



INVESTIGATING THE PROTECTIVE PROPERTIES OF CONCRETE CONTAINING ASH FROM COAL COMBUSTION IN A FLUIDIZED BED

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Abstract. The article reports the results of research on the protective properties of concrete with the addition of ash from hard coal combustion in a fluidized bed at a power plant in Katowice. Research was carried out on concentrated water extracts from disintegrated concrete using a polarization technique. The results were compared with those obtained in a similar way from concrete extracts without additives and with criteria including the delimiting values of the parameters of the electrochemical process. The results have shown that concrete incorporating 15% and 30% ash as cement replacement correctly protect reinforcement against corrosion.

Keywords: protective properties of concrete, concrete supplement, cement replacement materials, ash from fluidized bed combustion, reinforcement corrosion, polarization curves, corrosion current, corrosion potential.

1. Introduction

The power industry in Poland is based mainly on solid fuels – mostly hard coal. Combustion products constitute waste and their management is an important economic and technical problem (Coufal 1999). So far, combustion practice has formed, among other things, fly ash, which is a useful mineral supplement to concrete. Research conducted over the last few years has shown that fly ash has pozzolanic properties and that it can be taken into account in concrete formulas as a binder component (Jiang *et al.* 1999; Fu *et al.* 2002). The use of fly ash in concrete technology is included in standards (EN 450: 2005, EN 206-1: 2000).

With the present desire to limit the emission of harmful compounds into the atmosphere, power stations and heat and power stations are undergoing modernization that consists of installing fluidized beds, in which the process of fuel combustion runs at temperature lowered to 850 °C. As a result of this solution, the emission of nitric and sulphur oxides is lowered. However, ashes from combustion in a fluidized bed are

different from those obtained in a conventional way, especially in relation to a phase type. Although concrete with the addition of fly ashes is characterized by good compressive strength and reinforcement protective properties against corrosion, these positive properties cannot be directly obtained with the inclusion of ashes from fluidized bed combustion. Hence, currently, experimental work is being undertaken the aim of which is to qualify the conditions permitting the general supplementation of ashes from a fluidized bed to the production of the structural types of concrete (Pacewska *et al.* 2002; Giergiczny, Pużak 2008; Łagosz *et al.* 2008; Domagała, Zybura 2009).

The aim of this paper is to show that replacing cement with ash from fluidized bed combustion furnace does not cause deterioration in the protective properties of concrete in regard to steel reinforcement.

The linear polarization method was conducted to define the basic parameters of the corrosive process. The ability of concrete in the passivation of the steel surface was determined in concentrated water extracts

from concrete modelling porous liquid. Concrete contained ash from the hard coal combustion power station in Katowice. The ash was applied in two proportions – 15% and 30% by weight of cement, whereas water to binder ratio (together cement and ash) was constant and maintained at 0.55. The obtained values were compared with the results of analogous measurements conducted in a model solution from reference concrete without additives in water to binder the ratio of 0.55. Research on three kinds of concrete is considered.

2. Method and Scope of Investigations

Research was conducted on steel reinforcement grade BSt 500S (DIN 488-1: 2006) modelling the protective influence of concrete with water solutions. Model solutions reflected conditions occurring in concrete which is not subject to aggressive influences from the environment. Research had an electrochemical character and was conducted using the polarization method in a three-electrode circuit (Choi 2006; Ha *et al.* 2007).

Electrochemical measurements were recorded offering three solutions. One solution was taken from concrete free of ashes and the obtained results were used as a reference level. The two remaining solutions were prepared from concrete mixes with the addition of ashes from a fluidized bed.

Water samples were extracted from nine 10×10×10-cm size cubical specimens crumbled after crushing them in a testing machine at a later stage. 3 series of samples were formed including 3 cubes in every series. The individual series of samples were constituted from concrete created according to different formulas, varying ash content and altering the class of Portland cement. The types of concrete were marked applying the symbols:

- A0 – ash-free reference mix,
- A15K – with 15% ash content,
- A30K – with 30% ash content.

All types of concrete were based on a mix of natural fine aggregates of 0–2 mm river sand, a coarse aggregate of 2–8 mm gravel and high early durability cement. The plasticizers BASF Liquol BV18 and BASF Glenium SKY591 (www.basf-admixtures.pl) were used for preparing concrete. The composition of concrete mixes is given in Table 1.

The embedded samples were kept in moulds for three days. After removal from the moulds, the samples were described and placed for the period of 25 days in a climatic chamber at a temperature of 20 °C and relative moisture $\geq 95\%$.

3. Technique and Procedures of Research

The vacuum concentration method was used to prepare model solutions (Wieczorek 1993). The concentration process imitates conditions present in the concrete pores under the influence of humidity and temperature changes causing a periodical increase in the concentration or thinning of the liquid adsorbed by pores and a change in the chemical constitution of the solution connected with new equilibrium states between the solid and liquid phases of concrete. The specific relation between water and hardened paste corresponds to the actual humidity of concrete while the aggregate is treated as inert material. The preparation of the model solution is derived from the vaporization of water extract induced by intensive pressure on ground and hardened concrete which is in continuous contact with the dissolved solid phase. The concentration of the solution was adjusted proportionally to the humidity of concrete accepting that in average, the working conditions of reinforced concrete constructions makes about 5% of its mass. It is estimated that all lixiviate solutions from concrete must be concentrated 3.4 times.

In preparing water extracts, every sample of crumbled concrete was sifted through a 0.25 mm sieve placed in a container adding distilled water by weight in proportions 1:1. The thick solution was stirred every

Table 1. Composition of concrete mixes and compressive strength of concrete at 28 days

Concrete	Compressive strength [MPa]	Water-binder ratio	Materials [kg/m ³]						
			Cement	Fluidized ash	Water	Aggregate	BV18	SKY591	
A0	41.2	0.55	CEM I 42.5R	320	–	176	1865	2.9	1.0
A15K	32.8	0.55	CEM I 32.5R	272	48	176	1857	2.9	1.8
A30K	41.5	0.55	CEM I 32.5R	224	96	176	1847	2.9	2.9

few hours for one full day. Later, it was trickled through a filter of average thickness. Trickling was aided by low pressure in a suction flask joined to a vacuum pump. Then, water extract was concentrated in a rotary vacuum evaporator (see Fig. 1).

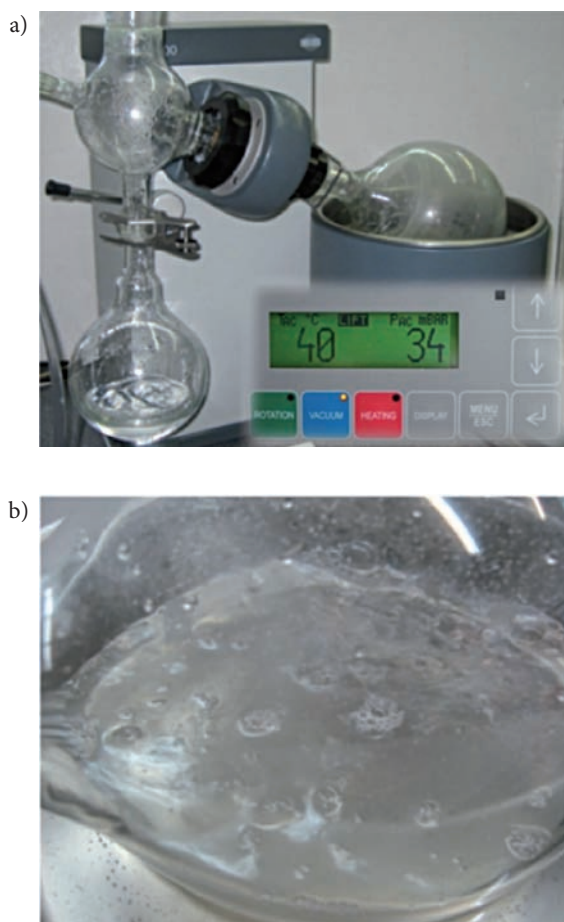


Fig. 1. The method of concentrating model pore liquid in a rotary vacuum evaporator: a) laboratory stand, b) solution boiling at room temperature

In the vacuum evaporator, the pressure was lowered to 34 hPa. Such conditions made it possible to bring concentrated liquid to the boiling point at a temperature of about 27 °C. Vaporizing was helped by a radiator that accelerated steam condensation and intensified the process. Because boiling solution causes a drop in its temperature, the flask containing the model pore liquid was immersed in a water bath the temperature of which was about 10 °C higher than that of the solution inside the flask. From every crushed cube, the sample of 200 ml of concentrated extract was obtained for research on the protective proprieties of concrete.

Electrochemical tests were conducted applying the polarization method in a three-electrode circuit according to the scheme shown in Fig. 2.

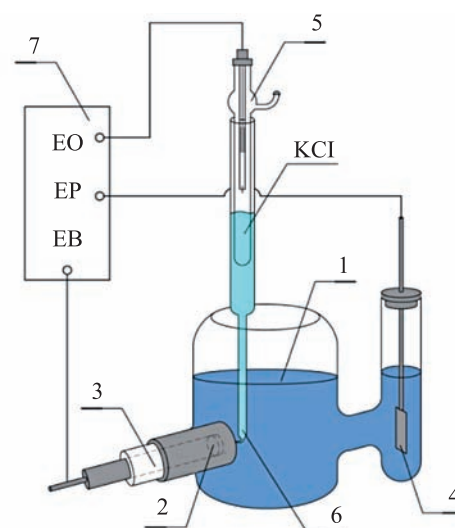


Fig. 2. The scheme of apparatus for research on the protective properties of model pore liquid

Model pore solution 1 was placed in an electrochemical vessel while steel sample 2 lay in holder 3. In the electrochemical vessel, there was an auxiliary electrode 4 in the form of a platinum-covered titanic plate as well as reference silver-silver chloride electrode 5 together with Lugin's capillary tube 6. Lugin's capillary tube protected against the occurrence of diffusive potential between two electrode solutions. The sample of reinforcing steel 2 (working electrode) was made in the form of a rod of 10 mm diameter and 5 mm thickness. The active surface of the working electrode was polished, degreased with acetone and dried. Spur handle 3 assured the working electrode in a surface area of 0.35 cm². Measurements were made using computer controlled potentiostat 7 supplied by Gamry Instruments Inc. featuring a PC/300 card serving the application DC105 for direct current analysis.

After establishing the value of stationary potential, polarization was begun changing the potential value at a rate of 0.25 mV/s. Every series of measurements consisted of three concentrated model solutions as well as of three independently produced samples reinforcing steel. Analogical measurements obtained from model solutions with concrete containing ash from brown coal combustion in a fluidized bed are reported in our earlier studies (Domagala, Zybur 2009).

Moreover, prior to every electrochemical analysis, a measurement of the pH value of the model solution was executed. This procedure was conducted employing the Mettler Toledo pH-meter with the added measuring electrode dipped in a container filled with water solution from the above analysed concrete. After the pH value stabilised, the reading of pH-meter was noted.

4. Test Results

The results of every electrochemical measurement were obtained as a computer printout of the shape of cathodic and anodic polarization curves as well as the value of corrosion potential E_{corr} and corrosion current density i_{corr} .

Polarization curves representing the corrosive properties of reinforcement protected with reference concrete A0 are shown in Fig. 3, with concrete A15K in Fig. 4 and with concrete A30K in Fig. 5.

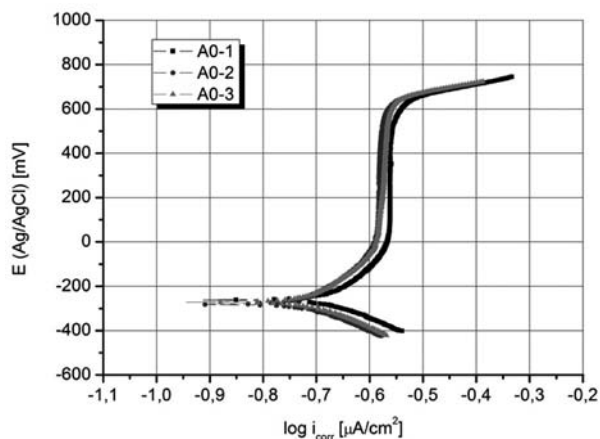


Fig. 3. Polarization curves obtained from model solutions with reference concrete A0

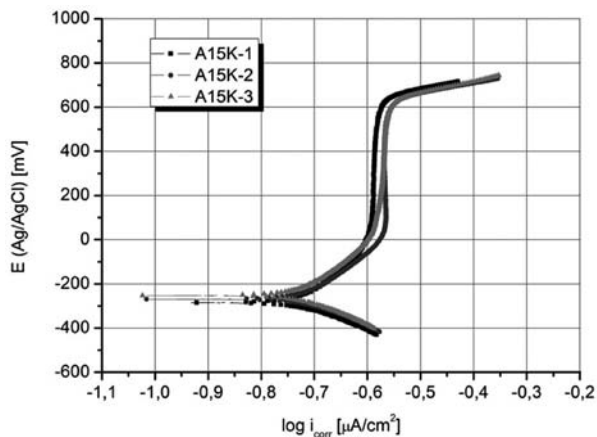


Fig. 4. Polarization curves obtained from model solutions with concrete containing 15% ash additive – A15K

The analysis of the resulting polarization curves was conducted according to principles presented in Fig. 6.

The value of corrosion current density i_{corr} and corrosion potential E_{corr} are the results of the extrapolation of the straight sections of polarization curves expressed as a logarithmic scale of current density. The abscissa of

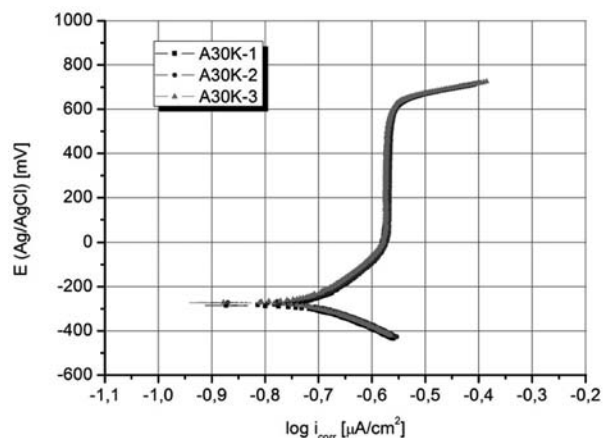


Fig. 5. Polarization curves obtained from model solutions with concrete containing 30% ash additive – A30K

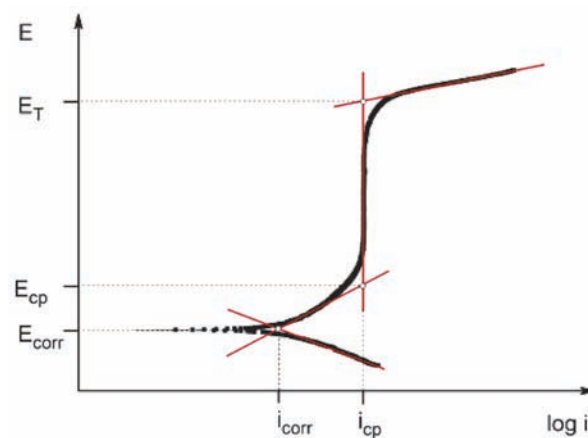


Fig. 6. The principle of determining electrochemical process parameters from the shape of polarization curves

the point of the intersection of both straight sections marks the logarithm of the value of corrosion current density i_{corr} whereas the ordinate corresponds to the value of corrosion potential E_{corr} . Moreover, on the basis of the shape of polarization curves, the values of critical passivation current density i_{cp} , critical passivation potential E_{cp} and transpassivation E_T were graphically established.

A summary of the results of the electrochemical research and pH measurements of model solutions are presented in Table 2.

5. Discussion

Parameters characterizing the process of reinforcing steel corrosion incurred in model solutions from concrete containing ashes from fluidized combustion were compared with values determined during potentiodynamical measurements in solutions from reference

Table 2. Statement of electrochemical research results

Concrete	Specimen	pH	Potential [mV]			Current density [$\mu\text{A}/\text{cm}^2$]	
			E_{corr}	E_{cp}	E_{T}	i_{cp}	i_{corr}
A0	1	12.53	-262.2	-46.4	611.5	0.27	0.19
	2	12.49	-280.4	-37.9	612.2	0.26	0.07
	3	12.50	-271.4	-31.1	615.3	0.27	0.08
A15K	1	12.41	-284.2	-26.6	613.3	0.26	0.07
	2	12.35	-268.1	-22.3	615.0	0.27	0.07
	3	12.41	-251.8	-0.7	611.7	0.27	0.06
A30K	1	12.53	-284.9	-42.0	610.2	0.27	0.10
	2	12.52	-272.2	-42.8	614.9	0.27	0.13
	3	12.53	-271.5	-37.3	616.1	0.27	0.09

concrete (A0) following recommendations for standard (EN 480-14: 2006).

Although standard (EN 480-14: 2006) deems it is sufficient to compare the value of current density i_{corr} only, however, in the present study, all remaining electrochemical parameters including critical passivation current density i_{cp} , corrosion potential E_{corr} , critical potential of passivation E_{cp} and transpassivation potential E_{T} have been also analysed.

The most recurrent values close to the reference level are characteristically corrosion potential E_{corr} and transpassivation potential E_{T} . The values of critical passivation potential E_{cp} marking the beginning of the passive zone on polarization curves showed a slightly larger variation. The addition of ash from fluidized combustion raised the value of critical passivation potential in comparison with reference concrete (A0), although note that in model solutions from concrete containing a 15% addition of ash, the value of critical passivation potential was higher than that in solutions from concrete in which 30% of cement was replaced by ash.

The results of polarization measurements show that on effect of using ash from the fluidized bed as a replacement of 30% of cement mass imperceptibly enlarged the value of corrosion current i_{corr} , whereas 15% addition of ashes caused a different tendency influencing on a decrease in corrosion current density. The value of critical passivation current density i_{cp} estimated in individual model solutions were comparable, and therefore it is hard to differentiate individual results on the basis of this parameter.

In respect to differences between the results of measurements obtained in individual solutions, one should stress their small changes that do not show the existence of variable tendencies in relation to those obtained as level reference values. That is why it can be supposed that the exchange of a piece of cement for

ash from a fluidized bed did not influence significantly the shape of electrochemical processes at the point of contact with steel–model pore solutions and did not worsen the protective properties of concrete in relation to reinforcement.

In analysing polarization curves, the criteria contained in the monograph (Wieczorek 2002) were also considered. According to the introduced criteria, concrete is characterized with correct protective properties when corrosion potential $E_{\text{corr}} > -378.5$ mV, corrosion current density $i_{\text{corr}} < 1 \mu\text{A}/\text{cm}^2$, critical passivation current density $i_{\text{cp}} < 5 \mu\text{A}/\text{cm}^2$ and transpassivation potential $E_{\text{T}} > 428.5$ mV. The values of potentials passed originally with regard to the saturated calomel electrode were in reference to the saturated silver–silver chloride electrode applied in research. The results of measurements noted in individual water extracts from concrete also reflect the quoted criteria confirming the statement that the examined steel was in the passive state.

The pH value of concrete covering has a significant influence on the electrochemical state of steel reinforcement. A delimiting value, below which the depassivation of steel surface occurs is recognised as $\text{pH} = 11.8$ (Wieczorek 2002). The determined pH values of individual model solutions oscillating in the range of 12.35 (A15K-2) ÷ 12.53 (A0-1, A30K-1, A30K-3) give evidence of good protective properties of all studied types of concrete in relation to reinforcing steel.

The results of investigations barring reference to the latest standard (EN 480-14: 2006) were additionally compared with recommendations contained in the currently applicable Polish standard (PN-86/B-01810: 1986] suggesting the following values defined in relation to silver–silver chloride electrode: corrosion potential $E_{\text{corr}} > -328.5$ mV and critical passivation potential $E_{\text{cp}} > -278.5$ mV while transpassivation potential is contained in the range of $428.5 < E_{\text{T}} < 678.5$ mV. Mo-

reover, corrosion current density should not exceed $i_{corr} < 15 \mu\text{A}/\text{cm}^2$. Electrochemical parameters determined in all analysed model solutions also fulfil the revised criteria of the Polish standard (PN-86/B-01810:1986) which, however, are recognised as somewhat liberal at present (Wieczorek 2002).

6. Conclusions

With the aim of managing the waste of products from modernized power stations derived from combustion coal in fluidized beds, a test has been undertaken on the use of ash as cement replacement material in structural concrete. The assessment of protective properties in regard to concrete reinforcement, including ash from the hard coal power station in Katowice, has been conducted using the potentiodynamic method in model solutions. The obtained results have been compared to reference concrete without additives, in accordance with the standard (EN 480-14: 2006) applying additional criteria.

Based on the shape of polarization curves, corresponding to the individual types of concrete, the basic parameters characterizing its ability in the passivation of steel surface have been assessed. Corrosion current density has shown a range from the smallest value $i_{corr} = 0.06 \mu\text{A}/\text{cm}^2$ noted in a solution from concrete with 15% addition of ash (A15K-3) to the largest value $i_{corr} = 0.19 \mu\text{A}/\text{cm}^2$ measured in a model liquid from reference concrete (A0-1). These values are considerably smaller than the generally recognised delimiting value $i_{corr} < 1 \mu\text{A}/\text{cm}^2$ considered as an indication of the non occurrence of reinforcement steel corrosion (Saraswathy, Song 2006; Wieczorek 2002). The smallest value of critical passivation current density $i_{cp} = 0.26 \mu\text{A}/\text{cm}^2$ has been estimated in water extract from concrete, including a 15% addition of ash (A15K-1) while the maximum value of critical passivation current density $i_{cp} = 0.27 \mu\text{A}/\text{cm}^2$ occurred in the solution from reference concrete (A0-1). This parameter similarly testifies to the correct protective properties of all analysed types of concrete (according to (Wieczorek 2002) $i_{cp} < 5 \mu\text{A}/\text{cm}^2$). The most recurrent values, which are close to the level of reference values, have characterized corrosion potential E_{corr} and transpassivation potential E_T as fulfilling in every case criteria $E_{corr(Ag/AgCl)} > -378.5 \text{ mV}$, $E_{T(Ag/AgCl)} > 428.5 \text{ mV}$ for the proper protection of reinforcing steel against corrosion (Saraswathy, Song 2006; Wieczorek 2002).

Also giving good evidence for the ability of the individual types of concrete in the passivation of steel rein-

forcement surface are the values of $pH = 12.35 \div 12.53$ measured in individual model solutions and considerably exceed $pH = 11.8$ recognised as a delimiting value below which steel depassivation occurs.

Comparing the results achieved in concentrated water extracts from the types of concrete modified with fly ash additives and from reference concrete and taking into account additional criteria engaging the delimiting values of electrochemical parameters can infer, the use of ashes from hard coal combustion in fluidized beds as cement replacement material did not worsen the protective properties of concrete in relation to steel. Concrete containing 15% and 30% of these ashes in relation to the mass of cement protects steel bars against corrosion correctly.

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BETONO SU SKYSTO KURO KROSNYJE SUDEGINOTOS ANGLIES PELENAIS APSAUGINIŲ SAVYBIŲ TYRIMAS

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Santrauka. Straipsnyje pateikti betono su Katowice gamykloje skysto kuro krosnyje sudegintos anglies pelenais apsauginių savybių tyrimų rezultatai. Taikant poliarizacijos technologiją buvo tiriamas vandens koncentratas, išskirtas iš suirusio betono. Rezultatai palyginti su panašių tyrimų rezultatais, kai taikant tokią pačią technologiją buvo tiriamas betonas be priemaišų. Rezultatai taip pat buvo palyginti pagal kriterijus, įvertinančius ribines elektrocheminio proceso parametrų reikšmes. Rezultatai parodė, kad, betone 15 ar 30 proc. cemento pakeitus pelenais, armatūra būna tinkamai apsaugota nuo korozijos.

Reikšminiai žodžiai: apsauginės betono savybės, betono priedai, cementą pakeičiančios medžiagos, skysto kuro krosnyje sudegintos anglies pelenai, armatūros korozija, poliarizacijos kreivės, korozijos srovė, korozijos potencialas.

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