

Issues using potential decay techniques to assess a cathodic protection system of steel in concrete caused by macrocell corrosion.

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ABSTRACT : An experiment was undertaken to simulate steel in concrete macrocell corrosion and to measure the macrocell corrosion rates under dry and wet circumstances and its affect on potential decay (depolarisation) readings when using a CP-system. Two steel in concrete specimens were prepared of which one specimen with passive bars and the second specimen with active bars and coupled together. The experiment conducted simulated a situation in which passive bars are surrounded in close vicinity by active bars which are polarised by a galvanic anode. It was performed to understand the affect of current distribution on depolarisation readings. Results indicated clearly a change of current direction coming from the active bars in a wet environment when the anode's current supply was switched-off when starting the instant-off measurement readings. Depending on the humidity and surface area of the active bars in relation to the passive surface area it should be clear that the amount of current produced by the active bars will have noticeable influence on the potential decay (depolarisation) readings.

1 INTRODUCTION

Cathodic Protection have been used for many years to inhibit corrosion of reinforced concrete. One of the main challenges when designing a CP-system specifically for reinforced concrete is to understand the parameters affecting the performance and the working area which is also called the anode's "throwing power" which can be studied by analysing polarisation and depolarisation potentials of the structure in a predefined zone around the anode. This paper describes an experiment which was performed to clear up some dubious depolarisation issues resulting from a previous experiment in which newly developed anodes were tested. The purpose of this experiment is to give a better understanding of these phenomena by simulating a situation in which active and passive bars are combined in concrete specimen.

2 EXPERIMENT PROCEDURES

An experiment was conducted to simulate a situation in which active bars are surrounded in close vicinity by passive bars which are polarized by an anode to understand the affect on current distribution and depolarization readings. The anode chosen was a zinc sacrificial surface applied anode which is a zinc sheet with pre-applied ion-conductive adhesive as can be seen in Figure 2. The main reason to use such an anode system was its simplicity, ease of application and having no physical and mechanical impact on the concrete samples, avoiding any electric field irregularities or electric field concentrations which may affect the potential decay measurements.

Two concrete samples shown in Figure 1 were prepared with the following composition : portland cement 300 kg/m³, 0-15 mixed aggregates, superplasticizer 1,17 ltr / 100 kg cement, water cement factor of 0,6 , and only sample 2 with mixed in

calcium chloride (CaCl_2) with a 3% Cl^- on m/m cement weight. The dimension of the concrete samples are: (L x W x H) 10 x 10 x 4 cm. Each of the samples contain 2 bars with a diameter of 10 mm and a total steel surface area of 25 cm^2 . The zinc sheet has a total surface area of 100 cm^2 .

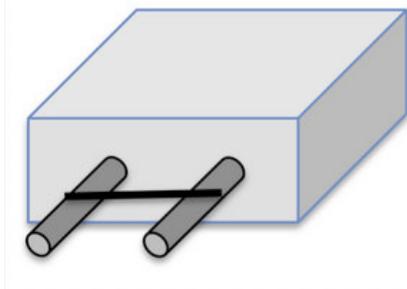


Figure 1. Concrete samples

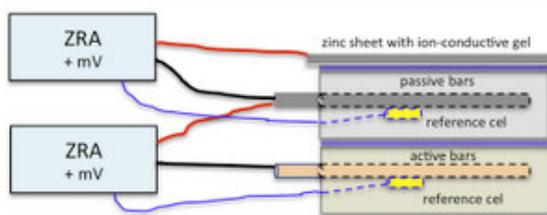


Figure 2. Experimental set-up

Between the two concrete samples a 1 mm sheet of ion-conductive adhesive was placed to secure electrolytic continuity, good adherence and avoiding interruption of the electrolytic field within both samples. The reference cels used are silver/silver chloride [Ag/AgCl] with a Haber-Luggin capillary.

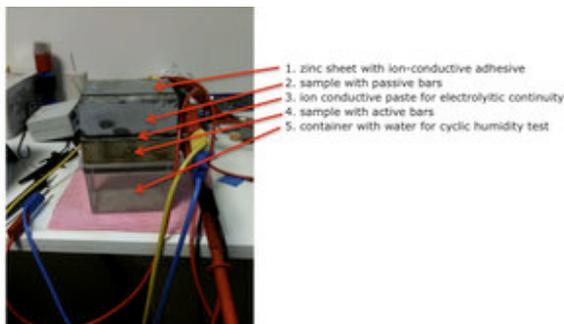


Figure 3. Picture of the experimental set-up.



Figure 4. Lab set-up with two ZRAs measuring the current distribution and direction.

3 RESULTS

The system has been connected and the data has been logged for every 10 minutes for a total of 44 hrs. Figure 5 shows that the current measured between the samples and the zinc anode is called A_1 , which is an imposed current by the zinc anode. A positive current sign means an electron flow from the zinc anode to the samples. A negative current sign means an opposite direction of electron flow. A_2 is the current flow between sample 1 and sample 2. A positive current sign means an electron flow from sample 1 to sample 2. A negative current sign means an opposite direction of electron flow.



Figure 5. Sample 1 has passive bars, and sample 2 has active bars

3.1 Step 1 (open circuit macrocell condition)

The first 10 minutes the potential of both samples were logged. Both samples were not electrically connected neither was the anode. Both samples were also kept in an environment with 65% RH and 20°C . Figure 6 shows a sketch of the situation including

Table I and Figure 7 showing the potentials and current measured



Figure 6. Sketch of the samples

TABLE 1

Potentials and currents measured during step 1

| SAMPLE 1 | | | | SAMPLE 2 | | | |
|----------|------|--------|-------------------|----------|-------------------|--|--|
| hrs | min. | CSE mV | A ₁ uA | CSE mV | A ₂ uA | | |
| 0 | 0 | 165 | 0 | -490 | 0 | | |
| | 10 | 168 | 0 | -487 | 0 | | |

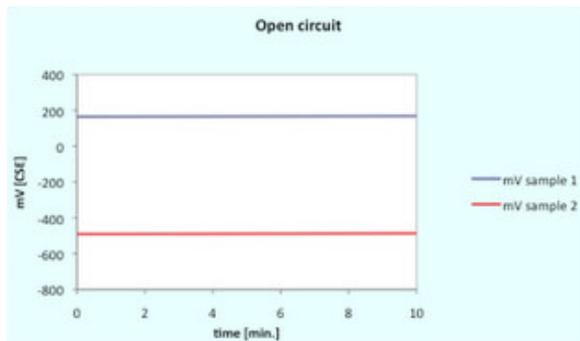


Figure 7. The results from Table 1 presented graphically

3.2 Step 2 (closed circuit macrocell condition without anode current)

The next step involved a closed circuit between sample 1 and sample 2. In this condition the electron flow A_2 measured was caused by the macrocell condition. Both potentials and current were measured till the values stabilised. The results are shown in Table 2 and presented graphically in Figure 9 and 10.



Figure 8. Electron flow of the macrocell condition

TABLE 2

Potentials and currents measured during step 2

| SAMPLE 1 | | | | SAMPLE 2 | | | |
|----------|------|--------|-------------------|----------|-------------------|----------------|--|
| hrs | min. | CSE mV | A ₁ uA | CSE mV | A ₂ uA | | |
| 10 | 168 | 0 | | -487 | 0 | Bars connected | |
| 20 | | -123 | 0 | -481 | -51 | | |
| 30 | | -173 | 0 | -491 | -52 | | |
| 40 | | -179 | 0 | -493 | -48 | | |
| 50 | | -177 | 0 | -490 | -49 | | |

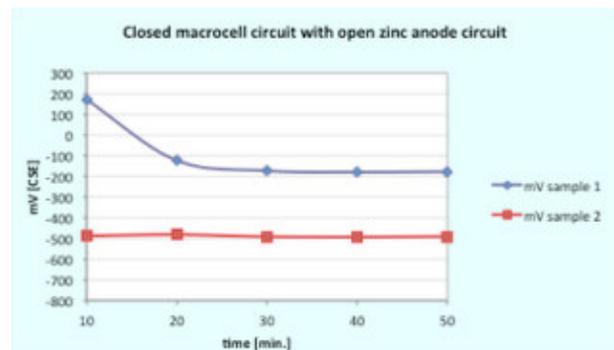


Figure 9. The potentials [mV] from Table 2 presented graphically

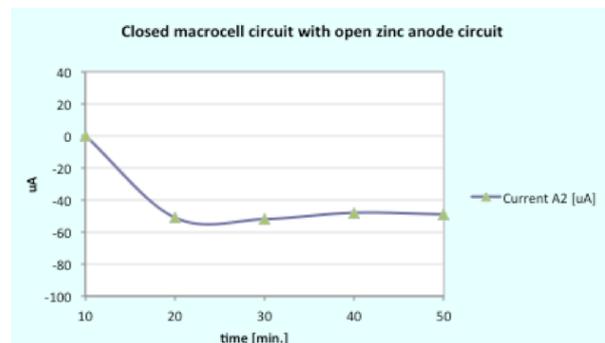


Figure 10. The current [μ A] from Table 2 presented graphically

3.3 Step 3 (closed circuit macrocell condition with anode current)

Step 3 involved a closed circuit between sample 1, sample 2 and the anode. In this condition an electron flow A_1 and A_2 were measured as shown in Figure 11. The zinc anode was able to supply not only an electron flow to sample 1 but also to sample 2 (A_2). Both samples were dry. The results can be found in Table 3 and presented graphically in Figure 12 and 13.

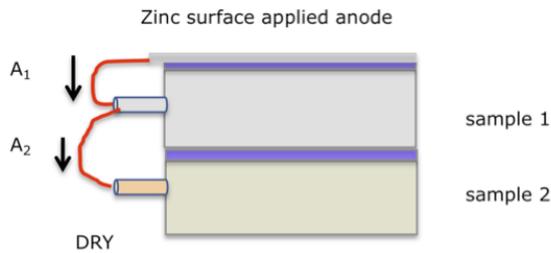


Figure 11. A_1 and A_2 show the electron flow measured.

TABLE 3

Potentials and currents measured during step 3

| hrs | SAMPLE 1 | | | SAMPLE 2 | | anode connected |
|-----|----------|--------|---------------|----------|---------------|-----------------|
| | min. | CSE mV | A_1 μ A | CSE mV | A_2 μ A | |
| 1 | 50 | -177 | 0 | -490 | -49 | |
| | 60 | -437 | 114 | -495 | 35 | |
| | 70 | -545 | 111 | -517 | 36 | |
| | 80 | -572 | 108 | -520 | 34 | |
| | 90 | -536 | 105 | -518 | 31 | |
| | 100 | -585 | 101 | -519 | 33 | |
| 2 | 110 | -527 | 95 | -519 | 35 | |
| | 120 | -531 | 91 | -517 | 31 | |
| 3 | 180 | -571 | 73 | -520 | 27 | |

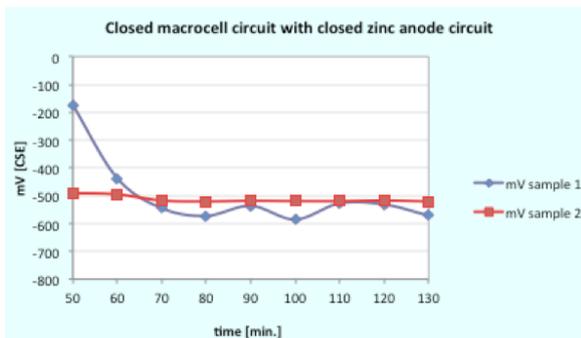


Figure 12. The potentials [mV] from Table 3 presented graphically.

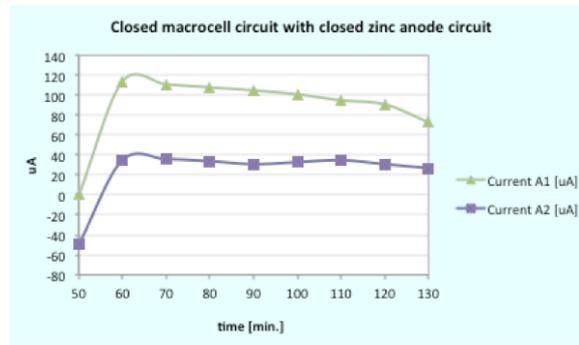


Figure 13. The currents [μ A] from Table 3 presented graphically

3.4 Step 4 (closed circuit macrocell condition with anode current)

Step 4 involved similar situation as step 3 a closed circuit between sample 1, sample 2 and the zinc anode. However the sample with the active bars was effected by high humidity. The sample was put on top of a container filled with water as shown in Figure 14. Immediately the humidity starts to penetrate the sample with active bars as can be seen in Table 4 and presented graphically in Figure 15 and 16.

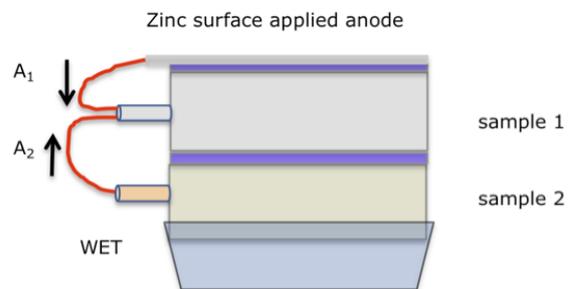


Figure 14. Sample 2 placed on top of a water container.

TABLE 4

Potentials and currents measured during step 4

| hrs | SAMPLE 1 | | | SAMPLE 2 | | |
|-----|----------|--------|-------------------|----------|-------------------|---------------|
| | min. | CSE mV | A ₁ uA | CSE mV | A ₂ uA | |
| 3 | 180 | -571 | 73 | -520 | 27 | Sample wetted |
| 4 | 240 | -580 | 67 | -522 | 21 | |
| 5 | 300 | -590 | 63 | -521 | 18 | |
| 6 | 360 | -564 | 59 | -522 | 13 | |
| 7 | 420 | -593 | 57 | -521 | 6 | |
| 8 | 480 | -626 | 57 | -521 | 1 | |
| 9 | 540 | -554 | 55 | -522 | -4 | |
| 10 | 600 | -602 | 56 | -522 | -9 | |
| 11 | 660 | -619 | 55 | -522 | -12 | |
| 12 | 720 | -547 | 54 | -520 | -15 | |
| 13 | 780 | -619 | 53 | -520 | -17 | |
| 14 | 840 | -606 | 55 | -519 | -18 | |
| 15 | 900 | -554 | 55 | -521 | -16 | |

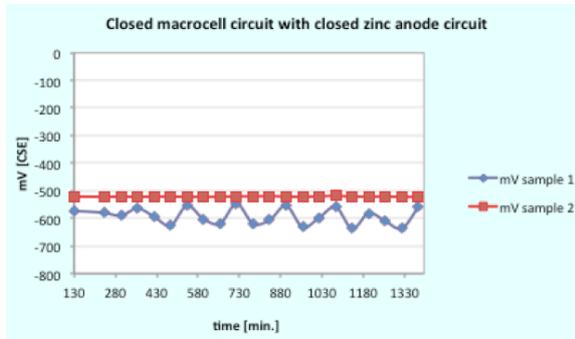


Figure 15. The potentials [mV] from Table 4 presented graphically

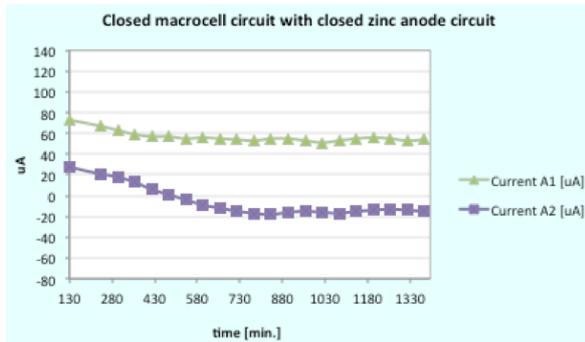


Figure 16. The currents [uA] from Table 4 presented graphically

3.5 Step 5 (closed circuit macrocell condition with anode current)

Figure 17 shows step 5 which is actually the same situation as described step 3. In this situation the sample with the active bars has been taken off from the container with water and slowly got back to a dry environment. The results are found in Table 5 and presented graphically in Figure 18 and 19.

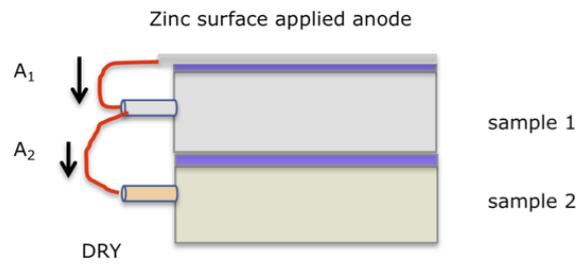


Figure 17. Situation turned as in Figure 11 in Step 3

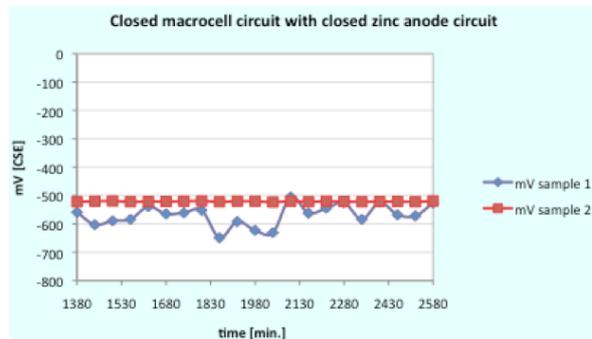


Figure 18. The potentials [mV] from Table 4 presented graphically

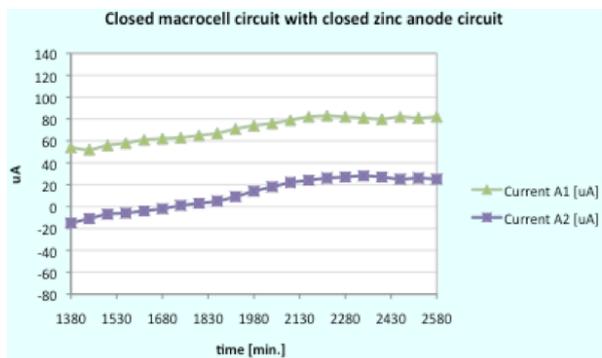


Figure 19. The currents [uA] from Table 4 presented graphically

4 DISCUSSION

Unfortunately there is a lack of discussions about design criteria to get reliable monitoring readings of CP-systems for steel in concrete. Specifically for galvanic anodes the position of reference cell in relation to the anode can be critical when judging whether a system is working or not. On the other hand surrounding circumstances which sometimes are not well judged can have quite an impact on the values measured and undervalue the performance. This is what happened during previous experiments in getting better understanding of the throwing power, current densities and overall performance of newly developed discrete sacrificial anodes to see whether they complied with the ISO12696 criteria.

This original experiment was based on a total of four concrete slabs each with dimension 100 x 100 x 15 cm of which two of these slabs were contaminated with chlorides. One Slab was used to simulate a concrete slab with traditional repairwork. This particular slab was heavily contaminated with chlorides and the top of this slab (appr. 10 cm) was replaced by a traditional mineral repair mortar. These slabs contained reference cells on strategic locations to get depolarisation readings at different distances from the anodes. The depolarisation readings were quite disappointing and not in agreement with the current readings of the anodes which were impressive, specifically in the region with active corroding bars due to the low polarisation resistance of the active corroding bars. Similar effects were also noticed in previous studies (Bertolini et al) in which single anodes were analysed for its performance and "throwing power" immediately after switching off the current during instant-off readings.

After having studied and analysed the results of the original experiment as described above, there were already assumptions indicating that the readings were possibly affected by the actively corroding bars in close vicinity of the reference electrodes. Similar situations may occur in case where per unit surface area too few anodes with too low anode surface area

are used in combination with active bars in wet zones. This will lead also to situations resulting in insufficient polarisation capacity of the anodes simply because they follow the mixed potential theory. The mixed potential theory indicates very clearly that sacrificial anodes needs a minimum required surface area in proportion to the steel surface area for gaining sufficient steel polarisation (Giorgini & Papworth), (Kelly & Scully).

Therefore it was decided to conduct a new experiment to simulate a situation in which passive bars are surrounded in close vicinity by active bars in combination with a CP-system to understand the current distribution and its affect on depolarisation readings. When considering the current densities and potentials presented in the data it is helpful to consider the overall potential as the sum of several electrochemical processes called overpotentials or polarisations, which are : activation polarisation also called charge transfer polarisation or charge transfer overpotential η_{act} to overcome the charge transfer resistance R_{ct} , concentration polarisation η_{conc} to overcome diffusional resistance due to mass transport limitations R_D and ohmic polarisation η_o to overcome ohmic resistance also called solution or electrolytic resistance R_S (Cherry).

Activation polarisation is actually the potential required to trigger the reaction at the surface and keeping it running. It can be described by the Tafel Equation (1):

$$\eta_{act} = -\beta_c \ln x (i_c / i_{corr}) \quad (1)$$

Concentration polarisation occurs during the depletion of charge-carriers at the electrode surface. The mass transport of these charge-carriers could become rate controlling. It can be described in Equation (2) :

$$\eta_{conc} = R \times (T/n) \times F \ln(1 - [i_c / i_{corr}]) \quad (2)$$

Ohmic polarisation is actually the potential gradient caused by solution or electrolyte resistance. Ohmic overpotential is described by Ohm's law and is often called Ohmic drop as presented in Equation (3) :

$$\eta_a = I \times R_a \quad (3)$$

The total overpotential gives Equation (4) :

$$\begin{aligned} \eta_{\text{total}} &= (\eta_{\text{act}} + \eta_{\text{conc}}) + \eta_a \\ &= \left[-\beta_c \times \ln\left(\frac{i_c}{i_{\text{corr}}}\right) + \left(\frac{R \times T}{n \times F}\right) \times \right. \\ &\quad \left. \ln\left(1 - \left[\frac{i_c}{i_{\text{corr}}}\right]\right)\right] + I \times R_a \end{aligned} \quad (4)$$

to overcome :

$$R_{\text{tot}} = [R_{\text{ct}} + R_D] + R_S$$

of which

$$[R_{\text{ct}} + R_D] = R_p$$

makes Equation (5) :

$$R_{\text{tot}} = R_p + R_S \quad (5)$$

Each individual parameter can be derived from the polarisation curves shown in figures 23 - 26 which illustrate steps 2, 3 and 4. To understand these individual parameters within a corrosion process, it may help to visualise the elements of the circuit as electrical components to simulate the corrosion process. The most common equivalent circuit used in electrochemistry is called the Randles circuit as shown in Figure 20. Additional to all individual resistances there is also a capacitive element C_{dl} due to the double layer present at the electrode / solution interface which acts like a capacitor.

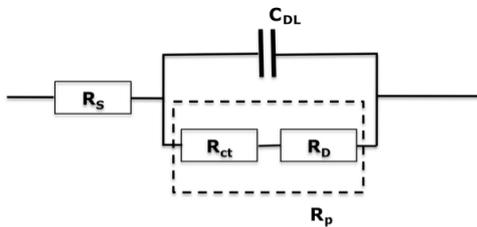


Figure 20. Randles circuit

We will not go into detail how to determine each of these individual parameters because the goal of this experiment is to visualise that part of overpotential which is caused by the macrocell corrosion current.

When studying the results caused by macrocell corrosion it becomes obvious that the polarisation values are strongly effected by the macrocell corrosion currents. This means that it effects equally the depolarisation or potential decay readings. Figure 21 shows the overall curve of all 5 steps together and clearly shows the effect on polarisation due to macro corrosion currents.

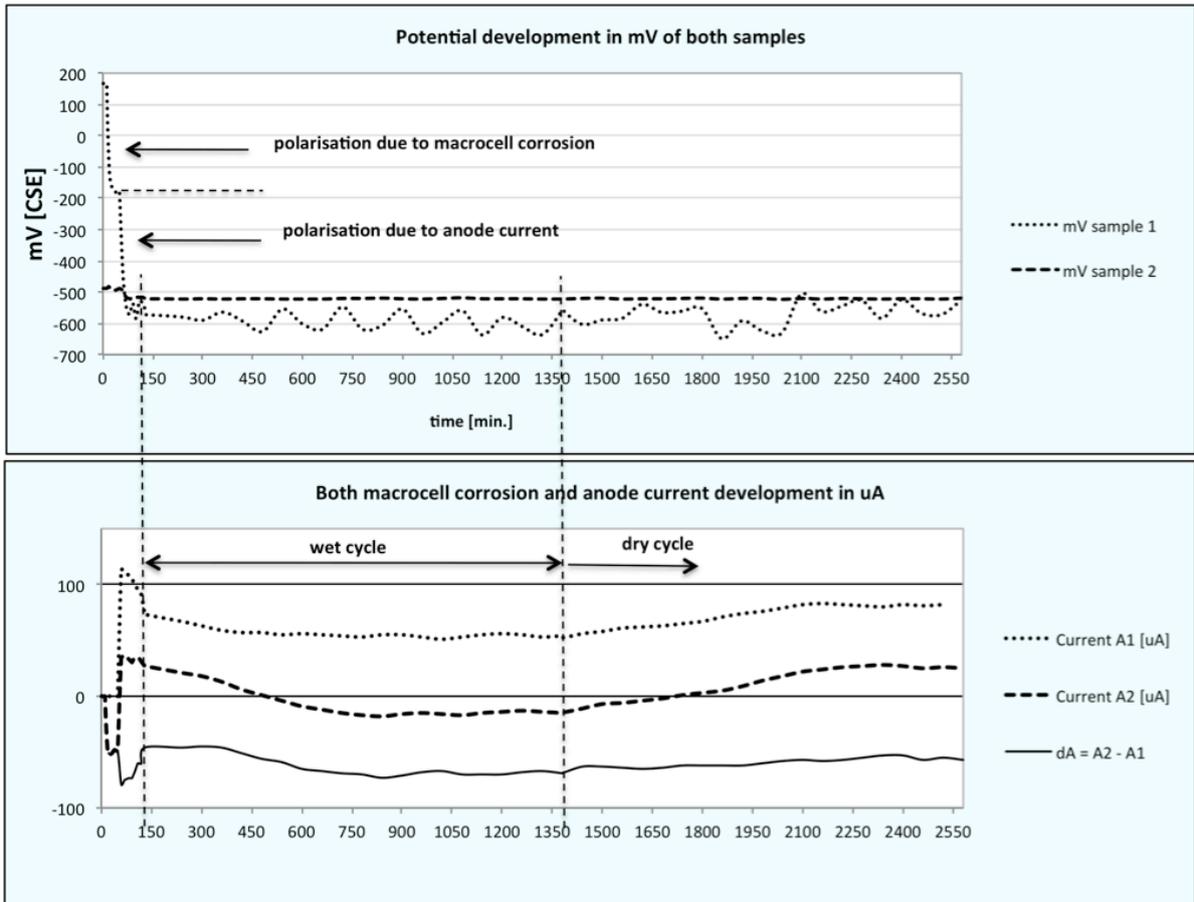


Figure 21. The currents [uA] and potentials [mV] from all steps presented graphically

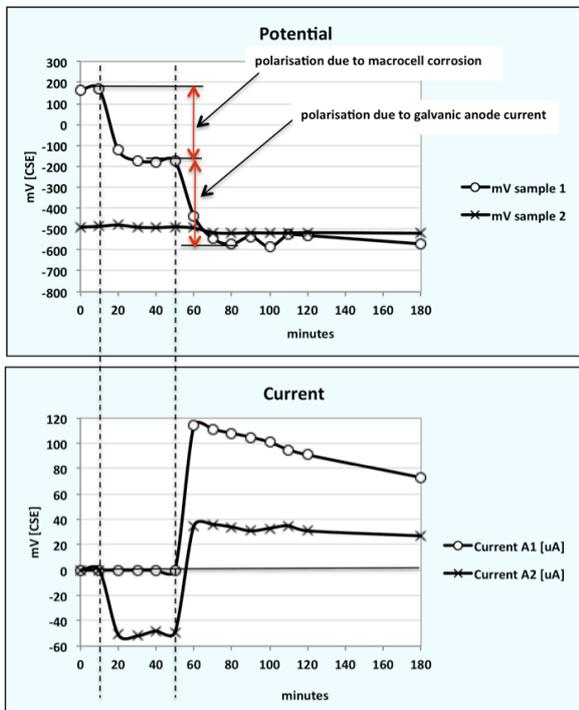


Figure 22. The currents [uA] and potentials [mV] from all steps presented graphically.

When zooming in on the first 180 minutes it is even possible to quantify the exact amount of polarisation caused by the macrocell corrosion current. It can be clearly seen in Figure 22 the strong effects of these macrocell corrosion currents and hence the error of depolarisation or potential decay readings during monitoring if these currents are not excluded.

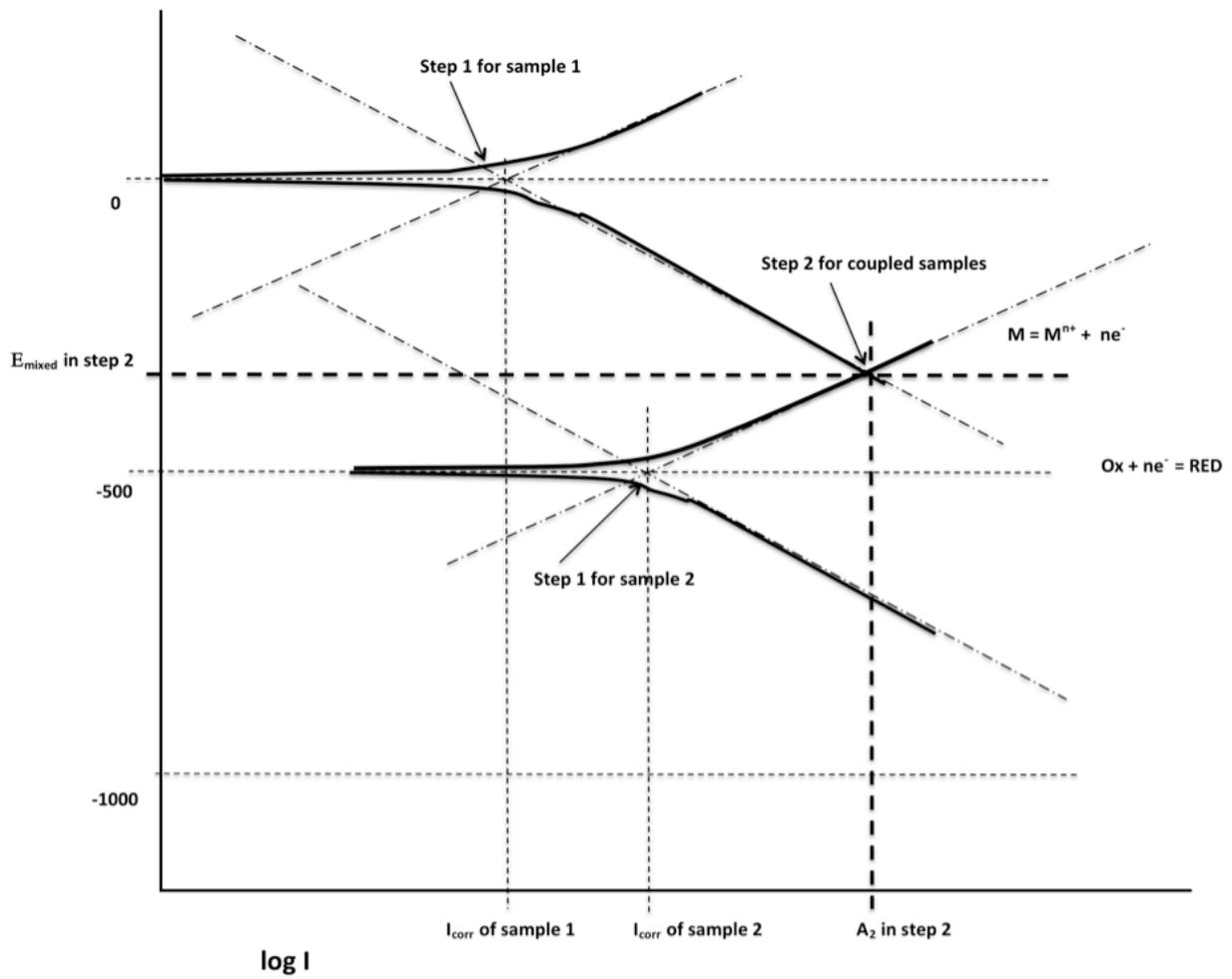


Figure 23. Schematic Evans diagram and polarisation curves illustrating step 2

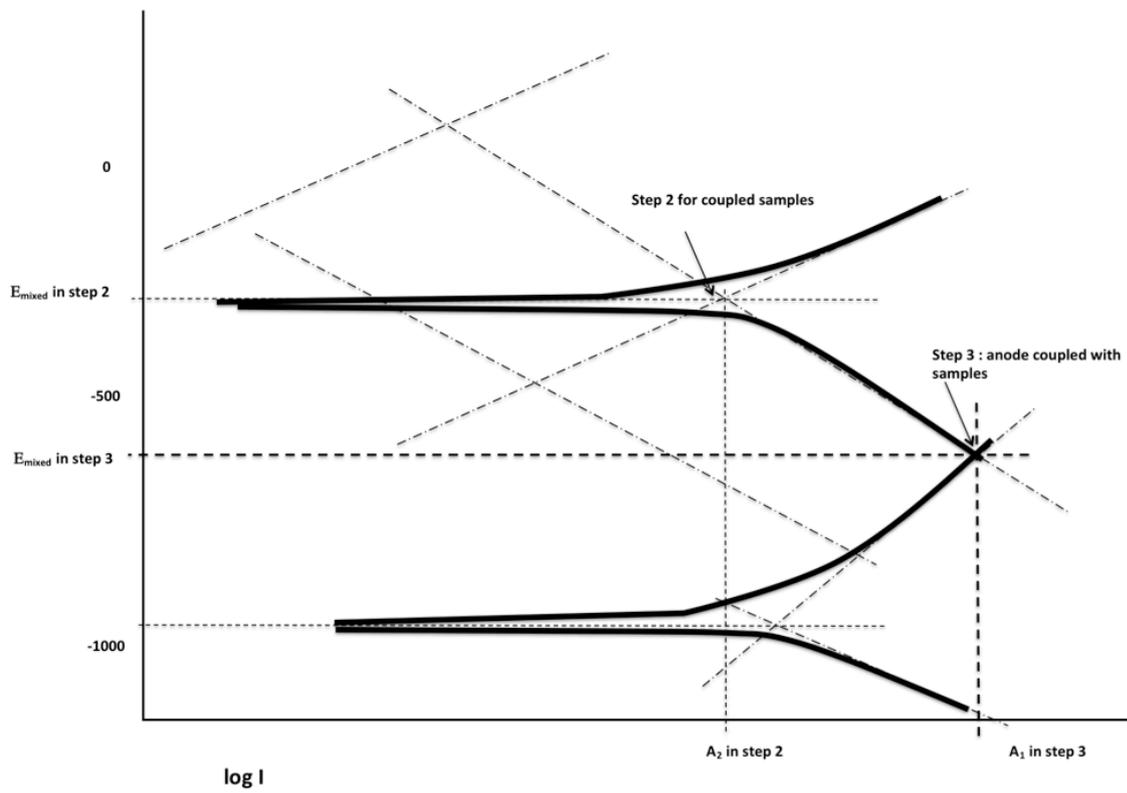


Figure 24. Schematic Evans diagram and polarisation curves illustrating step 3

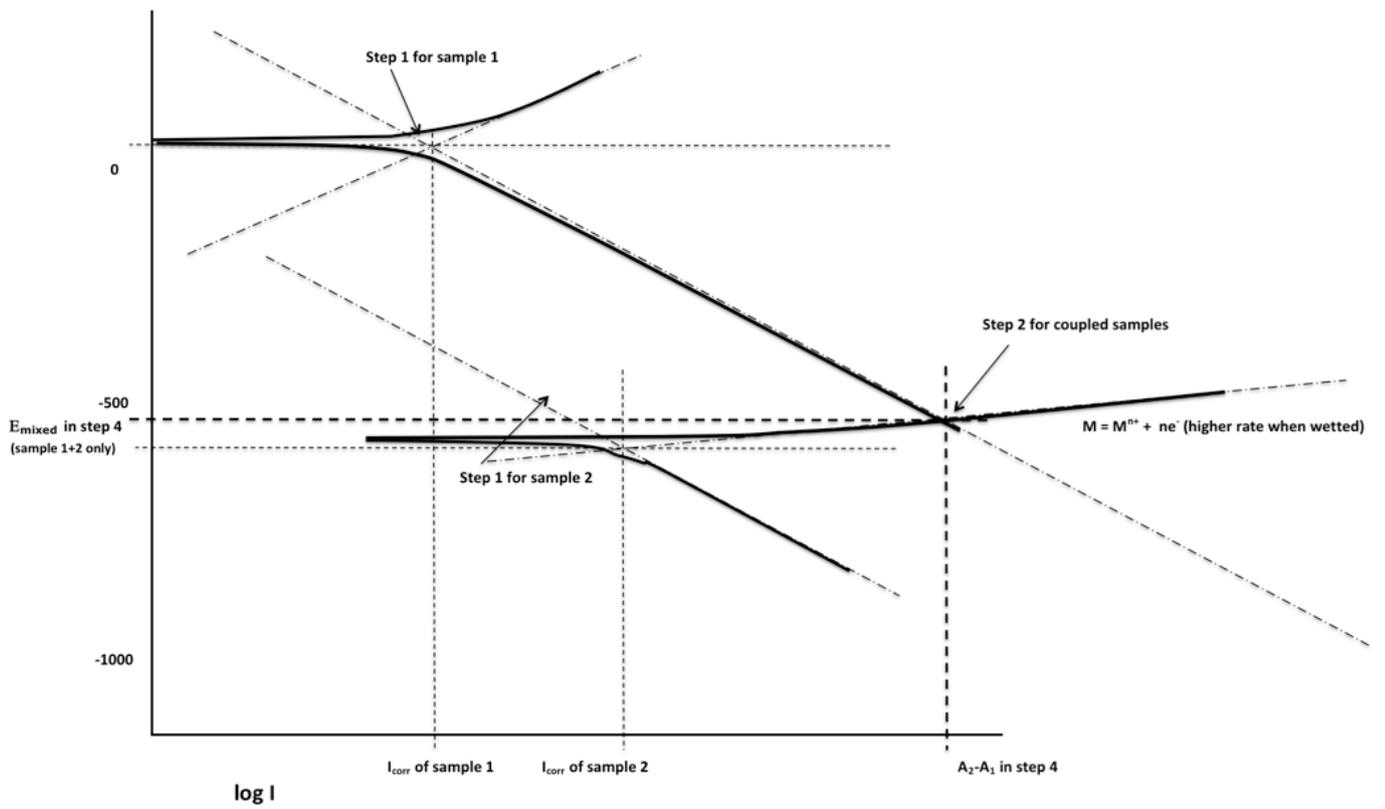


FIGURE 25. Schematic Evans diagram and polarisation curves of the two concrete samples coupled illustrating step 4, assuming the anode would not participate in the coupling.

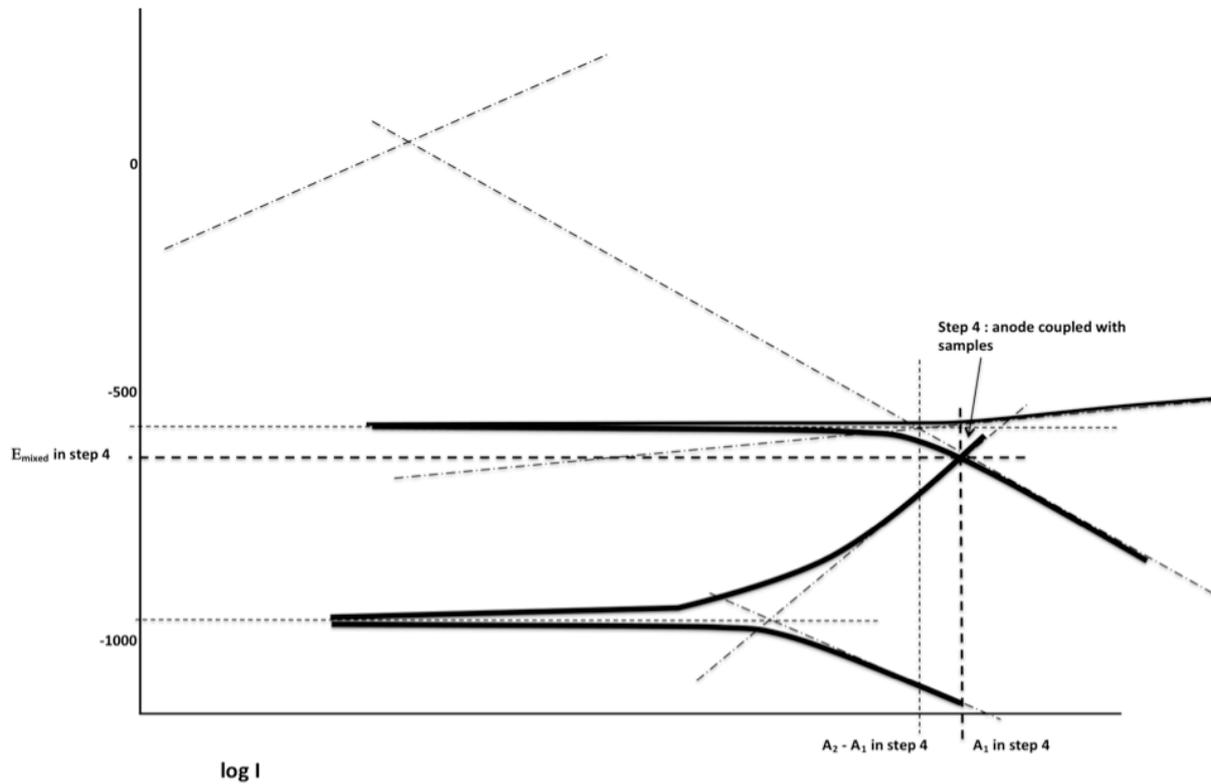


Figure 26. Schematic Evans diagram and polarisation curves illustrating step 4.

5 CONCLUSIONS

This experiment showed very clearly the effect of macrocell corrosion on steel polarisation in concrete samples.

It also showed that the combination of passive and active bars in each close vicinity produce such an amount of corrosion current being able to give strong polarisation effects hence errored depolarisation readings.

It is therefore strongly recommended that CP-designers consider these effects in their CP-system designs to avoid errored readings and misinterpretations.

6 REFERENCES

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- Kelly, R.G. & Scully, J.R. 2003. Electrochemical techniques in corrosion science and engineering.