluidized Bed Combustion* ASME, 19 (1999).
[8] W. Roszczynialski, W. Nocun-Wczelik, and M. Gawlicki, "Fly ash from fluidized bed coal combustion as complex cement addition", *Proc. Three-Day CANMET/ACI International Symposium on Sustainable Development and Concrete Technology* ACI SP-202, (2001).
[9] J. Havlica, J. Brandstetr, and I. Odler, "Possibilities of utilizing solid residues from pressured fluidized bed coal combustion (PSBC) for the production of blended cements", *Cement and Concrete Research* 28 (2), 299–307 (1998).
[10] M.A. Glinicki and K. Ladyzynski, "Influence of activated fluid bed combustion fly ash on properties of structural concrete", *Int. Conf. Ashes from Power Generation*, 119–133 (2001), (in Polish).
[11] B. Mather, "A discussion of the paper", *Theories of Expansion in Sulfoaluminate-type Expansive Cements: Schools of Though, Cement and Concrete Research* 14 (4), 603–609 (1984).
[12] S. Diamond, "Delayed ettringite formation", *Processes and Problems: Cement & Concrete Composites* 18 (3), 205–215 (1996).

[13] H. Lee, A.M. Cody, R.D. Cody, and P.G. Spry, "PCC pavement deterioration and mineral growth", *Transportation Conf. Proc.*, 71–75 (1998).

[14] J. Skalny, "Internal sulfate attack – points of agreement and disagreement", *Int. RILEM TC 186-ISA Workshop on Internal Sulfate Attack and Delayed Ettringite Formation*, 265–276 (2002).

[15] L. Delem, T. Van Dam, K.R. Peterson, and L. Sutter, "Evaluation of premature deterioration of concrete bridge barriers by petrographic examination", *83rd Annual Meeting, Transportation Research Board*, 19 (2004).

[16] I. Odler, "Free lime content and unsoundness of cement", in: *Materials Science of Concrete. Special volume: Calcium Hydoxide in Concrete*, ed. J. Skalny, J. Gebauer, and I. Odler, pp. 237-244, American Ceramic Society, Westerville, 2001.

[17] EN 197-1:2000, *Cement Part 1: Composition, Specification and Conformity Criteria for Common Cements*.

[18] EN 196-2:2005, *Methods of Testing Cement – Part 2: Chemical Analysis of Cement*.

[19] I. Külaots, A. Hsu, R.H. Hurt, and E.M. Suuberg, "Adsorption of surfactants on unburned carbon in fly ash and development of a standardized foam index test", *Cement and Concrete Research* 33 (12), 2091–2099 (2003).

[20] PN-88/B-06250, *Plain Concrete*, Polish Committee for Standardization, (in Polish).

[21] R. Krzywoblocka-Laurow, "Testing of phase composition of concrete", *Instruction* 357/98, Building Research Institute (ITB), Warsaw, 1998, (in Polish).

[22] R. Krzywoblocka-Laurow, "Determination of phase composition of common cements CEMI", *Instruction* 370, Building Research Institute (ITB), Warsaw, 2002, (in Polish).

[23] R. Krzywoblocka-Laurow, "Estimation of quality of cement CEM I on the basis of phase composition", *Proc. US – Poland Workshop on Diagnosis of Concrete Materials and Structures for Infrastructure Facilities*, 77–81 (2004).