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Determining the effectiveness of cathodic protection based on pH-measurement: A new method for determining the pH at the steel surface in coating defects from the soil surface

Bestimmen der Wirksamkeit des kathodischen Korrosionsschutzes mit Hilfe einer pH-Wert Messung: Eine neue Methode für die Ermittlung des pH-Werts an Fehlstellenoberflächen von der Erdoberfläche aus

Déterminer l'efficacité de la protection cathodique sur la base de la mesure du pH : nouvelle méthode pour déterminer le pH à la surface de l'acier dans les défauts de revêtement à partir de la surface du sol

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Abstract

Most recent investigations have shown that an IR-free potential more positive than the protection criteria does not necessarily indicate corrosion in many cases. This leads typically to unnecessary excavations or unnecessary increase in protection current. An effective cathodic protection is accompanied in most cases by an increase of the pH at the steel surface, which allows for the formation of a passive film. The formation of the passive film is normally responsible for IR-free potentials more positive than the protection criteria. Hence the knowledge of the surface pH and the passivating conditions at the steel surface in coating defects would significantly increase the reliability of the effectiveness measurements. The theoretical background of a method that allows for determining these parameters from the soil surface is presented. Additionally examples of successful field application are discussed.

Zusammenfassung

Neueste Untersuchungen haben gezeigt, dass ein IR-freie Potential, welches positiver als das Schutzkriterium ist, nicht notwendigerweise mit Korrosion einhergeht. Dies führt typischerweise zu unnötigen Freilegungen oder unnötiger Erhöhung des Schutzstroms. Ein wirksamer kathodischer Korrosionsschutz ist in vielen Fällen begleitet von einer Erhöhung des pH-Werts an der Stahloberfläche, welcher zur Bildung eines schützenden Passivfilms führt. Dieser ist für die vergleichsweise positiven IR-freien Potentiale verantwortlich. Folglich ermöglicht die Kenntnis des pH-Werts an der Stahloberfläche und deren passivierenden Eigenschaften eine deutliche Verbesserung der Beurteilung der Wirksamkeit des kathodischen Korrosionsschutzes. Der theoretische Hintergrund der Messmethode, welche die Ermittlung dieser Parameter von der Erdoberfläche aus erlaubt, wird vorgestellt. Zudem werden Beispiele von erfolgreichen Feldanwendungen präsentiert.

Résumé

De récentes études ont démontré qu'un potentiel sans IR davantage positif que les critères de protection n'étaient pas nécessairement, dans de nombreux cas, synonyme de corrosion. Cette situation entraîne généralement des excavations inutiles ou une augmentation inutile du courant de protection. Une protection cathodique efficace s'accompagne dans la plupart des cas d'une hausse du pH à la surface de l'acier, favorisant la formation d'un film passif. La formation du film passif est normalement à l'origine de potentiels sans IR davantage positifs que les critères de protection. Dès lors, la connaissance du pH en surface et des conditions passivantes à la surface de l'acier en cas de défauts de revêtement pourraient considérablement accroître la fiabilité des mesures d'efficacité. Ce document présente le contexte théorique d'une méthode permettant de déterminer ces paramètres à partir de la surface du sol. Des exemples supplémentaires d'applications sur le terrain réalisées avec succès sont abordés.

1. Introduction

In recent years various investigations have shown, that the effectiveness of cathodic protection can readily be explained by means of an increase of the pH-value at the steel surface, rather than the lowering of the potential [1, 2]. These data are supported by extensive field tests [3-5] that demonstrated the effectiveness of cathodic protection as long as the on-potential more negative than $-0.85 V_{CSE}$. This criterion was originally suggested by Robert Kuhn [6] and was extensively used also in Europe. Nevertheless corrosion damages were reported in the past, which occurred with the application of this criterion. These effects resulted in the development of the IR-free potential and the associated threshold values in EN 12954. Some of these values were empirically determined [7]. Numerical modelling shows that these threshold values can only be explained in the presence of a passive film [2, 8, 9]. The discussion of the various influencing factors makes clear that the key factor in cathodic protection is the increase of the pH and the formation of a passive film rather than the lowering of the potential. However, if the pH at the steel surface cannot increase due to increased convection or bacterial activity, an IR-free potential of $-0.95 V_{CSE}$ has to be applied in order to assure corrosion protection by means of immunity. The theoretical and empirical data are well in line with the requirements of EN 12954. They also clearly demonstrate that meeting these criteria assures the effectiveness of cathodic protection. However, not meeting the protection criteria for the IR-free potential does not necessarily indicate the occurrence of corrosion.

This problem is illustrated by means of model calculations for the corrosion potential of $-0.75 V_{CSE}$ of a steel surface of 10 cm^2 in a near neutral soil of $50 \Omega\text{m}$ (Fig. 1), the IR-free potential of $-0.70 V_{CSE}$ of steel in well aerated high resistive soil at an on-potential of $-1.3 V_{CSE}$ (Fig. 2), and the IR-free potential of steel of $-0.86 V_{CSE}$ in soft open water of $50 \Omega\text{m}$ at an on-potential of $-1.3 V_{CSE}$ (Fig. 3).

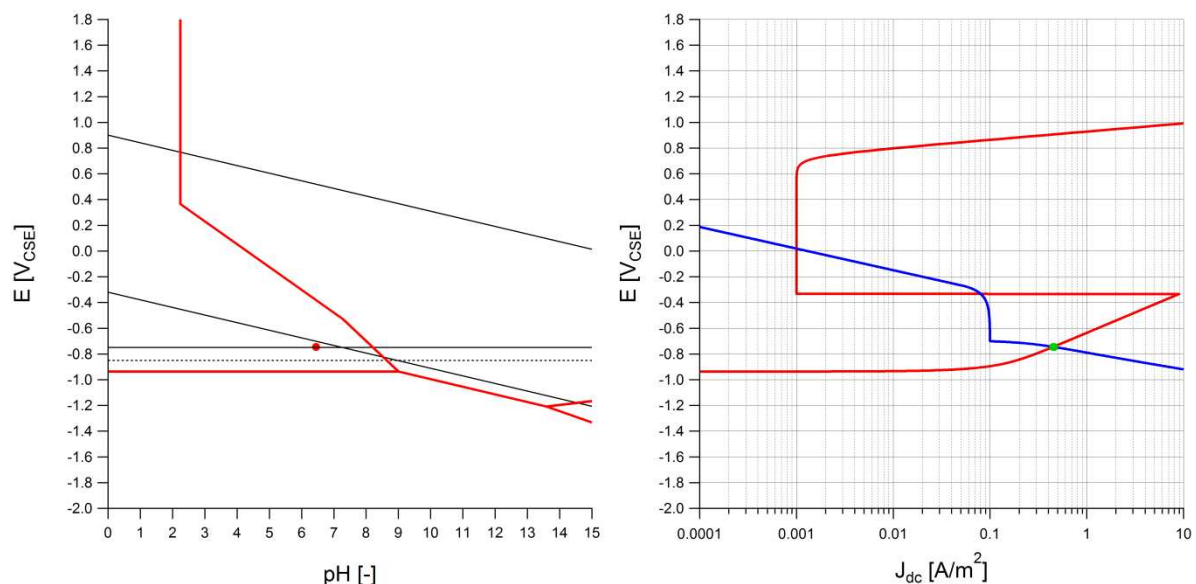


Fig. 1 $E_{IR-free}$ calculated for a soil resistivity of $50 \Omega\text{m}$. Left: Pourbaix diagram with the red dot showing the conditions at the steel surface. The dashed horizontal line represents the protection criterion of $-0.85 V_{CSE}$ according to EN 12954 and the solid horizontal line the corrosion potential/on-potential of $-0.75 V_{CSE}$ that is expected under the given circumstances. Right: Polarization curves for anodic (red) and cathodic reactions (blue) on steel at the corresponding pH value.

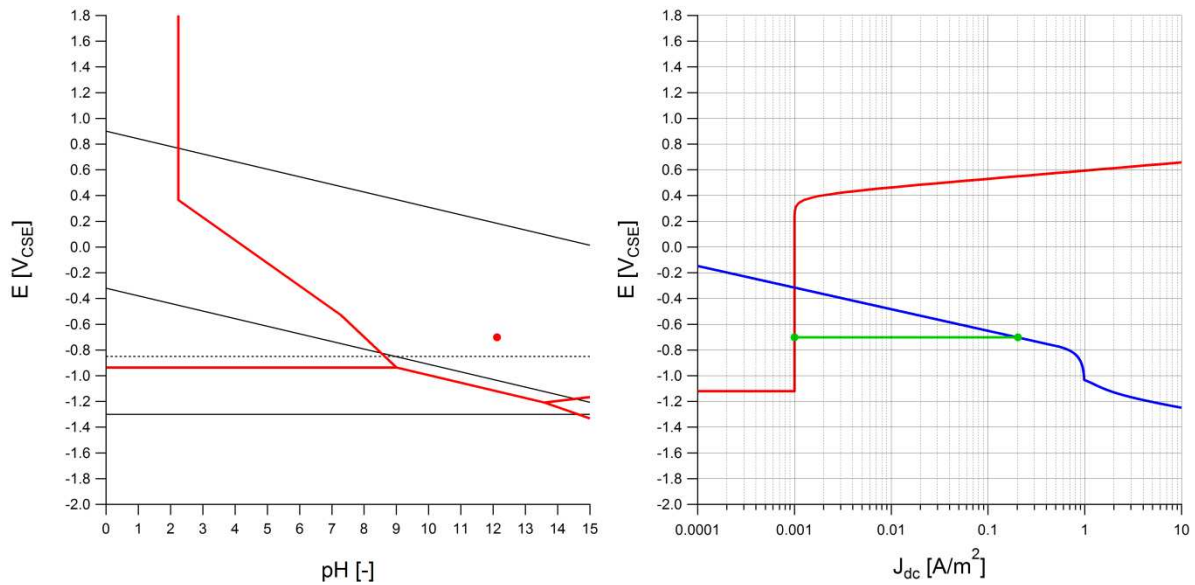


Fig. 2: $E_{IR-free}$ calculated for a soil resistivity of 5000 Ωm and a diffusion limited oxygen reduction current at an on-potential of -1.3 V CSE. Details to the plot are described in Fig. 1.

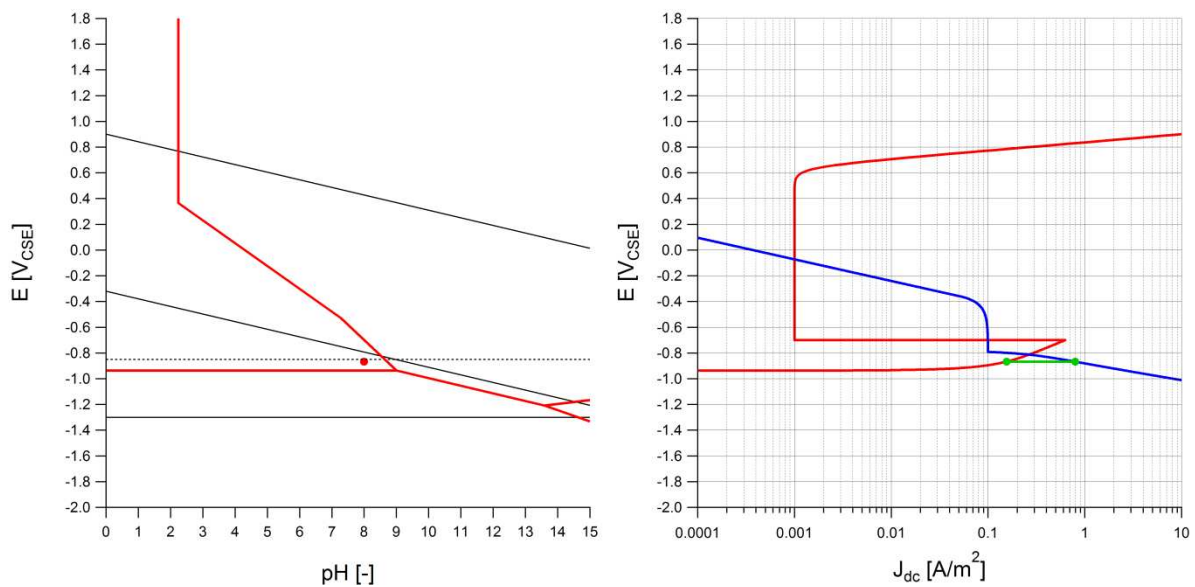


Fig. 3: $E_{IR-free}$ calculated for a water resistivity of 50 Ωm at an on-potential of -1.3 V_{CSE}. The increase of the pH-value is limited to 8. Details to the plot are described in Fig. 1.

The example demonstrates clearly that corrosion protection is only achieved in the case the IR-free potential of -0.7 V_{CSE} where the soil allows for an increase of the pH and the formation of a passive film. In case of open water that does not result in the formation of calcareous deposits the IR-free potential of -0.86 V_{CSE} is meeting the protection criterion of EN 12954, but still corrosion is occurring. This is due to the fact that the convection of water results in a fast dilution of the hydroxide ions formed by the protection current, which prevents the increase of the pH at the steel surface and the formation of a passive film. Based on this analysis an assessment of the effectiveness of cathodic protection

Considering the increased economic pressure on assessing the effectiveness of cathodic protection and excavating coating defects on pipelines with insufficient IR-free potential, there is significant need for a measuring technique that allows for determining the pH-value at the steel surface of coating defects. A new method for pH-measurement is presented in the following.

2. Theoretical background

In discussing the effect of cathodic protection it is found that the IR-free potential is well suited for assessing the effectiveness of cathodic protection. However, its significance is strongly limited in assessing the cases without effectiveness. Only if the pH-value at the steel surface cannot increase, an IR-free potential more positive than $-0.95 V_{CSE}$ indicates the occurrence of corrosion. If the pH is increased and a passive film can form on the steel surface, the IR-free potential is irrelevant for the assessment of non-effectiveness of the cathodic protection. This explains the generally observed bad correlation between insufficiently negative IR-free potentials and the damage situation found in excavations, both on coupons and pipelines. The effect can readily be explained with the increased pH-value at the steel surface resulting in the formation of a passive film. It is in line with the theoretical considerations [2]. The formation of the passive film provides the corrosion protection independent on the IR-free potential. Hence, it would be more efficient to determine the pH value or the presence of passivating conditions rather than the IR-free potential. The measurement of the pH on coupons has already been reported [1]. The systematic application of this method in the past 10 years in Switzerland has demonstrated the suitability of the method. However, the measurement of the pH-value on the steel surface of coating defects on the pipeline from the soil surface is significantly more difficult.

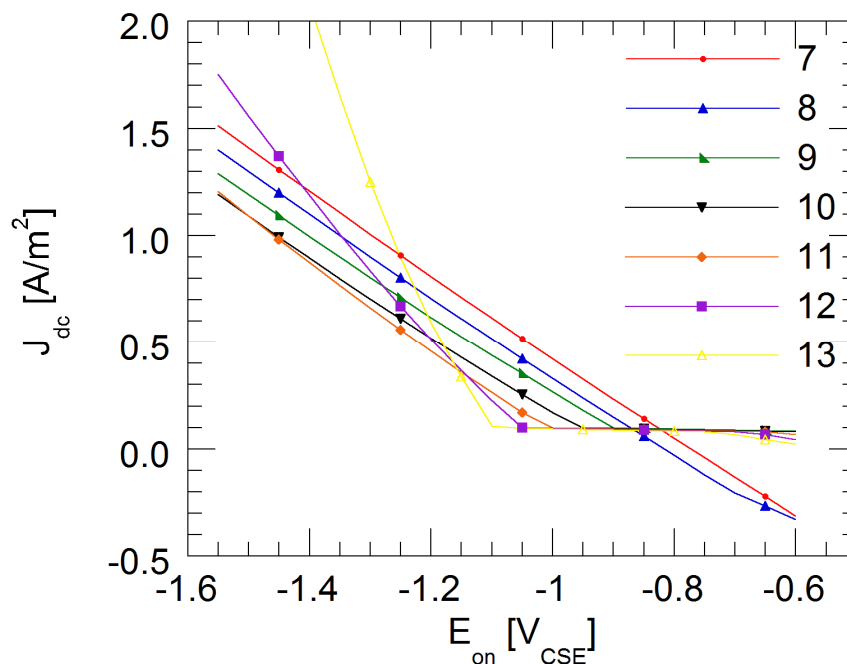


Fig. 4: Dependence of the current density from the on-potential at a defect surface of 10 cm^2 , a soil resistivity of $33 \Omega\text{m}$ and a limiting oxygen diffusion current of 0.1 A/m^2 . Cathodic currents have a positive sign.

Using model calculations [2, 8] it is possible to address the problems associated with the pH-measurement. By calculating the dependence of the current density in a coating defect from the on-potential at various soil resistivities and soil aeration for different defect sizes in soils with various pH-values, an improved understanding of the behavior is obtained. An example for the calculation is shown in Fig. 4. Clearly the pH at the steel surface is influencing the dependence of the current density from the on-potential. This is a result of the dependence of the electrochemical reactions from pH. Additionally it is found that the behavior at lower pH-values is linear, while there is a significant deviation from linearity at higher pH-values. The deviation is a result of the formation of the passive film that limits the anodic current flow.

Based on the model calculation the variation of the on-potential and the concurrent measurement of the current density allow in principle for the calculation of the pH-value and the judgement of the passivating conditions at the steel surface. However, it is not possible to directly measure the current density at coating defects on the pipeline. Since the absolute value is not relevant for the analysis, the ohmic potential drop between two reference electrodes can be analyzed instead according to Fig. 5. The potential drop is proportional to the current density in the coating defect and sufficient for the evaluation of the results. For determining the passivating properties of the soil at the steel surface an anodic polarization of the pipeline is required. If a passive film is present at all the coating defects on the structure this is not critical. Optimizing the control of the potential and the measuring procedure can limit the extent of corrosion in the case of low pH-values

3. Experimental procedure

In laboratory investigations the validity of model calculations could be confirmed. For demonstrating the applicability in field tests various coupons were connected with a pipeline. The defect surface was 600 cm² due to the expected dimension of coating defects on that specific pipeline. One of the coupons was placed in the nearby river shortly before the measurement. This should prevent the formation of calcareous deposits and the increase of the pH due to dilution of the hydroxide ions in the river water. An additional coupon was buried in soil and a third coupon was previously covered with concrete before burying in soil as well. These two coupons were connected with the pipeline two weeks prior to the measurement resulting in a certain increase of the pH at the steel surface due to the cathodic protection current.

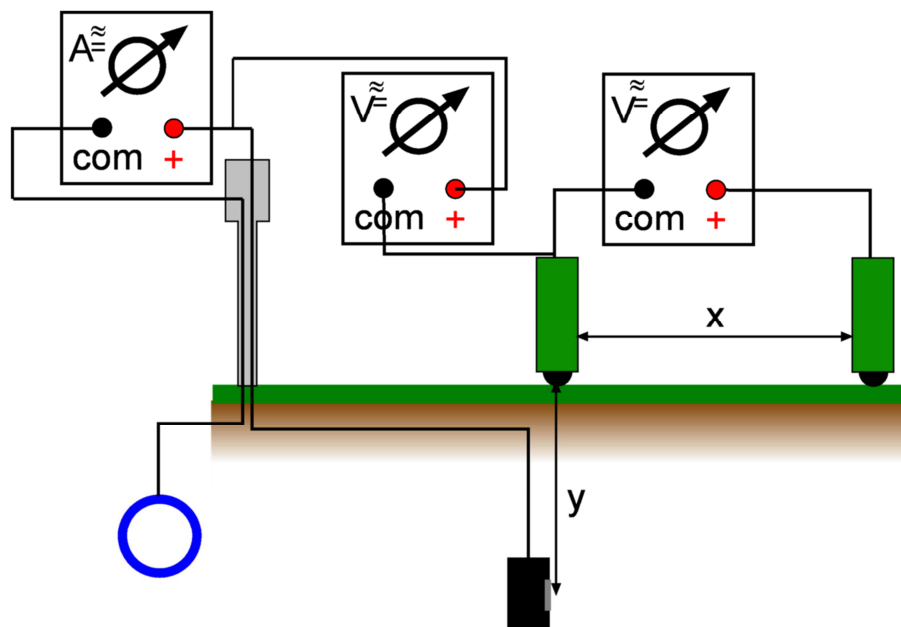


Fig. 5: Experimental set-up for determining the ohmic potential drop as a function of the on-potential.

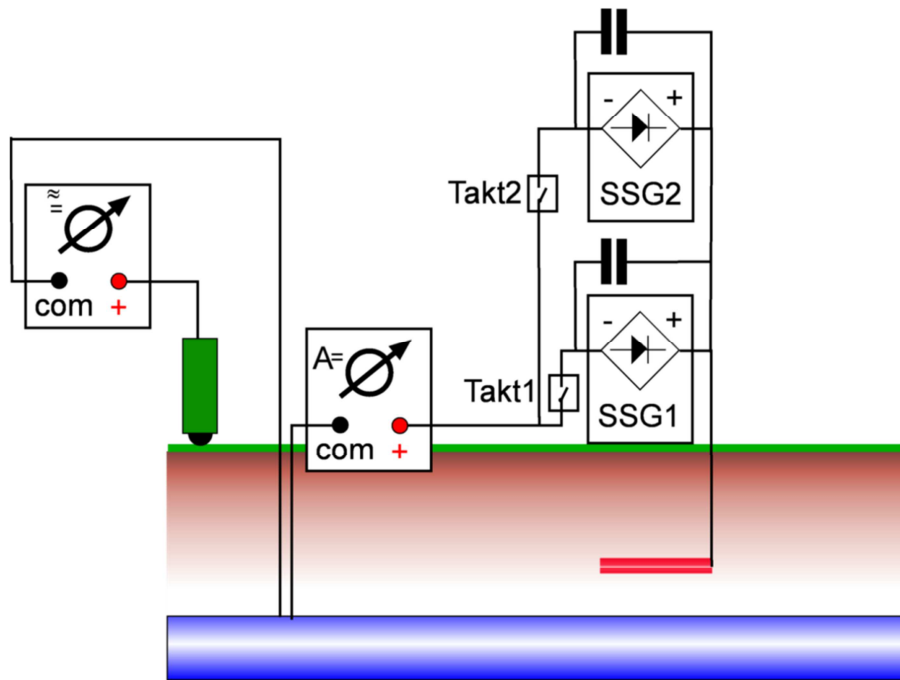


Fig. 6: Experimental set-up for the control of the on-potential.

Both, the current flow in the coupon and the potential drop were determined as a function of the on-potential. For the adjustment of the on-potential the experimental set-up in Fig. 6 was used. All measurement and switch functions were performed by Minilog 2 from Weilekes Elektronik.

4. Results and discussion

The results of the measurement on the three coupons are shown in Fig. 7. A linear behavior is found for the coupon in water, as it was expected for low pH values based on the calculations in Fig. 7. In contrast, a clear deviation from linearity is obtained in the case of the coupon in concrete, as it is typical for passive steel.

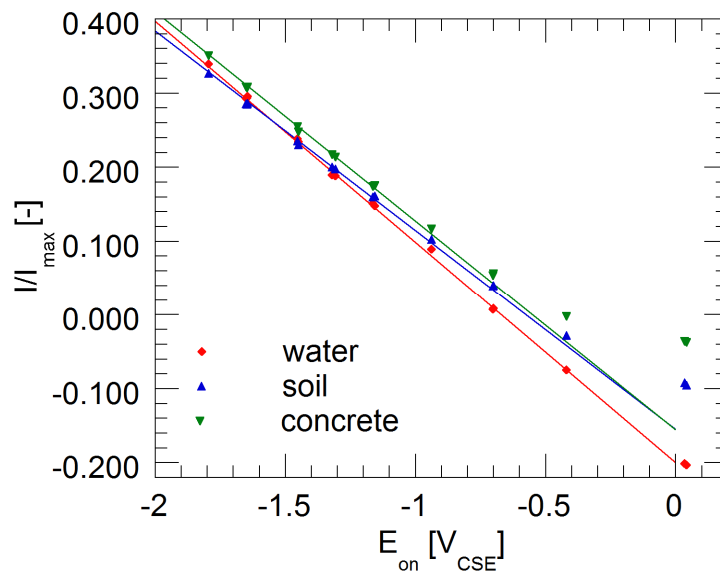


Fig. 7: Current-potential characteristic determined on three coupons in their corresponding environment.

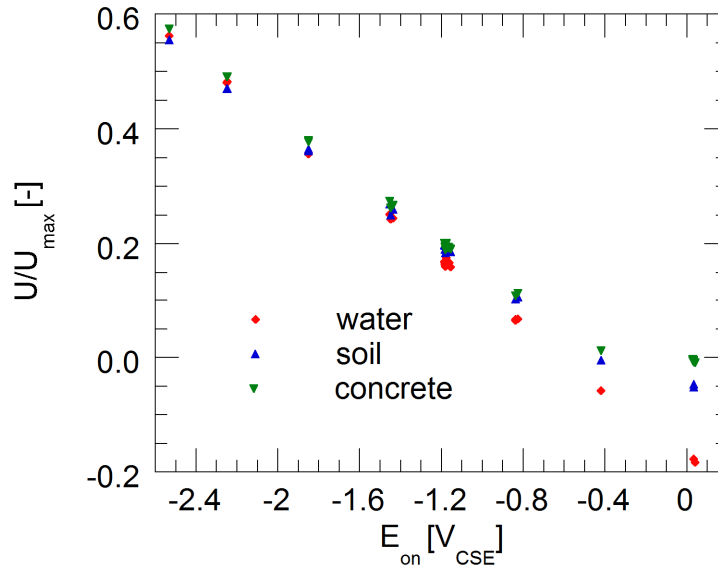


Fig. 8: Gradient potential characteristic determined on three coupons in their corresponding environment.

The buried coupon in contact with soil shows a deviation from linearity as well. The deviation is, however, less pronounced. The results qualitatively confirm the expected behavior in Fig. 4. It is possible to clearly identify the properties of the environment in contact with steel based on the current measurement with respect to the alkalinity and passivating properties.

The evaluation of the data by means of the numerical model provides additional information regarding the situation at the steel surface (Table 1). The calculated pH-values are within the expected range. For concrete a value of about 13.5 was expected. In soil the cathodic protection during 2 weeks at the on-potential of -1.3 VCSE was sufficient to increase the pH value to 12.6. This values is plausible based on the model calculations [2]. In contrast, the polarization in near neutral water did increase the pH as is confirmed by the calculated pH value. Interestingly the IR-free potentials for the coupons are more positive than the one of the corroding coupon. This effect is confirmed by the model calculations as well [2]. It is a direct result of the passivity and the control of the potential by the charge transfer controlled oxygen reduction.

Table 1: Evaluation of the corrosion situation of coupons by means of the current.

	Coupon in water	Coupon in soil	Coupon in concrete
pH-value [-]	6.0	12.6	13.8
IR-free potential [V _{CSE}]	-0.67	-0.58	-0.55
Current-potential characteristic	active	passive	passive

Table 2: Evaluation of the corrosion situation of coupons by means of the gradient.

	Coupon in water	Coupon in soil	Coupon in concrete
pH-value [-]	5.1	>10	>10
IR-free potential [V _{CSE}]	-0.61	-0.44	-0.43
Gradient-potential characteristic	active	passive	passive

In the case of coating defects on the pipeline a direct current measurement is not possible. Instead the analysis of the corrosion situation must be made by means of the voltage gradient. The dependence of the normalized gradient from the on-potential is shown in Fig. 8 and the calculated values are presented in Table 2. The results found in the analysis of the gradients are similar to those with the current. The values for the pH and the IR-free potential are affected by even small differences between the reference electrodes. This problem is well known from the intensive measurement. In the case of non-linear foreign gradients this method can lead to erroneous results. The same applies to the present method for the calculation of the pH-values and limits the precision of the evaluation. A key advantage, however, of the proposed method is the evaluation of the linearity. The linearity can be checked independent on the absolute value of the gradient. Hence, it can be expected that the analysis of the coating defects with respect to passivity is possible even on small defect sizes and in presence of larger foreign gradients.

5. Conclusion

The presented model concept is capable of explaining the significance of the on-potential for the analysis of the effectiveness of cathodic protection. Additionally it explains why corrosion occurs in absence of a passivating environment, which can occur at the steel surface in convection of water or in the case of activity of sulfate reducing bacteria. The discussion demonstrates that a direct measurement of the pH or the passivity is a more reliable approach for assessing the effectiveness of cathodic protection, rather than the IR-free potential. This is confirmed by the results of the discussed field test, where the IR-free potential alone would have resulted in an erroneous analysis of the corrosion situation. The new measurement principle based on the model calculations is capable of resolving this problem. It allows for identifying the coating defects with insufficient cathodic protection by assessment of the pH and the passivity.

The measurements demonstrate the applicability of the proposed measurement technique in the field. It allows for judging the corrosion situation of the steel surface. In ideal cases it is even possible to determine the pH value of the steel surface in a coating defect of a buried pipeline. In contrast to the intensive measurement technique, which has been used for the assessment of the effectiveness of the cathodic protection, the proposed method is independent of the absolute value of the gradient. This should result in an increased reliability even in the case of small coating defects and foreign gradients.

6. Acknowledgement

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7. Literature

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