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Discussion of the mechanism of a.c.-corrosion of cathodically protected pipelines: The effect of the cathodic protection level

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Summary

In recent investigations it was found that the level of cathodic protection has an influence on the a.c. corrosion rate observed on coupons. In order to obtain data for optimizing the cathodic protection parameters, the corrosion rate was investigated at various On potentials and interfering a.c. voltages. Based on the obtained results it was possible to demonstrate that the corrosion rate can significantly be decreased if the Off potential is more negative than -0.85 V CSE and the On potential is in the range of -1.2 V CSE. Moreover it was possible to demonstrate that the high a.c. corrosion rate on coupons can readily be decreased if the cathodic protection level is adjusted. In order to obtain an understanding of the processes involved and to clarify the influence of alkalinity on the corrosion rate, the effect of cathodic current density on the pH-value on the metals surface of coupons was analyzed with a new in-situ pH measurement technique. The effect of pH, spread resistance and electrochemical reduction is discussed with respect to the experimentally observed corrosion rate.

Introduction

The phenomenon "a.c. corrosion" was investigated very detailed since the observation of the first corrosion damages induced by a.c. corrosion on cathodically protected pipelines in 1988 [1, 2]. Despite of all these investigations performed since then, the involved mechanisms are still not completely understood.

In general, it is well established that the a.c. corrosion can only occur if the a.c. current density exceeds 30 A/m^2 [3-5]. However, it was found that higher current densities do not necessarily lead to corrosion attack. While the a.c.-current densities determined on coupons do provide information on the corrosion state, the a.c. potential measured on pipelines was 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 a.c. potential {Büchler, 2003 #2146}. The development of the coulometric oxidation turned out to be a promising technique to determine the amount of a.c. corrosion taking place on coupons [7]. The characterization and analysis of coupons subjected to a.c.-interference in field applications allowed for evaluating the reliability of the coulometric oxidation in determining the occurrence of a.c.-corrosion on coupons.

In recent investigations it was demonstrated that the operation parameters of the cathodic protection strongly influence the corrosion rate [8-11]. By running laboratory tests in artificial soil solutions at various cathodic protection levels and evaluating the corrosion rate it was possible to determine their influence on the corrosion rate. The possible mechanisms involved are discussed.

Experimental setup

For the coulometric oxidation of coupons a Jaissle Potentiostat Galvanostat PCT 1002 in combination with a computer was used. The investigated surface area was 1 cm^2 in all tests. Artificial soil solutions were prepared from reagent grade chemicals and de-ionized water.

Table 1:   Composition of the artificial soil solution

NaHCO$_3$	2.5 mmol/l
NaSO$_4$*10H$_2$O	5 mmol/l
NaCl	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. All potentials are referred to saturated Copper/Copper sulfate electrode (CSE).
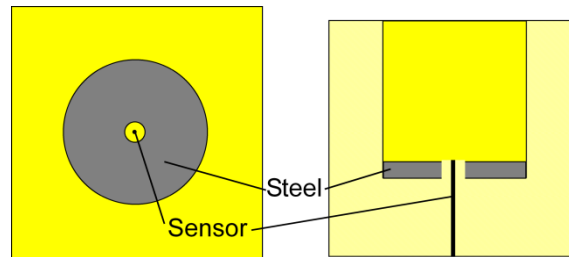

Fig. 0:   Experimental set-up for determining the pH-value in front of the steel surface. The steel plate had as surface of 1 cm^2.

The pH in front of the coupon was determined by means of a pH sensor [12]. The pH-sensor was placed in the center of the steel surface (Fig. 0). The pH-value was determined based on the oxygen evolution on the sensor. Additionally the spread resistance of the sensor was used to estimate the pH-value. The confined geometry resulted in a linear current distribution, linear diffusion, and linear migration. The experiment was performed in quartz sand and artificial soil solution according to Table 1.

Results and discussion
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 conditions 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 [13]. 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 deaerated 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 of about pH 16, 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.
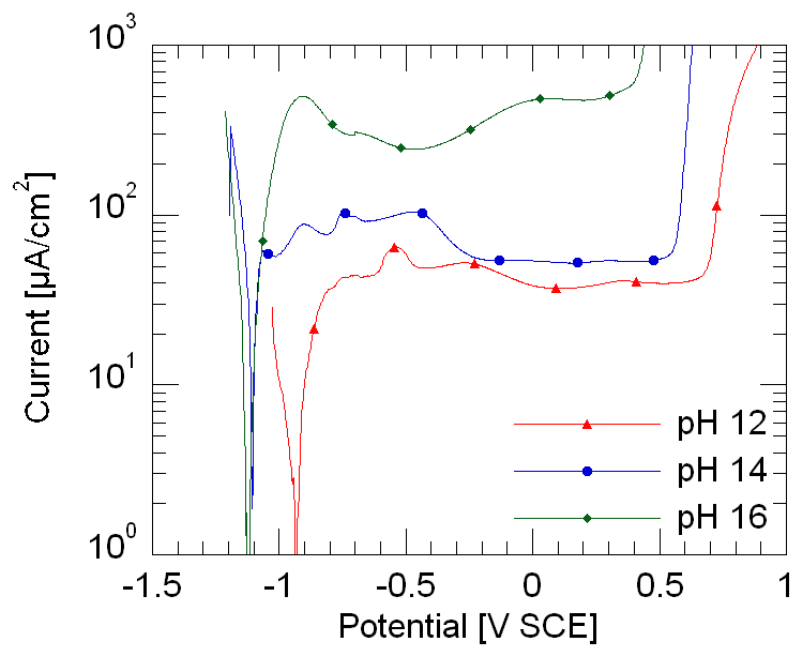
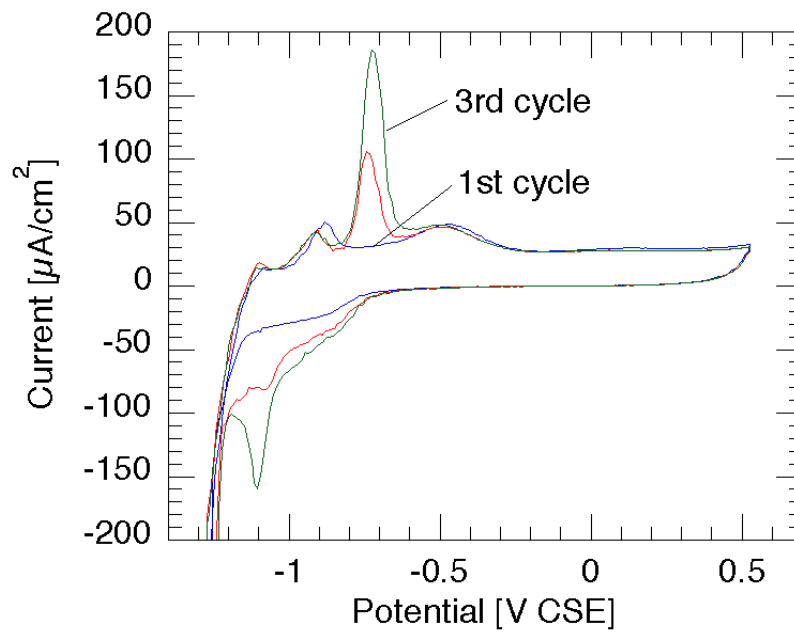*Fig. 1: Polarization scan of steel in de-aerated alkaline solutions (dU/dt=10mV/s).*

Fig. 2: Cyclic voltammetry of iron in de-aerated 0.1 M NaOH of pH 13 (dU/dt=10mV/s).
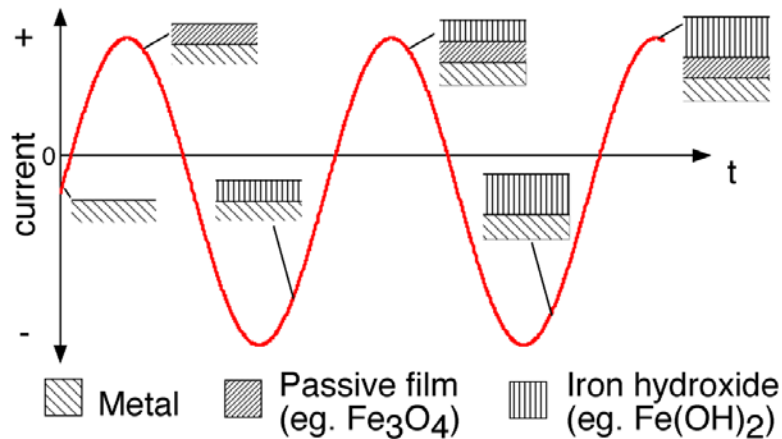
Fig. 3: Schematic representation of the processes taking place on steel under a.c.-interference on a cathodically polarized steel surface in alkaline environment.

It is generally assumed that a.c. 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 voltammograms in de-aerated 0.1 M NaOH of pH 13 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.

 Based on these results it can be assumed that the iron dissolved during anodic polarisation due to a.c.-interference in alkaline solution is not soluble and is therefore accumulated in front of the coupon [12]. In soil this process is even more pronounced, since the hydrodynamic is more limited. Moreover, the cathodic protection current assures that at least parts of the accumulated iron ions are reduced to Fe(II). Therefore, the amount of accumulated corrosion products in front of the coupon can be determined with the so called coulometric oxidation. 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 a.c.-currents are shown in Fig. 4. A galvanostatic anodic current load of 100 µA/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) [14, 15]. 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 behaviour 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 in Fig. 4 indicates the amount of Fe(II) accumulated in front of the coupon, which is an indicator for the amount of a.c.-corrosion [7, 16]. Additionally the experiment shown in Fig. 4 clearly shows the presence of pH-value in front of the coupon that is sufficiently high for passivation of steel.

This increase of the pH is a result of the cathodic protection current. The effect of the cathodic protection on potential and pH of the steel surface is schematically shown in Fig. 5. The reduction of oxygen and the formation of hydrogen result in a decrease of the potential, while the hydroxide ions formed by these reactions cause an increase of the pH- value.
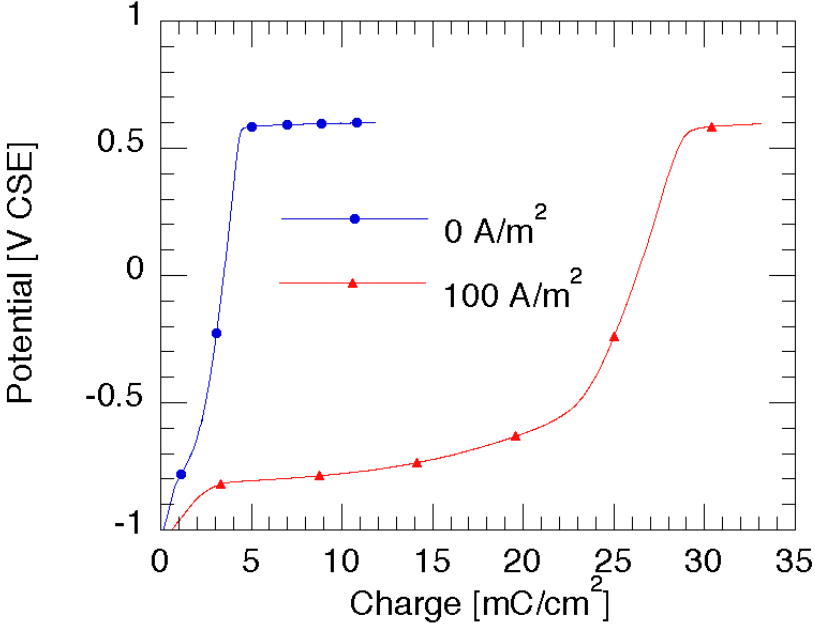

Fig. 4: Coulometric oxidation of coupons polarized for 7 days in artificial soil solutions and quartz sand with 3 A/m² d.c current density and different a.c.-current densities.
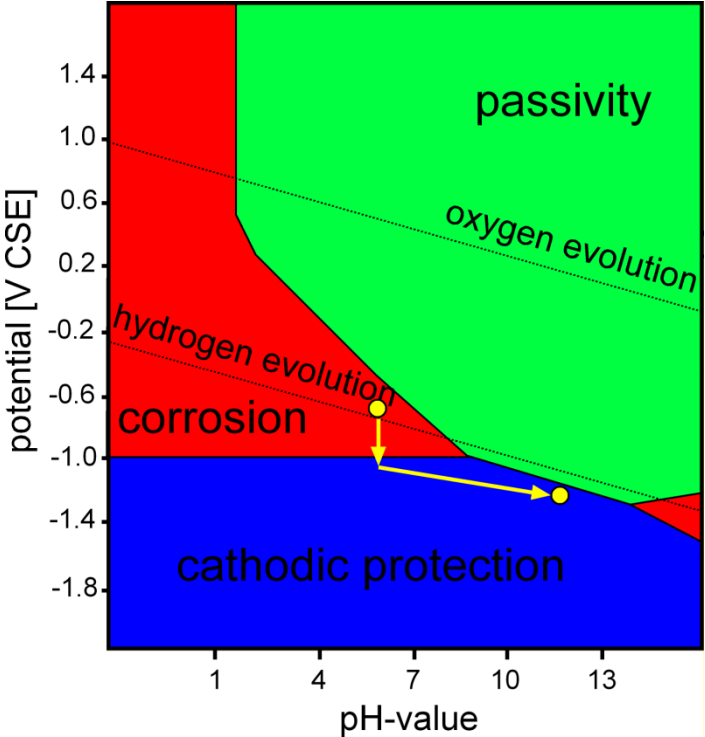

Fig. 5: Effect of cathodic protection on potential of steel and pH-value in front of the steel surface.

In order to evaluate the effect of the cathodic protection level on the corrosion rate various laboratory investigations were performed in quartz sand flooded with artificial soil solutions. This artificial soil had a resistivity of 17 Ωm which corresponds to an extremely conductive soil. From the point of view of conductivity, the artificial soil may be considered to be a worst case situation. The tests were run at various On potentials of the cathodic protection system and at 14 and 30 V a.c.-voltage. Furthermore two different sets of coupons of 1 cm^2 were used. Type 1 had a remaining coating of 7 mm thickness simulating a punctuation through the coating and the protective cement layer, while type 2 was planar with surface of the surrounding polymer coating simulating an open defect excluding the pore resistance in the coating. Both situations represent extreme cases of coating defects.

The results of the determined corrosion rate compared to the On potential for the coupon type 1 is shown in Fig. 6. Clearly a difference in corrosion rate could be detected between the two a.c. voltages. However, a strong effect of the On potential could be detected as well, confirming the contribution of the cathodic operation parameters to the a.c.-corrosion rate. Based on the available data a minimal corrosion rate is obtained between On potentials of about -1.2 to -0.9 V CSE. At higher potentials the corrosion rate increases presumably due to an insufficient cathodic protection. However, the increase in corrosion rate at lower potentials is even stronger. Partly this effect may be due to the decrease in spread resistance caused by the increase of pH at lower cathodic protection potentials.

Apparently the difference in geometry strongly affects the corrosion rate. The strong difference between the two types of coupons at negative potentials may be explained with the increase in cathodic protection current due to the difference in spread resistance. In Fig. 7 the corrosion rate of all investigated coupons is plotted vs. the d.c. current density. An increasing d.c. current density results in increased corrosion rates. It is interesting to note that the difference between the two levels of a.c.-voltage disappears at sufficiently high d.c.-current density. This observation is in good agreement with the high corrosion rates observed in field applications at a.c.-voltages below 10 V and at current densities higher than 10 A/m^2, which showed high corrosion rates [7]. In Fig. 8 the corrosion rate is plotted versus the a.c. current density. Clearly, an increase in corrosion rate is observed with increased a.c. current densities. However, even at a.c. current densities as high as 300 A/m^2, corrosion rates below 10 µm/year are observed.
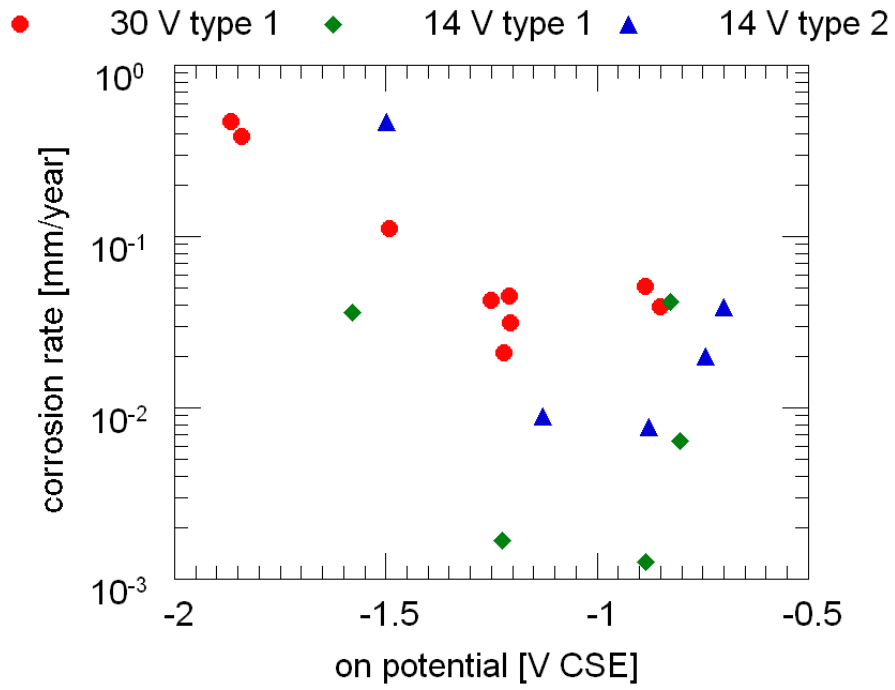
Fig. 6:   Corrosion rate of coupons at 30 and 14 Va.c. at various On potentials.
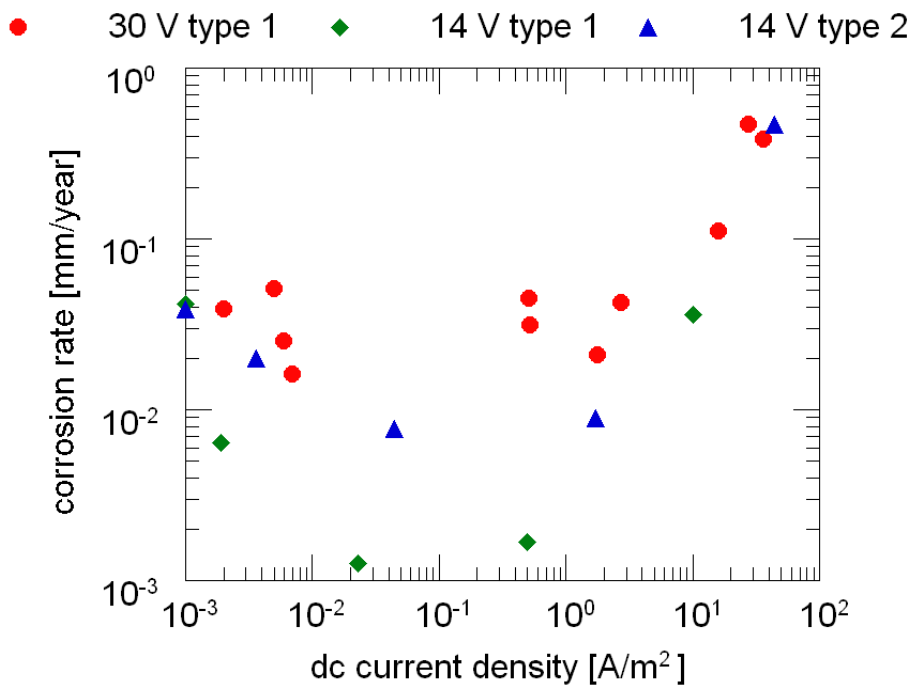

Fig. 7:   Corrosion rate of coupons of type 1 and type 2 at 14 and 30 Va.c. plotted vs. the cathodic current density.
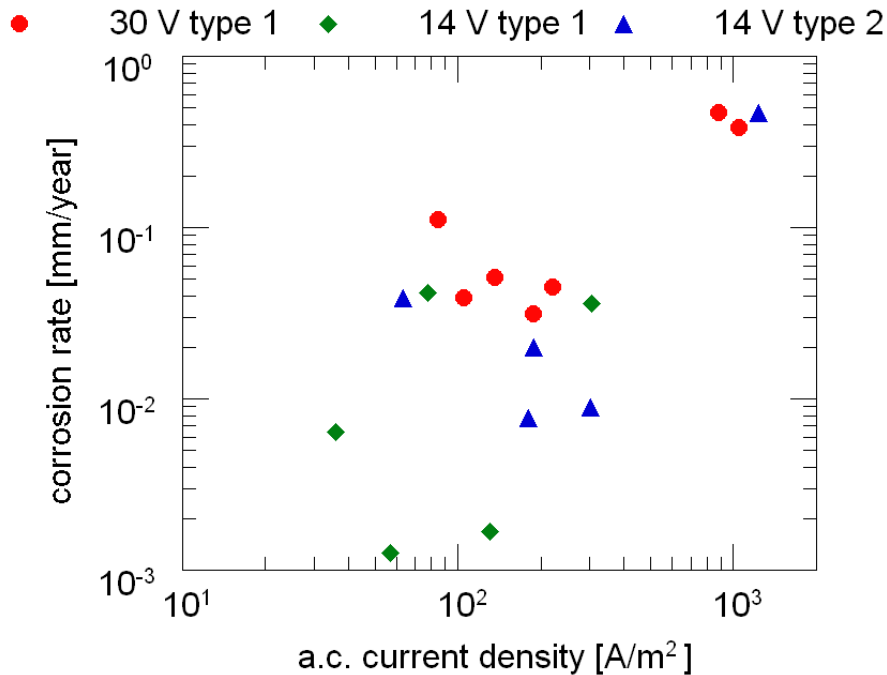
Fig. 8: Corrosion rate of coupons of type 1 and type 2 at 14 and 30 Va.c. plotted vs. the a.c. current density.

The obtained data clearly demonstrate the influence of both the a.c. voltage and the cathodic operation conditions. The influence of the a.c. current density is well known and its contribution to the corrosion rate is generally explained with higher anodic polarization during the anodic part of the half wave. In the past it was attempted to decrease the a.c. corrosion by increasing the d.c. current density [17]. The higher d.c. current density decreases the amount of charge passed during the anodic half wave. If the d.c. current density is sufficiently high to prevent the passage of any anodic current during the a.c. cycle, the corrosion process described in Fig. 3 can be completely stopped. However, in order to eliminate any anodic current, On potentials in the range of several volts are required, resulting in significant hydrogen evolution and an increased risk of cathodic disbonding of the coating. Based on the obtained results in Fig. 6-8, an increase in d.c. current density that does not completely eliminate anodic charge transfer results in a strong acceleration of the corrosion rate.

Hence the question rises regarding the negative effect of the cathodic current on corrosion rate. Generally, the decrease of the spread resistance resulting in a higher a.c. current density is assumed to be responsible for the increased corrosion rate. Moreover, the increase of the pH-value in front of the metal surface above 14 and the formation of iron hydrates is often discussed as possible reason for the increased corrosion rate (c.f. Fig. 5).

Decrease of the spread resistance: Based on Fig. 7 and 8 a high a.c. current density is observed in combination with an increased d.c current density. Nevertheless, even at a.c. current densities that are well above the generally accepted threshold for a.c. corrosion of 30 A/m^2 no significant corrosion may be observed. With the decrease of the spread resistance increased current densities will occur resulting in higher amount of charges passed during the anodic half wave at constant potentials. Hence, higher d.c. current densities would bare an increased risk for corrosion.
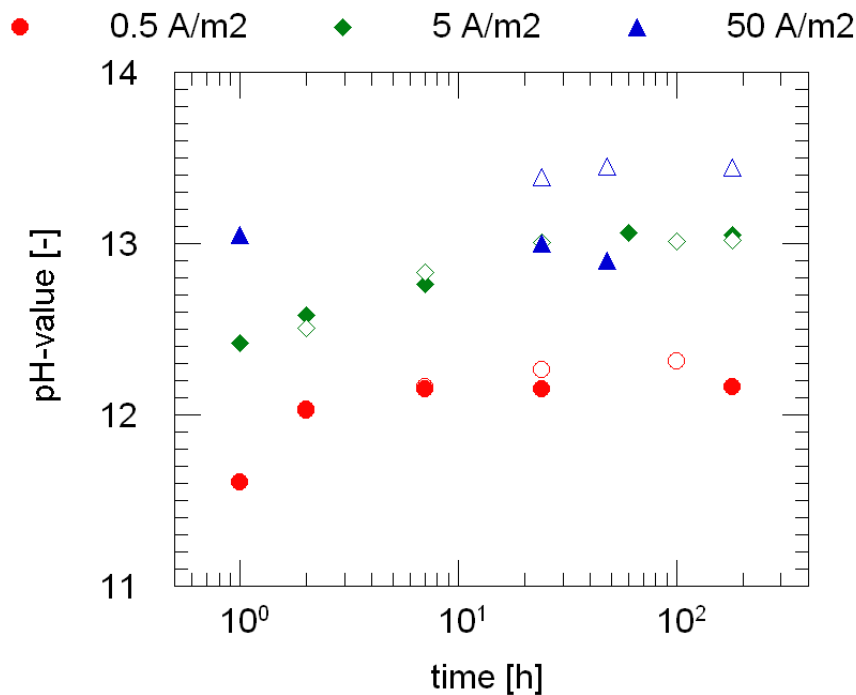
Fig. 9: Development of pH over time at different d.c. current densities. The open symbols were determined based on the measurement of the spread resistance of the sensor.

Increase of the pH-value: In discussing the effect of the pH value it is important to determine the pH-value that is obtained on the steel surface. The results of the pH-measurement at various d.c. current densities are shown in Fig. 9. The results clearly demonstrate an increase of the pH-value over time. At all current densities the pH-value reaches a constant level within a week. While a good agreement between measuring the spread resistance and the potential for oxygen evolution was observed at lower current densities some problems were encountered in determining the oxygen evaluation at 50 A /m^2. This was attributed to the high concentration of hydrogen interfering with the measurement. Nevertheless, it can be concluded that the pH-value does not exceed 14 even for d.c. current densities that were found to result in very high corrosion rates (Fig. 7). The limited increase of the pH in front of the metals surface is explained with the increased migration of the hydroxide ions into the bulk electrolyte. As soon as a steady state between formation and migration is found, no further increase of the pH will be observed. An increase in current will cause a higher formation rate but will also increase removal of hydroxyl ions due to migration. After exposure to cathodic current for one week, the steel samples were passivated by coulometric oxidation. The amount of charge required for passivation was comparable for all current densities. This observation confirms that the pH-value is not exceeding 14 as observed in the Fig. 9.

Based on the obtained results it may be concluded that the formation of iron hydroxides and thus the increase in pH is not primarily responsible for the occurrence of a.c. corrosion. As a consequence, tests were run in quartz sand soaked with 1 M NaOH of pH 14. The a.c. current density 500 A/m^2 and no cathodic protection current was applied. Over a test period of 3 months no significant corrosion was observed confirming that neither the a.c. current density nor the alkaline environment is responsible for the increased corrosion rate. Based on these results the cathodic protection current must have an inherent effect on the corrosion process that is not associated with the changes in the conductivity and pH.

This contribution of the cathodic current to the corrosion rate could be explained as follows: It is in principle possible to eliminate the corrosion process by preventing the dissolution of the once formed passive film. If no cathodic dissolution (i.e. reduction) of the passive film takes

place, no or only limited additional oxidation will take place during the next anodic half wave. The higher the cathodic current density, the more efficient is the cathodic dissolution of the passive film. As a consequence, more oxidation of iron will be required in order to form this film in the following anodic half wave. Assuming the formation and dissolution of a passive film consisting of one single atomic layer during every a.c. cycle, a corrosion rate of 3.1 mm/year would be obtained. The experimentally observed corrosion rates can indeed be in this range in the case of high d.c. current densities (Fig. 7). It may be concluded that typically only parts of the passive film are reduced. With increasing cathodic current density the dissolution of the passive film and therefore the corrosion rate will be increased since more passive film has to grow to compensate for the cathodically dissolved part.

As a consequence it must be concluded that a certain passive film is always present on the steel surface. This conclusion is confirmed by the Pourbaix diagram shown in Fig. 5. Based on this thermodynamic consideration hydrogen evolution is anodic of the area of cathodic protection. Thus at sufficiently high pH and low cathodic current density it has to be expected that the steel surface is covered with a passive film. The formation of a passive film will additionally be favored by the rectification of the a.c. current caused by the asymmetry of the anodic and cathodic current-potential dependence (c.f. Fig. 2). An a.c. current will therefore cause a shift of the potential in anodic direction resulting in an enhancement of the oxide film formation.

The cathodic reduction and dissolution of this passive film is hindered, since the cathodic reduction current is primarily consumed for hydrogen evolution. Hence, only parts of the cathodic current will be available for reduction and dissolution of the passive film. In contrast, the anodic oxidation will primarily be consumed for iron oxidation for new passive film formation in the case of a previous cathodic removal of the passive film at high d.c. current (apart of the current used for capacitive charging). As a consequence, the anodic reaction in Fig. 3 is strongly favored over the cathodic reduction reaction due to the lack of a competing reaction.

Based on these considerations the increase of a.c. corrosion with increasing d.c. current density could be explained by the increased dissolution of the passive film present on the steel surface. This proposed model could explain the experimental effects observed so far with a.c. corrosion.

Conclusions

The laboratory investigation of a.c. corrosion in artificial soil clearly demonstrates the strong effect of the On potential on the corrosion rate. At high protection current densities obtained at negative On potentials the effect of the corrosion rate is higher than 0.1 mm/year and the effect of a.c. voltage level is negligible. Even at low a.c. voltage high corrosion rates may be observed. Hence the cathodic protection parameters have to be optimized in order to minimize the a.c. corrosion rate. The d.c. current density must be below 5 A/m^2 in order to significantly decrease the corrosion rate. Presumably even lower current densities are desirable especially in the case of certain defect geometries that lead to heterogeneous current distribution on the steel surface. In this case the local current density may be underestimated based on the average current density of the entire defect. Based on the available data neither the spread resistance nor the high pH may entirely explain the negative effect of the d.c. current density on the corrosion behavior. A mechanism is proposed and discussed that is capable of describing the available data. It is known that the a.c. corrosion can be stopped if the formation of a passive film is entirely prevented by applying very negative On-potentials. Similarly it can be concluded that a.c. corrosion may be decreased if the dissolution of the once formed passive film is decreased. This is possible by decreasing the cathodic protection current.

Acknowledgements

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