

# Impedance spectroscopy monitoring of a polyurethane coating on mortar exposed to NaCl solution

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Polyurethane coated OPC mortar specimens exposed to 1M NaCl solution were studied by impedance spectroscopy and SEM over a period of 4 years. Results showed a rapid reduction of the coating resistance over the first half year, followed by a slow decrease thereafter. The coating deteriorated starting from the surface in contact with the NaCl solution and the deterioration front reached the coating/substrate interface after around three years. Different stages of deterioration were clearly identified by impedance spectroscopy. The study demonstrates that impedance spectroscopy is a versatile and informative non-destructive method to assess and monitor the performance of surface treatments on concrete. © 2000 Kluwer Academic Publishers

## 1. Introduction

Surface coatings on concrete are being increasingly used for protection of reinforced concrete structures against aggressive environments [1–5]. A surface coating acts as a partial barrier between the external environment and the substrate concrete cover, limiting the penetration of aggressive substances such as chloride or carbon dioxide into concrete, therefore extending the time to reinforcement corrosion. The effectiveness of a surface coating depends on its intrinsic physical and chemical properties, the rate that it deteriorates, the application methods and the quality and surface condition of the substrate concrete.

Unlike coatings for metal substrates, surface coatings on concrete are in contact with both the external environment and an alkaline concrete substrate. Factors affecting their performance associated with the external environment include ultra violet radiation, moisture and temperature cycles and chemical exposure [6–10]. Factors associated with the substrate include its moisture content and the pH and composition of the pore solution. In addition, pressure and chemical composition differences between the external environment and the internal pore solution may lead to osmotic phenomena.

For concrete structures exposed to marine, deicing salt or other chloride-rich environments, a quantitative assessment of the chloride diffusion resistance of surface treatments and the ability to monitor the deterioration of surface treatment materials are important for surface treatment development, performance monitoring and service life prediction. However, conventional chloride diffusion test methods applied to surface treatments, such as chloride profiling [11] and the diffusion cell test [8, 12], take a long time to obtain results and are

insensitive to property changes which take place during a test, offering little information on the deterioration of surface treatments. As a consequence, there is little known about the deterioration of surface treatments on concrete and this lack of understanding has been one of the obstacles to surface treatment development and widespread application.

Impedance spectroscopy has been shown to be a versatile, quantitative and informative technique to assess the chloride diffusion resistance of surface treatments [13]. Previous work has shown that this method is able to separate the impedances of a surface treatment layer and the substrate and that it has a good correlation with long term test results [13]. Furthermore, it is rapid and non-destructive and therefore should be well-suited to monitoring.

Polyurethane coatings have such high resistance to chloride diffusion that use of conventional tests is impractical. In this study, impedance spectroscopy was used to investigate the long-term performance of a polyurethane coating exposed to 1M NaCl solution.

## 2. Experimental

### 2.1. Mortar substrate

The ordinary Portland cement (OPC) mortar substrate used had 0.45 free water/cement, 2.5 sand/cement with a maximum aggregate size of 2.36 mm. Specimens were cast as 100 mm diameter 50 mm thick discs. They were demoulded after 2 days sealed in the moulds and were then stored in a sealed condition at  $22 \pm 2^\circ\text{C}$  to an age of 28 days. 10 mm thick slices with the cast surface faces were then cut from the discs. The specimens were conditioned at 86% RH and  $22 \pm 2^\circ\text{C}$  for 1 week prior to being surface treated.

## 2.2. Surface treatment

The polyurethane coating was a hydroxy acrylic resin and aliphatic isocyanate based material. The material was mixed with hardener (catalyst) before application and was applied by brush, directly on the cast surface of the conditioned specimens. The coverage was  $0.35 \text{ kg/m}^2$  applied in two coats and the application was controlled by the weight of material applied using an accurate (to 0.01 g) electronic balance. Surface treated specimens were left in open air in the laboratory at  $22 \pm 2^\circ\text{C}$  and  $50 \pm 5\%$  RH for 24 h to dry prior to further conditioning.

## 2.3. Conditioning of surface treated specimens

After the 24 h drying period following surface treatment, the specimens were transferred to humidity control boxes and were conditioned at 86% RH and  $22 \pm 2^\circ\text{C}$  for 2 weeks.

In order to avoid the influence of chloride ion uptake as a result of water absorption and to ensure that all the specimens to be tested had the same degree of saturation, the specimens were subjected to vacuum water saturation prior to tests. Vacuum saturation involved vacuuming the treated specimens dry for 1 h, then introducing distilled water into the vacuum chamber and maintaining the vacuum for 12 h. Finally the specimens were kept in water without vacuum for 12 h.

## 2.4. Test set up

The conditioned specimens were housed in diffusion cells as shown in Fig. 1. The surface treated face was exposed to 1M NaCl solution and the opposite face to 0.3M NaOH solution. Both the solutions were saturated with  $\text{Ca}(\text{OH})_2$ . The NaOH solution provided a reservoir of alkalinity to simulate an internal concrete environment. The effective area exposed to the solutions was  $50.2 \text{ cm}^2$ . After the specimens were installed in the cells, the areas of the specimens outside of the cell (i.e. exposed to air) were coated with two applications of epoxy resin. 3 replicate specimens were used. Impedance measurements were carried out using a Schlumberger 1260 frequency response analyser. A 0.1V AC voltage with frequency sweeping from 20 MHz to 1 Hz was applied via graphite electrodes immersed in either side of the diffusion cells. The test cells were stored in a temperature controlled laboratory ( $22 \pm 2^\circ\text{C}$ ) and impedance measurements were made

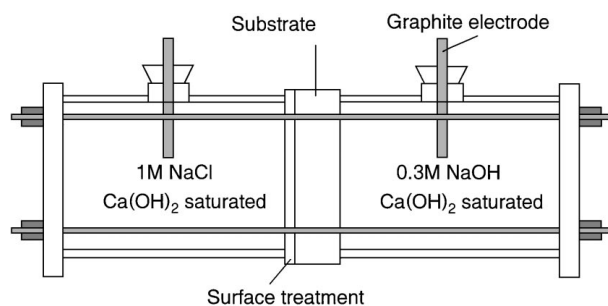


Figure 1 Cell used for impedance measurements.

regularly over a period of 4 years. Impedance spectra obtained were analysed using ZSIM software [14] by Schlumberger Instruments.

Prior to measuring the impedance of surface treated specimens, a nulling test was performed using a test cell filled with 0.3M NaOH solution without a specimen installed. The nulling test data were used in subsequent measurements to subtract automatically the impedance of the test leads, graphite electrodes and the test cell.

## 2.5. SEM examination

Specimens were taken out of the cells after 2 and 3 years of testing. The specimens were rinsed with water and were partially dried at room temperature. They were then broken to expose fractured cross-section surfaces for examination using a JEOL JSM-5410LV low vacuum SEM. The two years old specimen was further resin impregnated and polished for SEM examination.

## 3. Results

### 3.1. Impedance spectra of polyurethane coating and OPC mortar substrate

Fig. 2 shows the impedance spectra of polyurethane coating treated and untreated specimens 4 days after installation in their cells. It is clear that the impedance spectrum of the substrate is located in a very high frequency range (1–10 MHz) while that of the polyurethane coating is in a relatively low frequency range (1 Hz–100 kHz). The impedance of the substrate was very small (about 50 ohms) with respect to that of the polyurethane coating and it was therefore omitted in impedance spectrum analysis.

### 3.2. Variation of impedance spectra of polyurethane coating with time

Fig. 3 shows the variation of the average resistance (of 3 specimens) of the polyurethane coating during the first 500 days. Fig. 4a and b show the change of impedance spectra of a polyurethane coating treated mortar specimen with time. The resistance of the coating decreased rapidly during the first 6 months and continued to decrease, but at a lower rate. The shape of the spectrum showed interesting variation over the testing period. The spectrum started with a depressed semi-circle and then gradually transformed to two partially overlapping semi-circles after about 3–4 months and finally became a single depressed semi-circle again after about three years.

### 3.3. Visual and SEM observations of polyurethane coating

Blisters of up to 0.5 mm in diameter were apparent on the coating surface after 7 days of testing and some blisters remained over the 4 years testing period.

Fig. 5a–c show the backscattered electron images of the fractured and polished cross-section surfaces of the specimen after two years immersion and the fractured cross-section surface of the specimen after three years immersion respectively. The coating is around 0.35 mm thick. In Fig. 5a, two layers of the coating and

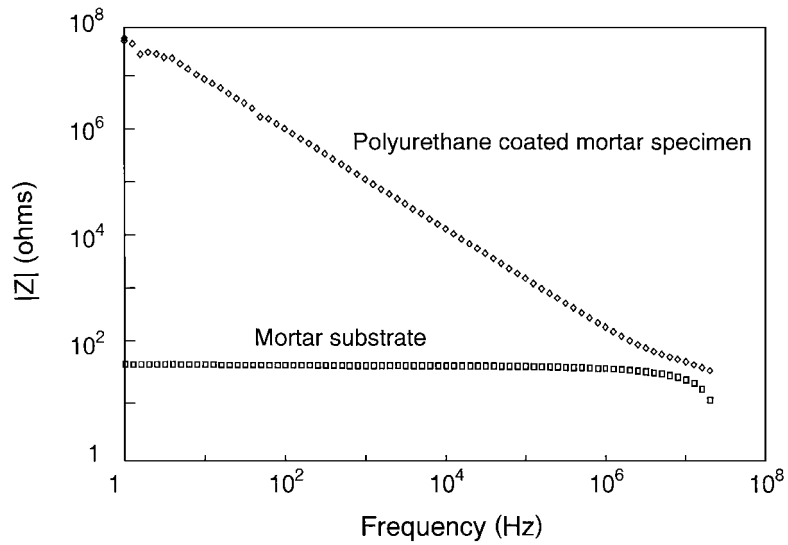


Figure 2 Impedance spectra of untreated and polyurethane coating treated mortar specimens 4 days after exposure to 1M NaCl solution.

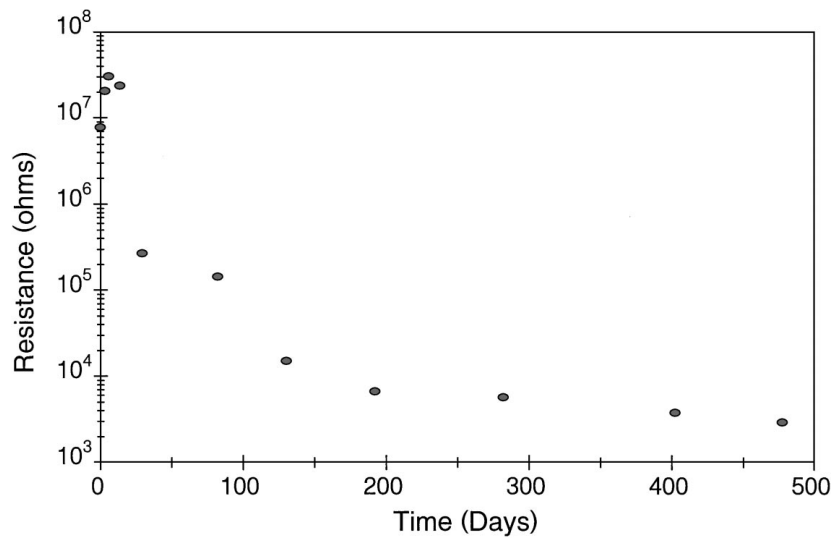


Figure 3 Variation of polyurethane coating resistance over the first 500 days.

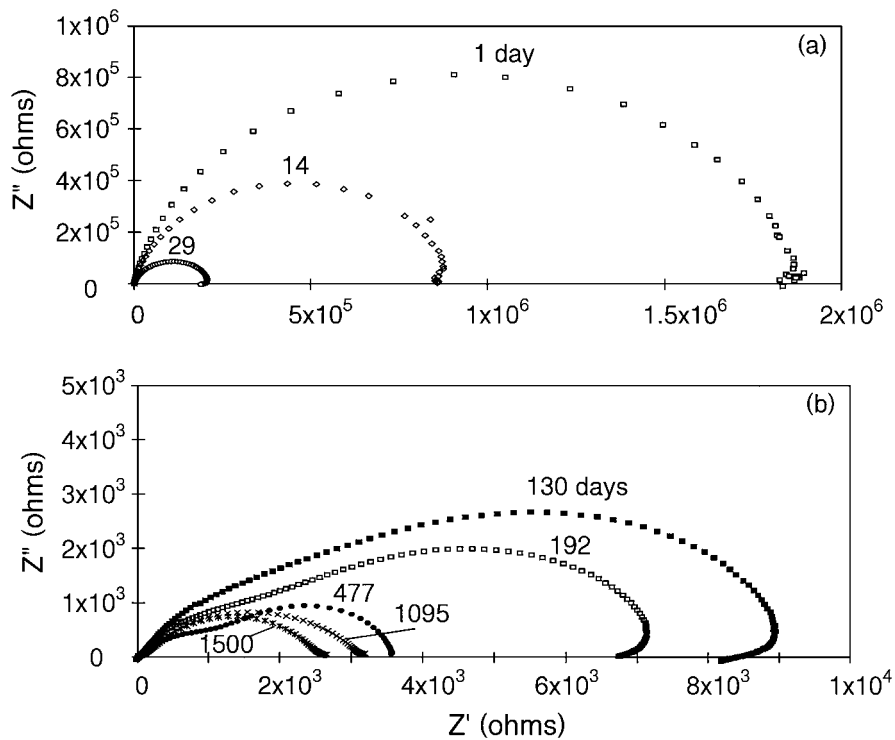
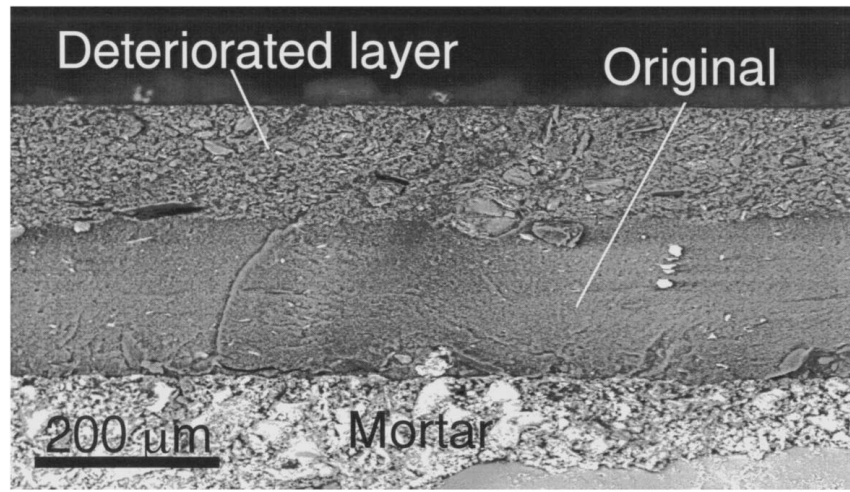
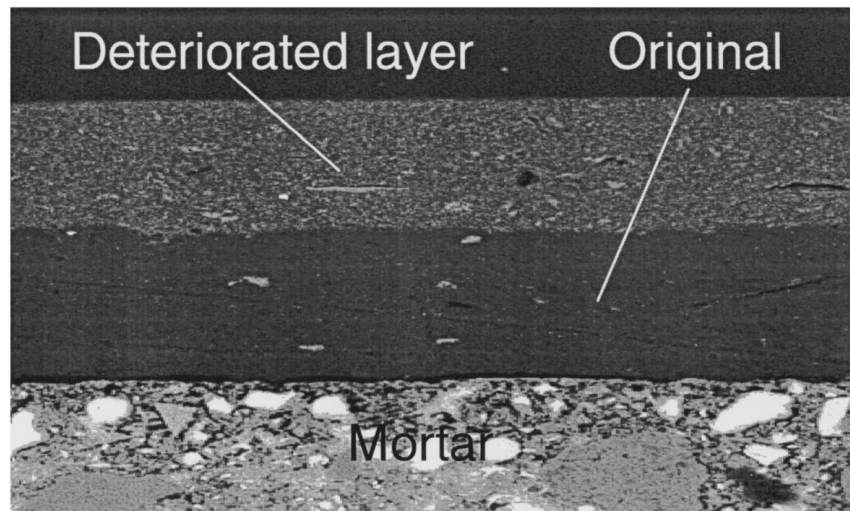


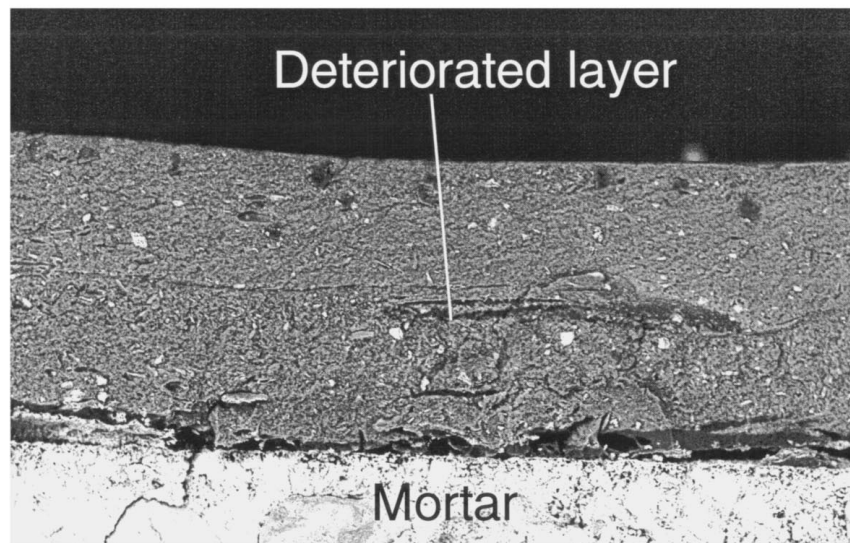
Figure 4 Variation of impedance spectrum of polyurethane coating with time.



(a)



(b)



(c)

Figure 5 SEM images of the specimens after 2 and 3 years of exposure to 1M NaCl solution. (a) fractured surface, 2 years old, (b) polished surface, two years old and (c) fractured surface, 3 years old.

the boundary are visible, the outer layer being more coarse than the inner layer. After polishing, the two layer structure of the coating remained clearly visible as shown in Fig. 5b despite the topographic effect of the fractured surface on image contrast having been elim-

inated, indicating a compositional difference between the two layers. In Fig. 5c, only one coarse layer is observed, although the interface between the two coats applied can be seen. This suggests that the coating layer deteriorated from the outer surface in contact with the

NaCl solution and that the deterioration front reached the interface of the coating and the substrate mortar after around three years.

## 4. Discussion

### 4.1. Equivalent circuit for polyurethane coating exposed to NaCl solution

The continuous reduction in resistance of the coating over the exposure time indicates that the coating underwent deterioration. The two time constant feature of the impedance spectra measured between around 100 and 1000 days implies that the coating divided into two layers of different dielectric properties. This has been confirmed by SEM examination. Based on these results a simple equivalent circuit consisting of two ZARC elements [15] connected in series is proposed for fitting the impedance spectra. ZARC element is a parallel circuit of a resistor and a Constant Phase Element (CPE). The impedance of the coating layer is

$$Z = Z_o + Z_d = \frac{R_o}{1 + (j\tau_o\omega)^{n_o}} + \frac{R_d}{1 + (j\tau_d\omega)^{n_d}}$$

where  $Z$  is the impedance,  $R$  is the resistance,  $\tau$  is a CPE element constant,  $n$  is the index which determines the constant phase angle,  $\omega$  is the angular frequency and subscripts  $o$  and  $d$  denote the original and deteriorated coating layers respectively. Impedance analysis results for a typical specimen are given in Table I.  $\omega^T$  in the table is the frequency of the top point of the impedance arc in a Nyquist plot.

It is clear from Table I that the low frequency impedance arc seen in Fig. 3 indicates the original polyurethane coating material. With the increase of exposure time, a high frequency impedance arc emerged, representing the deteriorated polyurethane layer.

### 4.2. Variation of electrical resistance of polyurethane coating with exposure time

It can be seen from Table I that the variation of the total resistance of the coating can be divided into three periods. In the early period of exposure (one month or so), a single depressed semi-circle was measured and the resistance decreased sharply by almost one order of magnitude. It is thought that this rapid drop of resistance

mainly resulted from the formation of blisters. Deformation of the coating in blistered areas is likely to lead to micro cracks within the coating layer, which would substantially reduce the resistance. The main reason for blistering is likely to be osmosis. Because the mortar substrate [16, 17] and polymer coating [18] are both membrane materials and two different electrolytes and concentrations were used in the diffusion cells, water tended to migrate from the 0.3 NaOH solution to the 1M NaCl solution.

The second period of resistance decrease was related to the transformation of the original polyurethane coating to the less resistant deteriorated layer. It is interesting to note from the SEM images that the boundary between the two layers is very clear, indicating two distinctly different states of the polyurethane coating material. The inner original coating material had a good bond with the substrate, implying that there was no deleterious interaction taking place between the coating material and the alkaline pore solution, cement paste or aggregate. As the deterioration started from the outer surface in contact with the NaCl solution, it can be concluded that the deterioration is linked to the NaCl solution. The clear interface between the two layers implies that the deterioration process was predominantly at the interface of the two layers and that the deteriorated layer was more penetrable than the original one so that reactive species could penetrate through the layer to reach the interface or reaction products could diffuse out into solution. The mechanism of this transformation is not known yet. Two possibilities are dissolution of one of the components of the coating system, for example a pigment, or depolymerization of the polymer base material. During this period, as the thickness of the inner original layer gradually decreased, so did its impedance. The impedance of the deteriorated layer also slowly decreased during this period despite the increase of its thickness. This suggests continuous deterioration of the layer. After three years, the coating had completely transformed to its deteriorated form, this being reflected in the Nyquist plot of the impedance spectrum by a single depressed semi-circle at a higher frequency range than that of the original layer spectrum.

The third period followed the complete transformation of the layer. It can be seen from Table I that the resistance  $R_d$  increased from  $1.5 \times 10^3$  ohms at 477 days to  $3.1 \times 10^3$  ohms at 1095 days and  $\omega_d^T$  fell from 18 to 7 kHz over the same period. This property change is believed to result from the interaction of the deteriorated coating material with the alkaline NaOH solution penetrating the coating after full deterioration of the original low penetrability coating.

Despite the substantial reduction in resistance, the resistance of 2000–3000 ohms after 3 years is still quite high in relation to other surface treatments [13], indicating that the coating provides good protection to concrete in conditions close to those adopted in these tests.

The variation of the resistance over the testing period suggests that the chloride diffusion coefficient of the coating is time dependent. In terms of service life prediction, this time dependence should be taken into

TABLE I Impedance analysis results

Exposure time (days)	Total resistance, $R$ (ohms)	$R_o$ (ohms)	$\omega_o^T$ (Hz)	$R_d$ (ohms)	$\omega_d^T$ (Hz)
1	$1.9 \times 10^6$	$1.9 \times 10^6$	63	—	—
15	$8.9 \times 10^5$	$8.9 \times 10^5$	126	—	—
29	$2.2 \times 10^5$	$2.2 \times 10^5$	424	—	—
130	$9.5 \times 10^3$	$6.7 \times 10^3$	475	$2.8 \times 10^3$	18930
192	$7.6 \times 10^3$	$5.6 \times 10^3$	533	$2.0 \times 10^3$	18930
477	$3.6 \times 10^3$	$2.1 \times 10^3$	475	$1.5 \times 10^3$	18930
1095	$3.1 \times 10^3$	—	—	$3.1 \times 10^3$	7535
1500	$2.5 \times 10^3$	—	—	$2.5 \times 10^3$	9486

account and, in this respect, impedance data are of value in providing such information.

It should be emphasised that the deterioration of the coating was related to the exposure conditions of the test. It would be interesting to investigate the behaviour of the coating in other exposure regimes, for example, for different concentrations of the solutions or for simulated real environments. In addition, the osmosis behaviour of the coating needs further study as it played an important role in the sharp reduction in resistance during the early part of the test.

## 5. Conclusions

- Impedance spectroscopy was found to be a convenient and informative method of monitoring coatings on cementitious substrates.
- The polyurethane coating studied deteriorated starting from the surface in contact with NaCl solution. The deteriorated material was more porous and had a lower resistance than the original material. Complete transformation of the 0.35 mm thick coating took about three years and prior to this a two layer system was identified by impedance spectroscopy and was confirmed by SEM. An early sharp reduction in resistance is believed to be due to the formation of blisters in the coating.
- Despite the reduction in resistance over the testing period, the polyurethane coating still retained a high resistance in relation to other surface treatments used to protect concrete from chloride ingress.

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