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**The physical-chemical significance of the IR-free potential**

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## **Abstract**

The effectiveness of the cathodic protection according to EN 12954 is demonstrated by measuring the IR-free potential of the steel. The present paper is discussing the physical chemical significance of the parameter with respect to the corrosion protection by means of theoretical considerations and numerical simulation.

## **Zusammenfassung**

Der Nachweis der Wirksamkeit des kathodischen Korrosionsschutzes gemäss EN 12954 erfolgt durch Messung des IR-freien Potentials. Die chemisch-physikalische Bedeutung dieses Parameters wird in Bezug auf die Korrosionsschutzwirkung mit Hilfe von theoretischen Betrachtungen und numerischen Berechnungen diskutiert.

## **Résumé**

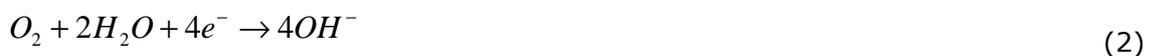
L'efficacité de la protection cathodique selon EN 12954 est démontrée en mesurant le potentiel sans chute ohmique de l'acier. Le présent article aborde l'importance physico-chimique du paramètre en ce qui concerne la protection contre la corrosion, par le biais de considérations théoriques et d'une simulation numérique.

## 1. Introduction

The effectiveness of cathodic protection is demonstrated by measuring the IR-free potential ( $E_{IR-free}$ ) at the steel soil interface. If the experimentally determined value of  $E_{IR-free}$  is more negative than the values in table 1 of EN 12954, the corrosion rate is smaller than 0.01 mm/year. The problems associated with determining this value are often significant in practical applications. However, at least as important as the measuring technique is the understanding of the physical-chemical meaning of this parameter and the respective threshold values. For discussing possible differences in the measuring technique it is important to understand possible influencing parameters. The purpose of the present paper is to discuss relevant parameters and compare them to numerical simulations.

## 2. The cathodic protection of steel

When steel is brought into contact with an aqueous electrolyte an oxidation reaction can take place according to reaction (1) while oxygen is reduced according to reaction (2). This reaction is not only influenced by the pH-value of the electrolyte, but also by the electrochemical potential at the interface metal/electrolyte. The oxidation reaction will only take place if the potential at the interface is more positive than the equilibrium potential of reaction (1). The equilibrium potential and the pH dependence of the reactions can be calculated by means of the Nernst equation. The graphic representation of the relevant reactions and the thermodynamically stable conditions is possible by means of the Pourbaix diagram [1].



When the potential of the steel surface is decreased by an impressed cathodic current ( $J_{dc}$ ) at more negative potentials than the equilibrium potential of reaction (1), the direction of reaction (1) is inverted. Instead of corrosion, the formation of solid iron becomes thermodynamically possible. Hence, the corrosion process is completely stopped despite the presence of the oxidizing agent oxygen in the electrolyte.

In Fig. 1 the Pourbaix diagram for iron is shown. It is important to note that the equilibrium potential for the oxidation reaction (1), which is the transition from immunity to corrosion, of iron is at a potential more negative than the equilibrium potential for the hydrogen evolution according to reaction (3).



This has consequences for the mechanism of cathodic protection. When a cathodic current is applied to steel, the oxygen in the electrolyte is electrochemically reduced according to reaction (2). Once the oxygen is depleted at the metal surface, the rate of oxygen reduction becomes controlled by oxygen diffusion to the steel surface. If the cathodic current,  $J_{dc}$ , is sufficiently high or the diffusion rate of oxygen is low, the potential of the steel surface reaches the equilibrium potential for hydrogen evolution. As a consequence, hydrogen is formed according to reaction (3). This is indicated in Fig. 1.

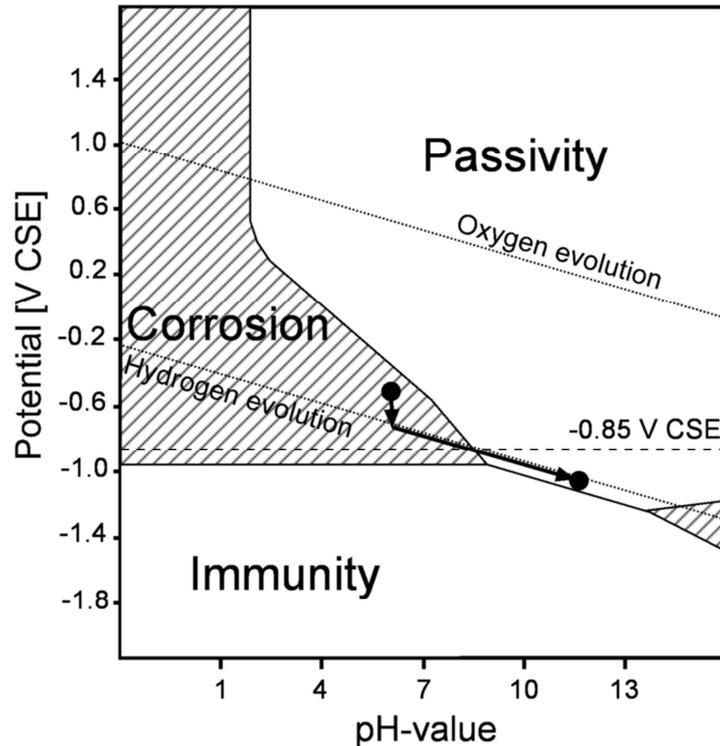


Fig. 1: Pourbaix diagram for iron. Shift of the potential due to an imposed protection current density of  $0.1 \text{ A/m}^2$

Any further decrease in potential requires high  $J_{dc}$ , since the Tafel slope of reaction (3) is around 120 mV/decade and supply of liquid water as a reactant is never rate limiting in an aqueous electrolyte. The described effects are demonstrated by the cathodic polarization scan, as shown in Fig. 2 [2, 3]. Based on this result it can be concluded that the decrease of the potential of the steel surface due to an imposed cathodic current is limited by the hydrogen evolution. The immunity range can only be reached at increased  $J_{dc}$ . Since reaction (3) and (2) result in the formation of hydroxide ions, the pH at the steel surface is increased over time. Thus, the steel potential follows the equilibrium line for hydrogen evolution (at common  $J_{dc}$ ). With increasing pH (which occurs owing to the release of hydroxide ions acc. to equations (1) and (2)), the field of passivity is reached in the Pourbaix diagram (Fig. 1). In this area formation of a protective passive film is thermodynamically expected. When reaching the field of passivity, the steel potential gets more negative than  $-0.85 \text{ V CSE}$ , which is the value originally reported by R. J. Kuhn [4, 5] that is discussed in detail in [6] and which still is the protection criterion according to EN 12954. Since this value is not in the immunity range, the question arises regarding the protection mechanism of steel under cathodic protection. According to the current understanding there are several effects that contribute to the corrosion protection of steel:

- Corrosion is only possible when the electrons formed in reaction (1) are consumed. The predominant oxidizing agent is oxygen. Hence the depletion of oxygen at the steel surface results in a decrease in the corrosion rate.
- The reduction reactions taking place on the steel surface increase the pH at the steel surface. If the pH is sufficiently high, the steel surface is covered by a protective passive film that strongly decreases the corrosion rate.
- The lowering of the potential of the steel surface decreases the driving voltage for reaction (1). Therefore, the corrosion rate is decreased. Moreover, any galvanic couples due to aeration elements along the pipeline are eliminated.

- At high protection current densities immunity can be reached and corrosion is stopped.

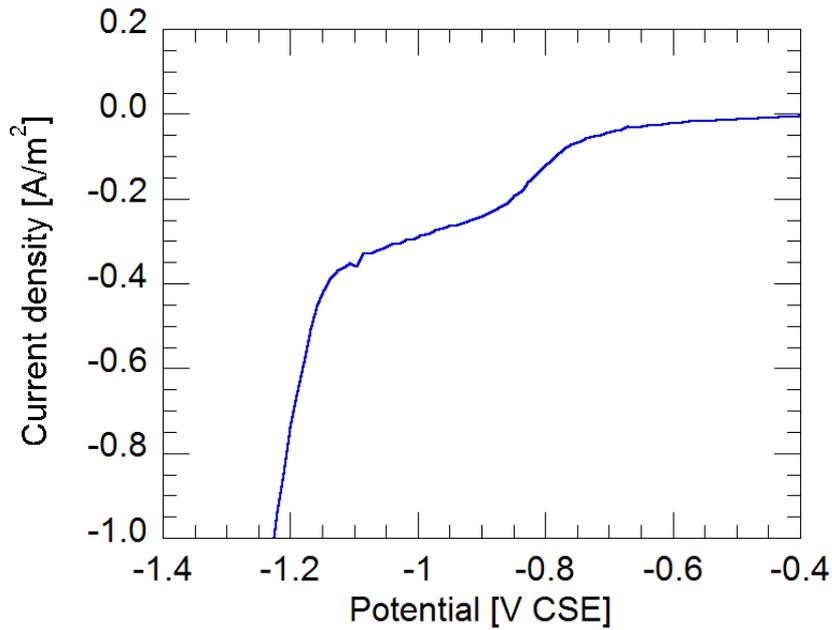


Fig. 2: Cathodic polarization scan of steel in 0.1 M NaOH with pH 13.

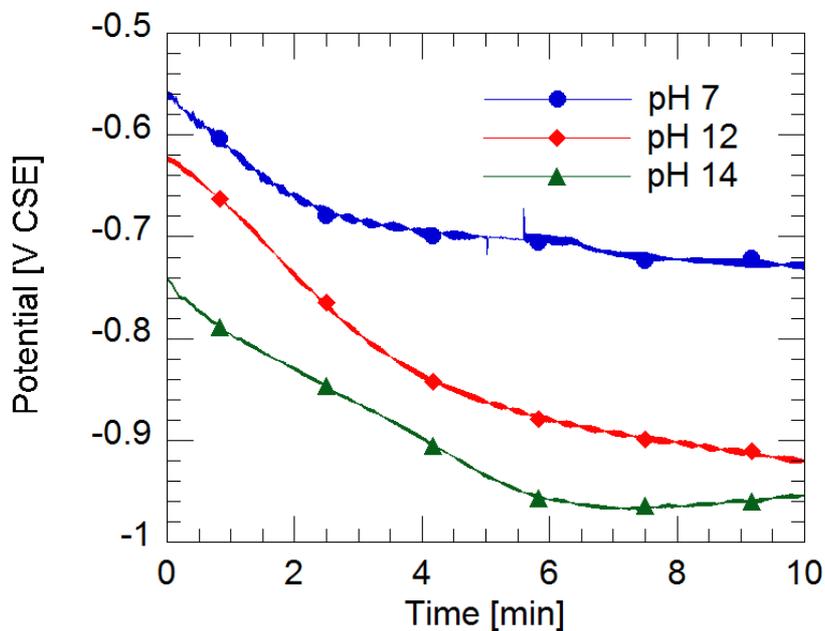


Fig. 3: Potential of steel during the purging of electrolytes with nitrogen.

As a consequence, the positive effect of cathodic protection is caused by the synergistic contribution of all effects [7]. Similar conclusions are reported in the literature [8, 9]. Based on the discussion of the processes taking place under cathodic protection, a potential more negative than -0.85 V CSE can only be reached when oxygen is depleted and the alkalinity is sufficiently high to allow the formation of a protective passive film. As a consequence, it could be

concluded that the protection criterion according to EN 12954 indirectly represents a mixed pH and oxygen criterion as has been demonstrated in [2, 3]. This is illustrated by the potential measurement of steel in electrolytes with various pH values (Fig. 3). The oxygen content of these electrolytes is decreased by purging with nitrogen. Clearly the potential decreases rapidly, when the oxygen content is lowered. In the case of the electrolyte with pH 12 the potential drops to a potential value more negative than  $-0.85$  V CSE after a few minutes. This effect is even more pronounced at pH 14, while in neutral solution the potential is decreased to a value in the range of  $-0.73$  V CSE. This experiment demonstrates that meeting the protection criteria of EN 12954 is possible without external current but by changing pH and oxygen content according to the theoretical considerations.

### 3. Consequences of the model concept for cathodic protection

The discussed mechanism has consequences on practical aspects of cathodic protection. This is especially relevant in the case of anodic stray current interference or in the case of interruption of the cathodic protection current due to failure of the CP system or deliberate earthing of the protected structure due to maintenance work. The processes taking place were investigated for coupons in various soils after the interruption of the cathodic protection current that was applied for 10 minutes. Typical results are shown in Fig. 4 for various soils. After switching off  $J_{dc}$ , an increase of the potential is observed. Depending on soil composition, the potential rises to values more positive than  $-0.85$  V<sub>CSE</sub>. The safety criterion for cathodic protection according to EN 12954 is exceeded already after short time. In all cases, the potential rise flattens within a few hours until it comes to a rapid drop of the potential [10, 11].

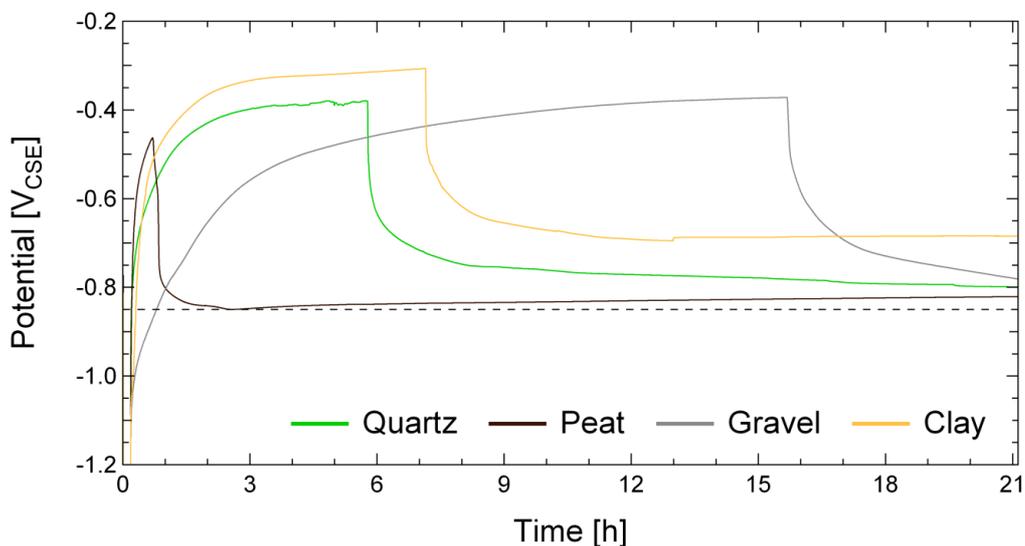
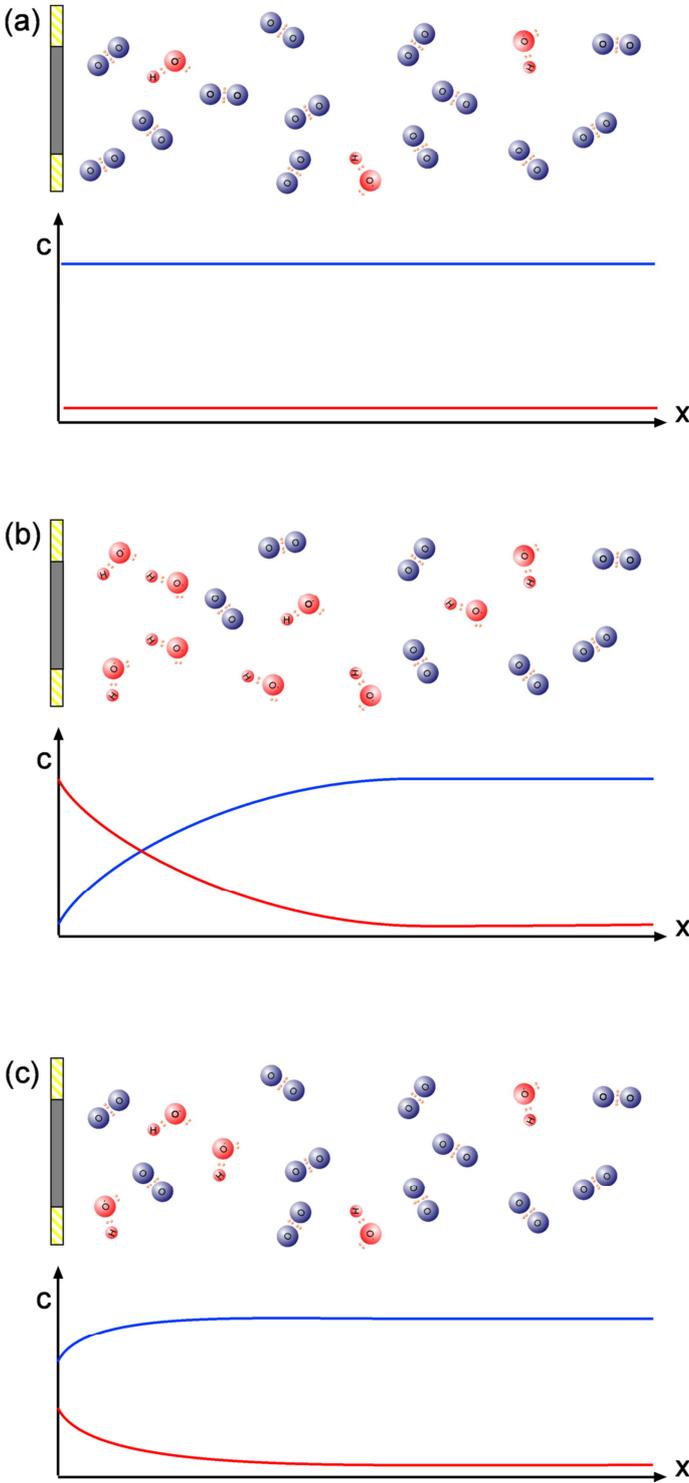


Fig. 4: Potential curves of circular coupons with  $1\text{cm}^2$  surface after a cathodic polarization at  $40$   $\text{A/m}^2$  for 10 minutes.

Taking into consideration the effects taking place during cathodic corrosion protection discussed above, the protective current will lead to a depletion of oxygen and an increase of pH at the steel surface. These changes in soil electrolyte composition in the immediate vicinity of the steel surface are shown in Fig. 5a and b. After turning off of the CP, oxygen from the environment will diffuse to the steel surface and hydroxide accumulated close to the steel will diffuse into the bulk solution. Both processes lead to a positive shift of the steel potential. According to the Pourbaix diagram (Fig. 1) this potential shift brings the steel surface into a region of passivity. Due to the

still comparatively high pH value, no corrosion is expected even if the potential is more positive than  $-0.85 V_{CSE}$ . This effect was discussed in detail in [12] for the case of stray current interference.



**Fig. 5:** Concentration distribution of oxygen ( $O_2$ ) and hydroxyl ( $OH^-$ ) in soil: a) homogeneous distribution before the start of the CP, b) Reduced oxygen and increased hydroxyl ion concentration on the steel surface with CP, c) increase in the oxygen and reduction of hydroxyl ion concentration by diffusion processes over time after switching off the CP.

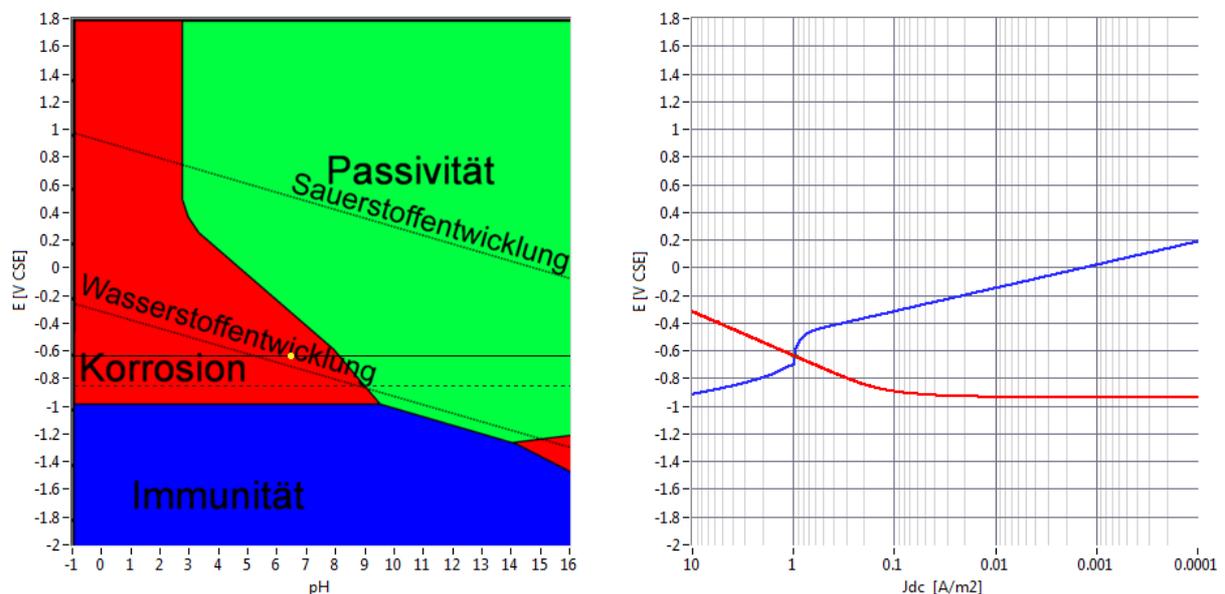
As the passive layer grows and increases in thickness, the potential will continue increasing. However, diffusion will also continue decreasing the hydroxide ion concentration at the steel surface. It is apparent from Fig. 1 that the potential increase and the decrease in pH are

competitive processes with respect to maintaining passivity. If the potential does not increase fast enough with respect to the fall in pH, the conditions for passivity may be lost, viz. as soon as the line separating the shaded (corrosion) and white (passivity) areas in Fig. 1 is crossed. In case chlorides are present in the system, maybe even at spurious concentrations, the ratio between hydroxide and chloride ions may become unfavorable before the shaded corrosion area is reached so that pitting corrosion is initiated.

In any case, with the initiation of corrosion, oxygen is again consumed at the steel surface and the potential of the coupon starts falling again. These exemplary experiments clearly show the close interaction between the electrochemical reactions, mass transport in soil, and soil properties with respect to oxygen and pH.

#### 4. Physical-chemical significance of the threshold values

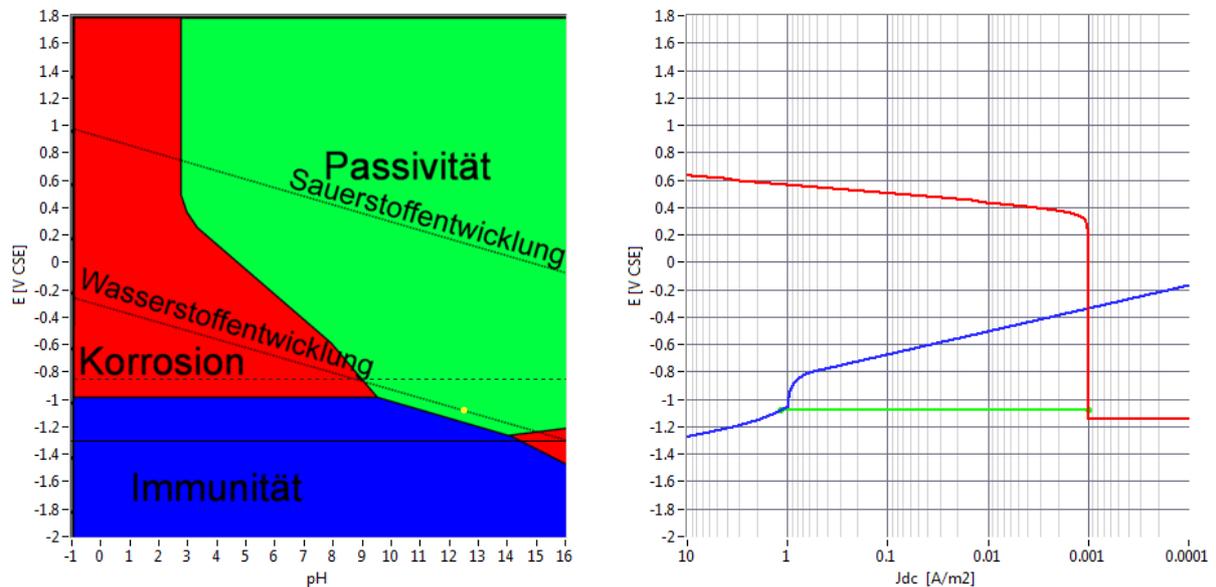
The above discussion demonstrates that the experimentally determined value of  $-0.85$  V CSE can readily be explained by means of sufficient pH increase and sufficient oxygen depletion at the steel surface. However, EN 12954 reports various threshold values that depend on soil conditions. They were determined by means of experimental field and laboratory tests [13]. Hence the question arises regarding their physical-chemical significance. In order to clarify this issue, a simulation software was developed that is capable of calculating the relevant parameters at the steel electrolyte interface such as pH, spread resistance and  $E_{IR-free}$  depending on the external parameters. The basis for the calculations are the experimental data reported in [7, 14, 15]. Various combinations are discussed in the following to demonstrate the relevant dependencies.



**Fig. 6:**  $E_{IR-free}$  calculated for a soil resistivity of  $50 \Omega m$ . Left: The dashed horizontal line represents  $E_p = -0.85$  V CSE according to EN 12954 and the solid line indicates a corrosion potential of  $-0.64$  V CSE. Right: Potential/current relationships of anodic reactions of steel (red) and cathodic reactions (2) and (3) (blue) at the corresponding pH.

The discussion is made in all cases for a circular defect with a surface of  $10 \text{ cm}^2$ . The parameters investigated were  $E_{on}$ , soil resistivity, and diffusion limited oxygen reduction current ( $J_{O_2}$ ). According to Fig. 6 the corrosion potential of steel in a near neutral soil with a resistivity of  $50 \Omega m$ , and a  $J_{O_2}$  of  $1 \text{ A/m}^2$  is  $-0.64$  V CSE. Values in this range are reported in [13]. The

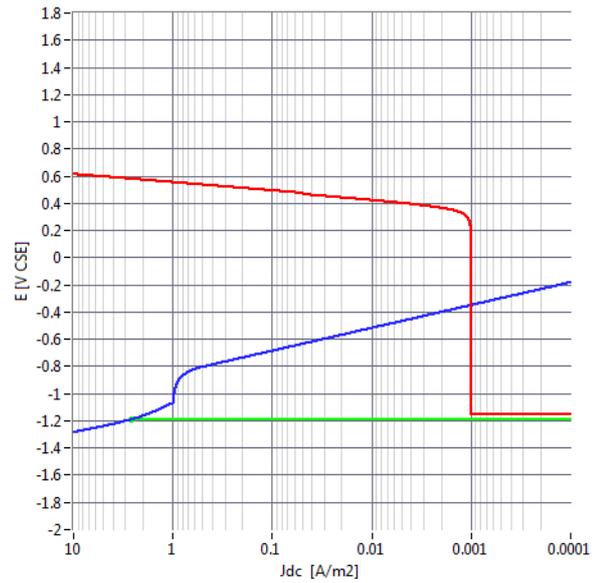
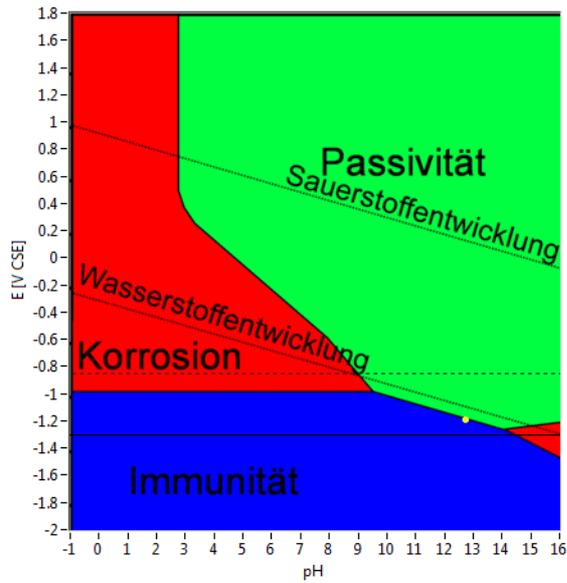
corrosion potential is at the intersection of the anodic current/potential curve for the dissolution of steel according to reaction (1) and the cathodic current/potential curve for oxygen reduction and hydrogen evolution. Based on Fig. 6 it can be concluded that  $J_{O_2}$  is controlling the corrosion potential.



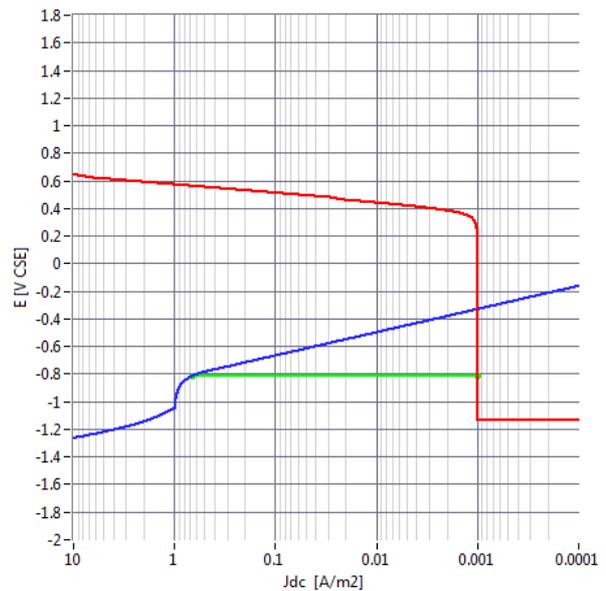
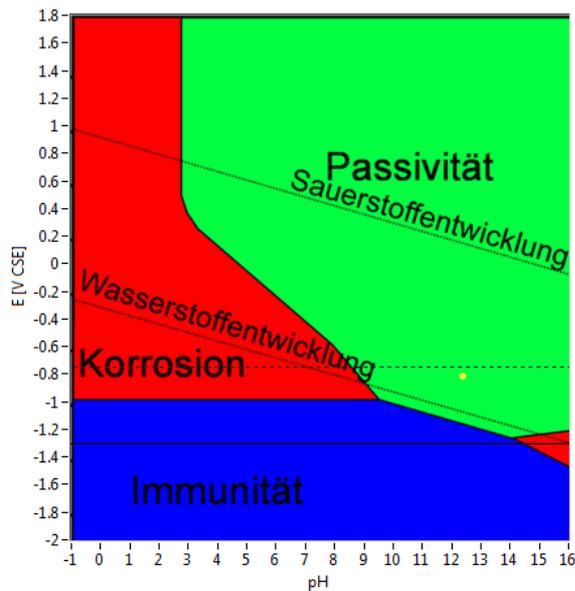
**Fig. 7:**  $E_{IR-free}$  calculated for a soil resistivity of  $50 \Omega m$ . Left: The dashed horizontal line represents  $E_p = -0.85 \text{ V CSE}$  according to EN 12954 and the solid line indicates  $E_{on}$  of  $-1.3 \text{ V CSE}$ . Right: Potential/current relationships of anodic reactions of steel (red) and cathodic reactions (2) and (3) (blue) at the corresponding pH. The green line represents  $E_{IR-free}$  and the length of the green line is the protection current density in the defect.

After imposing a cathodic protection with an  $E_{on}$  of  $-1.3 \text{ V CSE}$   $E_{IR-free}$  is shifted to more negative values and the pH is significantly increased as can be concluded from Fig. 7. The increase in pH, which is caused by  $J_{dc}$ , changes the anodic behavior of steel (red line in Fig. 7). Instead of charge transfer controlled metal dissolution, the formation of a passive film with an assumed passive current density of  $1 \text{ mA/m}^2$  is expected. The spread resistance influenced by the increase of pH at the steel surface and the surrounding soil results in a  $J_{dc}$  of about  $1 \text{ A/m}^2$ , as can be concluded from the length of the green line in Fig. 7. Most of the current is consumed for oxygen reduction and only a small amount is consumed for hydrogen evolution. Since the given conditions in Fig. 7 are close to the normal situation according to EN 12954 the  $E_p$  of  $-0.85 \text{ V CSE}$  may be applied. Based on the calculation it can be concluded that the protection criterion is fulfilled. The corrosion protection in this case is achieved by the increase of the pH and the formation of a protective passive film on the steel surface.

When the soil resistivity is only  $5 \Omega m$ , but  $E_{on}$  maintained at  $-1.3 \text{ V CSE}$ , the decreased spread resistance results in a smaller ohmic potential drop and a  $J_{dc}$  of about  $2.5 \text{ A/m}^2$ , as can be concluded from Fig. 8. This increased cathodic current density results in a higher pH at the steel surface and significant hydrogen evolution. Under these conditions the potential of the steel surface is in the immunity range. Hence it can be concluded that in this case the corrosion protection is caused by immunity rather than passivity.

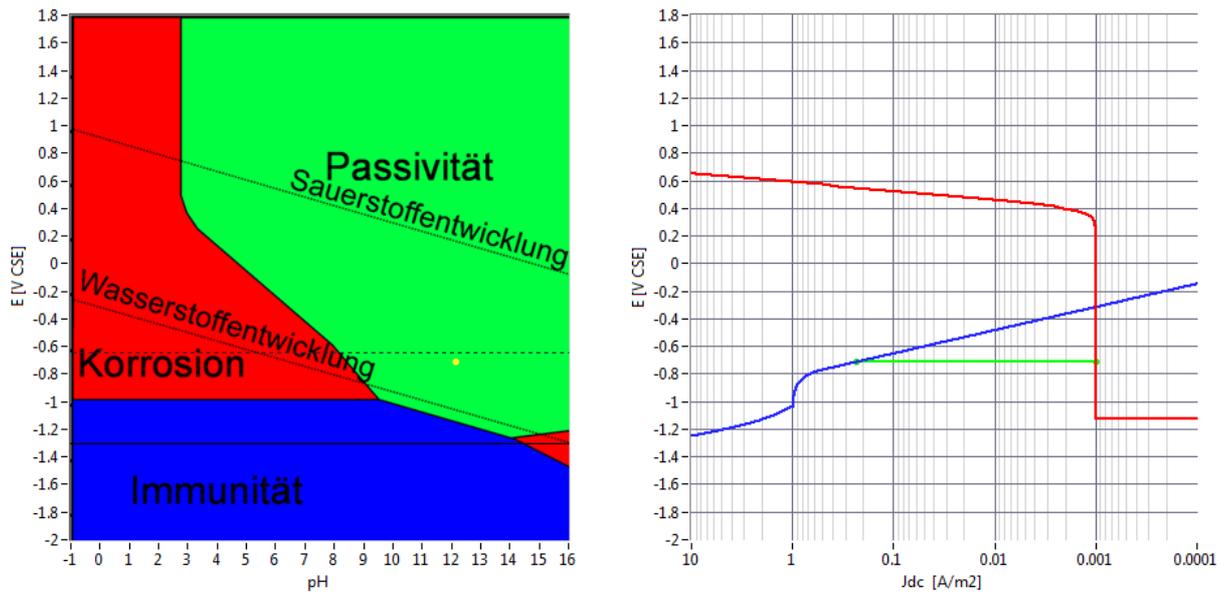


**Fig. 8:**  $E_{IR-free}$  calculated for a soil resistivity of  $5 \Omega m$ . Left: The dashed horizontal line represents  $E_p = -0.85 \text{ V CSE}$  according to EN 12954 and the solid line indicates  $E_{on}$  of  $-1.3 \text{ V CSE}$ . Right: Potential/current relationships. Detailed description is in Fig. 7.



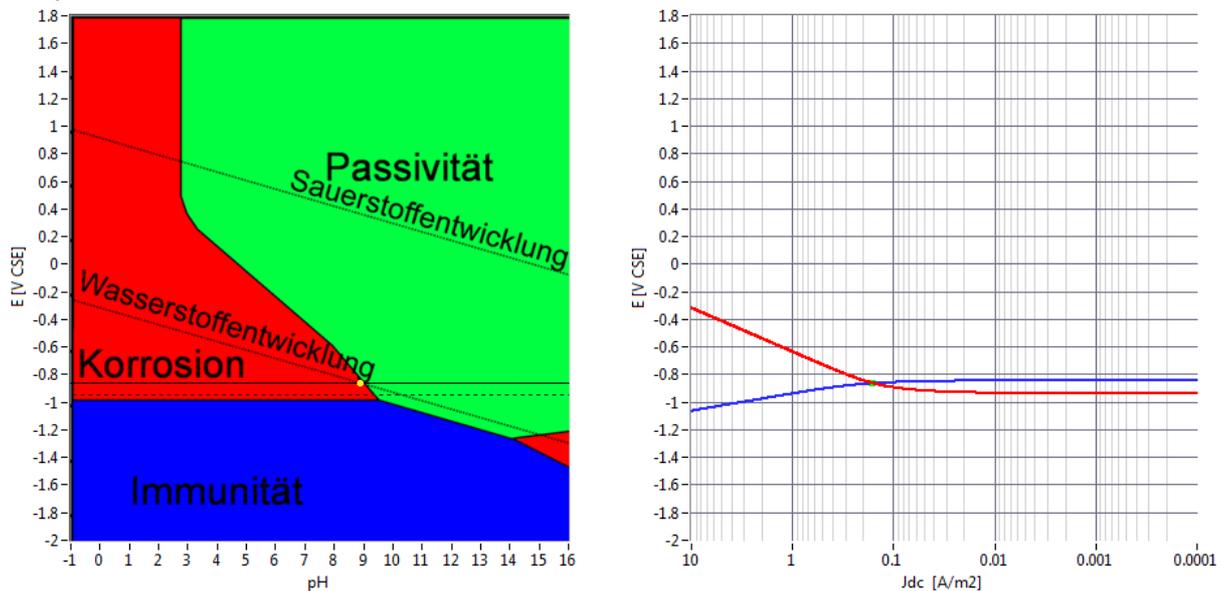
**Fig. 9:**  $E_{IR-free}$  calculated for a soil resistivity of  $500 \Omega m$ . Left: The dashed horizontal line represents  $E_p = -0.75 \text{ V CSE}$  according to EN 12954 and the solid line indicates  $E_{on}$  of  $-1.3 \text{ V CSE}$ . Right: Potential/current relationships. Detailed description is in Fig. 7.

Increasing the soil resistivity to  $500 \Omega m$  results in an increased spread resistance, a lower  $J_{dc}$  of about  $0.7 \text{ A/m}^2$ , and an  $E_{IR-free}$  that is more positive than  $-0.85 \text{ V CSE}$  (Fig. 9). However, these conditions allow the use of criterion  $E_p$  of  $-0.75 \text{ V CSE}$  according to EN 12954. As a consequence, the protection conditions are still met. Based on the calculation in Fig. 9 it can be concluded that the corrosion protection is achieved by passivity caused by the increase of the pH at the steel surface.



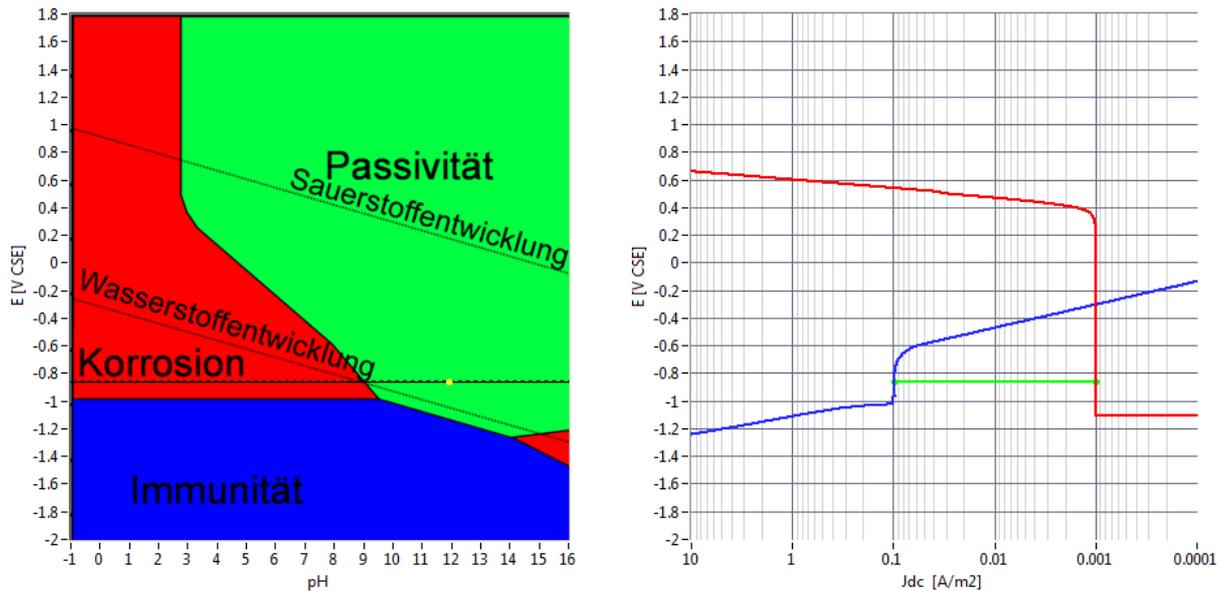
**Fig. 10:**  $E_{IR-free}$  calculated for a soil resistivity of 5000  $\Omega m$ . Left: The dashed horizontal line represents  $E_p = -0.65$  V CSE according to EN 12954 and the solid line indicates  $E_{on}$  of -1.3 V CSE. Right: Potential/current relationships. Detailed description is in Fig. 7.

Increasing the soil resistivity to 5000  $\Omega m$  results in a more increased spread resistance, an even lower  $J_{dc}$  of about 0.25 A/m<sup>2</sup> and an  $E_{IR-free}$  that is now more positive than -0.75 V CSE (Fig. 10). However, these conditions allow the use of an  $E_p$  of -0.65 V CSE according to EN 12954. As a consequence, the protection conditions are again met and the corrosion protection is achieved by passivity.



**Fig. 11:**  $E_{IR-free}$  calculated for a soil resistivity of 5  $\Omega m$ . Left: The dashed horizontal line represents  $E_p = -0.95$  V CSE according to EN 12954 for anaerobic conditions and the solid line indicates  $E_{on}$  of -0.87 V CSE. Right: Potential/current relationships. Detailed description is in Fig. 7.

The discussion demonstrates clearly that the protection criteria can readily be explained by means of the kinetic and thermodynamic data. It is important to note that the corrosion potential values of -0.64 V CSE in Fig. 6 in absence of cathodic protection may indicate corrosion while an identical  $E_{IR-free}$  under the conditions discussed in Fig. 10 is demonstrating corrosion protection. The difference is caused by the modification of the pH and the change in the anodic potential/current relationship of steel.



**Fig. 12:**  $E_{IR-free}$  calculated for a soil resistivity of  $5 \Omega m$ . Left: The dashed horizontal line represents  $E_p = -0.85$  V CSE according to EN 12954 and the solid line  $E_{on}$  of  $-0.87$  V CSE. Right: Potential/current relationships. Detailed description is in Fig. 7.

Under anaerobic conditions  $J_{O_2}$  becomes virtually zero. Applying an  $E_{on}$  of  $-0.87$  V CSE at a soil resistivity of  $5 \Omega m$ , results in an  $E_{IR-free}$  more negative than  $-0.85$  V CSE. Despite of this value still corrosion is expected to take place since the pH is not sufficiently increased to reach the passivity range (Fig. 11). This is due to the fact that the corrosion potential of steel under anaerobic conditions is very negative and, therefore, the protection current density is extremely small despite of the low spread resistance. According to the EN 12954 a protection criteria of  $-0.95$  has to be applied under these conditions, which is in line with the corrosion expected based on the calculation.

Increasing  $J_{O_2}$  to  $0.1$  A/m<sup>2</sup> results in a shift of the corrosion potential to more positive values that causes  $J_{dc}$  and therefore the pH at the steel surface to increase, as can be concluded from Fig. 12. In this case  $E_{IR-free}$  is more negative than  $-0.85$  V CSE. Hence the protection conditions of EN 12954 are met and the corrosion protection is achieved by means of passivity.

## 5. Conclusion

The discussion and calculations demonstrate that the criteria of EN 12954 and the results in [13] can be explained when considering the thermodynamic and kinetic parameters of steel in soil. It can be concluded that corrosion protection can be achieved by means of passivity or immunity. Based on the presented data it has to be expected that in typical operation conditions both protection methods are present on the various coating defects, depending on soil resistivity and diffusion limited oxygen reduction current.

Based on the discussion it can be concluded that  $E_{IR-free}$  is a mixed pH and oxygen measurement. However, for obtaining a sufficient corrosion protection primarily the increased pH at the steel surface is relevant rather than the potential. Therefore, the protection criteria have to be adapted depending on the aeration conditions of the soil. Based on the presented data it could be concluded that a direct pH measurement could be beneficial to determining the efficiency of cathodic protection. Possible methods for determining the pH-value at the surface of coupons were reported previously [3, 7, 16] and have proved to be an efficient and reliable

method for confirming CP efficiency in case the protection criteria are not met. Alternatively the use of ER-coupons may be used as a direct proof for the efficiency of the cathodic protection [17, 18].

Considering the discussed data it is also clear that on-potentials should always be more negative than -0.95 V CSE, if anaerobic conditions are expected. Otherwise, passivity cannot be assured on all coating defects and, therefore, anodic polarization of the anaerobic sites may occur.

## 6. Acknowledgement

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