

Chloride Ion Detection in Concrete through Galvanic Voltage and Resistivity

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ABSTRACT

The construction industry has a significant impact on the environment with increasing consumption of resources. The degradation of reinforced concrete structures when exposed to different environmental conditions affects the life-time of structures and presents significant challenges to the construction industry. More sustainable construction methods are necessary to improve durability and resilience of structures. Resilient structures can be achieved through the development of systems which are autonomously able to detect harmful chemical substances in time, to enable remedial action to be undertaken, thus avoiding structural degradation. This paper reviews and explores two methods of chloride ion detection; namely, the voltage produced by a galvanic pair of metals under the influence of chloride ions and the change in resistivity which an influx of chloride ions produces in the actual concrete. This paper explores the harnessing of such methods in the development of a sensory platform used for the detection of chloride levels beyond a threshold level. Such a platform should be able to perform autonomously from a power supply and have the potential for long-term monitoring of the concrete structure's performance.

KEYWORDS: Concrete, Galvanic corrosion, Resistivity, Chloride, Monitoring, Deterioration, Rebar corrosion.

INTRODUCTION

Diffusion Processes Involved in Species Transport in Concrete

The construction industry has a significant impact on the environment with increasing consumption of resources. The degradation of reinforced concrete structures when exposed to different environmental conditions affects the life-time of structures and presents significant challenges to the construction industry. More sustainable construction methods are necessary to improve durability and resilience of structures.

Resilient structures can be achieved through the

development of systems which are autonomously able to detect harmful chemical substances in time, to enable remedial action to be undertaken, thus avoiding structural degradation. This paper will discuss the applicability of two potential methods which can be used to detect the presence of chloride ions in concrete. Chloride ions cause rebar corrosion and hence, chloride ion concentration is an important parameter which needs to be monitored through structural health monitoring systems (Ismail and Lee, 2014).

Species, such as O₂, Cl⁻ and SO₄²⁻, penetrate concrete pores through various mechanisms. One of the methods of penetration is diffusion, which occurs through the establishment of a concentration gradient.

This gradient makes the species travel from the surface into the pores and then through the pores to the

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internal regions of the concrete. There, they come into contact with the rebar structure (Bertolini, 2013). The first method of chloride ion detection which will be discussed in this paper is the measurement of the concrete's electrical resistivity, which changes with the variation in chloride concentration. The second method which will be discussed is the change in open circuit voltage between the two elements of a galvanic pair of metals with the change in concrete's chloride ion concentration.

Theoretical Basis of the Experimental Program

Changes in the Material Resistivity with Change in Chloride Concentration

The measurement of electrical resistivity of specific materials has often been used to study material properties. When an electrode is embedded into a block of material and a voltage is applied, the current will flow in a radial route out of the electrode, in a defined hemispherical fashion, thereby producing a uniform distribution of current which is equipotential on any point of the hemispherical surface. As the current is moving through the material sample, potential contours are set up as shown in Fig. 1. There are various configurations of electrode set-ups which can be used for taking resistivity readings. Prior work in this area has mostly focused on the use of the Wenner configuration, which basically uses four equally spaced electrodes (Stanish et al.).

The basic set for the experimental work carried out in this paper was based on the Schlumberger- Palmer model. This model uses unequally spaced electrodes, which are set in such a way as to position the voltage electrodes much closer to the current electrodes than in the Wenner model, thus theoretically allowing the possibility of a higher potential to be obtained (Haddad and Warne, 2004). This aspect allows the achievement of better resolutions, especially in the case of low voltage applications.

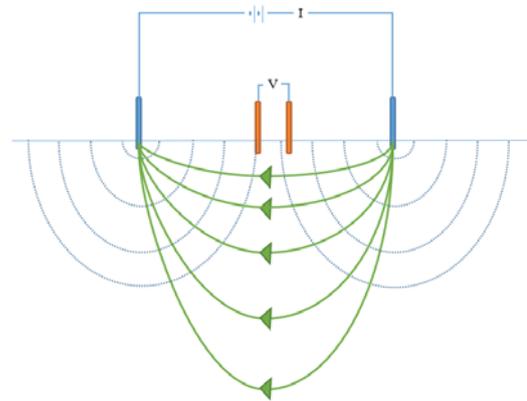


Figure (1): Four-electrode configuration following the Schlumberger- Palmer model. The solid green lines show the flow of current. Dashed blue lines show the electrical potential contours; blue electrodes-current; brown electrodes-voltage

Galvanic Voltage Measurement

A galvanic couple is formed by two dissimilar metals which have a conductive link and are positioned in an electrically conductive electrolyte as shown in Fig. 2.

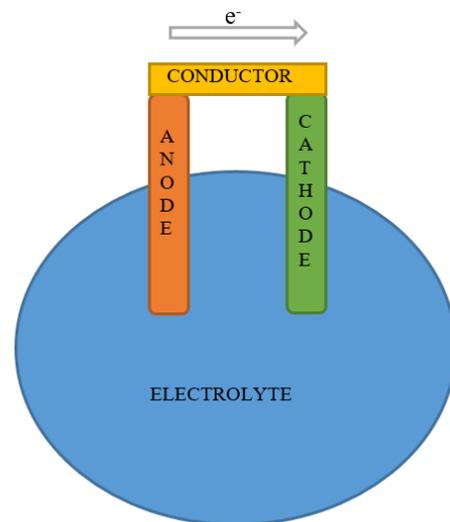


Figure (2): Requirements to form a galvanic pair

Metals which are in an electrolyte assume an electrode potential which varies according to the particular metals. Since different metals have different

potentials, current flow would occur from one metal to the other, if the circuit were to be closed (National Physics Laboratory, 1982).

In the case of this paper, the galvanic pair selected was a combination of 316 stainless steel and EN3B mild steel. When used together, the 316 stainless steel and EN3B mild steel pair forms a galvanic corrosion cell, whereby mild steel would act as the anode from which iron would be dissolved into the solution following Equation (1).



To form a galvanic cell set-up, Equation (1) would need to be balanced by the cathodic reaction, which occurs at the stainless steel electrode that forms the cathodic electrode. The rate at which galvanic corrosion reactions occur depends on variables, such as temperature and the composition of the electrolyte, such as electrolytic conductivity. As current flows between the two metals forming the galvanic pair, the electrode potentials on both electrodes start to shift through polarization. This goes on until the potential on each of the two electrodes would reach the same value. At this stage, current flow would then stop, since there would not be a potential difference to drive the electron flow.

Various works studying galvanic voltages have been carried out mostly using Ag/AgCl electrodes, but other galvanic pairs are also explored (Kelley and Jones).

The galvanic activity of the two metals forming the pair is strongly influenced by the electrical conductivity of the electrolyte. Chloride ion presence, forming the electrolyte solution found in the concrete pores, has a strong influence on its conductivity. For example, distilled water would have a conductivity of between 0.5 and $2\mu\text{S}/\text{cm}$, while a saturated sodium chloride solution would have a conductivity of around $250,000\mu\text{S}/\text{cm}$ (National Physics Laboratory, 1982).

METHODOLOGY

The general practical approach followed in this

paper was the production and subsequent electrical studies on three concrete mixes, each of which has a different sodium chloride concentration. During casting, each of the cast samples was fitted with the necessary electrodes used to measure galvanic voltages and changes in the isotropic resistivity.

Experimental Procedure

Samples of mortar (100mmx100mmx100mm) were produced, each having a different NaCl concentration. Sample type 1 (control) had no added NaCl in the mix, type 2 had 1% NaCl of cement weight or 0.24% of the overall weight added to the mix, while sample 3 had 5% NaCl of cement weight or 1.2% of the overall weight. The cement used was CEM 1 52.5N, together with crushed rock 0/4 aggregate sand sourced from a Coralline Limestone quarry in Malta. The water/cement ratio was 0.5. The sand/cement ratio was 2.7. Seven-day compression test result for mortar without salt was 41.24MPa, while it was 48.91MPa at 28 days. The mortar density at 7 days was $2,156\text{kgm}^{-3}$, while the density at 28 days was $2,121\text{kgm}^{-3}$.

Three sets of electrodes, as shown in Figure 3, were installed in each of the fresh mortar cube specimens, which were cast in the moulds and the whole assembly was compacted on a vibrating table until all air bubbles reached the surface. This ensured that no air bubbles would settle between the electrodes and the concrete, thereby causing a region of high resistivity. This could potentially have a bearing on the results. With reference to Fig. 3, electrode set A was installed to enable the resistivity measurement experiments, which are intended to observe changes in electrical resistivity with changes in chloride concentration. Electrode sets B and C were installed to enable galvanic voltage experimentation to be carried out, thereby correlating galvanic voltage with chloride concentration and electrode surface areas.

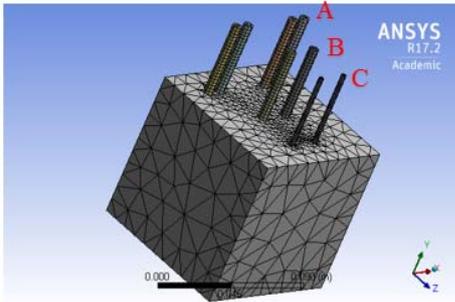


Figure (3): Sample with electrodes installed

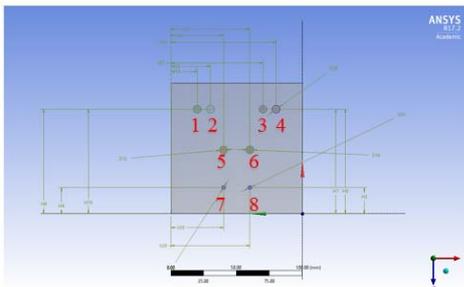


Figure (4): Sample with electrodes numbered

The three electrode groups are detailed in Table 1. Before installation, the electrodes were wiped to remove oil traces and sanded uniformly with sandpaper to roughen their surface. This surface roughening would thereby increase the contact areas which the electrodes have with the concrete material. Each electrode was embedded into the concrete to a depth of 5cm. The cube specimens were cast in moulds and demoulded after three days of curing. The samples were left in an ambient laboratory environment at 20°C. Electrical testing was started immediately as shown in Figure 5.

Electrical Testing

After casting of the 3 mortar samples, electrical testing was carried out. As previously mentioned in this paper, the experimental procedures focused on measuring resistivity and galvanic voltage changes which occur due to chloride presence.

Table 1. The electrode groups embedded in concrete

Group	Electrodes quantity and material	Electrode diameter	Electrode numbers (ref. to)
A	Four Stainless Steel AISI 316	6 mm	1,4 – Current Input 2,3-Voltage Reading
B	One Stainless Steel AISI 316 One Brightly Drawn Mild Steel EN3B	6 mm	5,6
C	One Stainless Steel AISI 316 One Brightly Drawn Mild Steel EN3B	3 mm	7,8

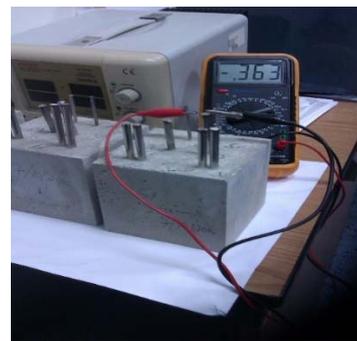


Figure (5): Electrical testing photos showing galvanic voltage measurement



Figure (6): Electrical testing photos showing resistivity measurements

Resistivity Testing

For this part of the experimentation process, the stainless steel electrodes, numbered 1,2,3,4 in Fig. 4, were used. Direct current at varying voltage was applied to electrodes 1 and 4 using a Pintek Triple output 200VA DC power supply. At each current step, the voltage on electrodes 2 and 3 was measured using a DVM 890 multi-meter.

Galvanic Voltage Testing

This was the second part of the testing process. For this part of the experimentation process, the two stainless steel/mild steel galvanic pairs 5, 6 (6mm diameter) and 7, 8 (3mm diameter), as shown in Fig. 3, were used. A DVM 890 multi-meter was used to read the instantaneous galvanic voltage across the electrodes 5, 6 and 7, 8 without electrically loading them to avoid polarization which would drop the open circuit voltage.

RESULTS AND DISCUSSION

Resistivity Testing

Voltages (DC) between 1 and 33 Volts were applied to electrodes 1 and 4 (refer to Fig. 4). The voltage across electrodes 5 and 6 was measured as was the current input into electrodes 1 and 4. These measured values were then inserted into a mathematical model, which was built using the Finite Element Analysis (FEA), modeling

software ANSYS R17.2 Academic Version. The stainless steel electrodes were modeled having an Isotropic Resistivity value of $7.7 \times 10^{-7} \Omega \text{m}$. Each electrode had a contact region modeled between the stainless steel and the concrete. Bonded contact types were selected for this contact region. Bonded contact ensures that there is no sliding and allows for linear solutions to the equations.

Other material properties for the concrete and the electrode metals were taken from the ANSYS Engineering Data Library. The steady state current conduction analysis toolbox platform was used to carry out the analysis. Electromagnetics physics preference meshing was selected with a minimum edge length of $1.885 \times 10^{-2} \text{m}$, to obtain 31,022 nodes delineating the 17,168 separate elements which make up the model. ANSYS was then used to model the complex electrical structure and calculate resistivity, through the use of FEA.

The process used to compute resistivity was carried out by setting an arbitrary isotropic resistivity value for the concrete and gradually varying the value until the mathematical results obtained from the FEM matched the results obtained from the experimental procedure for current flowing into electrodes 1 and 4 and the voltage across electrodes 5 and 6. The results of this mathematical exercise can be seen in columns 7 and 11 of Table 2.

Table 2. Results of galvanic testing combined with calculations carried out through ANSYS

C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
0%	23.8	4900	17.543	6.5617	10.9813	10.48	1097.5	2.829E-05	0.0310	0.031
1%	29.6	4600	23.223	8.2026	15.0204	14.80	1393.1	2.829E-05	0.0394	0.039
5%	28.4	2325	23.557	8.3961	15.1609	15.23	557.2	2.829E-05	0.0723	0.072

C1- Sample salt concentration (NaCl % of cement weight); **C2-** Applied voltage on the current electrodes 1&4 (V); **C3-** Calculated resistivity input in ANSYS

simulation ($\Omega \text{ cm}$); **C4-** Calculated voltage ANSYS electrode 2 (V); **C5-** Calculated voltage ANSYS electrode 3 (V); **C6 -** ANSYS calculated voltage

difference (V); C7- Actual measured voltage (V); C8- ANSYS calculated current density (A/m²); C9- Contact area of electrode (m²); C10- Calculated ANSYS current electrodes 1&4-(A); C11-Measured current input (A)

From Table 2, it can be seen that resistivity falls with an increase in sodium chloride levels, with the 0% specimen exhibiting the highest resistivity values and the 5% specimen exhibiting the lowest. The measured drop in resistivity with increased sodium chloride concentration is being plotted in the graph shown in Fig. 8.

As previously discussed, FEA software is being used to compute the resistivity values from the experimentally obtained voltage and current readings. Figure 7 shows the hemispherical voltage distribution around the electrodes in a cross-sectional view of a mortar specimen (0% sample) as computed by the ANSYS APDL.

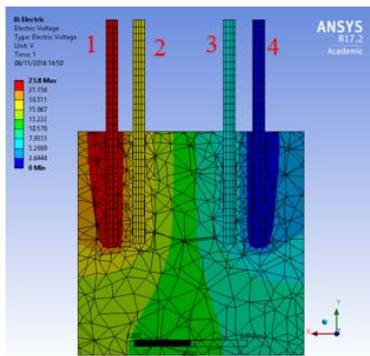


Figure (7): FEA cross-section showing the voltage contours in the 0% sodium chloride specimen

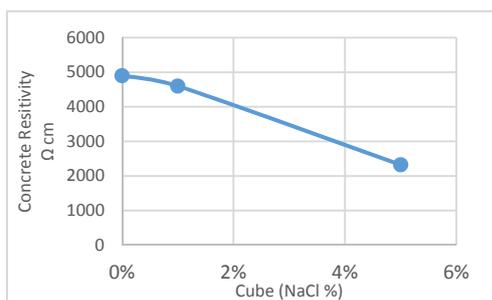


Figure (8): Concrete resistivity dropping with increase in sodium chloride concentration

Resistivity Cross Check Reading Using a 4-Point Wenner Probe

To verify the readings obtained, further readings using a standard 4-point Wenner probe were taken. For this verification exercise, samples of 100mm diameter/200mm length cylinders were cast using the same mix design as the 0% salt sample. Resistivity readings using a Proseq Resipod, Wenner Bridge were taken in different positions on the cylinders' sides. The values obtained were 4.2kΩcm and 4.1kΩcm for two cylinders. The Wenner probe values can be compared to the values obtained in Table 2 (C2) and are of the same order of magnitude as the resistivity of the 0% mortar sample. Thus, the results were validated.

Galvanic Voltage Testing

Voltage readings were taken instantaneously using a DVM 890 multi-meter across electrodes 5 and 6. Readings were also taken across electrodes 7 and 8. The readings obtained are plotted in Figure 9 and Figure 10, which show a net increase in galvanic voltage with the increase in salt content concentration for both electrode diameters.

These readings show an increase in open circuit voltage with increased salt concentration occurring in both the 6mm and 3mm diameter electrodes. This relationship between the galvanic voltage and the sodium chloride content % is shown in Figure 9 and Figure 10.

As can be seen, the galvanic voltage was measured over a period of time and presented a stable voltage value throughout the whole period. The open circuit voltage was also found not to be dependent on the electrode surface area.

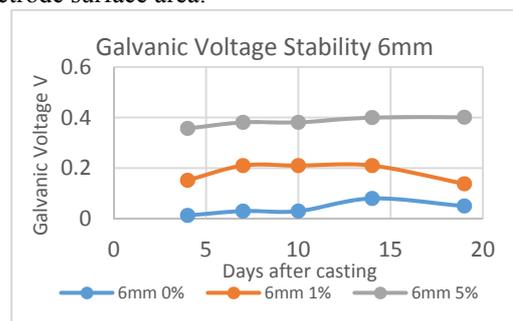


Figure (9): Galvanic voltage measurements on a number of days; electrode diameter = 6mm

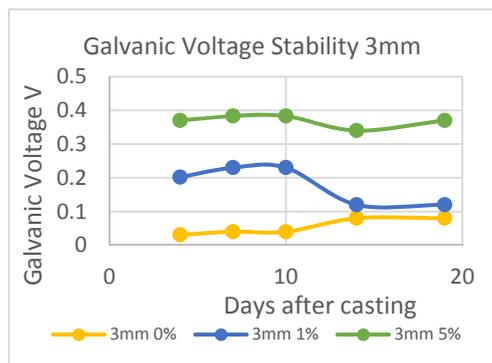


Figure (10): Galvanic voltage measurements on a number of days; electrode diameter = 3mm

CONCLUSIONS

This research presents the outcome of the two methods of chloride ion detection investigated based on the assessment of the voltage produced by a galvanic pair of metals under the influence of chloride ions; and the change in resistivity which an influx of chloride ions produces in the actual concrete. The resistivity and galvanic voltage tests both gave reliable and stable

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readings and it is therefore evident that both can be built upon to develop an efficient chloride ion detection system. It is also evident from the results obtained that both systems have the capability of detecting chloride ion presence due to sodium chloride concentration in the concrete.

The investigation presented sets the scene for additional research needs in the mechanisms involved, as well as the development of a more reliable system intended for use in different operating conditions, such as changing pore saturation. Studies to develop miniature sensors at the micro-level also need to be undertaken in view of developing a product, which is practical for use, small, light and economic for wide structural reinforced concrete applications.

This paper explores the harnessing of the methods in the development of a sensory platform used for the detection of chloride levels beyond a threshold level. Such a platform should be able to perform autonomously from a power supply and have the potential for long-term monitoring of the concrete structure's performance.

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