

Chloride ion detection through the voltage response of a galvanic pair

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Abstract. Chloride ion ingress into reinforced concrete structures is one of the primary causes of concrete degradation. Real-time monitoring of concrete structures for the ingress of chloride ions is therefore of paramount importance towards the achievement of durable and sustainable structures. It is therefore important that the chloride ion detection method used must be accurate and reliable. This paper will endeavour to show how embedded 316L stainless steel and EN3b mild steel galvanic electrode pairs will react to chloride ions present in the concrete pore solution. Through practical experimentation the correlation between the chloride ion concentration in the pore solution and galvanic voltage measurements between the electrode pairs was explored. An experimental setup was proposed, based on concrete samples with in-built fluid containment vessels holding sodium chloride solution, which was allowed to permeate through the pore structure of the concrete over a defined period of time. At particular time intervals core samples were taken at different depths in concrete samples, and the chloride ion content was determined with depth of penetration through titration on the extracted material. The chloride ion content results from titration tests were compared to the measured galvanic voltages. Within certain limits there was good correlation between the chloride ion concentration and the measured voltage readings across the galvanic electrode pair. Galvanic voltage measurements provide a relevant technique for the detection of chloride ions in concrete and in the design of a chloride ion sensory system. Validation testing was also carried out, where samples with known salt concentrations were prepared against which the results obtained could be compared.

Keywords: chloride ion penetration; galvanic corrosion; concrete degradation

1. Introduction

Chloride ions, Cl^- , as well as species such as O_2 , and SO_4^{2-} are able to penetrate the concrete pores through various mechanisms. One of the principal methods of penetration is diffusion which occurs when a concentration gradient is established. This gradient causes the species to travel from the surface of the structure, into the pores and then through the pores into the internal regions of the concrete. Once in the internal regions, the chloride ions come into contact with the rebar structure and cause the initiation of corrosion [1].



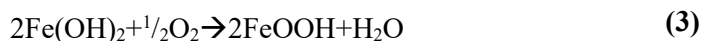
1.1. Theoretical basis

The pore solution in concrete is highly alkaline, with a pH of around 12.5 to 13.5. This pH value is due to the substantial amounts of the hydroxides of calcium, sodium and potassium which are dissolved in the pore solution. The highly alkaline environment of the pore solution passivates the steel, which forms a layer of gamma ferric oxide, thereby protecting the steel and preventing corrosion [2].

Chloride ions dissolved in the pore solution, result in subsequent localised corrosion, in specific areas which are not protected by passive film, thereby resulting in active zones which act as anodes. The surrounding areas on the other hand act as the cathodes in which the reduction of oxygen occurs.

The anodic and cathodic half-cell equations which tie together the galvanic process are represented below [3]:

Anodic half-cell reactions



Cathodic half-cell reactions



2. Methodology

2.1. Experimental procedure

The procedure followed during the experimental programme, was based on ASTM C1556-11a. This is the standard test method used for determining the apparent chloride diffusion coefficient of cementitious mixtures by bulk diffusion [4].

The test samples designed and built for this experimental process are shown in Figure 1. The procedure to construct the test samples started by preparing the electrodes required to form the galvanic pairs. The two metals used were EN3B Mild Steel, which act as the anodes and 316L Stainless Steel, which act as the cathodes. The edges of the electrodes were rounded to remove all pointed edges thereby ensuring that contact area is maximised, with solvents being used to remove any organic residues.

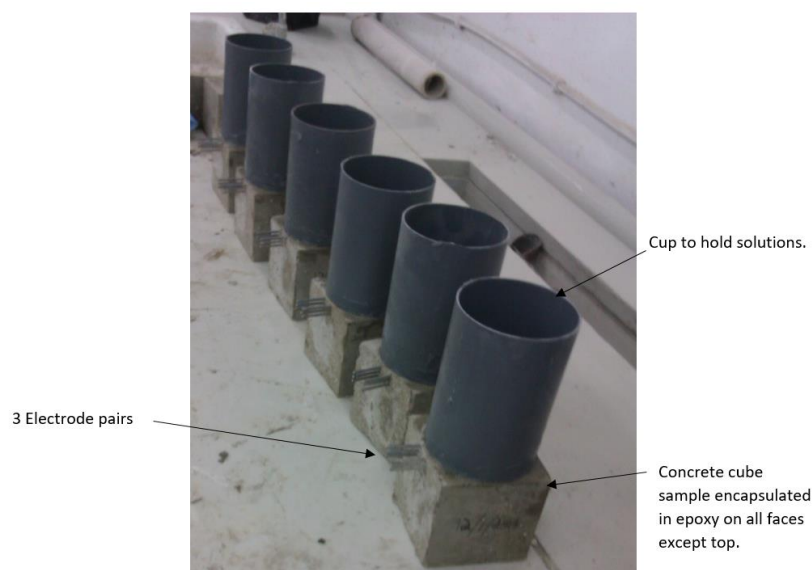


Figure 1. Concrete blocks with fluid containment vessels attached.

The electrode pairs which were spaced as shown in Figure 2 were set in moulds intended for 100mm cubic samples of mortar. 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 set at 0.5 with a sand/cement ratio of 2.7.

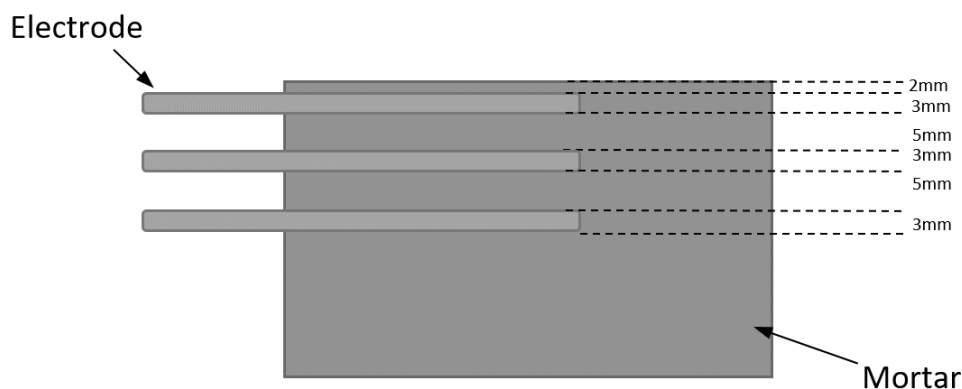


Figure 2. Diagram showing the spacing between electrodes in the mortar cube (not to scale).

A PVC fluid containment vessel was then attached with sealing adhesive to each concrete block, in order to ensure a watertight seal. This vessel allows the testing fluids to be contained and also allows galvanic voltages across the electrodes to be studied while the actual diffusion is occurring.

The exposed concrete surfaces were then coated with an epoxy structural system sealant. This sealant was necessary to minimise the possibility of fluid egress through the exposed surfaces thereby ensuring that the chloride ions move through the pore solution predominantly by diffusion rather than other bulk transport methods.

In line with the method as proposed in the ASTM C1556-11a the next step was to expose the samples to a solution of saturated calcium hydroxide $\text{Ca}(\text{OH})_2$ which was placed in the fluid containment vessels fitted on the concrete samples. The solutions were kept replenished up to the maximum mark in the fluid containment vessels. The exposure to the calcium hydroxide continued until the concrete mass did not increase by more than 0.1 mass% per 24 hours.

After the exposure to the calcium hydroxide, the samples' fluid containment tanks were emptied, cleaned with distilled water and then filled with the concentrated brine exposure liquid. The exposure liquid was prepared by mixing $165\text{g} \pm 1\text{g}$ of pure NaCl per dm^3 solution with distilled water. The exposure to the solution was continued for a number of days with the fluid containment vessels on all the samples being kept filled and replenished with solution to ensure that hydrostatic pressure on the surface of the concrete remains constant.

3. Results

The samples were studied over two time periods namely, Period 1 being between 1 and 19 days and Period 2 between 20 and 120 days. The first time period, Period 1, was monitored to study the correlation between the galvanic voltage readings and the chloride ion concentration in early age concrete before the pore solution starts to dry out. The latter time period, Period 2, was studied to see how galvanic voltage varies as the concrete matures in controlled ambient conditions.

Throughout the experimental period the voltages across each of the three electrode pairs was measured. For each measurement three spot readings was taken and the average was then calculated, with all samples giving results which were very similar. The average values were plotted as presented in Figure 3. With reference to Figure 2, Electrode set 1 was the galvanic pair at the top next to the fluid containment vessel, electrode set 2 was the middle galvanic pair set and electrode set 3 was the lowermost galvanic pair.

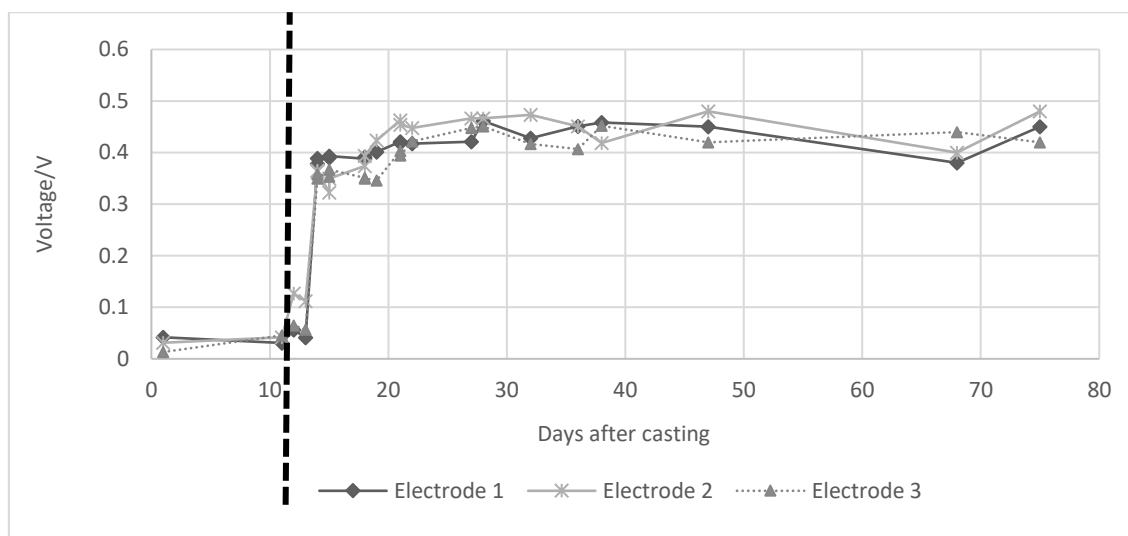


Figure 3. Galvanic voltage measured across electrodes for sample A1. Thirteen days (marked by dotted line) after casting exposure to chloride ions occurs. Each of the series shows the voltage values across an electrode pair.

As can be seen in Figure 3, the galvanic voltages measured before the exposure to chloride ions occurred, were all below the 0.3V threshold (actually all values measured were below 0.1V). As soon as exposure to chloride ions occurred the galvanic voltage increased instantly to values in the range between 0.35V and 0.45V. This meant that the presence of chloride ions and the voltage increase occurred at exactly the same time. It was also observed that the voltage increased at exactly the same time as when the chloride ion exposure occurred, in all the samples. Moreover the voltage across the galvanic pair instantly increased by more than a factor of four as soon as there is chloride ion contact with the metals.

The fact that the voltage increased in all the samples at the moment in which chloride ion exposure occurred, indicates that there is strong correlation between the galvanic voltage and the chloride ion concentration.

3.1. Titration analysis.

To calibrate the voltage increase with the chloride ion concentration values, the chloride concentration in the pore solution at the electrode positions was studied chemically using a volumetric procedure.

The volumetric procedure used was based on an argentometric titration process which involved the use of silver salts to determine the concentration of chloride ions present. The procedure used was based on BS 1881-124:1988 [5].

The concrete sample was cored at accurately measured depths and dust samples were collected for analysis. The dust samples were taken at 2mm depth intervals up to a depth of 14mm from the surface of the concrete block. Further samples were taken at depths of 25, 35, 45 and 50mm with around 8g of dust being taken for each depth.

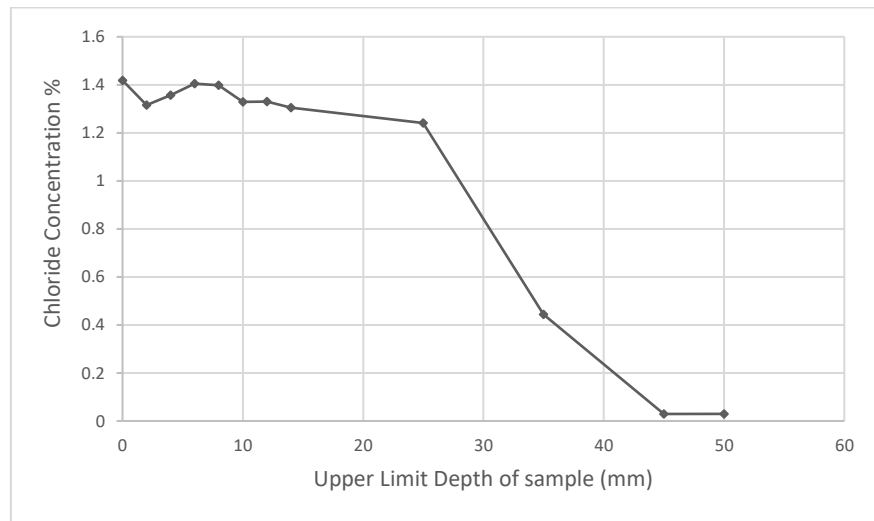


Figure 4. Chloride Concentration vs Depth of dust sample collection (After 23 days).

Figure 4 shows the profile of the chloride concentration changing with depth as obtained from the volumetric chemical analysis. It can be seen that as the sample depth increases, the chloride concentration decreases. This decrease becomes pronounced after the 25mm mark from the surface is exceeded. The deepest of the three electrode sets is situated at around 21mm from the concrete surface. The titration results therefore show that all the 3 electrode pairs, the lowest of which is set at 21mm from the sample surface, are situated in an area which reaches a chloride concentration of between 1.2% and 1.4% of the cement weight. The results therefore give an indication that the galvanic voltage across the electrode pair increases when the chloride ion concentration increases above 1.2% of the cement weight.

3.2. Validation Testing.

To confirm threshold chloride limits above which galvanic voltages start to increase above the 0.3V threshold, three samples with known sodium chloride concentrations added to the mortar mix were prepared as shown in Figure 5. These samples consisted of three mortar cubes with electrode sets A, B and C embedded. Each of the samples had a different sodium chloride salt concentration in the mortar mix.

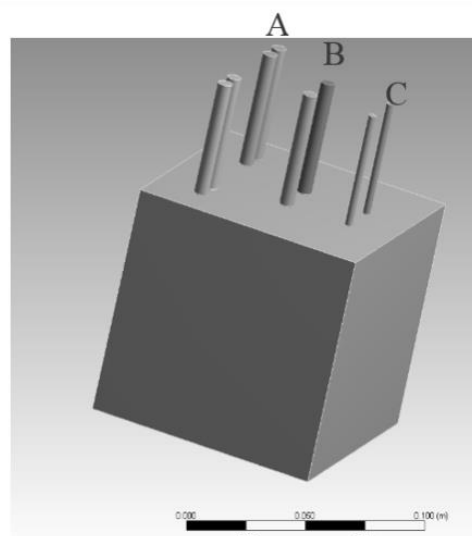


Figure 5. The three electrode groups embedded in the mortar.

One of the mortar cubes was made with mortar only i.e. 0% salt, the other one had salt equivalent to 1% of the cement weight added to the mortar mix, while the third sample had salt equivalent to 5% of the cement weight added. The material used and ratios (apart from the added salt concentrations) were the same as that used previously for experiments discussed in this paper. With reference to Figure 5 the electrode sets B and C were used in this experimental procedure to form the galvanic pairs. Electrode set A on the other hand formed by a set of four 316L stainless steel electrodes through which resistivity changes in the concrete with varying salt concentrations could be monitored through the use of the Wenner probe principle.

Electrode set B consisted of a 6mm diameter galvanic pair of electrodes, one of which was made of 316L stainless steel and the other EN3b mild steel. Electrode set C consisted of a galvanic pair made of the same metals as set B but with the electrodes being of a smaller 3mm diameter. The galvanic voltages measured between the electrodes pairs of each of the sets labelled B and C were recorded over a period of 115 days and the results were tabulated in Table 1.

Table 1. Galvanic voltages on the two stainless steel/mild steel galvanic pairs 5, 6 (6mm diameter) & 7, 8 (3mm diameter).

	Galvanic Voltage 6mm V			Galvanic Voltage 3mm V		
	6mm	6mm	6mm	3mm	3mm	3mm
Days after casting	0%	1%	5%	0%	1%	5%
4	0.01	0.15	0.36	0.03	0.20	0.37
7	0.03	0.21	0.38	0.04	0.23	0.38
10	0.03	0.21	0.38	0.04	0.23	0.38
14	0.08	0.21	0.40	0.08	0.12	0.34
19	0.05	0.14	0.40	0.08	0.12	0.37
38	0.01	0.11	0.39	0.02	0.06	0.27
49	0.01	0.10	0.33	0.02	0.05	0.21
59	0.03	0.17	0.28	0.05	0.06	0.28
68	0.08	0.19	0.37	0.07	0.06	0.25
88	0.05	0.09	0.27	0.08	0.12	0.21
95	0.03	0.07	0.24	0.06	0.08	0.17
115	0.05	0.10	0.25	0.03	0.02	0.18

The results shown in Table 1 over the first 19 days show that with a salt content of 1% the galvanic voltage between the galvanic pair of electrodes is higher than that noticed in the sample with 0% salt content. In the sample with the 5% salt content the galvanic voltage presented the high values similar to those measured in the experimental procedures as presented in section 2.1 when exposure to sodium chloride occurred. The values obtained in this sample, exceeded the correlated directly with the galvanic voltage values shown in Figure 3 thus confirming that chloride ion concentration above threshold causes galvanic voltage to instantly rise thereby validating the results of the chloride ion concentrations measured through the titration as shown in Figure 4.

The standard deviations for the voltages obtained in the period between day 4 and day 19 were calculated to study how closely grouped the results were when measurements were taken across a time period. The graph in Figure 6 shows tightly grouped voltage results, thereby indicating the suitability of the use of this method towards the construction of chloride ion sensory systems.

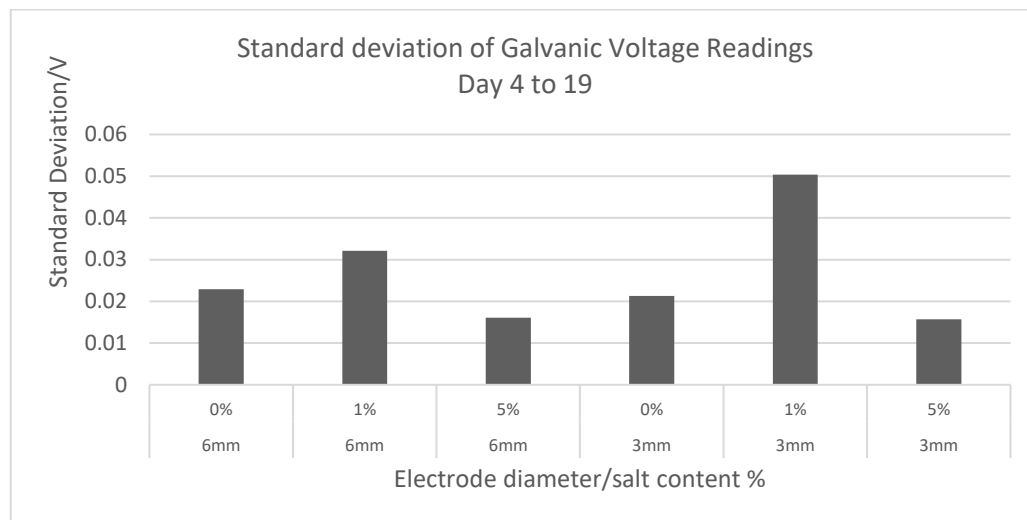


Figure 6. Standard deviation values of Galvanic Voltages obtained in the period between Day 4 to day 19 post molding.

The three samples were air dried in a controlled environment at an ambient temperature of 21°C and RH of 60%. It can be seen from Figure 7 that as the mortar matures, the galvanic voltage trend line for the 5% salt sample decreases and tends to converge with the trend lines of the 1% and 0% salt concentrations.

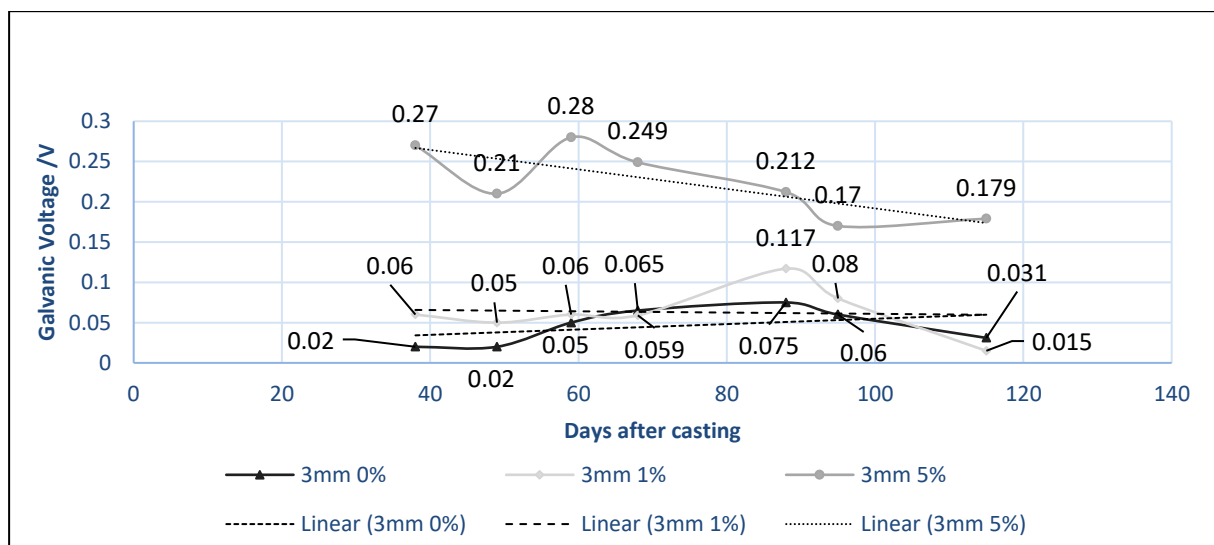


Figure 7. Galvanic voltages for the 3mm electrodes plotted against time.

There can be more than one reason for this reduction in galvanic activity as the sample matures. The main reason relates to the actual mechanism of ionic movement through the pore solution. For corrosion to occur there needs to be a path for ion transfer between the two electrodes. In the case of the selected galvanic pair there needs to be a liquid medium, through which the hydroxide ions formed at the cathode can move towards the anode, where the oxidation reaction with the iron occurs [2] [6].

Another reason for the reduction in galvanic activity with maturity of the sample, is the increase of the concrete's resistivity as the concrete dries. Testing using electrode set A, discussed in previous literature, confirmed that while resistivity is inversely proportional to ionic concentration, drying of the sample causes an increase in the concrete's resistivity [7] [8].

4. Conclusions

The results presented and discussed in this paper show that chloride concentrations in excess of circa 1.2% cause a galvanic electrode pair to present an increase in the voltage across it. This voltage increase may be measured and used to indicate the presence of chloride ions in the pore solution. Repeat testing has presented reliable results throughout.

A system based on a 316L stainless steel and En3B mild steel pair is therefore an effective solution which can be used to detect chloride ions above a threshold concentration of circa 1.2%. However the results also indicated that as the concrete dries up the galvanic voltage becomes a less reliable means of measuring chloride ion concentration. Methods of moisture retention in the sensor's active zone must therefore be explored for an effective sensory system to be developed.

Looking at the validation of results presented in section 3.2 it can also be seen that such a system has potential for future development and lends itself well towards effective miniaturisation. If one compares the first 20 days for both the 6mm and 3mm electrodes, very similar responses can be seen. This in the sense that for 5% salt content, both 3mm and 6mm diameter electrodes immediately exhibited a galvanic voltage above the 0.3V threshold. The other two samples (1% and 0% salt concentrations) never reached this voltage level across either of their electrode pairs. It can therefore be deduced that the electrode's surface area does not noticeably affect the open circuit voltage measurement.

The galvanic voltages obtained in this paper are similar to those achieved in other experimental procedures as found in prior literature which also recorded voltages of between 0.5 and 0.6V when the galvanic pairs were exposed to chloride ion solutions. Such literature also indicated that the oxygen level has a predominantly important effect on the galvanic activity and therefore the open circuit voltages measured. Tests in literature have shown that with increased oxygen concentration in solution the galvanic voltage can reach 0.87V in a mild steel/stainless steel galvanic [9]. Hence oxygen concentration enhancement methods, will be another area which would need to be studied and explored to be integrated in a sensory system in other future works carried out.

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