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# Advantages of the Simultaneous Use of Corrosion Inhibitors and Inorganic Coatings

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## Abstract

One widely used method for the protection of reinforced concrete is through coatings. For this purpose, both inorganic (based on water glass) as well as organic (siloxane, acrylic dispersion, epoxy resin, chlorinated rubber, acrylic rubber) coatings are used. The advantages of inorganic paints are lower absorption of sun radiation, non-burning, absence of fouling and microcrystalline texture. On the other hand, organic paints have the advantage of low permeability of carbon dioxide, sulphur dioxide and water. From our research, it was confirmed that organic paints provide better protection of reinforcing steel in concrete than the inorganic ones. However, the use of inorganic paints is expanding for environmental reasons and also because they can be applied for the rehabilitation of old structures. A way to increase the durability of inorganic paints is the use of a migrating corrosion inhibitor. The combined action of inorganic paint and corrosion inhibitor provides a satisfactory level of protection.

## Introduction

Under most conditions concrete provides good protection against corrosion of reinforcing steel, nevertheless, corrosion remains the most common cause of deterioration of reinforced concrete. In order for corrosion to occur, the presence of an electrolyte, such as the aqueous phase in concrete, is required. The final result of the corrosion process is the formation of a thick layer of rust, which exerts sufficient tensile forces within the concrete to cause cracking of the concrete cover [1].

In a alkaline solution, such as the calcium hydroxide solution in wet cement, a protective oxide film forms over the steel thus passivating it. Corrosion occurs when this protective film is impaired and oxygen is present. The stability of the film depends on the maintenance of a certain minimum pH value, above which access of oxygen will not cause corrosion. However, if the access of carbon dioxide reduces the pH to a value 10 or lower, the film is impaired, the natural passivity of concrete is thus reduced and under such conditions any access of oxygen will cause corrosion [1,2]. The presence of chloride ions stimulates corrosion by raising the pH required to stabilise the passive film to a value which may exceed that of a saturated calcium hydroxide solution. The intrusion of chloride ions depends on the porosity and permeability of the concrete material [1].

Coatings applied on concrete surface offer an effective and reliable solution for the protection of concrete material and the embedded reinforcing steel, either for a new construction or for rehabilitation of deteriorated concrete, even when it is contaminated with chlorides [3]. The use of protective surface coatings is generally applied for both conventional and lightweight concrete with or without the presence of chloride ions [3,4,5,6]. The different types of surface coatings that can be used for the protection of reinforced concrete include inorganic paints based on water glass, acrylic dispersions, epoxy resin and chlorinated rubber or acrylic rubber paints.

A special group of corrosion protection measures for concrete reinforcement are migrating corrosion inhibitors added to mortar during mixing. According to their action, the inhibitors can be classified into three groups:
* anodic inhibitors, which prevent the reinforcement corrosion by affecting the anodic process, such as nitrites and chromates,
* cathodic inhibitors, adsorbed on the reinforcement surface, create a barrier of molecular thickness, thus enhancing the kinetics of the electrode reactions, such as various amines and
* mixed inhibitors, which influence both the cathodic and the anodic process, such as migrating corrosion inhibitors.

The inhibitor should have good solubility characteristics and rapidly saturate the corroding surface. Also the physical and durability properties of concrete should not be adversely affected [7,8].

The purpose of this study is to compare the protective action of inorganic and organic coatings in the presence of chlorides. The combined effect on protective action of inorganic coatings used in conjunction with a corrosion inhibitor was also considered.

## Materials and Methods

The specimens were constructed using a cement type II-35 (pozzolanic), the chemical composition of which is shown in Table 1. The aggregate used was 0-5 mm pumice from Yali Island in S.E. Greece. Its typical chemical analysis and gradation are shown in Tables 1 and 2, respectively. Steel bars from steel type "Stahl 3" (DIN 488 T1-T6) and tap water were used. The mixture proportions were: aggregate/cement/water = 3/0.7/1. A solution of migrating corrosion inhibitor was used as an admixture (0.6 l/$m^3$) in the concrete mass.

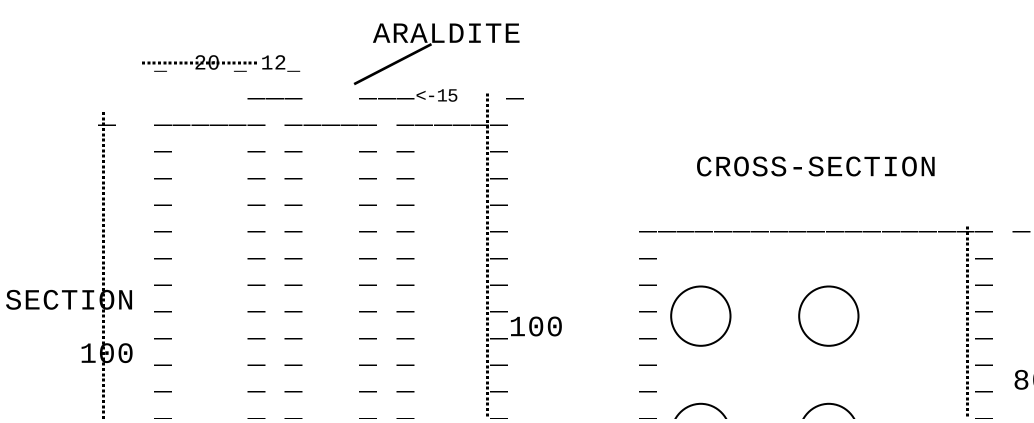
Table 1 Chemical analysis (%) of cement and pumice

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $K_20$ | $Na_2O$ | $SO_3$ | cor LOI | $CaO_f$ | Sb ($cm^2$/g) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| II-35 | 27.38 | 9.10 | 5.65 | 45.39 | 2.73 | 0.94 | 0.56 | 2.71 | 5.04 | 2.67 | 4275 |
| Pumice | 70.55 | 12.24 | 0.89 | 2.36 | 0.10 | 4.21 | 3.49 | 0.03 | | | |

Table 2 Typical gradation analysis of pumice

| Special Besser 0-5 mm | | |
|---|---|---|
| Grain Size (mm) | Ideal | Tolerance |
| 6.40 | 0 | 0 |
| 4.76 | 2 | 0.5 - 4 |
| 4.00 | | |
| 2.38 | 32 | 28 - 36 |
| 1.19 | 22 | 19 - 25 |
| 0.60 | 13 | 11 - 15 |
| 0.30 | 9 | 7 - 11 |
| 0.15 | 7 | 5.5 - 8.5 |
| | 15 | 12 - 17 |

Each test specimen was cast to a prism (80 X 80 X 100 mm) with four steel bars (cylindrical diameter 12 mm, height 100 mm) embedded in it (Fig.1). For the specimens' construction the surface of the steel bars was first cleaned from rust according to ISO/DIS 8407.3 and weighted. Subsequently, the bars were placed in moulds, as shown in Fig.1, where the mortar was cast and stored to dry at ambient conditions for 24 hours. Then the specimens, after being demoulded, were cured in tap water for 24 hours. Finally the specimens were stored for an additional 24 h at ambient conditions and thereafter the part shown in Fig. 1 was insulated with epoxy glue Araldite[R].



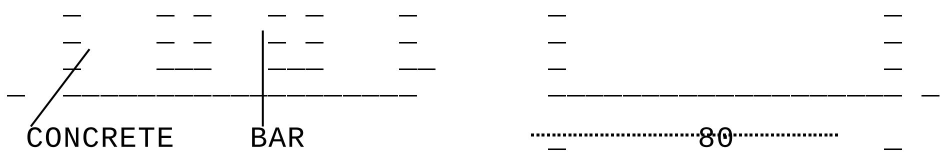



Fig.1 Shape and dimensions of specimens (mm)

Four different paints were used:

- emulsion paint (aqueous acrylic dispersion) with main pigment $TiO_2$ (G)
- emulsion paint (aqueous acrylic dispersion) with main pigment $Fe_2O_3$ (B1)
- chlorinated rubber paint with main pigment $Fe_2O_3$ (B2)
- inorganic paint with main pigment $TiO_2$ (W). All paints were applied by brush on the dried surface of the concrete specimen at two layers after a drying period between them of 24 h. Specimens without paint are referred as C and those with corrosion inhibitor as K.

Finally all specimens were partially immersed in 3.5% w/w NaCl solution up to 20 mm from their bottom, after 7 days of curing time, in order to simulate aggressive conditions and impose an accelerated rate of corrosion.

The following methods were employed in this study for the evaluation of the protective action of coatings against corrosion:

a) Half-cell potential versus time

During the exposure of the specimens in the corrosive environment the half-cell potential of steel bats was periodically measured versus a saturated calomel electrode.

b) Carbonation depth

The carbonation depth of the concrete material was measured on a vertical section of the specimen by the phenolphthalein indicator method.

c) Mass loss of bars

The corrosion rate of reinforcing steel was determined by measuring the mass loss of the steel bars. The steel bars were cleaned from any corrosion products with the same above mentioned procedure and were weighted. The average mass loss was calculated from the difference between the initial and the final weight of each steel bar.

d) Chloride diffusion rate

The rate of chloride diffusion rate through the cement was measured using a special device, in which a cylindrical concrete slice was placed in contact with a glass tube filled with a 3.5% w/w NaCl solution at one end and a glass tube filled with distilled water at the other end (Taywood Engineering Limited, "In-House Test Method A9: Measurement of ionic diffusion coefficient"). A specimen without paint was prepared for reference along with a series of concrete slices which were coated with the four categories of paints. The amount of chlorides diffused through the mortars was calculated by titration.

e) Impedance measurements

Specimens with all categories of paints (including those with inorganic paint and inhibitor) and without paint were immersed in 3.5% w/w NaCl solution and their impedance spectrum was examined in order to obtain information about the mechanism of corrosion, using the Solartron 1260 Impedance Gain-Phase Analyzer.

## Measurements and Results

Half-cell potentials of the painted concrete specimens after 10 months exposure in the corrosive environment are shown in Fig. 2 in comparison with the unpainted one. It is obvious that there is a tendency for the decreasing of potential from values of -100 to -200 mV to values -500 to -600 mV for all specimens. The change of potential to more negative values occurs at different times for each category of specimens. From this point of view the specimens coated with emulsion paint containing $TiO_2$ (G) exhibit a better behaviour with respect to corrosion resistance as compared to the others.

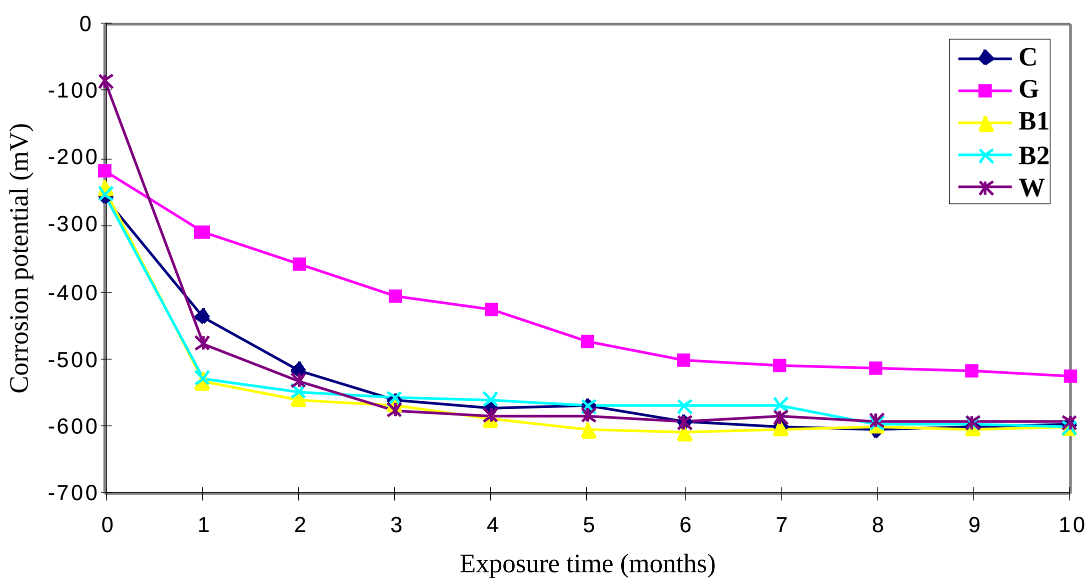



Fig.2 Half-cell potential versus time

The carbonation depth versus time for all specimens is shown in Fig. 3. From these measurements it can be observed that the depth of carbonation in concrete is reduced with the application of all paints. Again the acrylic dispersion with $TiO_2$ pigment provided a better protection, followed by the other organic paints and lastly the inorganic paint, as observed above.

The mass loss of rebars versus time for all specimen categories is shown in Fig. 4. The specimen without paint exhibits a comparatively greater mass loss. Indeed, it can be observed that all the paints provided sufficient and effective protection of concrete against aggressive corrosive exposure as compared to the reference without paint. The acrylic dispersion with pigment $TiO_2$ presents the better protective effect followed by the organic paints B1 and B2. The inorganic paint provided a comparatively lesser protection.

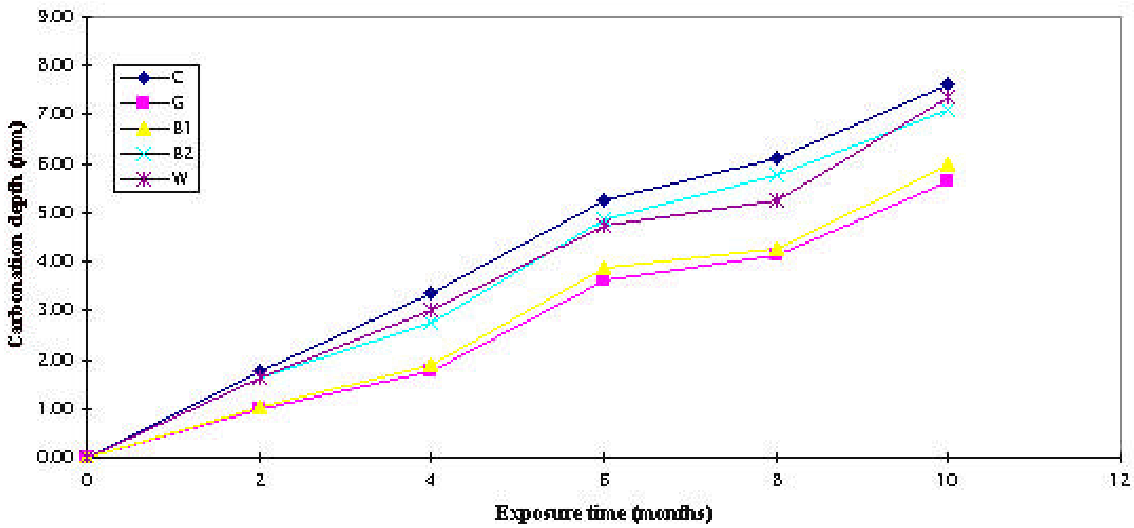



Fig.3 Carbonation depth versus time

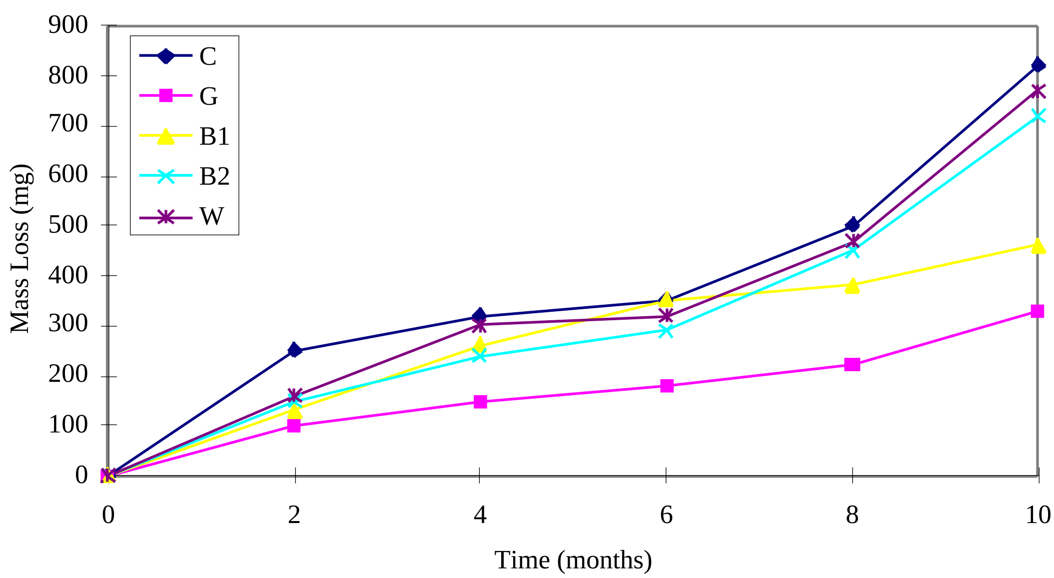



Fig.4 Mass loss of reinforcing steel bars

The chloride diffusion of all categories of specimens is shown in Fig. 5. It should be noted that all the paints inhibit the intrusion of chloride ions through the concrete. The organic paint based on chlorinated rubber exhibit the best results. A relatively higher diffusion rate of chloride ions is observed with the use of inorganic paint.

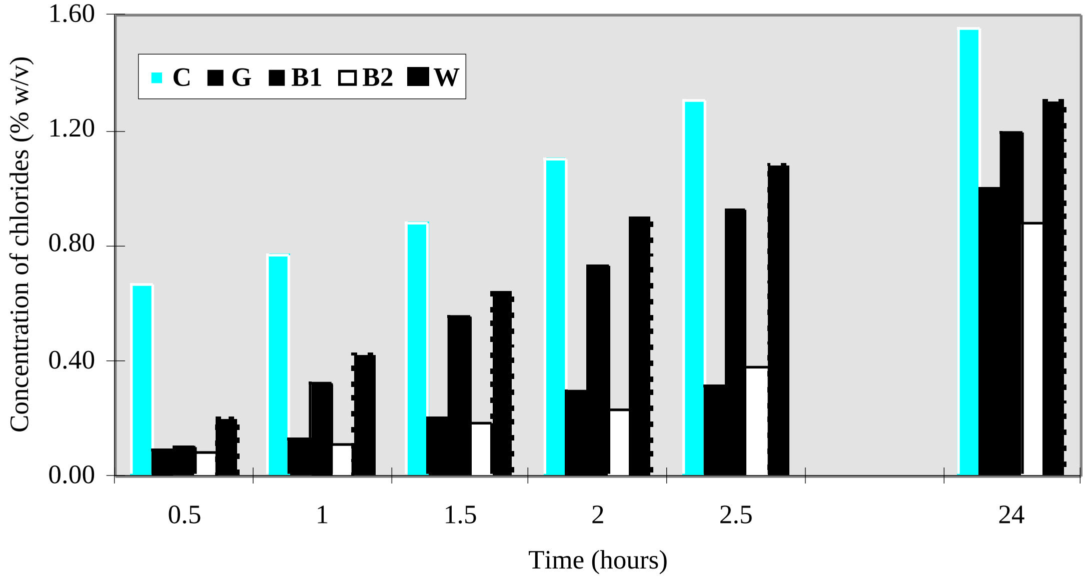



Fig.5 Chloride diffusion rate

In order to increase the relatively lower protective effect of inorganic coating, a migrating corrosion inhibitor (aminoalcohol) was additionally used. For comparative reasons the corrosion potential of the reinforcing steel bars of specimens with corrosion inhibitor is shown in Fig. 6. Up to three months of exposure time its potential shows more electropositive values than the specimens without paint and with the inorganic one, but after four months it almost reaches the same values as the other two.

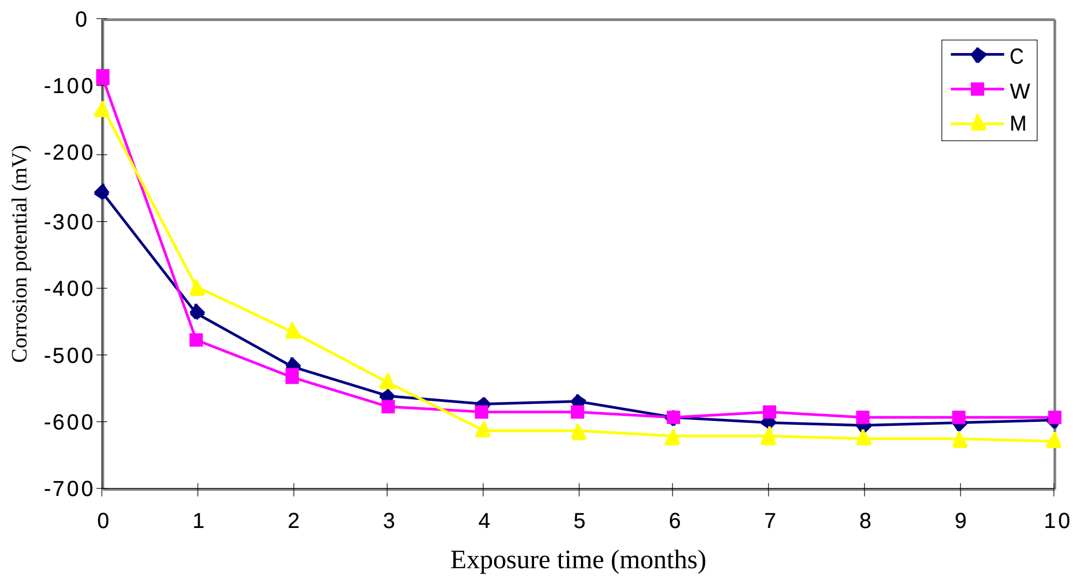



Fig. 6 Half-cell potentials versus time

The mass loss of reinforcing steel bars of the specimens with corrosion inhibitor is shown in Fig. 7. The improvement of the protective effect of the combination of inorganic coating and inorganic corrosion inhibitor is thus obvious.

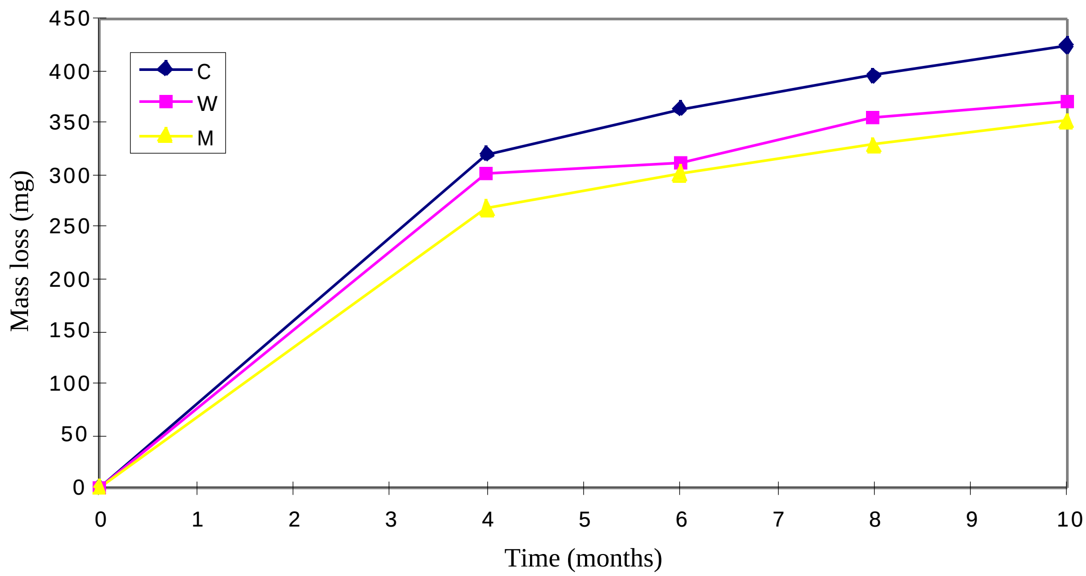



Fig.7 Mass loss of reinforcing steel bars time dependence

The impedance measurements of unpainted specimens, the ones with the inorganic paint and those with the combination of inorganic paint and corrosion inhibitor are shown in Fig. 8, after 10 days of immersion in the corrosive environment of 3.5% w/w NaCl solution. In this Nyquist plot, the imaginary part of resistance (Z'') is drawn versus the real part of resistance (Z'). The polarization resistance of the steel bars in the specimens with the combination of the corrosion inhibitor and inorganic paint is greater than those of the other two [9].

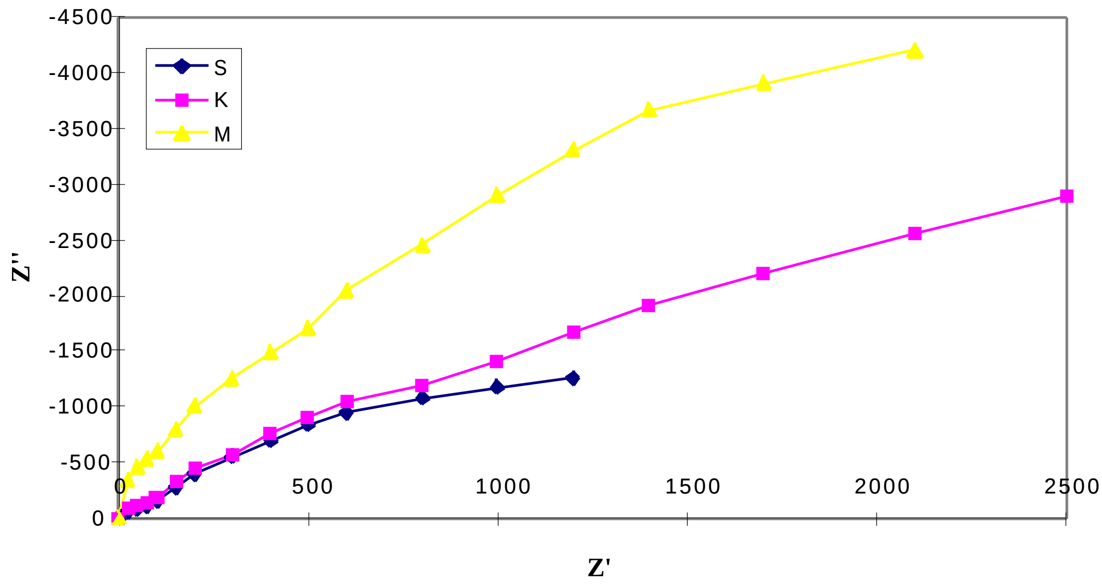



Fig. 8 Nyquist plot of specimens S, K and M in 3.5% w/w NaCl solution (_)

## Discussion

The acrylic dispersion paints generally provide the best protection against concrete carbonation. In the case of corrosion due to chlorides the chlorinated rubber paints exhibit sufficient protective effect, that is mass loss is less than half than that of the bare specimens [3,5].

On the other hand inorganic paints based on water glass can also be used as coatings on the surface of reinforced concrete, although they do not have a large range of coloration. Characteristic properties and advantages of inorganic paints are the following:

- Inorganic paints have micro crystallised texture with admirably aesthetic appearance and lower absorption of sun radiation.
- They do not flake off.
- The UV-radiation does not change the coloration.
- In the case of repainting, it is not possible to discriminate the change of coloration between old and new paint.
- They do not build up algae or micro-organisms.
- They do not have organic solvents and they do not bring out pollution.

In this investigation, it was observed that the use of inorganic paints provides a relatively lower protection of concrete surfaces than the organic paints, as is elsewhere referred [10]. also exhibited greater carbonation depths and higher chloride diffusion rates in comparison with the organic paints. Therefore, in the case where concrete is exposed to an aggressive environment the use of inorganic paints alone is not recommended.

However, migrating corrosion inhibitors (aminoalcohols) in combination with inorganic paints may provide an effective alternative in the application of protective coatings on concrete surfaces. Migrating corrosion inhibitors influence both the cathodic and the anodic process by the formation of a protective layer at the surface of steel, as they diffuse from the surface through the concrete mass surrounding the steel bars. After 10 months of exposure in the corrosive environment, the use of the corrosion inhibitor gives a protection level of 21%. From the results of the impedance measurements, a greater degree of protection could be expected. This fact is possibly due to the increased porosity of concrete specimens, which does not allow the corrosion inhibitor to offer its maximum capability of protection.

## Conclusions

The application of inorganic paints, as opposed to the organic, at the surface of reinforced concrete has the advantages of admirably aesthetic appearance, lower absorption of sun radiation, stable coloration and absence of fouling. Unfortunately when used alone they have the disadvantage of relatively lower protection effect against carbonation and chloride penetration and, under certain conditions this may lead to some deterioration of reinforced concrete.

Based on the measurements and test results obtained in this study, all the organic surface coatings provided satisfactory protection of reinforced concrete under aggressive corrosive exposure. The simultaneous use of a corrosion inhibitor and an inorganic paint is expected to increase the protection degree of the steel bars. In this work, the performance of the use of migrating corrosion inhibitor was tested. This combination reduces the corrosion of steel bars to a satisfactory level.

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