EFFECT OF FLUIDIZED BED COMBUSTION FLY ASH ON THE CHLORIDE RESISTANCE AND SCALING RESISTANCE OF CONCRETE

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Abstract

The subject of the investigations was the damage of concrete due to chloride ion penetration and surface scaling in presence of de-icing agents. The air-entrained concretes with 15% and 30% cement replacement by fly ash from fluidized bed combustion boilers (CFBC) were tested. Two kinds of CFBC fly ash were used, one obtained from hard coal combustion, the other one - from lignite.

The chloride migration coefficient was determined according to the Nordtest Method NT Build 492 and the scaling resistance - according to the CEN/TS 12390-9:2007, slab method. The concrete resistivity development was also measured and recorded.

Obtained results have showed a significant influence of partial cement replacement by CFBC fly ash on the chloride and scaling resistance of concrete.

It has been found that this replacement of Portland cement reduced the chloride diffusion coefficient and increased the concrete resistivity. The influence of CFBC fly ash on scaling resistance depends on the tested percentage (15 and 30% mass) content of cement replacement.

Key words: concrete, durability, chloride diffusion, scaling resistance, resistivity, fluidized bed combustion (FBC) fly ash

1. INTRODUCTION

Concrete structures exposed to saline sea water or deicing salts on coast areas, on roads and pavements during winter in severe climate are examples where a chloride and salt-frost resistant concrete is required in order to prevent damage. The concrete surface is exposed permanently or frequently to water containing chloride ions. At the beginning, the chloride diffuses into the concrete by different kinds of connected pores, and later the scaling starts by the micro-cracks and at a critical chloride concentration the steel corrosion is initiated

The chloride-induced corrosion of steel bars is a long-term effect and it is normally observed in practice after a few years. Therefore, special test procedures have been developed to simulate both, the chloride diffusion and scaling deterioration in a short period of time, [1]. The Non-Steady State Migration Test - NordTest Build 492, [2], and the slab test - CEN/TS 12390-9:2007, [3], were used.

Studies in the early 1970s [4] demonstrated that the addition of natural pozzolana to Portland cement (PC) could reduce the chloride diffusion coefficient of concrete by three times. Addition of fly ash has an even more significant effect on the diffusion coefficient and resistivity, [4], due to the reduction of permeability and diffusivity of concrete. The incorporation of fly ash increases porosity of the hardened cement paste at early ages, but the average pore size is reduced, and this often results in a less permeable cement paste. The dense transition zone between aggregate and matrix is also a result of the use of fly ash. The concrete containing fly ash is, therefore, less susceptible to the ingress of harmful chloride ions, [5].

In both phenomena, chloride and scaling resistance, the ingress of harmful ions can be reduced by fly ash as an additive or as a cement replacement. However, CFBC fly ash differs in physical and chemical properties from the traditionally used fly ashes, Table 1. Moreover, according to the definition indicated by European Standard, 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 this fly ash is beyond its scope, [6]. The CFBC fly ash is a relatively new by-product and its influence on the concrete durability is not well known. Preliminary tests where CFBC fly ash was used both as an additive and or a component of Portland cement revealed good properties of such blended concretes, [7].

In the paper the influence of fly ashes from CFBC on the chloride resistance and salt-frost resistance of concrete is analyzed. Two kinds of CFBC fly ash from two power plants in Poland have been studied. The effects of cement replacement by fly ash on compressive and tensile strength, air-void microstructure, resistivity and chloride and scaling resistance of concrete were investigated.

2. LABORATORY TESTS

2.1 Materials and mixture proportions

The aim of investigations was to determine the chloride and scaling resistance of the air-entrained concrete made with and without CFBC fly ash on chloride and scaling resistance. The concrete resistivity was also monitored during 360 days in order to obtain additional information on the connectivity of the pore system in the concrete surface layer. Five series of concrete specimens were made in the laboratory conditions.

Ordinary Portland cement CEM I 32.5 R from Małogoszcz cement plant, gravel from "Nivka" deposit, fractions 2-8 mm and 8-16 mm, and sand fraction 0-2 mm, were used. Concrete mixes were designed with constant water to binder ratio w/b = 0.45. To keep the relatively constant slump and porosity of fresh mix around 5% - 6%, different amounts of admixtures were applied. A plasticiser, a superplasticiser and an air-entrainer were used in amounts of 0.9%, 0.65% – 1.25% and 0.1% of the mass of binder (cement and fly ash), respectively, to achieve approximately the same workability and porosity of the fresh mix. The reference concrete did not contain any additive and the concretes with 15% and 30% cement replacement by fly ash from hard coal combustion in the thermal-electric power station "Katowice" (C15K and C30K) and from brown coal - lignite the in power plant "Turów" (C15T and C30T) were used. Chemical and physical properties of Portland cement type I, ordinary fly ash and CFBC fly ash are shown in Table 1, and in Table 2 - the mixture proportions of tested concretes and the compressive and tensile strength of hardened concrete.

Table 1. Chemical composition and other characteristics of PC, fly ash, and FBC fly ash, [8, 9]

Chemical compounds	PC type I	Fly ash	CFBC fly ash	
			from hard coal K	from lignite T
SiO_2	21.4	50.8	47.18	36.47
Fe_2O_3	3.5	8.6	6.8	4.4
Al_2O_3	5.7	23.9	25.62	28.4
TiO_2	NA	1.11	1.08	3.84
CaO	64.1	4.0	5.84	15.95
MgO	2.1	2.8	0.15	1.65
SO_3	2.1	0.8	3.62	3.8
Na_2O	0.5	0.8	1.18	1.64
K_2O	0.92	2.9	2.36	0.62
Cl^-	0.029	0.02	0.1	0.03
CaO_{free}	0.9	0.6	3.4	4.75
Specific gravity [g/cm^3]	3.15	2.16	2.68	2.75
Loss on ignition, 1000°C/1h	1.1	2.9	3.4	2.73

All concrete specimens were prepared in the Institute of Building Materials and Structures, the Faculty of Civil Engineering, Cracow University of Technology, under supervision of Professor Jacek Śliwiński, [8].

Table 2. Composition of the concrete mixes in kg/m^3 and the compressive and tensile strength

Mix	Cement	Additive		Aggregate	Water	Plasticizer	HRWR	AEA	Compressive strength, [MPa]		Tensile strength, [MPa]	
		T	K									
	Content [kg/m^3]								28 days	360 days	28 days	360 days
C0	380	-	-	1822	171	3.4	0.4	2.7	46.3	54.8	3.4	4.2
C15K	323	-	57	1813	171	3.4	0.6	2.5	47.2	57.3	3.8	4.2
C30K	266	-	114	1803	171	3.4	0.6	3.4	46.8	64.8	4.1	4.8
C15T	323	57	-	1810	171	3.4	0.6	3.8	45.3	60.9	3.7	4.2
C30T	266	114	-	1800	171	3.4	0.6	4.8	46.3	49.9	3.5	3.9

HRWR- high range water reducer, AEA- air-entraining admixture

The specimens were cast in cubical moulds 150x150x150 mm or in cylinder moulds – ø100 mm x 200 mm. Fresh mixes were consolidated by vibration. After 48 hours the specimens were demoulded and cured in high humidity conditions RH > 90% at temperature 18-20 ^{0}C until the age of 28, 90,180 and 360 days.

2.2 Testing procedures

Salt scaling tests were performed according to CEN/TS 12390-9:2007, [3]. Freeze/thaw exposure was carried on one-dimensionally on the upper horizontal surface of the specimens – cutting surface, while the remaining surfaces were isolated against humidity and heat transfer. After 28 days of curing the top exposed surface was covered with 3% saline solution. Then the cooling and thawing cycles, each of 24 hours, were applied. The scaled material was collected and weighed after given numbers of freeze/thaw cycles, and the results expressed as mass per unit area have been recorded. The test of the specimens according to the Standard ended after 56 cycles. The mean mass of scaled material after 28 and 56 cycles is used for evaluating the scaling resistance, according to the criteria presented in Table 3

Table 3. Criteria of the scaling resistance evaluation, [7]

Scaling resistance	Requirements
Very good	$m_{56} < 0.10$ kg/m^2
Good	$m_{56} < 0.20$ kg/m^2 or $m_{56} < 0.50$ kg/m^2 and $m_{56}/m_{28} < 2$
Admissible	$m_{56} < 1.00$ kg/m^2 and $m_{56}/m_{28} < 2$
Inadmissible	$m_{56} > 1.00$ kg/m^2 and $m_{56}/m_{28} > 2$

The chloride penetration test in this study is based on the standard of NordTest Build 492 - Non-Steady State Migration Test, [2]. Most of the chloride-migration tests used in Europe are comparable to this test, [1]. The principle of the test is that concrete is subjected to external electrical potential applied across the specimen and chloride ions are forced to migrate into concrete. The specimens are split open and sprayed with silver nitrate solution, which reacts to give white insoluble silver chloride on contact with chloride ions. This provides a possibility to measure the depth to which a sample has been penetrated. The test has an advantage of being unaffected by the chemistry of pore solution within different kinds of concrete.

The conformity criteria for concretes according to Non-Steady State Migration Test, [2] are based on the voltage magnitude, temperature of anolite measured on the beginning and the end of test and the depth of chloride ions penetration, Table 4.

Table 4. Estimation of the chloride resistance to chloride ions penetration, [10]

Diffusion coefficient	Resistance to chloride penetration
$< 2 \times 10^{-12}$ m^2/s	Very good
$2 – 8 \times 10^{-12}$ m^2/s	Good
$8 – 16 \times 10^{-12}$ m^2/s	Acceptable
$> 16 \times 10^{-12}$ m^2/s	Unacceptable

The Wenner method to test concrete resistivity is based on application of 4 probes on the concrete surface at equal spacing. The probes are connected to the concrete resistance test set. The test set allows to pass a known amount of current through the outer two probes and measures the voltage drop between the inner two probes. On the basis of the ohms law the output is equal to the resistivity value.

2.3 Results and discussion

The influence of freezing and thawing cycles in contact with 3% sodium chloride solution on resistance of concretes with different amount and type of FBC fly ash is shown in Fig. 1, each point of the diagrams represents a mean value from four specimens. Fig. 1 indicates that the specimens C30K and C30T failed the scaling test. As it was expected, the positive results were achieved for air-entrained concrete specimens C0 without any addition. The concretes made with 15% replacement of both kinds of FBC fly ash showed similar results after 56 cycles of cyclic freezing and thawing, i.e. about 0.6 kg/m^2.

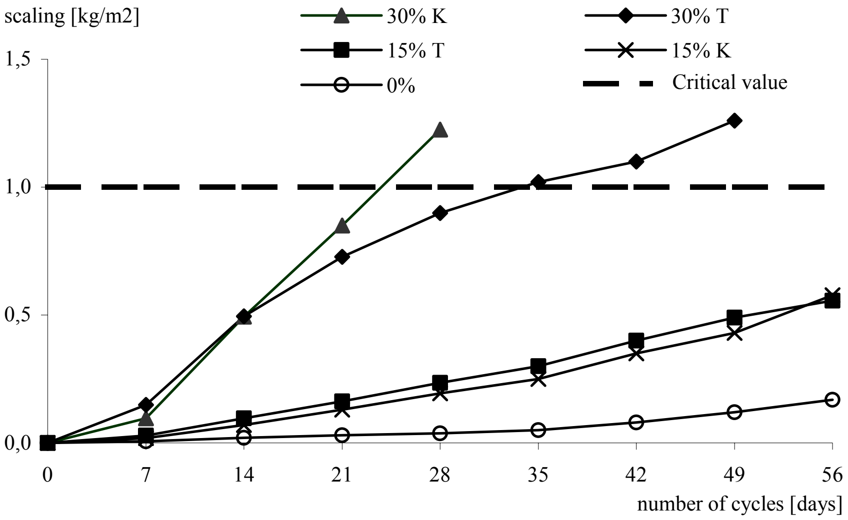

Figure 1: Results of the scaling resistance tested according to CEN/TS 12390-9:2007, [3]

Figure 2 and 3 present the influence of FBC fly ash on chloride resistance, tested during one year. The general tendency shows that fly ash beneficially influences on chloride diffusion coefficient.

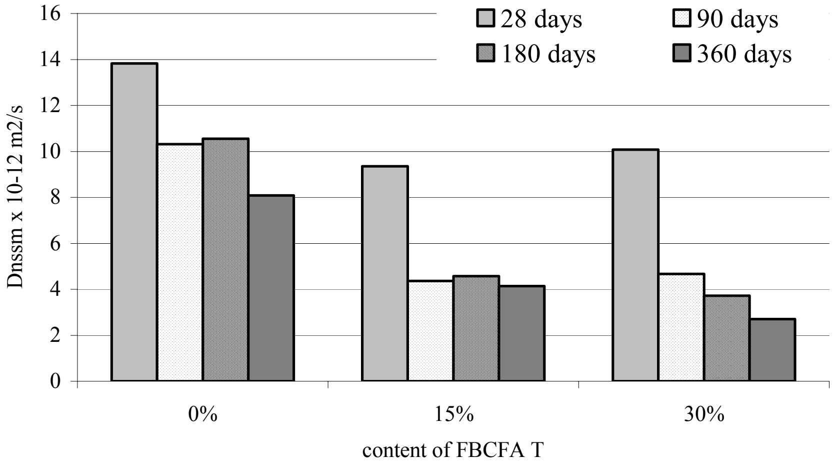

Figure 2: Chloride diffusion coefficient vs. FBC fly ash (from lignite) content, tested for 28, 90, 180 and 360 days

The replacement of cement by FBC fly ash from hard coal K caused better reduction the chloride diffusion coefficient, than fluidized fly ash from brown coal T. The differences in D_{nssm} between concretes with 15% and 30% of FBC fly ash from hard coal K could be neglected. The ordinary concrete C0 and FBC fly ash K - C30K and C15K exhibit systematic decreasing of chloride diffusion coefficient in time. In concretes with 30% of FBC fly ash from brown coal the value of D_{nssm} was higher than for concrete with 15%, and after 180 days the chloride resistance C30T was better than for C15T.

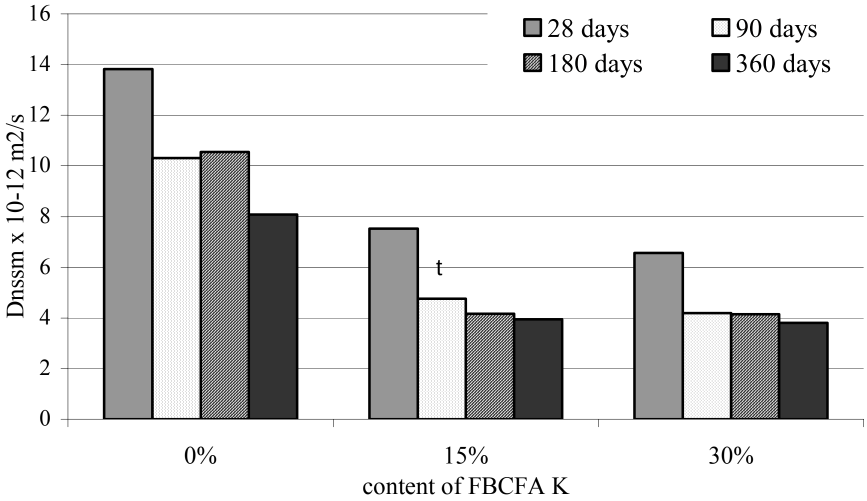

Figure 3: Chloride diffusion coefficient vs. FBC fly ash (from hard coal) content, tested for 28, 90, 180 and 360 days

The results of resistivity tests (Figure 4) showed that the cement replacement by FBC fly ash, both 15% and 30%, sealed the concrete microstructure. The highest resistivity values were obtained for concrete with 30% fly ash. After 120 days the increase rate became smaller. The resistivity of concretes with 30% replacement was four times higher than that of concrete without this replacement.

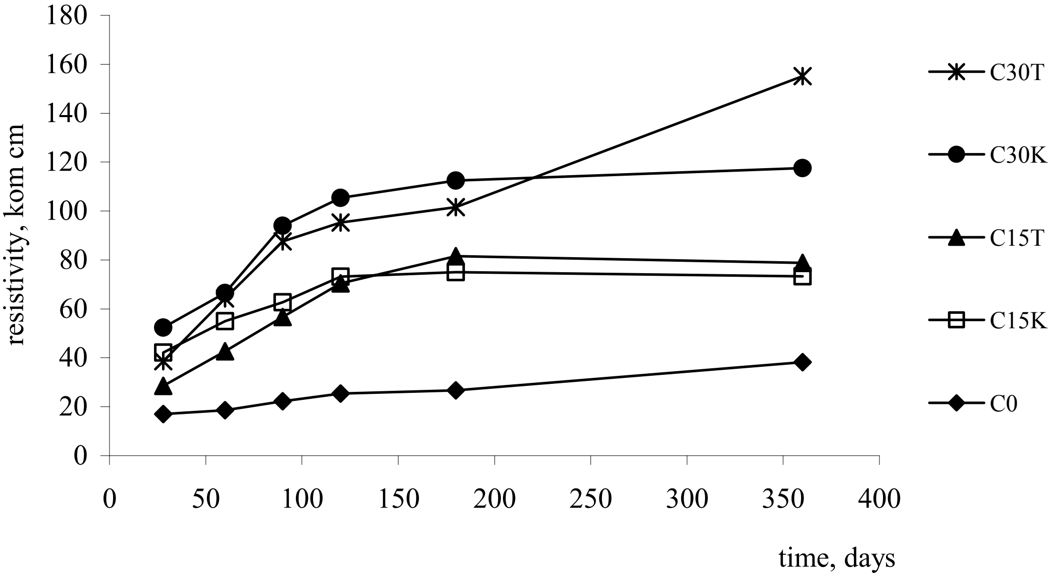

Figure 4: The resistivity of tested concretes vs. time

Additionally in Fig. 5 the chloride diffusion coefficient vs. resistivity is showed. The relationship between chloride resistance and resistivity in time is clearly visible. More dense and compact paste causes higher reduction of permeability of concretes, and this phenomenon is not time-dependent.

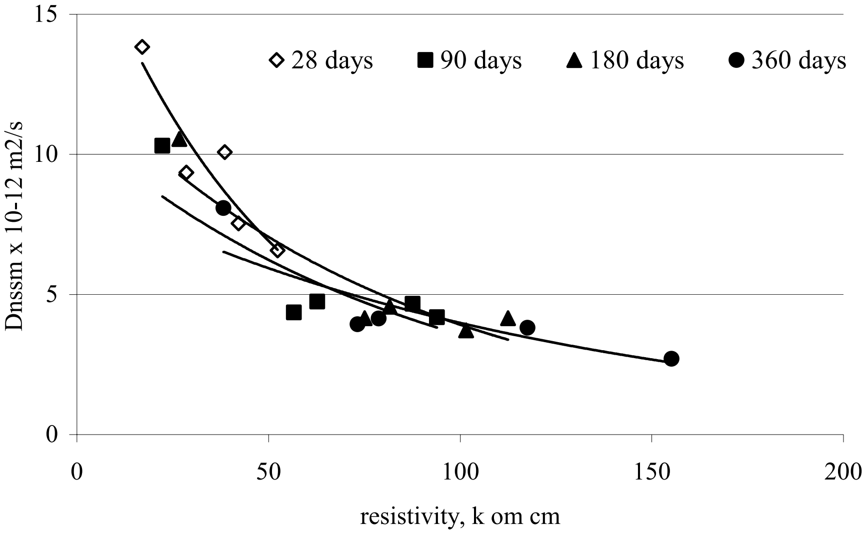

Figure 5: The chloride diffusion coefficient vs. resistivity tested in different period of time

4 CONCLUSIONS

The following conclusions can be drawn from this preliminary study:

- The cement replacement by both 15% and 30% of FBC fly ash causes better chloride resistance;
- The FBC fly ash from hard coal K shows better properties in reduction of chloride diffusion coefficient than FBC fly ash from brown coal T.
- The chloride diffusion coefficient decreased with increasing the resistivity;
- The Wenner method is an easy and simple test to determinate the resistivity of concretes surface layer but it does not explain how does FA influence on the scaling resistance;
- The 15% of FBC fly ash addition could be applied to reduce the scaling problem;
- The 30% cement replacement by FBC fly ash cannot be used for scaling resistant concretes;

Future research is needed in following directions:

- The optimum of FBC fly ash replacement which results in both, chloride and scaling resistant concrete;
- The highest possible content of FBC fly ash which can be applied to obtain chloride resistant concrete (taking into consideration the workability and rheology of fresh mix);
- The influence of the 10% and 20% cement replacement by FBC fly ashes on scaling resistance,
- The SEM observations of the difference in the microstructure of concretes with fluidized fly ashes (interfacial transition zone).

ACKNOWLEDGEMENTS

This work was supported by Project nr R04 013 01 sponsored by the Ministry of Research and High Education, Warsaw, Poland, to which the author is grateful.

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