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CORROSION OF UNDERGROUND PIPELINES ON COATING DEFECTS

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ABSTRACT

During checking excavations, detailed measurements of the conditions under the coating defects have been made: pH, potential, analysis of the solution trapped under the coating and soil analysis, characteristics of corrosive products etc. Measuring and sampling techniques suitable for work on site have therefore been developed.

In the laboratory, an experimental device has made possible to reproduce the different situations observed on site: open coating defects, with or without flow of underground water, and waterproof or oxygen permeable coating.

Several measurements have been carried out in the laboratory and a detailed analysis of the results is presented.

RESUME

Lors de fouilles de contrôle, des mesures détaillées des conditions sous les défauts de revêtements ont été faites: pH, potentiel, analyse de la solution enfermée sous le revêtement et analyse du sol, nature des produits de corrosion etc. Pour cela des techniques de mesures et de prélèvement adaptées au travail sur site ont été développé.

Au laboratoire, un dispositif expérimental a permis de reproduire différentes situations, observées sur le terrain: défaut de revêtement ouvert, avec ou sans circulation de l'eau souterraine, et revêtement étanche ou perméable à l'oxygène.

De nombreuses mesures ont été faites en laboratoire et une analyse détaillée des résultats est présentée.

ZUSAMMENFASSUNG

Bei Kontrollgrabungen wurden detaillierte Messungen der Bedingungen unter Ummantelungsmängeln durchgeführt: pH-Wert, Potential, Analyse der unter der Ummantelung eingeschlossenen Lösung und Bodenanalyse, Art der Korrosionsprodukte, usw. Zu diesem Zweck wurden Mess- und Entnahmetechniken entwickelt, die an die Arbeit vor Ort angepasst sind.

Im Labor ermöglichte eine Versuchsvorrichtung die Reproduktion verschiedener Situationen, die im Gelände beobachtet wurden: offener Mangel der Ummantelung mit oder ohne unterirdische Wasserzirkulation und sauerstoff-undurchlässige oder – durchlässige Ummantelung.

Zahlreiche Messungen wurden im Labor durchgeführt. Eine detaillierte Analyse der Ergebnisse wird präsentiert.

INTRODUCTION

Excavations of pipelines in places where corrosion had been detected by pigging have revealed some corrosion problems at various types of coating holidays.

The depth of corrosion at these defects and the age of the pipelines were known, but it was not known if the corrosion had developed during the whole of that time or if it was recent. One of the aims of this study is to answer that question so as to be able to manage the future of those pipelines in complete safety.

The present work is based on many investigations in the field and on a literature survey. A simulation experimental set-up with corrosion and chemistry sensors at coating defects was realized. These simulated defects were studied in different situations (soil chemistries, type of coating) and the evolution of corrosion was followed.

MATERIALS AND METHODS

Disbonding of coatings was simulated by assembling sheets of heat-sealing polymer materials and sheets of carbon steel. The size, gaps and types of the defects reproduced those observed during the field investigations: with or without renewal of the solution, with regular purges and with permanent circulation through two holidays.
The distance between the mouth and the tip (the farthest point from the opening) of the crevice under the disbonded coating was between 30 and 60 cm, which is mentioned in the literature as the most sensitive to corrosion. The gap between the steel and the disbonded coating was variable, from 0 to 2 mm. This corresponds to many defects observed on site.
The metal exposed in the crevice is divided into 12 squares of 50 x 50 mm x 25 µm which are interconnected by exterior connections to allow for local current densities between adjacent zones or from the exterior anode. The currents were measured by microammeters with zero resistance.
Potentials were measured at different depths in the crevice by three capillary junctions ending in the crevice near its mouth (zone A, 0 to 20 cm from the mouth), at middle length (zone B, 20 to 40 cm) and near the tip (zone C 40 to 60 cm).
Potentials were measured with the CP current "on" and "off". The capillary junctions allow the "on" potentials to correctly indicate the local potentials as influenced by CP. The "off" potentials were measured for confirmation.

The capillary junctions were also used to sample local crevice solutions for pH and other measurements.
Three of the 12 interconnected sheets of carbon steel are electrical resistance probes, made of a 25 µm thick sheet and positioned at the mouth, at middle length and at the tip. Thus, corrosion rate was measured by electrical resistance during the test and by weight loss at the end of the tests. The sensitivity of the electrical resistance probe is high and the results can be considered as instantaneous rates.

A series of specific precautions was taken to expose only one side of the steel plates, to allow an easy optical examination during the test, to allow verification of the corrosion rates measurements by weight loss without error due to electrical connections and to avoid chloride pollution from the reference electrodes and entry of oxygen through the capillary junctions.

The simulated disbonding was put in a 15 l glass container and connected to a 40 cm² steel surface, which is under cathodic control at –1100 to –1200 mV$_{sce}$ by means of a potentiostat.

One opening in the form of 5 cm long slits represents the mouth of the creviced coating defect. A second similar opening allows, at will, to purge the crevice (renew the volume of solution) or to install a permanent flow of solution through the crevice, as it may happen in reality.

Figure 1 is a schematic representation of the experimental set-up.

Different polymer materials were used to investigate the effect of permeability to oxygen:
-    a high oxygen permeability material :
low density polyethylene, thickness 80 µm, oxygen permeability 2.2 10^{-13} cm³.cm.cm^{-2}.s^{-1}.Pa^{-1} volumetric electrical resistance 10^{15} to 10^{18} ohm.cm
-    a low oxygen permeability material :
polyester, thickness 205 µm, oxygen permeability 0.015 to 0.04 10^{-13} cm³.cm.cm^{-2}.s^{-1}.Pa^{-1}, volumetric electrical resistance $> 10^{14}$ ohm.cm.

Bulk test solutions:
-    One low-conductive solution:
$NaHCO_3$ 5.10^{-4} M + $CaCl_2$ 5.10^{-4} M + $Ca_3(PO_4)_2$ 5.10^{-4} M
-    One conductive solution (NS4, reference solution used in Canadian studies):
KCl $1,64.10^{-3}$ M + $NaHCO_3$ $5.75.10^{-3}$ M + $CaCl_2.2H_2O$ $1.23.10^{-3}$ M + $MgSO_4.7H_2O$ $0.26.10^{-3}$M, pH brought to 7 by addition of HCl.

RESULTS

Three tests were conducted in typical conditions and are reported here:
-    a low oxygen permeability coating and a low conductive solution,
-    the same low permeable coating and a conductive solution
-    a coating permeable to oxygen and a conductive solution.

Low oxygen permeability coating in a low conductive solution

The potentials on the three zones of the crevice (near the mouth, at middle length and at the tip of the disbonding) decrease rapidly. After one day, the potentials stabilise at –850 mV$_{sce}$ at about 50 mm of the mouth and at –700 mV$_{sce}$ at middle length and at the tip (the end) of the crevice (figure 2).

A correction for the ohmic drop is necessary for the surfaces near the mouth, which receive the current. Without this correction, the apparent potential measured near the mouth is too low.

The current density received near the mouth of the crevice (on the first 50 mm long sample) is definitely and significantly cathodic (50 to 90 $\mu A/cm^2$). But already at 100 mm of the mouth, the cathodic current density is much lower (0.2 to 1.0 $\mu A/cm^2$) and eventually changes occasionally to anodic. The anodic polarisation inside the crevice is enhanced by a flow of solution in the crevice. The same is observed further down into the crevice (figure 3).

The pH at the mouth of crevice increases rapidly to 12-12.5. At mid-length and at the tip of the crevice, pH decreases first to 5-5.5, then increases slowly (more slowly at tip). When CP is interrupted, the pH at mouth decreases to 9.5 after 5 days. When the crevice is purged or when there is a flow inside the crevice, pH becomes similar to that of the bulk solution.

The metal in the depth of the crevice is slightly black. Corrosion is insignificant in the whole crevice, with the exception of periods of purges or flow in the crevice. A flow established after 27 days immediately led to corrosion rates up to 0.4 mm/y at mid-length.

Low oxygen permeability coating in a conductive solution

The potentials on the three zones of the crevice decrease below –800 mV$_{sce}$ (after 7 days for the middle and 14 days for the tip of the crevice), figure 4.

The current densities are larger and definitely cathodic near the mouth (up to 120 $\mu A/cm^2$). At 10 cm of the mouth the current is still cathodic but smaller (1 to 3 $\mu A/cm^2$). Further down the crevice, the current density is even smaller and of changing polarity (cathodic and anodic) during 10 to 15 days, after which it stabilises at a low cathodic value (figure 5).

The measurements of the instantaneous corrosion rate show zero for the zone A near the mouth, 200 $\mu m/y$ at beginning for zone B (middle) falling down to 10 $\mu m/y$ after a few days, and the same for zone C but more slowly.

The pH changes with time are similar to the previous test in less conductive solution: pH increases rapidly at the mouth when CP is applied (to pH 13), pH decreases first to 6.5 then increases to 13 after 20 days in the middle of the crevice and decreases to 6 and increases more slowly at the tip (11.5 after 29 days).

The steel surface showed a few black spots from the beginning of the test but no or negligible corrosion after 20 days.

Coating permeable to oxygen and a conductive solution.

Near the mouth, the potentials decrease slowly (stabilise at -870 mV$_{sce}$ after 10 days, while the potentials outside the crevice is –1100 to –1200 mV$_{sce}$). Further away from the crevice opening, the potential never reaches the protection potential (stabilises at –600 to –700 mV$_{sce}$).

The current density for the steel near the mouth is similar to that in conductive solution with a non-permeable coating (cathodic, up to 120 µA/cm²). The current densities further down in the crevice are much chaotic and mostly cathodic up to 15 cm into the crevice and also chaotic but often markedly anodic at a greater distance from the mouth. The variations in current density and polarity are often rapid (figure 6).

The corrosion rate near the mouth decreases to very low values (30 µm/y after 2 days and 0 at 10 days). But the corrosion rate further down in the crevice are large at the beginning (450 to 500 µm/y), decrease and increase again with time (400 and 600 µm/y after 15 days). The highest corrosion rate was observed at mid-length. The corrosion rate at the tip of the crevice, although important, was generally lower than at mid-length (figure 7).

The pH increased rapidly up to 13 near the mouth but remained low (pH 6) deeper in the crevice, during the whole test duration.

Red-brown corrosion products were visible from the beginning of the test. After 28 days, the test set-up was opened and perforation was observed locally on the 25 µm thick samples, at distances from the mouth equal or greater than 10 cm.

At the end of this test (after 28 days), 0.5 ml was sampled in each zone of the crevice and was analysed for pH, carbonate and bicarbonate equivalent and compared with the bulk solution.

The results are :

	Bulk	Mouth	Mid-length	Tip
pH	7	>13	6	6
OH^- (mg/l)	0	24	0	0
CO_3^{--} (mg/l)	0	258	0	0
HCO_3^- (mg/l)	183	0	366	396

DISCUSSION

The tests with a coating impermeable to oxygen showed that in disbonded areas where the coating is an obstacle to cathodic protection and when the solution is not circulating, the corrosion eventually comes to a stop, even very far away from the opening of the crevice. During a transitory period, some surfaces deep into the crevice are polarized slightly anodic, because of the absence of oxygen and consequently low potentials, while at a smaller distance from the mouth, potentials are slightly higher because CP is ineffective and because there is some oxygen brought in by diffusion from the bulk. With time, all oxygen is consumed (by corrosion, with precipitated corrosion products forming an obstacle to the oxygen diffusion), the pH increases in the whole crevice by diffusion of alkaline solution from the mouth and corrosion stops. Before that, it is probable that the precipitation of corrosion products produces a slight pH decrease (by hydrolysis of soluble iron), which is progressively neutralized by diffusion of the alkaline

mouth solution. In our tests, these modifications took a few hours for a little conductive bulk solution and about 20 days for a more conductive solution.

When the crevice is purged or when there is a flow of solution, corrosion increases rapidly. This was observed also in the field: no corrosion was observed on a factory coating disbonded over a large area with a gap of 1 mm, filled with stagnant water. But on the same pipe, a few dm away, under a disbonded insulating tape applied on site to protect the welds and open to a flow of solution, serious corrosion was observed with local pH around 6 [1].

The test with an electrically insulating coating which is permeable to oxygen indicated that the potentials hardly decrease in the immunity region (below –800 mV$_{sce}$) even rather close to the crevice opening. Further down in the crevice, immunity is not attained, no alkalization is observed and corrosion remains important during the course of time. Only the surface close to the mouth (5 cm) received a large current density (120 µA/cm²). Already at 10 cm, the cathodic current density was smaller than 5 µA/cm². Anodic zones were identified at different distances from the mouth (for example 20, 30 and 60 cm) and corrosion rates there decreased when CP was interrupted. Cathodic zones existed at intermediate distances (for example 34, 45 and 55 cm). In addition, several of these zones changed polarity during the test (anodic to cathodic or vice-versa) while the potentials were rather constant. These changes are attributed to local differences in oxygen availability and to hydrolysis and precipitation of corrosion products with local pH changes. The correlation between potentials, current density, pH and analysis of solution and corrosion products needs to be further clarified. The same type of experimental set-up could serve this purpose.

A flow of solution under the disbonded coating may produce large corrosion rates. In this study, the potentials attained because of a flow of an aerated solution were much higher (-400 to –200 mV$_{sce}$) than the potentials under a disbonded coating permeable to oxygen (-700 mV$_{sce}$).
However, the corrosion rates measured are in the same range whether corrosion is due to oxygen permeation (0.3 to 0.5 mm/y) or to a flow of solution (up to 0.4 mm/y). These figures are similar to other data or defects with a flow [2].

Corrosion observed under disbonded coatings was never homogeneous, but local with the shape of craters or corroded patches, as mentioned in [3]. A number of factors may explain this: crevice gap, local flow, concentration of corrosion products, precipitation and the resulting local pH, local currents etc.

The data collected in this study could be used in models to assess corrosion rate in the longer-term [3].

CONCLUSION

With the conditions selected for the tests performed, it was possible to simulate correctly situations encountered on site. The results obtained provide more complete information on the problem. The experimental set-up proved convenient. However, more detailed information could be obtained by making more frequent and simultaneous measurements of potentials, current density, pH, solution analysis, observation of precipitation processes and analysis of corrosion products.

If the coating is impermeable to oxygen, and if there is no circulation of solution, corrosion under long disbonding defects in the coating eventually comes to a stop after some time, even very far away from the opening of the defect.

This is attributed to two major factors: the progressive consumption of all the oxygen present due to the penetration of the CP and to diffusion of oxygen from the crevice tip, and the progressive alkalization of all the solution under the disbonding due to diffusion of the alkaline solution near the mouth. In our tests, this took a certain time (up to 20 days depending on the conductivity of the solution). Before stabilization, local corrosion events can occur temporarily, because of local pH changes due to hydrolysis and precipitation of corrosion products, obstacles to oxygen diffusion, local anodic polarization etc.

When there is circulation or frequent purges of the solution in the defect, high instantaneous corrosion rates are immediately observed. Figures of the order of 0.4 mm/y were measured. These figures are similar to other date from the literature [2].

If the coating is permeable to oxygen and makes an obstacle to cathodic protection, significant corrosion was observed. Only the zone close to the crevice mouth was finally protected and saw its pH rise after about fifteen days. Further down into the crevice, the potentials never reached the typical protection level of –800 mV$_{sce}$. In addition, sizeable anodic coupling current densities were measured which caused local corrosion in the range of 0.3 to 0.5 mm/y in the conditions of our tests.

The definite importance of the nature of the polymer coating is underlined. Polyethylene is typically permeable to oxygen. Unfortunately, polyethylene was extensively used at a time (between 1954 and 1995 [4]) for factory coating and as tape, especially for repair at the girth welds. It is only recently that these tapes were modified for lower oxygen permeability.

Tracing the use of oxygen permeable tapes or coatings is one tool for managing the problem of corrosion at disbondings of buried pipelines under cathodic protection. Measurement of oxygen permeability is now part of the routine examination procedure.

More work is needed to clarify the significance of the often observed ferrous carbonate deposits and of modifications of the local chemistry under disbonded coatings. More work is also necessary to clarify the reasons and sequences of local anodic polarization on some zones inside the disbonded crevice. More experiments using basically the same test set up could help for this.

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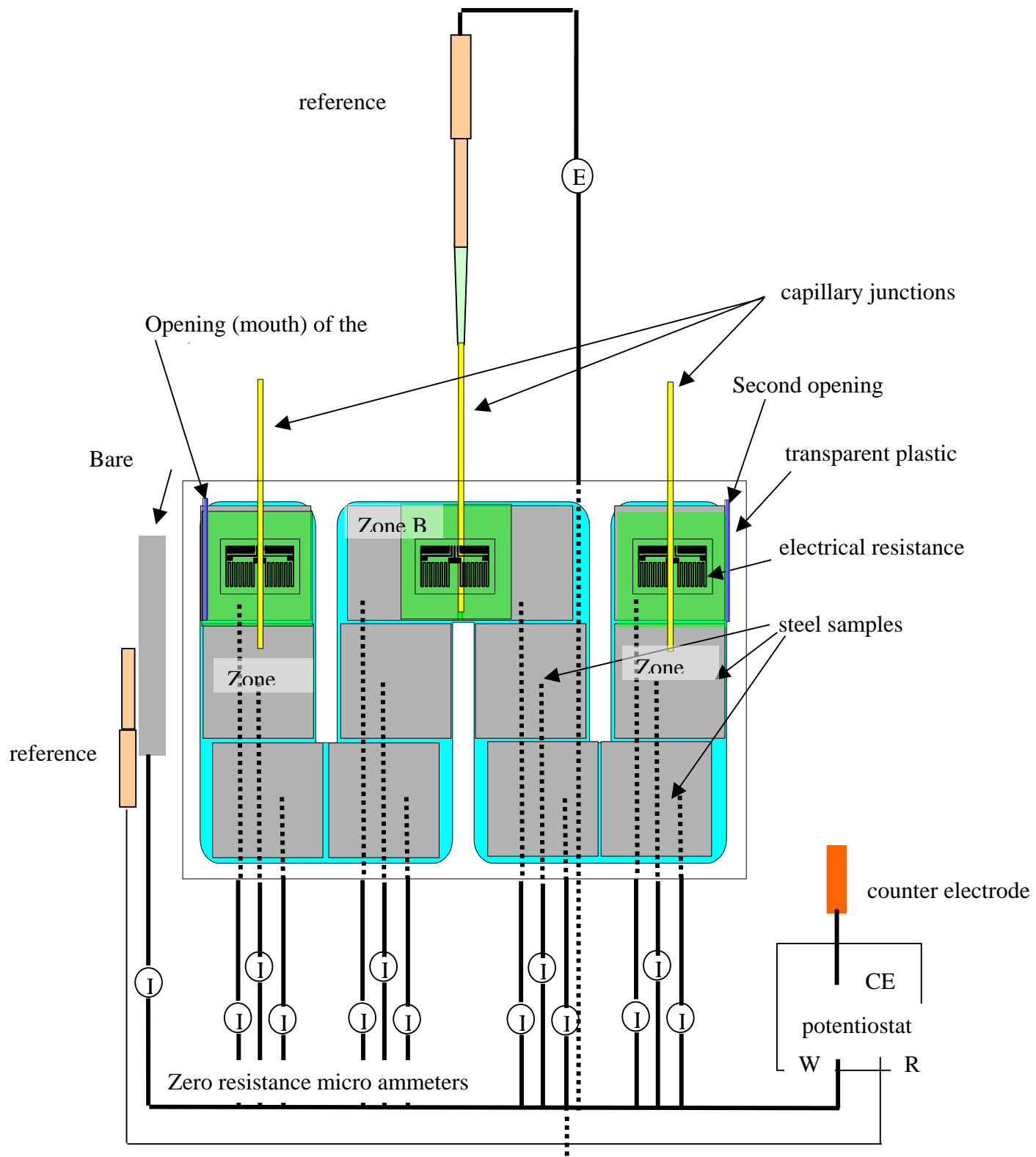
Figure 1: Schematic representation of the experimental set-up
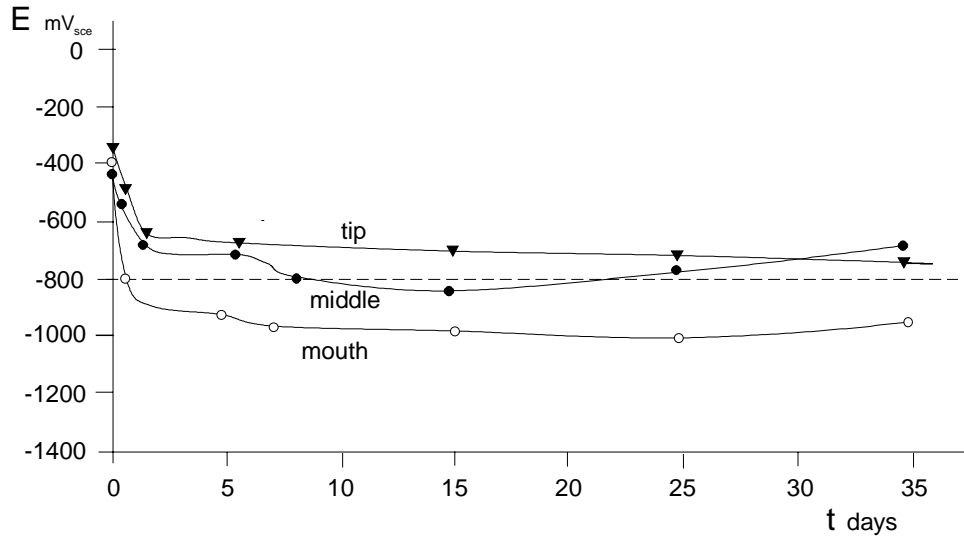
Figure 2: Potentials near the mouth, at middle length and at the tip of the disbonding as a function of time, under CP. Low oxygen permeability coating in a low conductive solution.
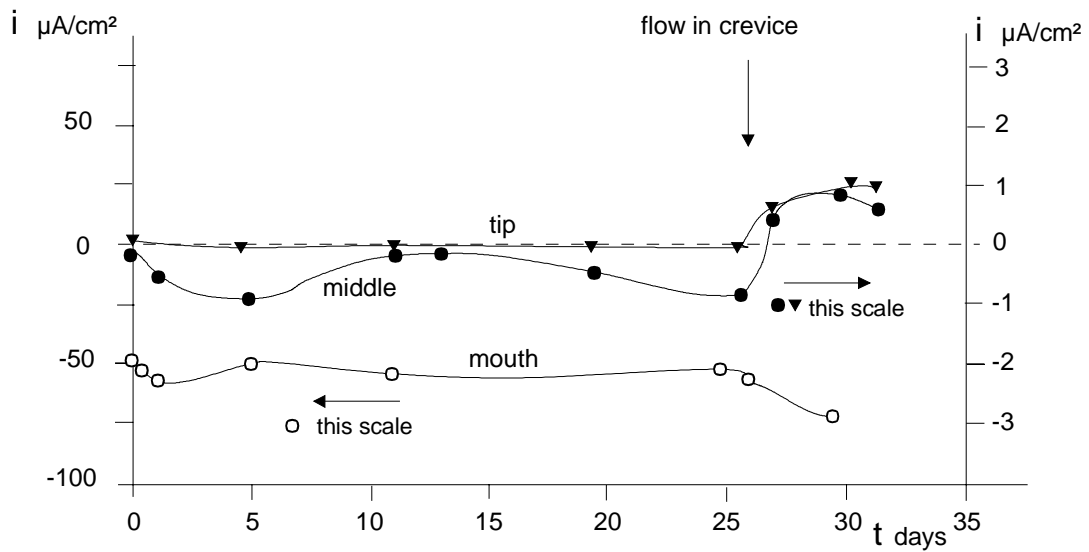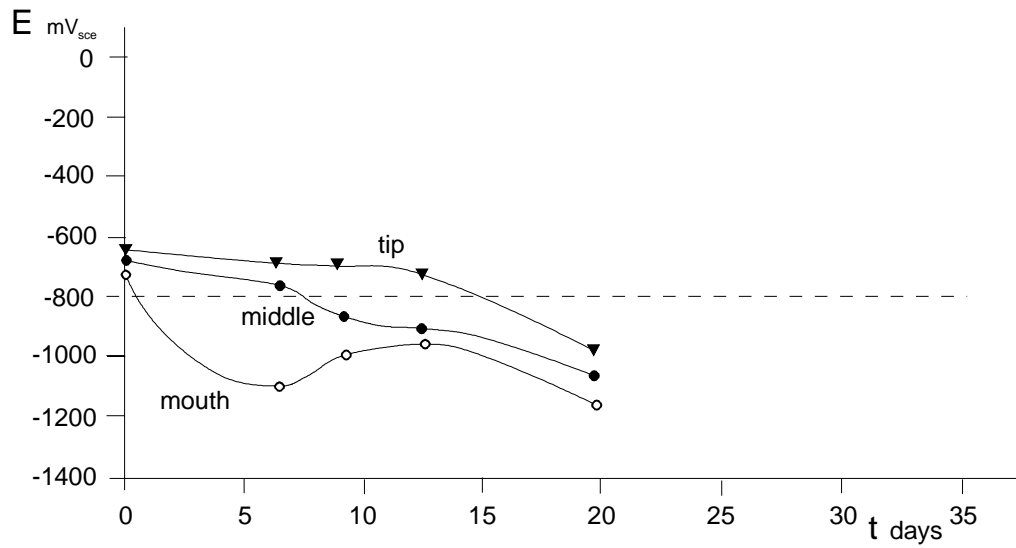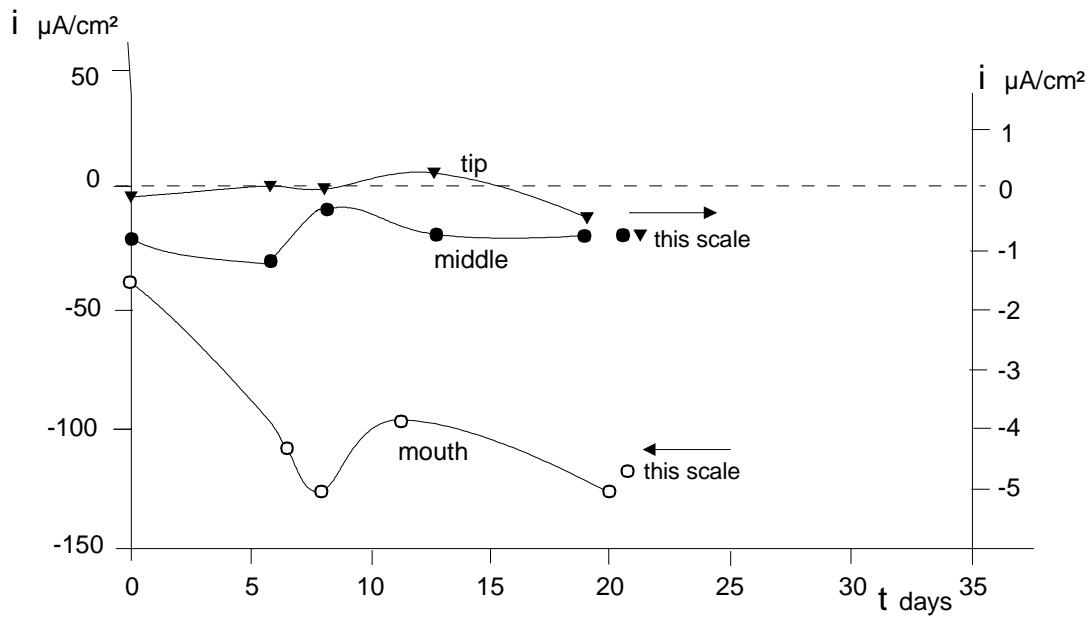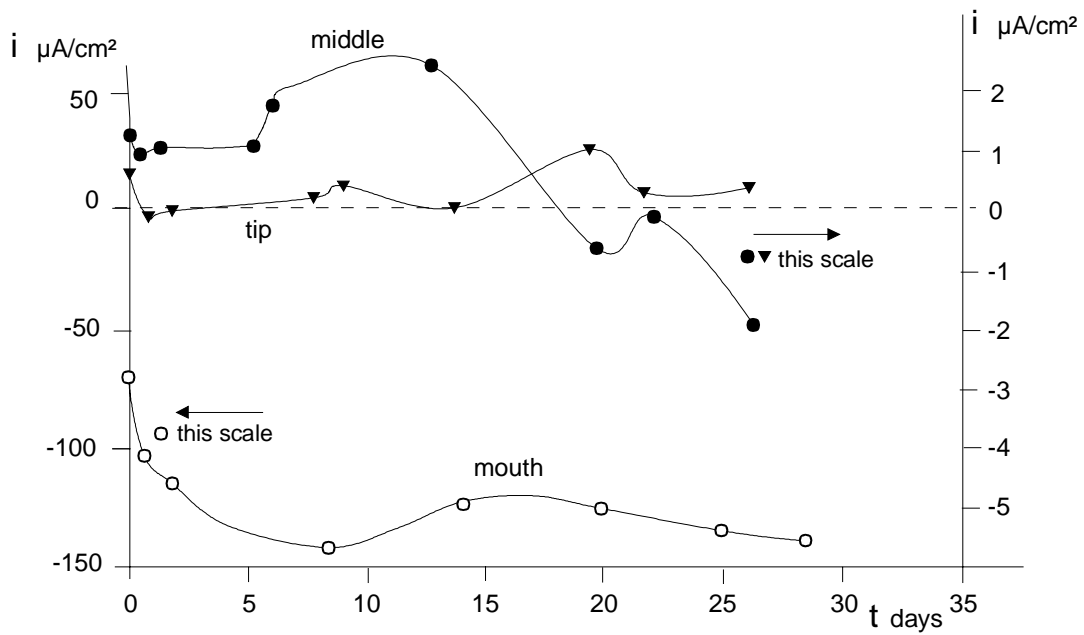

Figure 3: Current density at different distances in the crevice as a function of time
Effect of a flow in the crevice

Figure 4: Potentials near the mouth, at middle length and at the tip of the disbonding as a function of time, under CP. Low oxygen permeability coating in a conductive solution.

Figure 5: Current density at different distances in the crevice as a function of time. Low oxygen permeability coating in a conductive solution.

Figure 6: Current density at different distances in the crevice as a function of time. High oxygen permeable coating in a conductive solution.
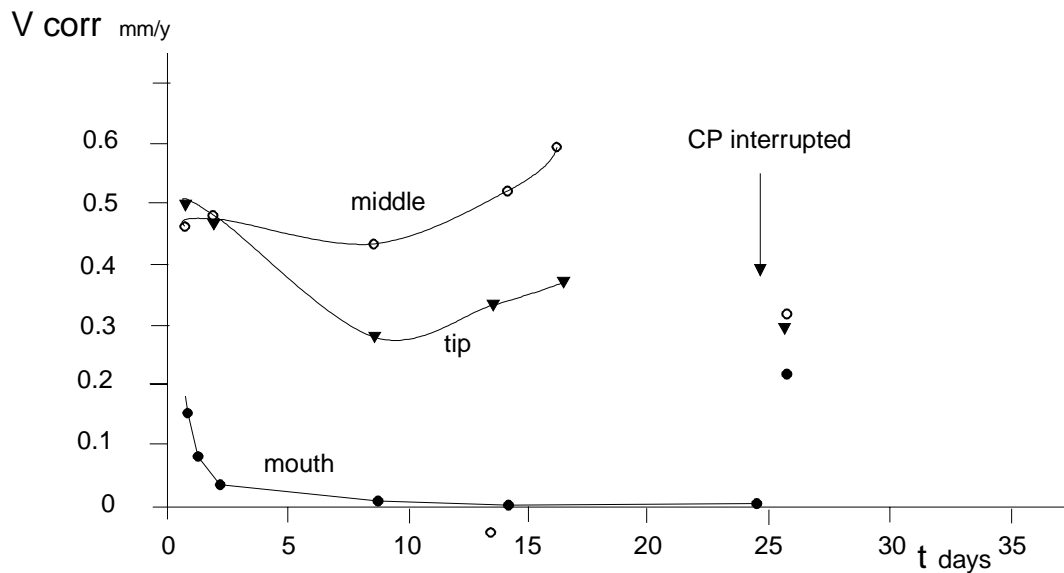
Figure 7: Corrosion rates in the crevice as a function of time. High oxygen permeable coating in a conductive solution.