

CEOCOR DRESDEN – SECTOR A

Paper n. 07

A NEW ELECTROCHEMICAL METHOD FOR THE DETECTION OF AC-CORROSION

M. Büchler, F. Stalder, and H.-G. Schöneich*

SGK, Swiss Society for Corrosion Protection, Technoparkstr. 1, CH-8005
Zürich, Switzerland

*Ruhrgas AG, Essen, Germany

Abstract

Corrosion due to induced ac-voltages on cathodically protected pipelines represents a significant risk to the durability and safety of these structures. To date, the only generally accepted criterion for the determination of the corrosion risk due to ac-currents is based on the use of coupons and the measurement of the ac-current density. However, it was found that the spread resistance of the coupons can significantly vary over time due to formation of chalk layers or the formation of hygroscopic alkali hydroxides in the soil. Moreover, the induced ac-voltage depends on the operation status of the power lines or the train system. Therefore, significant variation of the ac current density can be observed over time resulting in a possible underestimation of the of the corrosion risk in inspection measurements. These problems can be overcome by new electrochemical methods allowing for the detection of ac corrosion. Results of laboratory and field investigations are discussed.

Zusammenfassung

Korrosion aufgrund von induzierten Wechselspannungen auf kathodisch geschützten Leitungen stellt ein bedeutendes Risiko für die Dauerhaftigkeit und Betriebssicherheit dieser Strukturen dar. Bisher ist die Wechselstromdichte, welche an Messproben bestimmt wird, das einzige generell akzeptierte Kriterium zur Beurteilung der Korrosionsgefährdung. Es wurde jedoch gefunden, dass der Ausbreitungswiderstand von Messproben im Verlaufe der Zeit aufgrund der Ausbildung von Kalkschichten oder der Bildung von hygroskopischen Alkalihydroxiden erheblich variieren kann. Weiter ist das Ausmass der Wechselstromdichte in hohem Masse vom gegenwärtigen Betriebszustand des Beeinflussers ab. Es können daher erhebliche Variationen in der Wechselstromdichte auftreten, welche zu einer möglichen Unterschätzung der Gefährdung beim Zeitpunkt der Messung führen können. Diese Probleme können mit einer neuen elektrochemischen Methode überwunden werden. Ergebnisse aus Labor- und Felduntersuchungen werden vorgestellt.

Résumé

La corrosion due aux tensions alternatives induites sur les lignes cathodiquement protégées représente un risque significatif à la longévité et à la sûreté de ces structures. Jusqu'ici, le seul critère généralement admis pour la détermination du risque de corrosion dû aux courants alternatives est basé sur l'utilisation des coupons et la mesure de la densité du courant alternative. Cependant, on a constaté que la résistance des coupons peut changer dû à la formation des couches de craie ou aux hydroxides d'alcalis hygroskopiques. D'ailleurs, la tension alternative dépend du statut d'opération des lignes de puissance ou du système de train. Par conséquent, on peut observer la variation significative de la densité de courant alternative. avec le temps ayant pour résultat une sous-estimation possible du risque de corrosion dans des mesures d'inspection. Ces problèmes peuvent être surmontés par une nouvelle méthode électrochimique tenant compte de la détection de la corrosion courant alternative. Des résultats des investigations de laboratoire et de champ sont discutés.

INTRODUCTION

The phenomenon "AC corrosion" was investigated very detailed since the observation of the first corrosion damages induced by AC corrosion on cathodically protected pipelines in the 1988 [1, 2]. Despite of all these investigations, the involved mechanisms are still not understood and reliable techniques for the determination of the corrosion risk are not available.

In general, it is well established that the AC corrosion can only occur if the AC current density exceeds 30 A/m^2 [3-5]. Nevertheless, corrosion attack was also observed on samples with significantly lower current density [6]. This may be caused by the formation of a chalk layer on the coupon surface, which decreases the available surface area and, as a consequence, results in an increased local current density. Moreover, it was found that also high current densities do not necessarily lead to corrosion attack. While the ac-current densities determined on coupons do provide information on the corrosion state, the ac potential measured on pipelines were found to be merely an indicator than a criterion. In extended field investigations corrosion attack was found on samples that had less than 5 V ac potential [6]. The measurement of the so-called instantaneous off potential is reported to offer access to the polarization of the metal surface due to the ac current [7]. As the information is independent on the surface area it would allow to obtain information about the corrosion state of coupons independent on the partial covering of the surface with a chalk layer. However, it was found that corrosion attack also occurs on samples where the instantaneous off potential is below the cathodic protection potential [6]. In more recent work it was shown that the increased data acquisition rate of up to 2 MHz did not result in a more reliable indication of the occurrence of ac-corrosion [8]. Moreover, it was found that the results strongly depend on the chemical composition of the soil. Especially the presence of calcium ions caused a significant change of the depolarization behavior of metal surface.

As a consequence, a detailed investigation of the processes taking place on the metal surface during cathodic protection in combination with ac influence was performed. The results obtained in these investigations are presented.

EXPERIMENTAL

For the simulation of the electrochemical behavior of steel, electrochemical experiments in various NaOH solutions were performed. The investigated surface area was 1 cm^2 in all tests. A Jaissle Potentiostat Galvanostat PCT 1002 in combination with a computer was used for the electrochemical control. These electrolytes were prepared from reagent grade chemicals and de-ionized water. In some cases oxygen was removed from the electrolyte by purging with nitrogen. All potentials are referred to saturated Copper/Coppersulfate electrode (CSE).

Table 1: Composition of the artificial soil solution

| | solution with calcium |
|---|-----------------------|
| NaHCO_3 | 2.5 mol/l |
| $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ | 2.5 mmol/l |
| $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | 2.5 mmol/l |
| $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ | 5 mmol/l |

For the simulation of the behavior in soil, coupons were exposed to artificial soil solution in quartz sand. The composition of the electrolyte is given in Table 1. The coupons were cathodically polarized with 3 A/m^2 and subjected to an ac-current load of 100 A/m^2 . A detailed description of the experimental setup is given elsewhere [9].

RESULTS AND DISCUSSION

The detailed investigation of the instantaneous off-potential measurement shows clearly the predominant influence of the soil composition. In order to obtain a better understanding of the involved processes a detailed investigation of the influencing parameters was performed.

It is well known that the cathodic protection results in an increase of the pH-value in front of the metal surface due to oxygen reduction and hydrogen evolution. Depending on the current density, the spread resistance, the morphology of the soil and the hydrodynamic condition very high pH-values can be obtained. It is often pointed out that at high pH values the formation of soluble iron compounds is thermodynamically possible [10]. Hence, the formation of a passive film is not possible at elevated pH and low potentials. Additionally, the potential for cathodic protection is decreasing with increasing pH. In order to investigate the electrochemical behavior of steel in highly alkaline environment polarization scans in de-aerated electrolyte solutions were performed. The results are shown in Fig. 1. With increasing pH-value an increased passive current density is observed. In the case of saturated NaOH solution the current density is increased for more than a factor of 10. Hence, increased dissolution rates have to be expected in the case of potentials anodic of the cathodic protection potential. The results in Fig. 1 additionally demonstrate that the cathodic protection potential is decreased with increasing pH. Therefore, a coupon that is electrochemically polarized to -1.1 V CSE will change from a cathodic protection to an anodic situation when the pH value of the metal surface is increased over time.

It is generally assumed that ac corrosion is caused by short-term anodic polarization of the metal surface. This anodic polarization results in metal dissolution. In order to investigate the electrochemical processes occurring during alternating anodic polarization cyclic voltamograms in de-aerated 0.1 M NaOH were recorded. The results are shown in Fig. 2. The first cycle shows passivation comparable to the results obtained in Fig. 1. In the second cycle anodic oxidation peaks at -0.72 V CSE and cathodic reduction peaks at -1.1 V CSE are occurring. Their size increases with every consecutive cycle. This behavior can be explained as follows (Fig. 3): After the formation of a protecting passive film in the first anodic cycle the cathodic polarization results in the reduction of the oxide film to a porous Fe(OH)_2 . In the consecutive cycle a new passive film is formed and the porous layer is oxidized to FeOOH . This porous layer does not exhibit any protective properties since the passive current density is identical with every cycle. In the consecutive reduction both, the FeOOH and the passive film are reduced to Fe(OH)_2 . Therefore, the thickness of the porous layer is increased with every oxidation/reduction cycle. There are indications that a similar process is occurring on cathodically protected coupons. Some excavated coupons were covered with several hundred micrometers of dark iron oxides.

Based on this result it can be assumed that the iron dissolved in alkaline solution is not soluble and is therefore accumulated in front of the coupon. In soil this process is even more pronounced, since the hydrodynamic is even more limited. Moreover, the cathodic protection current will assure that at least parts of the accumulated iron ions are reduced to Fe(II) . If these considerations are correct, the amount of accumulated corrosion products in front of the coupon can be determined with an electrochemical measurement. In numerous investigations it was found that the galvanostatic oxidation is the most efficient method. The results for coupons exposed to artificial soil solution in quartz sand for seven days under cathodic

protection current density of 3 A/m^2 and different ac-currents are shown in Fig. 4. A galvanostatic anodic current load of $100 \mu\text{A/cm}^2$ was applied and the potential development was recorded over time. The sample exposed to 100 A/m^2 showed first some increase in potential, which is followed by a plateau. Based on the results in Fig. 2 it is known that this plateau can be attributed to the oxidation of Fe(II) to Fe(III) [11]. At about 25 mC/cm^2 a steep increase in potential occurs, which stops sharply when the oxygen evolution is occurring. With increasing charge the potential stays almost constant. For the coupon exposed to 0 A/m^2 a similar behavior is observed. The increase of the potential takes place at significantly smaller charge. No corrosion was observed on the coupon exposed to 0 A/m^2 while significant corrosion was observed on the coupon with 100 A/m^2 . Therefore it can be concluded that the position of the increase of potential Fig. 4 indicates the amount of Fe(II) in accumulated in front of the coupon, which is an indicator for the amount of ac-corrosion.

In Fig. 5 a similar experiment with coupons connected for 2.5 years to a cathodically protected pipeline are shown. The ac-current density was in the range of $40\text{-}120 \text{ A/m}^2$ indicating ac-corrosion to take place. Before the galvanostatic oxidation measurement the coupons were disconnected from the pipeline. An anodic current of 50 mA was imposed by the potentiostat between the coupons and an earth rod that was used as a temporary cathode. Since a significant potential drop is occurring, the current was interrupted in periodic intervals of 5 seconds for 1 second. The potential was recorded immediately after interrupting the current by measuring the potential between a reference electrode at the surface and the coupon. The increase of the potential required about 80-300 times more charge than the coupon in exposed to 100 A/m^2 for seven days in the laboratory test. This is indicating a significantly higher amount of Fe(II) that was accumulated during the 2.5 years of exposure in front of the coupon. Hence, the corrosion attack is significantly higher.

Based on the obtained results it can be concluded that the determination of the amount of Fe(II) in front of a coupon is possible under field conditions. The galvanostatic oxidation is, therefore, a new method allowing determining the corrosion state of a coupon. Since the method determines the amount of iron ions accumulated in front of the coupon, it is independent on the momentary ac-influence of the coupon.

Additionally, the galvanostatic oxidation allows determining the potential at which oxygen evolution is taking place. The results in Fig. 1 show clearly that the oxygen evolution depends on the pH of the solution. This pH dependence is described by equation (1) [10]. The hydrogen evolution depends on the pH-value in a similar way. However, no reliable correlation was found (cf. Fig. 1), since the reaction interferes with the formation of magnetite, as can be concluded from the Pourbaix diagram of iron [10].

$$E = 1.40 - 0.059 \text{ pH [V CSE]} \quad (1)$$

Based on systematic measurements of the oxygen evolution in electrolytes, in concrete, and on excavated coupons the results in Fig. 6 were obtained. The measurements show a linear correlation. Experimentally the values in equation (2) were found in calibration measurements in electrolyte solutions.

$$E = 1.51 - 0.074 \text{ pH [V CSE]} \quad (2)$$

These values deviate from the theoretical ones. This effect may be attributed to electrochemical over-potential for the oxygen evolution. Based on equation (2) it is possible to determine the pH value in the experiments shown in Fig. 5 and 6 (Table 2). The exposure of a coupon to a cathodic current for 7 days results in a significant increase of the pH in front of the metal surface. This effect is even more pronounced for the coupons exposed to cathodic protection for 2.5 years.

Table 2: pH-values determined on the measurements shown in Fig. 5 and 6.

| Fig. | Sample | pH-value |
|------|----------------------|----------|
| 5 | 0 A/m ² | 10.6 |
| | 100 A/m ² | 10.7 |
| 6 | 46 A/m ² | 12.4 |
| | 60 A/m ² | 12.2 |
| | 120 A/m ² | 12.3 |

Based on the presented results it can be concluded that the galvanostatic oxidation allows determining both, the amount of Fe(II) accumulated in front of the metal surface and the pH value of the soil. This type of pH measurement is unique, since the electrochemically active pH-value is determined in front of the metals surface. In the case of certain mass transport conditions this value can be strongly different to the pH a few millimeters away from the coupon.

The obtained results allow some conclusion about the misleading results in the instantaneous off potential measurement. In the Fig. 1, 4 and 5 it is shown that significant anodic currents can flow through a coupon without causing a polarization of the coupon anodic of the protection potential of -0.85 V CSE. As a consequence, even lower potentials could indicate the occurrence of ac-corrosion. In order to obtain more reliable information it would be necessary to consider the pH of the soil. This observation is confirmed by more recent investigations[12]. However, the detailed investigation of various parameters showed clearly, that the depolarization behavior of steel is too complex to allow the determination of the anodic polarization within a single off-potential measurement [13].

CONCLUSIONS

The electrochemical investigation of steel under simulated cathodic protection conditions showed the increased solubility of iron oxides with increasing pH-value. Moreover, it was found that alternating passivation and reduction, as it is found under ac-polarization, results in metal dissolution. This is even the case if the pH of the electrolyte allows the formation of a passive film. In the case of alkaline conditions, these corrosion products are accumulated in front of the metal surface. The amount of corrosion and the thickness of the accumulated corrosion products are increased with every cycle of the ac-potential. Since the amount of accumulated Fe(II) can be determined with galvanostatic oxidation, the degree of ac-corrosion can be determined. This assumption is correct, if the pH is sufficiently high for the precipitation of the iron ions and if the cathodic reduction current is sufficiently high. If the cathodic reduction current is too low, the oxygen dissolved in the soil will oxidize part of the Fe(II). The new measurement can be performed on coupons currently used on most pipeline systems. Additionally, the measurement allows the determination of the pH in the soil within the electrochemically active electrolyte volume.

The investigation of the electrochemical behavior of steel in alkaline solutions demonstrated clearly, that at elevated pH an off-potential of -0.85 V CSE does not necessarily indicate sufficient cathodic protection. The determination of the pH-value in the soil is therefore important for the evaluation of the corrosion risk.

ACKNOWLEDGEMENTS

This work was possible thanks to the generous support of the research fund of the Swiss electrical power companies (PSEL), Ruhrgas AG, SBB AG, BAV, ERI, Swissgas AG and Transitgas AG.

REFERENCES

1. G. Heim, G. Peez, *3R International* **27**, 345 (1988).
2. B. Meier, *GWA* **69**, 193 (1988).
3. D. Bindschedler, F. Stalder, *GWA* **71**, 307 (1991).
4. G. Heim, G. Peez, *gwf*, 133 (1992).
5. D. Funk, W. Prinz, H. G. Schöneich, *3R International*, 31 (1992).
6. M. Büchler, C.-H. Voûte, J. Bieler, F. Stalder, *GWA* **8** (2001).
7. R. Gregoor, A. Pourbaix, in CEOCOR 5th international conference, CEOCOR, c/o C.I.B.E., Brussels, Belgium, (2000).
8. M. Büchler, C.-H. Voûte, F. Stalder, in CEOCOR 6th international Congress, CEOCOR, c/o C.I.B.E., Brussels, Belgium, (2003).
9. C.-H. Voûte, F. Stalder, *GWA* **80** (2000).
10. M. Pourbaix, *Atlas of electrochemical equilibria in aqueous solutions* (NACE, Houston, TX, 1974).
11. M. Büchler, P. Schmuki, H. Böhni, *J. Electrochem. Soc.* **144**, 2307 (1997).
12. H.-G. Schöneich, T. Heim, M. Melis, *3R International* **42**, 696 (2003).
13. M. Büchler, *in preparation*.

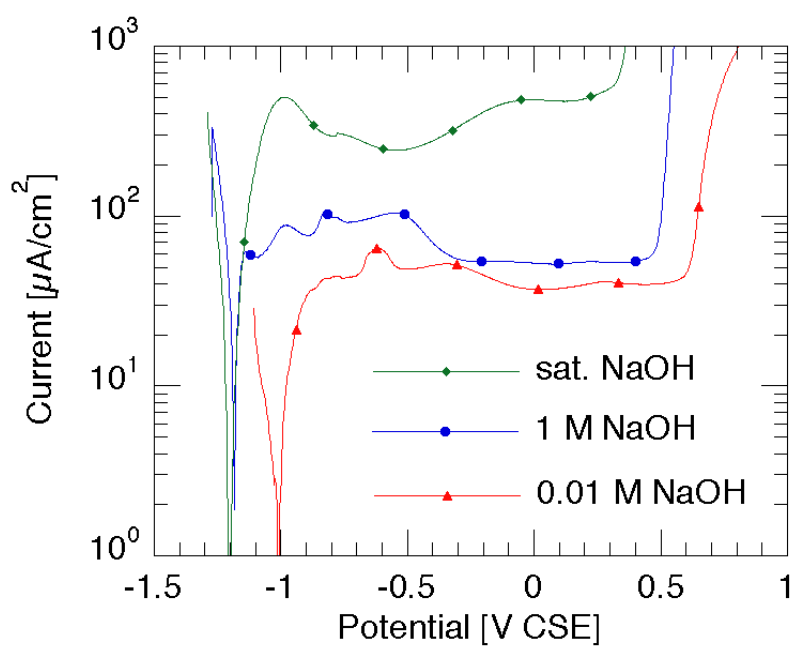


Fig. 1: Polarization scan of steel in de-aerated alkaline solutions.

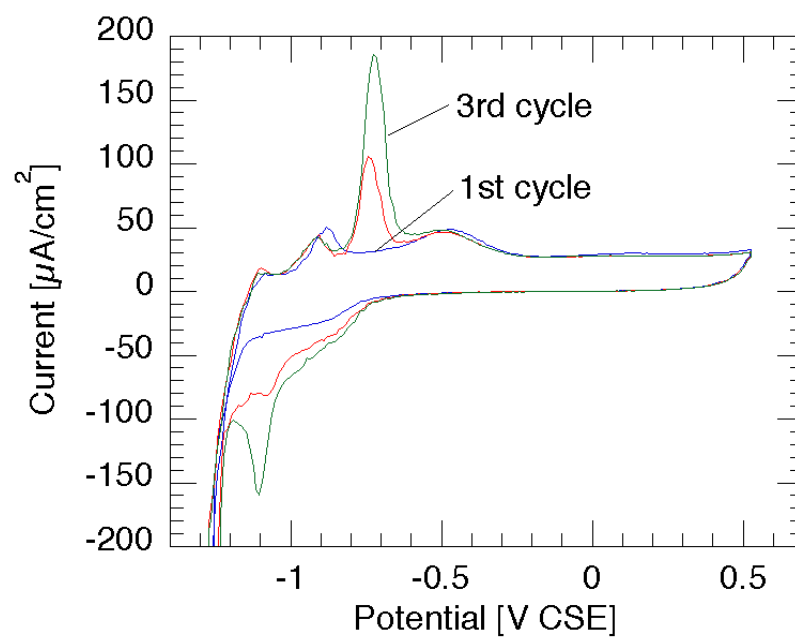


Fig. 2: Cyclic voltammetry of iron in de-aerated 0.1 M NaOH.

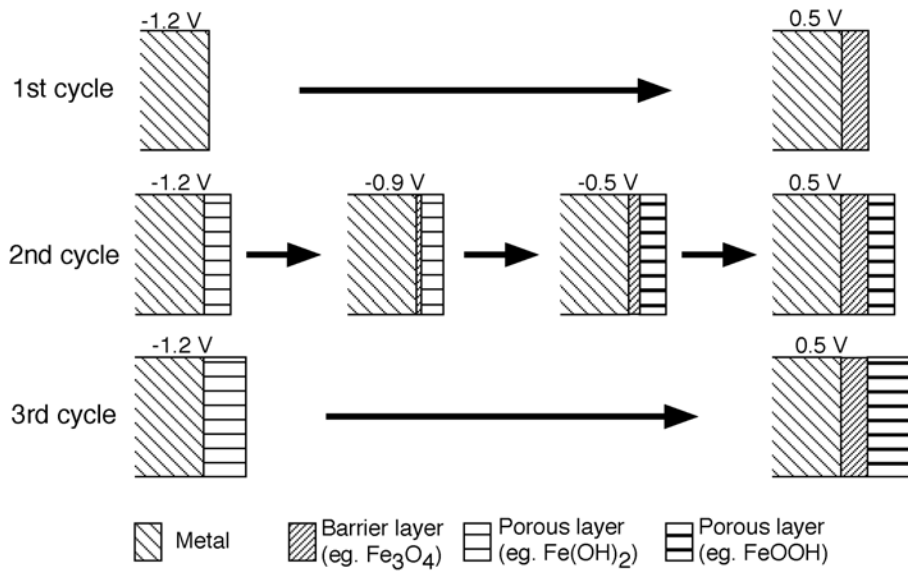


Fig. 3: Schematic representation of the processes taking place on steel during cyclic voltammetry in alkaline solutions.

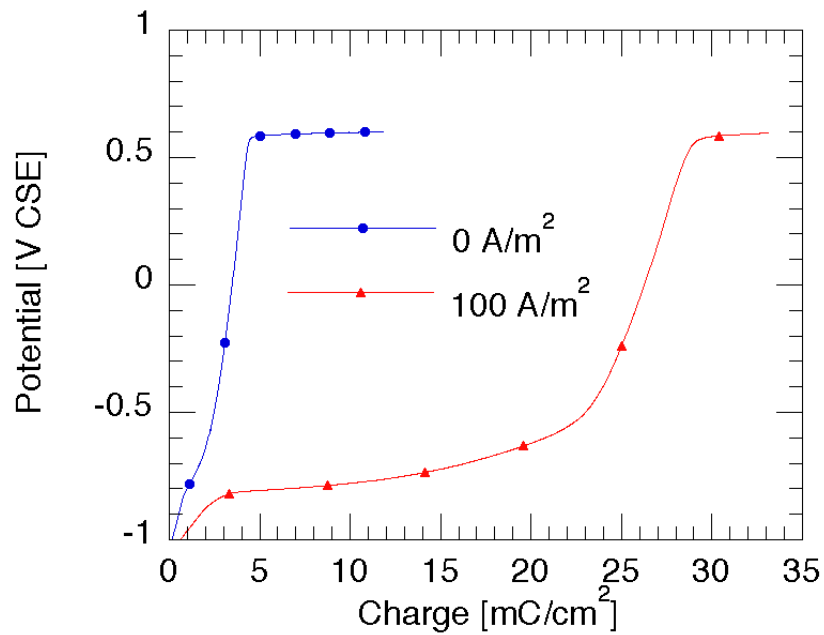


Fig. 4: Galvanostatic oxidation of coupons polarized for 7 days in artificial soil solutions and quartz sand with 3 A/m² and different ac-current densities.

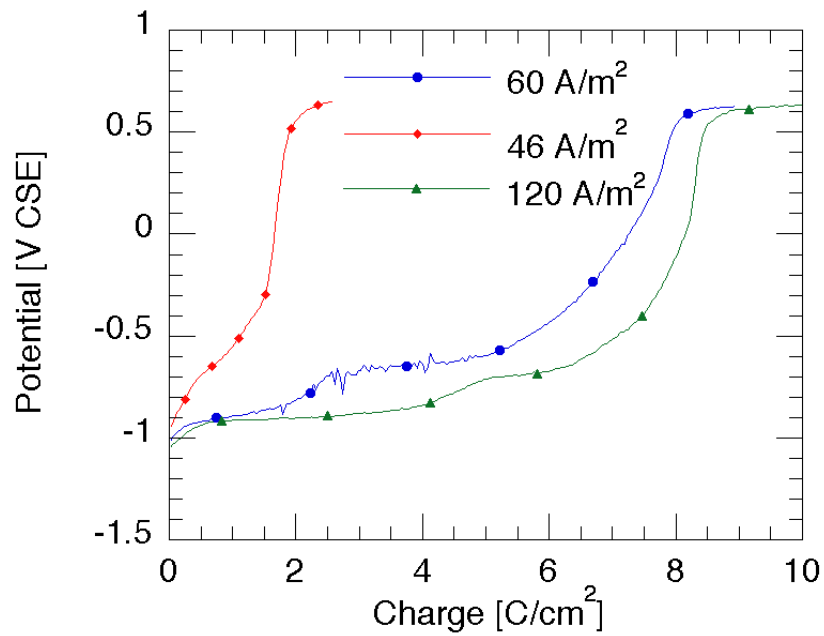


Fig. 5: Galvanostatic oxidation of coupons connected to a pipeline for 2.5 years with 50 mA/cm^2 . The ac-current density before the measurement is listed.

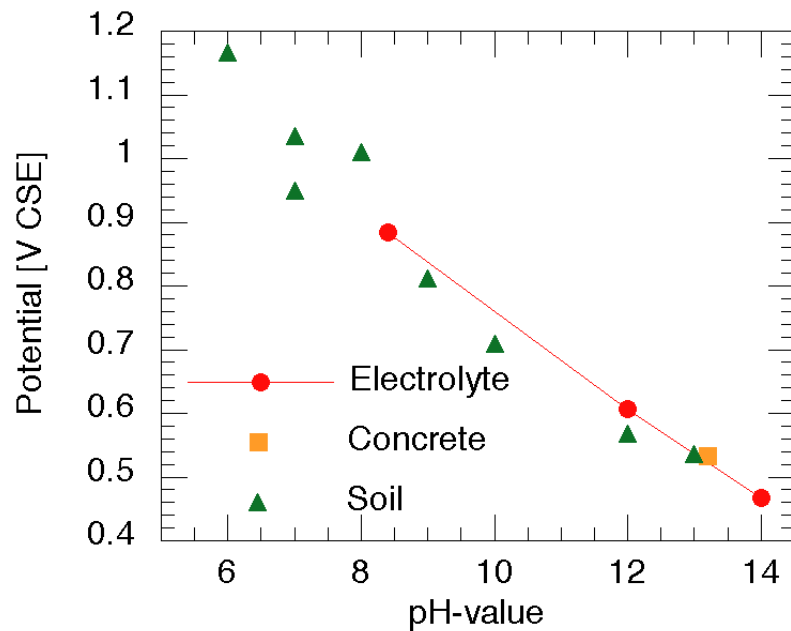


Fig. 6: Potential of oxygen evolution for steel in electrolytes, steel in concrete, and excavated coupons in soil in relation to the measured pH value of the environment.