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Monitoring of Concrete Resistance to Chloride Penetration

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The investigation was carried out in order to monitor the continuous behaviour of concretes containing fly ash in a chloride exposure regime. Chloride penetration was simulated by subjecting samples to cyclic loading with salt solution and drying or to freeze-thaw cycles in presence of chloride salt. The results of long-term monitoring of electrical resistivity changes were confronted with the results of chloride penetration resistance of concrete using rapid test (RCMT). The resistivity monitoring was conducted during 12 months and the resistance to chloride penetration by means of rapid test was determined after 28, 90 and 180 days of curing. Based on the test results, the beneficial effects of cement type, fly ash content related to cement mass as well as the time of exposition has been discussed.

Keywords: monitoring, concrete, fly ash, electrical resistivity, chloride penetrability, charge passed, diffusion coefficient.

1. INTRODUCTION

Chloride induced corrosion of steel in concrete is one of the most common reason for deterioration of reinforced concrete structures. Chloride permeability of concrete is such an intrinsic property that it needs to be assessed independently, especially in the design and construction of structures to be built in a salt-laden environment.

The main source of chlorides in concrete is chloride ions ingressing from outside. In the case of highway structures and bridges as well as parking garages, de-icing salts (NaCl and $CaCl_2$) can cause this. Another source of chloride ions is seawater in contact with concrete. Chlorides can also be deposited on the surface of concrete in the form of very fine airborne drops of seawater, carried by wind. Brackish ground water in contact with concrete is also the source of chlorides. Chlorides penetrate concrete by diffusion of the ions in the water, as well as by capillary suction and by absorption. Prolonged or repeated ingress can, with time, result in a high concentration of chloride ions at the surface of reinforcing steel [1]. It is apparent the progressive ingress of salts towards the reinforcing steel takes place under alternating wetting and drying or freezing and thawing. The cyclic action accelerates durability problems, for it subjects the concrete to the movement and accumulation of harmful materials [1 – 3].

Although the primary mechanism of chloride transport for near-surface unsaturated concrete is absorption, the accumulation of chlorides in this layer leads to further penetration of chlorides into concrete by diffusion. As a consequence, diffusion becomes the most dominant mechanism of chloride ions transport at greater depths.

Different test methods are available for assessing the resistance of concrete to chloride ingress and these tests provide either a chloride ion diffusion coefficient or an index of the concrete resistance to chloride ion penetration [4, 5].

The diffusivity of porous materials, such as concrete, is determined conventionally by diffusion cells or by immersion in a solution, assuming steady-state (Fick's first law) chloride ion diffusion across the cement paste specimen, or assuming non-steady-state diffusion (Fick's second law) across the concrete specimen. However, the mentioned methods are time-consuming, often requiring months or years to obtain results, particularly in the case of high performance concretes [5]. It is not possible to evaluate concrete property at the early age. The methods, based on natural diffusion process, are unsuitable for field structures, as they are laboratory-based techniques. The conventional methods cannot meet engineering requirements, thus rapid tests to evaluate existing structures and new materials and treatments are needed. The disadvantage such as time consuming has been overcome by the application of an electrical field that accelerates the movement of chloride ions in the way that the time of testing can be shortened from several months to a few hours.

The chlorides penetrability was evaluated using rapid non-steady-state migration experiment (RCMT) making the diffusivity evaluation possible.

The monitoring of concrete resistance to chloride penetration is also possible on the basis of electrical resistivity measurements. From theoretical and experimental works there appears to be the correlation of between concrete resistivity and chloride ingress. The electrical resisistivity of concrete structure exposed to chloride indicates the risk of early corrosion damage, because a low resistivity is related to rapid chloride penetration and to high corrosion rate [6, 7]. Concrete resistivity is a geometry-independent material property that describes the electrical resistance, that is the ratio between applied voltage and resulting current in a unit cell. The current is carried by ions dissolved in the pore liquid. Increased pore saturation (wet concrete) as well as increased number of larger diameter pores (higher water-to-cement ratio) decrease resistivity [4]. For constant moisture content, the resistivity is increased by longer

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curing (hydration), lower w/c ratio and by addition of reactive materials such as alternative cementing materials: fly ash, blast furnace slag, metakaoline and silica fume [8]. Resistivity also increases when the concrete dries out and when it carbonates, particularly in Portland cement.

The results of investigation aiming to monitor the changes in electrical resistivity of concrete subjected to chloride penetration in various moisture and temperature conditions are presented in the paper. The results of long-term monitoring of resistivity changes were confronted with the chloride penetration resistance of concrete determined by means of rapid test (RCMT). Based on the test results, the effects of cement type, fly ash content related to cement mass as well as the time of exposition have been discussed.

2. EXPERIMENTAL DETAILS

2.1. Materials and specimens preparation

When alternative cementitious materials, such as fly ash, ground granulated blast furnace slag or silica fume are used in concrete, not only the porosity is reduced but also the pores become finer and the change in mineralogy of the cement hydrates leads to a reduction in the mobility of chloride ions [8]. However, the secondary reaction products are formed slowly in concrete containing alternative cementitious materials, thus the resistance to chloride ions penetration also increases slowly with time [9, 10]. There is not enough available data concerning long-term performance of concrete with mineral additions in chloride exposure regime.

The tests were carried out for concrete with fly ash, which kept the requirements of standard EN 450-1 [11].

Two types of cement were used: Portland cement CEM I 32.5 R (C1) and blast furnace slag cement CEM III/A 32.5 NA (C2). The mineralogical composition of clinkers in cements used is presented in Table 1. The blast furnace slag used in C2 cement contained 44.8 % CaO, 39.1 % SiO_2, 7.1 % Al_2O_3, 1.7 % Fe_2O_3, 0.23 % SO_3, 6.2 % MgO. The content of slag in C2 cement was 62 %.

Table 1. Mineralogical composition of clinkers in cements used

Clinker	C_3S [%]	C_2S [%]	C_3A [%]	C_4AF [%]
C1 cement	62.1	14.5	8.6	9.3
C2 cement	60.4	15.5	9.1	8.8

The fly ash from local power plant was used. The phase composition of the fly ash was determined using X-ray diffraction analysis. Two main crystalline phases: β-quartz and mullite were determined. The fly ash also contained anhydrite, calcium oxide and very small amount of calcite and gypsum. The content of CaO (free), obtained from analytical test, was 0.25 %. The loss of ignition, monitored during 25 days of coal burning in power plant, did not exceed 4.8 %. The specific gravity of mineral addition was 2.23 kg/dm^3.

The fine aggregate used was river sand with a maximum diameter of 2 mm, the coarse aggregate – basalt grit with a maximum diameter of 8 mm.

The tests were carried out on specimens prepared of mixtures with different values of fly ash content: 10, 20 and 30 % related to cement mass (FA/C), as well as on unmodified control specimens. The part of fly ash (20 %) was taken into account as a binder and the remaining part – as filler. The cement content in control concrete was 350 kg/m^3. Water to binder ratio in the all concrete mixtures was constant (w/b = 0.50). The concrete was cast in the moulds and compacted by wibration. The specimens were stored 24 hrs in the moulds and, after demoulding, cured under water at 18 °C ±2 °C until the test age.

2.2. Experimental procedures

Rapid chloride migration test (RCMT)

The electrochemical method, often referred to as the Rapid Chloride Migration Test (RCMT), was applied in this study to determine the value of chloride migration coefficient [12]. An external electrical potential was applied axially across the disk sample and forces the chloride ions outside to migrate into the specimen. The theoretical basis for calculating chloride diffusivity in concrete was described in [13].

The voltage used and test duration depends on the measured initial current, thus the effect of specimen heating is eliminated. The concrete disks were subjected to about 30 V voltage through external stainless steel electrodes located on the opposite sides of sample.

The catholyte solution was 10 % NaCl and the anolyte solution was 0.3 mol/dm^3 NaOH. At the end of the test (after 24 hours) the concrete disk was split longitudinally into two half-cylinders. The newly exposed surface was sprayed with indicator solution ($AgNO_3$) to determine the depth of chloride penetration. The colorimetric method with $AgNO_3$ has a colour change at a chloride concentration of $c_d = 0.07$ mol/dm^3. The chloride penetration depth was measured from the visible white silver chloride precipitation at 7 points along the surface. The average penetration depth x_d is the output parameter of the test procedure.

The data was used to calculate the non-steady-state chloride migration coefficient D_{nssm} ($\times 10^{-12}$ m^2/s) from simplified equation (1), proposed in [12]:

$$D_{nssm} = \frac{0.0239(273+T)L}{(U-2)t}\left(x_d - 0.0238\sqrt{\frac{(273+T)Lx_d}{U-2}}\right), \quad (1)$$

where: U is the value of applied voltage (V); T is the average value of temperature in the anolyte solution (°C); L is the thickness of the specimen (mm); x_d is the average value of penetration depths (mm); t is the test duration (hour).

The temperature of solutions was monitored during testing. The temperature of the specimens and solutions should be maintained in the range of 20 °C – 25 °C. In high temperature the chloride ions transport is significantly accelerated and therefore it leads to erroneous conclusions.

The concrete disks 50 mm thick with a diameter of 105 mm were used in the test. In order to avoid heterogeneity, the specimens were vacuum-saturated prior to the test. Every series of specimens consisted of three replicates.

The non-steady-state migration coefficient cannot be directly compared with chloride diffusion coefficients obtained from the other test methods but it is very useful in rapid quantitative measurement of the resistance of tested material to chloride penetration [5].

Electrical resistivity of concrete

Electrical resistivity measurements are an effective non-destructive method for monitoring the changes in concrete structure. The specimens of (100×100×50) mm with the pairs of stainless steel electrodes, with active surface of 10 cm^2, embedded in hardened concrete, were used for evaluating the electrical resistivity [4]. The thickness of concrete cover around electrodes was ~2 cm.

The electrical resistivity development was monitored for concrete specimens exposed in various conditions:

- cyclic wetting and drying conditions, permitting moisture movement through concrete pores. The wetting period in 3 % NaCl solution was kept for 7 days and the time of drying, at 40 % RH and 18 °C ±2 °C, was 7 days. During the wetting period, the samples were partially (to 4/5 of their depth) submerged in solution, which should intensify the chlorides migration caused by absorption and capillary suction.
- cyclic freezing and thawing in the presence of 3 % NaCl solution. The duration of single freeze/thaw cycle was 24 hrs. Before exposition, the samples were stored 90 days in water and then they were saturated with NaCl solution by capillary suction.

Every 28 days the resistivity was determined. Since electrical resistivity is a function of the moisture content, just before the measurement all specimens were stored during 48 hrs in climatic chamber at 95 % RH and 18 °C. The test was conducted during 12 months. The changes in resistance between the pairs of electrodes were measured using 1 kHz – 2 kHz AC, electrode polarization effects were reduced to negligible proportions for all mixes [14]. The resistivity values were obtained by multiplying the measured resistance by a conversion factor (the cell constant). The cell constant was calculated considering the effective area of the steel electrodes and their distance of separation. Every series of specimens consisted of four replicates.

The properties of hardened concrete such as compressive strength, water absorbability, sorptivity and capillary suction of water were also analyzed.

3. TEST RESULTS AND DISCUSSION

3.1. Basic properties of hardened concretes

The test results of selected physical and mechanical properties of hardened concretes are presented in Table 2. As it is shown from Table 2, the fly ash addition, in considered range of FA/C values, has very little influence on water absorbability of concretes tested but the addition reduces the capillary suction of water and sorptivity of C2 cement concretes. The observed results of concrete strength test prove fly ash influence on the strength development at all ages. It is found, in general, that the rate of strength development is slower for mixtures containing fly ash, at early ages. The rate of strength increase in concretes with fly ash is significant between 28- and 180-days. The increase in strength between 28 and 90 days of curing is slower for C2 cement (blast furnace slag cement) concretes but after 180 days of storage the compressive strength of C2 cement concrete with fly ash is comparable with strength of C1 cement (Portland cement) concretes. Finally, the concretes containing the addition reached greater values of compressive strength than control concretes.

3.2. Resistivity of concrete subjected to cyclic wetting and drying

The changes in electric resistivity of concretes exposed to cyclic wetting in 3 % NaCl solution and drying, accelerating moisture movement through concrete pores, are shown in Figs 1 and 2.

All the specimens show the increase in concrete resistivity as a function of time, due to the microstructural changes in the hydrated cement paste and the consequent reduction in porosity of the cement paste. Since the rate of change of electrical resistivity of the control specimens of both cements is rather low in comparison to that of the fly ash-blended specimens, it could be inferred that it is the pozzolanic reaction of the fly ash that results in a high rate of change of resistivity.

Table 2. Selected properties of concrete tested

Cement type	FA/C	Capillary suction [% wt.]	Water absorb. [% wt.]	Sorptivity [% wt.]	Compressive strength [MPa]		
					28 days	90 days	180 days
C1	0.0	1.25	5.57	2.60	53.3	54.0	55.4
	0.1	1.33	5.01	2.90	52.3	55.5	63.5
	0.2	1.34	5.11	2.82	52.1	59.3	68.4
	0.3	1.29	5.41	2.71	50.6	57.5	62.5
C2	0.0	1.59	5.52	2.75	46.3	51.3	51.9
	0.1	1.42	5.34	2.04	46.7	53.3	54.7
	0.2	1.36	5.57	1.88	41.2	59.1	65.8
	0.3	1.25	5.58	1.57	43.5	58.2	63.8

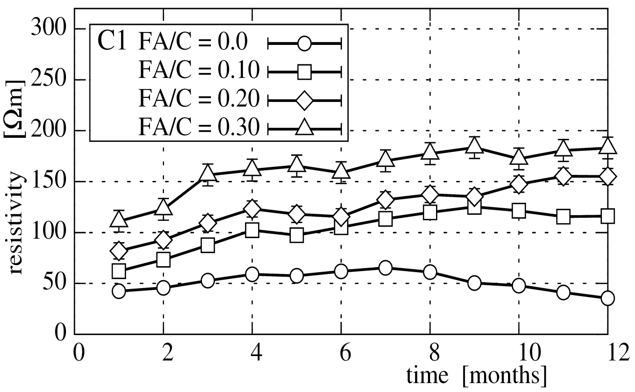

Fig. 1. Development of resistivity of C1 cement concretes exposed to cyclic wetting and drying

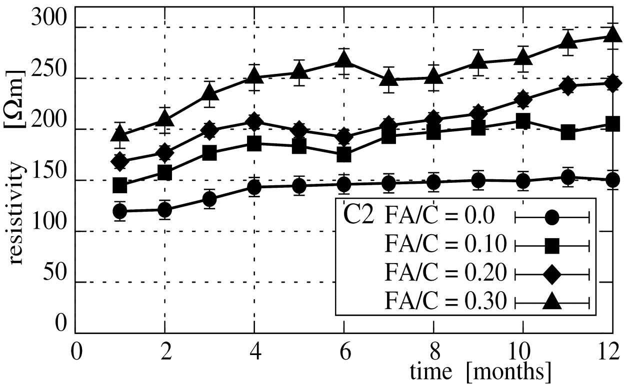

Fig. 2. Development of resistivity of C2 cement concretes exposed to cyclic wetting and drying

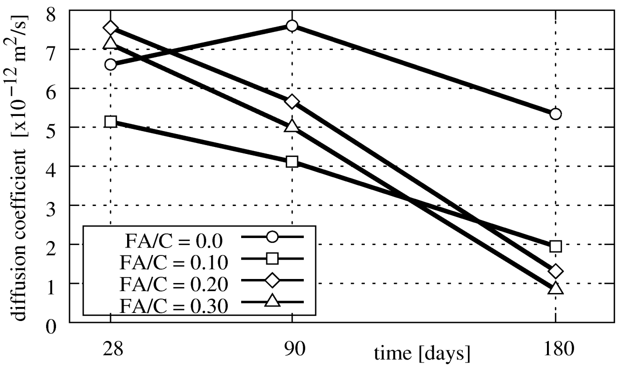

Fig. 3. Chloride diffusion coefficient from migration test in non-steady-state conditions – C1 cement concretes

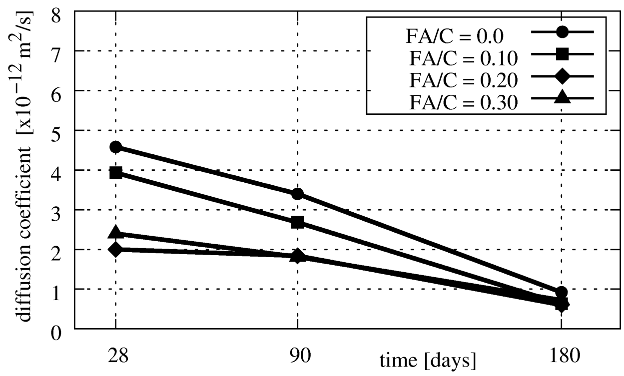

Fig. 4. Chloride migration coefficient in non-steady-state conditions – C2 cement concretes

The fly ash addition significantly influences the rate of concrete resistivity changes. During wetting/drying cycles, electrical response resulting for concrete specimens containing the addition increased gaining the values even several times greater than the resistivity of control concrete. Moreover, the values of resistivity obtained were directly proportional to the addition content in concrete mix (FA/C). Generally, C2 cement (blast furnace slag cement) concretes were characterized by higher value of resistivity than C1 cement (Portland cement) concretes.

However, comparing the electrical resistivity of concretes with fly ash and without addition, the significantly stronger influence of fly ash on resistivity was observed in the case of C1 cement concretes. The resistivity of C1 concrete of FA/C = 0.30 gained the value three times greater than the resistivity of control concrete. Such distinct differences were not found in the case of C2 cement concretes. After 9 months of test, the gradual decrease in resistivity of C1 cement concrete without addition was observed. The inconvenient influence of NaCl solution on resistivity of concrete with fly ash was not pointed out.

3.3. Diffusivity of concretes

The RCM test was used to determine the chloride diffusivity directly in quantitative way. The determined diffusion coefficients from migration test in non-steady-state conditions are presented in Figs 3 and 4.

The beneficial effect of hydration time was observed in relation to chloride penetration resistance. The fly ash addition as well as the presence of slag in cement has significant influence on chloride migration coefficient. The analysis of the investigation results, for both cements used, showed the beneficial effect of extended time of curing and the fly ash addition content on chloride diffusivity in concrete.

In the case of C1 cement concretes (Fig. 3), containing fly ash, during ~150 days (from 28 to 180 day of storage) the value of migration coefficient decreased even ~7 times. It is difficult to determine univocally the relation between FA/C ratio and migration coefficient for C1 cement concretes tested after 28 and 90 days of curing, probably because of the inaccuracy of chloride penetration depth measurements using colorimetric method, whereas, the results obtained after 180 days indicate very low concrete diffusivity.

In the case of C2 cement concretes (Fig. 4) smaller values of coefficient than for C1 cement concretes were observed as early as after 28 days of curing. Afterwards, with age, the coefficient values decreased. However, after 180 days of storage, these values were comparable ($<1.0\times10^{-12}$ m^2/s), for C2 cement independently of fly ash dosage [15].

For unmodified concrete with C1 cement the diffusion coefficient did not change significantly, keeping up the value above 5×10^{-12} m^2/s.

In an attempt to explore the possibility of relating the concrete resistivity to the resistance to chloride penetration in concrete containing fly ash, the concrete properties were compared. In Figs 5 and 6, the selected values of resistivity determined were plotted against the diffusion coefficient from migration test.

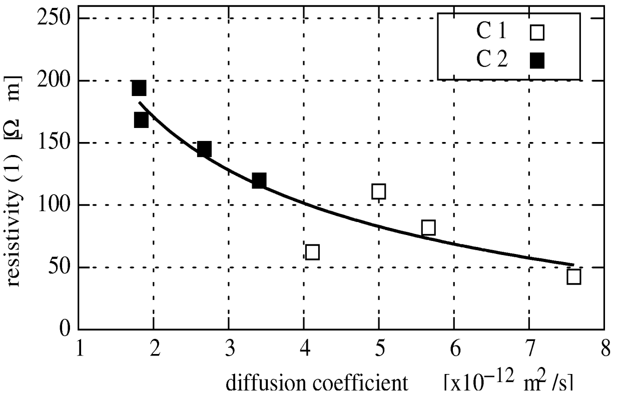

Fig. 5. Relationship between initial resistivity after 1 month of exposition and diffusion coefficient after 90 days of curing

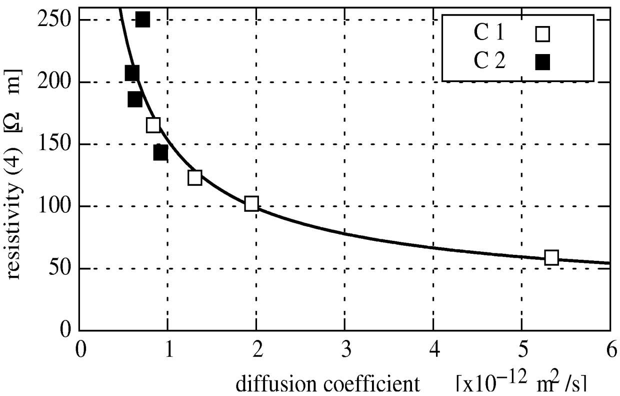

Fig. 6. Relationship between resistivity after 4 month of exposition and diffusion coefficient after 180 days of curing

The initial values of electrical resistivity, after 1 month of exposure in cyclic wetting and drying conditions, were compared with diffusion coefficient after 90 days of curing and the resistivity after 4 month of exposure, when the rate of resistivity change was significant, with diffusion coefficient after 180 days of curing. The concretes tested were at the same age. The general trend can be observed; the degree of dependence was higher for concretes after 180 days of curing. The trend lines show that the resistivity change with time could be useful for evaluation the chloride ion penetration resistance of concretes containing fly ash.

3.4. Resistivity of concrete exposed to freezing and thawing

The data concerning the variation of electrical resistivity with FA/C ratio and time of exposition for both cement types, after cyclic freeze/thaw, were plotted in Figs 7 and 8.

The synergistic action of freeze/thaw cycles and chloride ions caused significant decrease in electric resistivity, although the curing time of concrete before test was extended. The exposure regime was the main factor

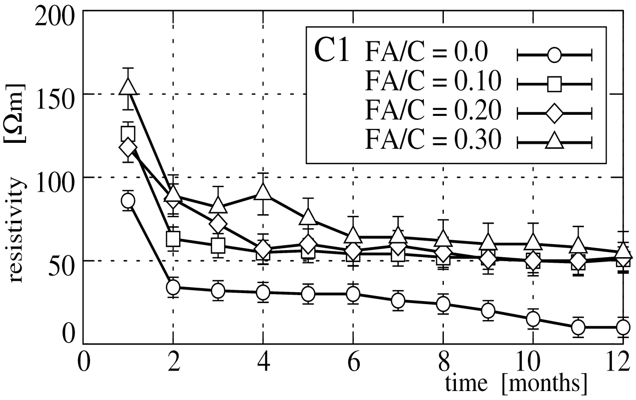

Fig. 7. Resistivity of C1 cement concretes exposed to cyclic freezing and thawing

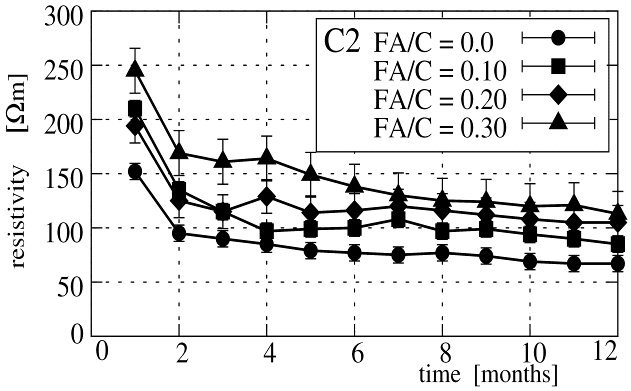

Fig. 8. Resistivity of C2 cement concretes exposed to cyclic freezing and thawing

affecting concrete resistivity. After initial distinct drop,observed for all concrete specimens, the resistivity value became stable in aggressive environment. Only in the case of C1 cement concrete without fly ash (FA/C = 0.0) intensive destruction due to freezing and thawing was pointed out. The C2 cement (blast furnace slag cement) concretes exhibited substantially higher electric resistivity than C1 cement (Portland cement) concretes.

4. CONCLUSIONS

The investigation was carried out in order to monitor the long-term behaviour of concretes in a chloride exposure regime. The concrete samples made of two types of cement and containing fly ash in varying proportions were examined. The durability of concrete was tested under influence of cyclic wetting and drying as well as freezing and thawing with chlorides.

Based on the results obtained from the present experimental investigation, the following conclusions can be drawn:

1. The resistivity of concrete was found to be closely connected with cement type and mineral addition content related to cement mass as well as the time of storage. During long-term test, it was observed that blending cement with fly ash caused significant changes in electric resistivity of concrete exposed to various conditions simulating service life conditions. The blast furnace slag cement (C2) concretes showed

higher electric resistivity than Portland cement (C1) concretes and the resistivity value was directly proportional to FA/C ratio.
2. The resistance to chloride penetration was found to increase with time but the value of diffusion coefficient from migration test depended on cement type. The long-term beneficial effect on chloride diffusivity was found to be better in concretes with higher percentages of fly ash. The correlation of concrete resistivity to the chloride diffusivity was observed for concretes with both types of cement used. The resistivity monitoring could be effective method of evaluation of concrete resistance to chloride penetration in simple way in the non-destructive test.
3. The considerable effect of slag and fly ash is reflected in permeability and diffusivity of ions. The introduction of fly ash addition to blast furnace slag cement concrete makes it possible to achieve required compressive strength and the excellent resistance to chloride penetration. The beneficial effect of fly ash and slag cement combination is evident as early as after 28 days of curing, although the hydration process, pozzolanic reaction and changes in microstructure continue to occur. The use of fly ash or slag will considerably increase the service life of structures exposed to chloride environments.

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