

The historic evolution of cathodic protection criteria

Die historische Entwicklung der Kriterien für den kathodischen Korrosionsschutz

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Abstract

In the context of a.c. corrosion some aspects of cathodic protection needed to be reconsidered and resulted in an improved understanding of the corrosion process under interference conditions. While these new concepts are well accepted in the case of a.c. corrosion, their implications on cathodic protection criteria are not yet fully understood. Therefore the literature on cathodic protection criteria is revisited and discussed in the light of the most recent results. This review shall provide a contribution to the ongoing discussion on criteria for cathodic protection and stray current interference.

Zusammenfassung

Im Zusammenhang mit der Wechselstromkorrosion wurden verschiedene Aspekte des kathodischen Korrosionsschutzes durch neue Erkenntnisse ergänzt. Dies führte zu einem verbesserten Verständnis der unter Beeinflussung ablaufenden Prozesse. Während diese Ergebnisse im Bereich der Wechselstromkorrosion generell akzeptiert sind, besteht noch kein umfassendes Verständnis bezüglich deren Auswirkungen auf die kathodischen Schutzkriterien. Die Literatur bezüglich Schutzkriterien wird im Zusammenhang mit diesen neuen Erkenntnissen diskutiert. Dies soll einen Beitrag zur aktuellen Diskussion der Kriterien für kathodischen Schutz und Streustromkorrosion liefern.

1. Introduction

Cathodic protection (CP) has been systematically applied on pipelines since 1928 [1]. Despite the long and successful application of this technology, there is still significant controversy about the applicable protection criteria, the corresponding threshold values and the underlying mechanisms. While there is general agreement that the protection is achieved through electrochemical polarization, there was only limited consideration to the type of polarization and the respective characteristics.

In the last years various investigations with respect to cathodic protection have confirmed the understanding, that the pH is an important parameter in providing the corrosion protection [2-5]. In many cases relatively small protection current densities result in a significant increase of the pH-value at the steel surface of coating defects of pipelines. This increase of the pH favors the formation of a passive film, which significantly limits any further corrosion [3-5]. By means of model calculations, that are based on thermodynamic and kinetic data, all currently used protection criteria in CP can readily be explained when taking into account the relevance of the pH and the formation of a passive film [6-9]. Based on these considerations the mass transport at the steel surface is a key determining factor in the effectiveness of CP.

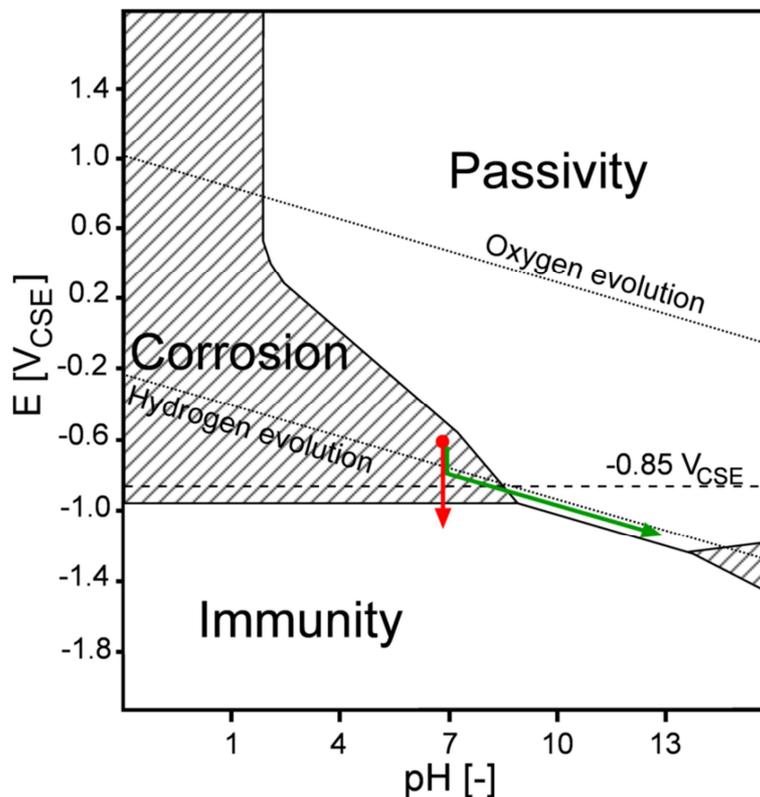


Figure 1: Polarization of steel with cathodic current according to Leeds [10]. Green: Concentration polarization of a well bedded coating defect; Red: Activation polarization of a poorly bedded coating defect. Solid lines delineating the thermodynamic stability of the various areas assume the conventional concentration of 10^{-6} M Fe^{2+} .

An increase of the pH-value at the steel surface, however, can only occur, when the pipeline is bedded in fine sand and soil, or if the precipitation of calcareous deposits from water with increased hardness is taking place. Under these circumstances the convection of water at the coating defect will be limited and the hydroxide ions that are formed at the steel surface by the cathodic current entering the steel surface can only be transported by means of diffusion and migration. Hence, they will accumulate and the pH-value at the steel surface will increase. Under these conditions relatively small protection current densities are required to cause a

change in concentration of hydroxide ions at the steel surface. This type of polarization corresponds to a concentration polarization as shown by the green line in Figure 1. In contrast, the presence of streaming and especially soft water, as it can be expected in rough bedding material, will result in a rapid dilution of the generated hydroxide ions. Alternatively, the increase of the pH can be limited by the activity of sulfate reducing bacteria [2]. The increase of the pH-value and the formation of the passive film will not occur under these circumstances. Therefore, corrosion protection can only be achieved by activation polarization into the immunity domain. Since the immunity domain is cathodic of the hydrogen equilibrium potential line, the polarization into immunity is only possible with highly increased current densities. This case is illustrated by the red line in Figure 1.

The illustration of the two extreme cases of polarization ignores the fact that any activation polarization will give rise to some concentration polarization and all concentration polarization will have some activation polarization. In Figure 1 the extreme cases of these two types of polarization are shown. For further differentiation the key differences are discussed below:

Limited mass transport due to bedding in soil and sand, or formation of calcareous deposits on coating defects resulting in concentration polarization:

- The required current density for the increase of the pH-value and the formation of a passive film is in the range of 1 mA/m^2
- After passivation of the steel, a current density will be established that is determined by external parameters, such as the on-potential, the diffusion limited oxygen reduction current and the spread resistance of the coating defect
- In the presence and maintenance of passivity an IR-free potential more positive than any conventional protection criterion (e.g. more positive than $-0.85 V_{\text{CSE}}$) does not have to be interpreted as corrosion
- In the presence of passivity, limited anodic interference has only a minor impact on the corrosion behavior

In case of fast mass transport due to contact with streaming and especially soft water or neutralization of the formed hydroxide ions due to microbial activity, the polarization is achieved through activation polarization:

- A reduction of corrosion rate is achieved by shifting the IR-free potential in the negative direction, i.e. in the immunity domain
- The required current densities for achieving the immunity domain are in the range of 1 A/m^2 or higher due to the kinetics of the hydrogen evolution reaction
- IR-free potentials more positive than the protection criterion of $-0.95 V_{\text{CSE}}$ indicate corrosion
- In the case of activation polarization, anodic interference has a dramatic impact on the corrosion behavior due to the potential being consistently in the area where soluble Fe^{2+} is thermodynamically stable.
- Under typical operation conditions of CP it can be difficult to achieve protection of larger coating defects in higher resistive soil

The above list is not exhaustive. A more detailed discussion is given in [11]. These parameters demonstrate the importance of mass transport and hence the bedding of the pipeline. Effective CP is comparably easy to achieve on a well bedded pipeline where limited mass transport

favors concentration polarization. In contrast, in the case of poor bedding conditions and fast mass transport, it can be very difficult to achieve sufficient corrosion protection by means of activation polarization. For larger coating defects in high resistivity soil unrealistically negative on-potentials may be required to achieve sufficient corrosion protection. This makes it questionable whether or not achieving immunity by means of activation polarization is possible in all cases.

For the design, control and effectiveness of CP systems and the requirements for coatings and backfill of pipelines it is of the utmost importance to have an understanding of the predominant and relevant controlling parameters. This is even more important for interference conditions. In order to gain a more profound understanding of these various aspects, the evolution of cathodic protection is investigated based on literature and the consequences on the application of the technology are discussed.

2. Historic evolution

2.1. Introduction

The relevant difference between concentration and activation polarization has severe consequences on the application of cathodic protection and the assessment of its effectiveness. If there is a lack of understanding of the involved processes, it will not be possible to develop appropriate protection criteria. In the light of these concepts it is therefore relevant to revisit literature and compare those results with the proposed concepts. The following discussion will be based on the various aspects of the above concepts.

2.2. Increase of pH and passivation with concentration polarization

All the relevant processes described in Figure 1 for concentration polarization were essentially discussed by Evans in 1923 for the corrosion of steel in heterogeneous aeration [12]. In order to illustrate his concept, the relevant effects are discussed by means of the Evans droplet test as shown in Figure 2:

A piece of steel with a water droplet on top will develop within a few minutes a localized corrosion process based on the reduction of oxygen according to reaction (1) and the oxidation of iron according to reaction (2).



The heterogeneous aeration due to the different diffusion distances for oxygen causes an increase of the pH at the edges of the droplet while oxygen depletion in the center will result in increased corrosion. This mechanism originally reported by Evans was summarized by Pourbaix [13] in 1974 as follows:

"When a piece of iron is immersed in a practically neutral non-buffered solution, which is aerated in one region (edges of the droplet) and not aerated in another (center of the droplet), it is noticed that this differential aeration produces an increase in the corrosion rate in the non-aerated regions, and a decrease in the corrosion rate in the aerated regions, with a flow of

electric current between these regions. On account of the increase of the pH due to the reduction of oxygen, the aerated regions will be passivated and the non-aerated regions will not be passivated."

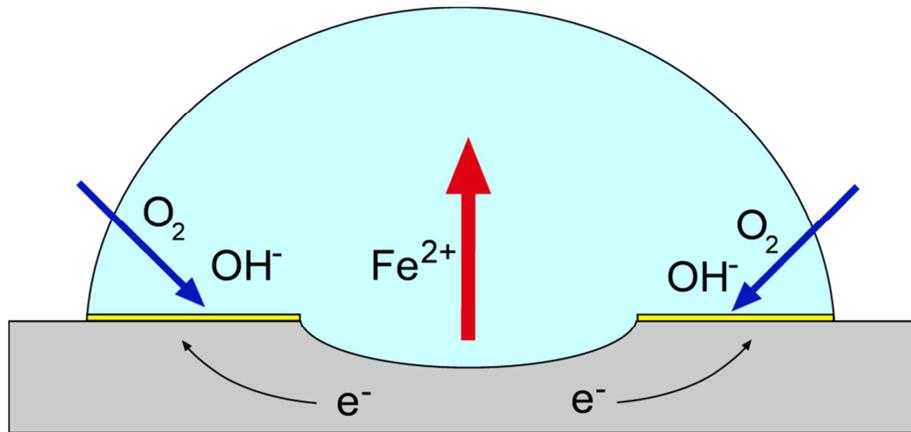


Figure 2: Schematic illustration of the Evans droplet test causing local increase of pH due to heterogeneous aeration and subsequent passivation (yellow).

This description by Pourbaix is in good agreement with the effects illustrated in Figure 1 for concentration polarization. In other words the Evans droplet test is a case of cathodic protection by means of a galvanic anode in the form of a poorly aerated steel surface. This very concept of increase of pH and formation of a passive film is confirmed by the Max Planck Institute für Eisenforschung in the case of cut edge tests of galvanized steel [14]. It was found that the good corrosion protection caused by the limited cathodic current densities delivered by zinc can only be explained based on a pH increase and subsequent passivation.

In 1928 Kuhn introduced cathodic protection as a means to control corrosion on pipelines. He introduced the value of $-0.85 V_{CSE}$ for the on-potential and stated for the current entering on the cathodic areas [1]:

"It causes a film of hydroxide to form, which protects these areas from corrosion"

The process of accumulation of hydroxide ions and increase of pH is most effective in non-buffered solutions with hindered mass transport, since otherwise the increase of the pH is limited and passivation will be delayed. Evans indeed observed that the current density required for achieving cathodic protection is dependent on the convection of the electrolyte. At increased flow rates higher current densities are required to compensate for the dilution of the hydroxide ions, as Evans stated in 1946 [15].

Based on these observations it can be concluded that some of the first discussions of the electrochemical corrosion processes of steel already took into account the effects of change of concentration at the steel surface and the resulting passivation.

2.3. The problems associated with activation polarization

The key problem associated with activation polarization is the fact that the immunity domain of iron is cathodic of the hydrogen evolution equilibrium line and hence outside the stability domain of water. Polarizing into the immunity, therefore, requires significantly increased protection current densities. Achieving cathodic protection by means of activation polarization is, therefore, difficult and requires increased current densities. This problem was recognized by von Baekmann in the first edition of his Handbook in 1971 [16]. The discrepancy between the

theoretically expected high current densities with the comparably small ones observed in the practical application led him to the conclusion that the hydrogen evolution is kinetically hindered by an over-potential:

"The existence of such an over-potential, i.e. a kinetic inhibition for the hydrogen evolution, is an important precondition for the applicability of CP. Otherwise the hydrogen evolution would represent an important potential barrier. Otherwise the required negative potentials for immunity could not be reached."

However, investigations have clearly shown that there is no relevant over potential for hydrogen evolution on steel [17]. Consequently in the third edition of the Handbook 1988 [18] this explanation is no longer found. Instead the mechanism of cathodic protection is described as follows:

- Immunity cannot be reached
- Hence the protection criteria can only be determined empirically
- The strong decrease of the corrosion rate with decreasing potential in oxygen containing solutions is caused by the formation of oxide covering layers with the involvement of OH⁻ and O₂

This description is in good agreement with the discussed effects in Figure 1. The polarization into immunity is practically not possible and the change in concentration of hydroxide ions is considered to be at least relevant in certain cases. However, the fact that no model is proposed for the mechanism of cathodic protection has severe implications. If the criteria are purely empirical, they are only applicable for the very conditions under which they were determined. It follows immediately that the thresholds for the IR-free potential of -0.75 and -0.65 V_{CSE} of EN 12954 and ISO 15589-1 may only be applied in the case of coating defects that are well bedded in fine sand, since those were the very conditions under which these thresholds were determined [19]. Interestingly, for well bedded conditions in combination with concentration polarization these values can readily be confirmed by recent model calculations [6-9]. Therefore, these criteria in EN 12954 implicitly require optimized mass transport conditions and concentration polarization. The same applies for the current densities stated in the ISO 15589-1.

2.4. The IR-free potential and the pH-value

One of the first investigations with respect to the relevance of the threshold of -0.85 V_{CSE} was performed by Schwerdtfeger and McDorman [20] in 1951. They observed that the corrosion potential of steel in anaerobic electrolytes lays between the equilibrium line for reaction (2) at -0.95 V_{CSE} and the hydrogen evolution line (Figure 3). The values gradually decrease with increasing pH, reaching -0.85 V_{CSE} at pH-values of 9. These results are in agreement with the expected corrosion potential of iron under hydrogen evolution [6-9]. They are moreover consistent with the line shown in Figure 1 for concentration polarization, since their data demonstrate that an IR-free potential of steel more negative than -0.85 V_{CSE} is linked to a pH larger than 9. Moreover, these data demonstrate that the steel does not exhibit a relevant over potential for hydrogen evolution, since a kinetic inhibition for hydrogen evolution would result in more negative potentials. This has relevant technical implications: The electrodeposition of iron by polarization into immunity is limited to few specific applications due to the required current densities well above 10 A/m². Hence, the very conditions that prevent an extensive application of electrodeposition of iron make the cathodic protection of steel by activation polarization into immunity impractical [18].

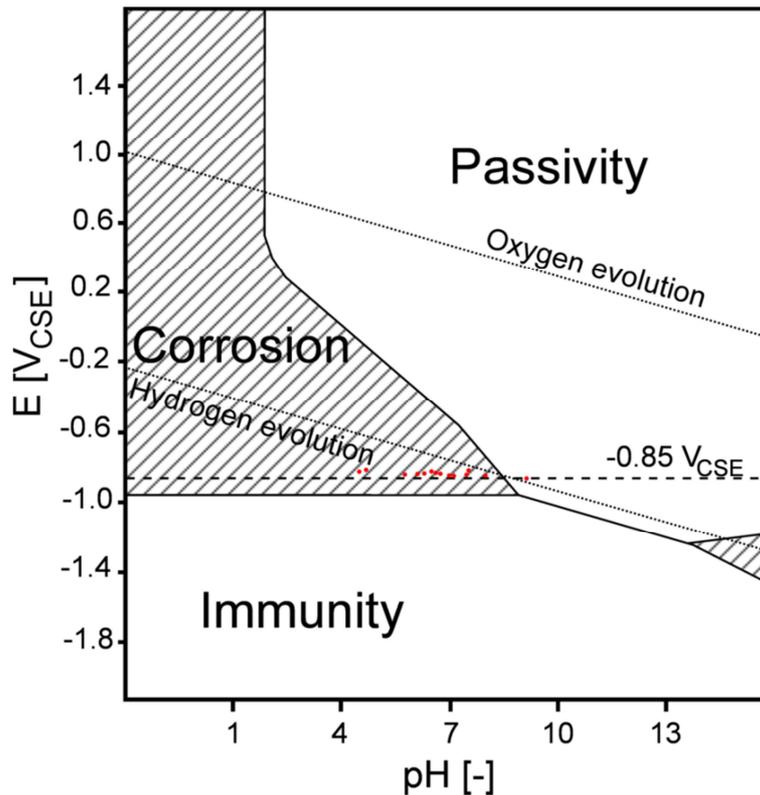


Figure 3: Corrosion potentials of steel in anaerobic electrolytes as a function of pH replotted from [20]

Another investigation related to the IR-free potential and the pH at the steel surface was performed by Thompson and Barlo in 1983 [21]. Steel samples were polarized in anaerobic, aerated and oxygenated electrolyte to either -0.92 or $-1.12 V_{CSE}$. The mass transport was limited by a porous ceramic, allowing for accumulation of hydroxide ions at the steel surface. Based on these measurements, the applied IR-free potentials resulted in a relevant increase of the pH and a limitation of the corrosion rate below 0.01 mm/year in all cases (Figure 4). Based on these data the corrosion protection was achieved by either passivity or immunity at increased pH.

They evaluated their data with respect to protection current density and pH at the steel surface [21] as shown in Figure 5. Additionally, data obtained in artificial soil determined at higher current densities are shown [3]. Current densities as low as 1 mA/m^2 are sufficient to provide an increased surface pH and passivation of the steel surface under conditions of hindered mass transport. Moreover, it is found that protection current densities in the range of 0.1 A/m^2 result in pH values around 12 under these conditions and, therefore, allow for concentration polarization.

In 1988 Freiman et al. [22] recognized the discrepancy between concentration and activation polarization and the lack of differentiation between these two cases:

"Modern theories of cathodic protection for underground steel structures assume that the metal always corrodes in the active state, and the role of cathodic polarization is reduced to a reduction in potential to those values with which the anodic dissolution rate becomes below the technical permissible value or it almost equals zero. As a rule no consideration is given to an increase in pH of the layer near the electrode at the metal surface (pHs) due to a reduction in the rate of formation of acid corrosion products with retention or even some acceleration of the cathodic discharge of O_2 molecules. However, with pHs ≥ 10.7 and quite low concentrations of active ions (sulfates and chlorides) in the soil the metal should be converted into the passive state not despite cathodic polarization, but due to it."

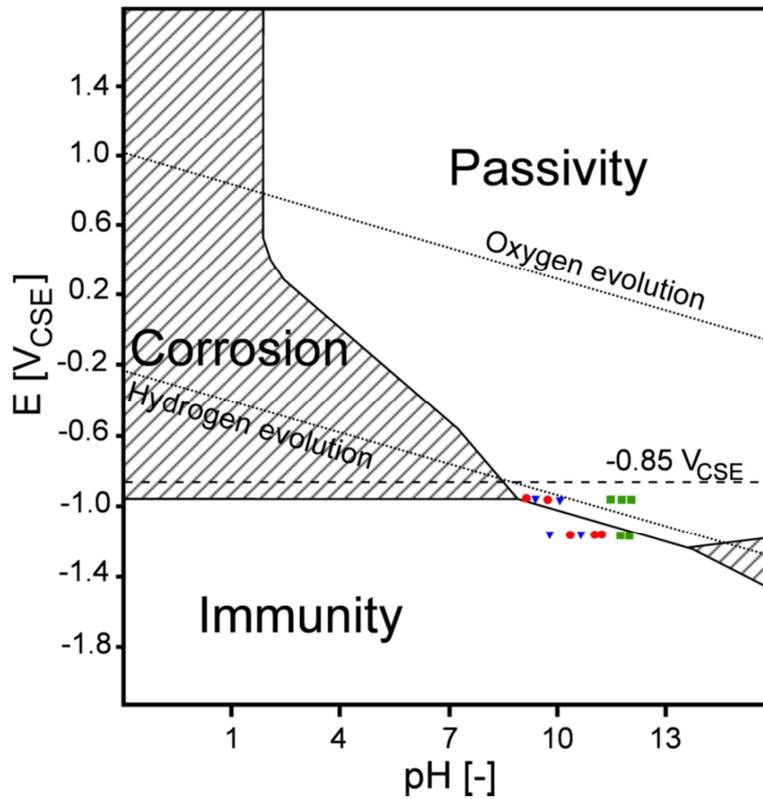


Figure 4: The pH values obtained after polarization in mass transport limited electrolytes replotted from [21]. All corrosion rates were below 0.01 mm/year. Red: anaerobic; blue: aerated; green: oxygenated.

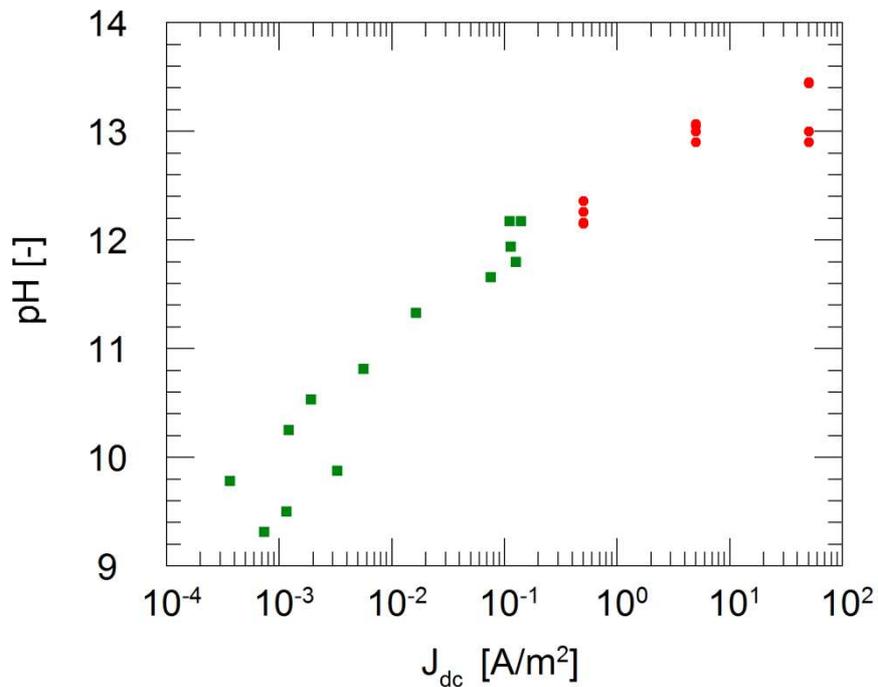


Figure 5: Correlation between the protection current density and the surface pH under conditions of restricted mass transport and hence concentration polarization. Green: Thompson and Barlo [21]; red: Büchler and Schöneich [3].

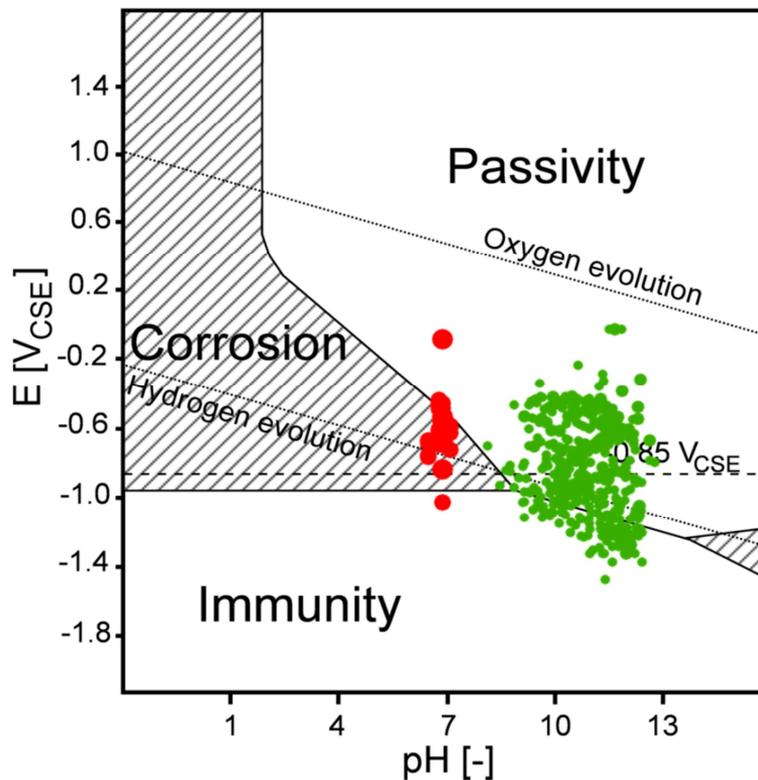


Figure 6: Representation of the corrosion rate from field tests [23] in the Pourbaix diagram. The corrosion rates for the green dots are smaller than 0.03 mm/year, while the red dots exhibit higher corrosion rates.

This conclusion is in line with the effects discussed in Figure 1. They are confirmed by the extensive field investigations of CP and the related protection criteria performed by Barlo in 1994. Coupons were cathodically protected under defined conditions during 5 years in Australia, Canada and the USA [23]. In Figure 6 the IR-free potentials and the pH values calculated from the relationship in Figure 5 are plotted. The pH of the corroding coupons was estimated to be in the neutral domain. The results for the coupons with small corrosion rates (green dots) show a sufficiently increased pH for passivation. This explains the small corrosion rates even at IR-free potentials more positive than $-0.85 V_{CSE}$. Based on these data it is clear that the corrosion protection can readily be determined based on the pH value rather than on the IR-free potential. Interestingly, applying the same approach to the data collected in Germany between 2011 and 2013 [24] resulted in an even better correlation between pH and corrosion protection. As long as the average current density was cathodic (larger than 1 mA/m^2) and the average on-potential was more negative than $-0.85 V_{CSE}$, no corrosion was observed. This good agreement between the field test [24] with the model concepts in Figure 1 can readily be explained by the special care that was taken with respect to bedding of the coupons: they were oriented upward by an angle of 45° to prevent loss of contact with the soil in the case of soil settling. Hence, the bedding conditions were ideal, the mass transport was highly limited and the buildup of an increased pH with concentration polarization was possible even at small current densities. This confirms the relevance of the mass transport for the corrosion behavior.

The problems associated with a limited pH increase are nicely illustrated by the investigation of Kajiyama and Okamura in 1999 [2] as shown in **Fout! Verwijzingsbron niet gevonden..** The acid produced by the sulfate reducing bacteria (SRB) required activation polarization in order to achieve protection, while in absence of SRB an increase of pH and protection through passivation was readily possible. These data are again in good agreement with the proposed

model concept in Figure 1 and can readily be explained by means of concentration and activation polarization, respectively.

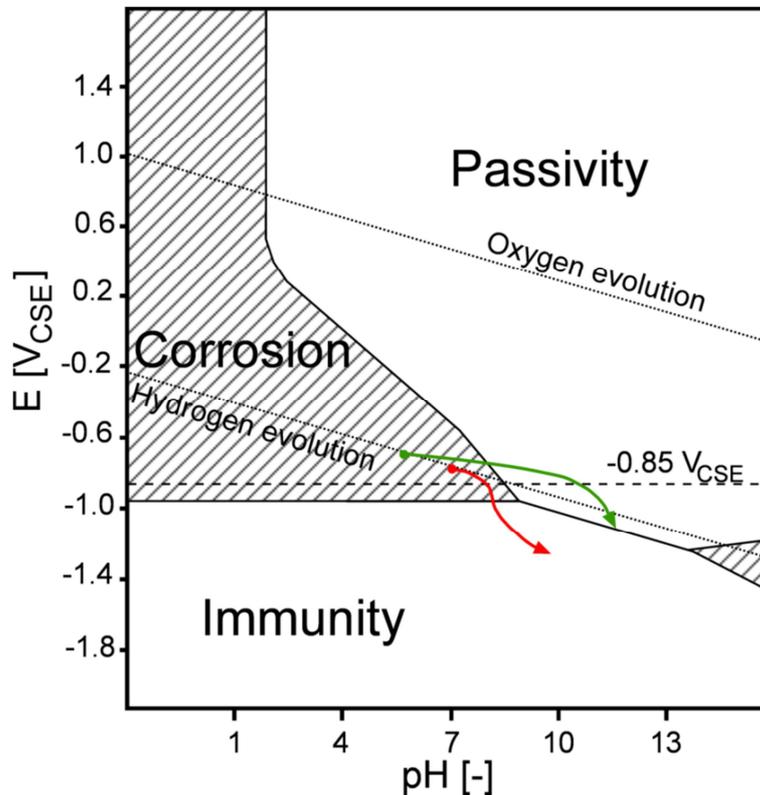


Figure 7: The pH and IR-free potential dependence determined for soils with (red) and without (green) sulfate reducing bacteria according to [2].

The results of Schwerdtfeger and McDorman (Figure 3), of Thompson and Barlo (Figure 4) and Kajiyama and Okamura (**Fout! Verwijzingsbron niet gevonden.**) demonstrate a link between the pH and the IR-free potential as suggested by Leeds in 1992 (Figure 1). Kasahara, Sato and Adachi [25] also demonstrated a similar relationship between the IR-free potential, current density and pH. In the case of limited mass transport (sand bedding) and absence of sulfate reducing bacteria the protection current as small as 1 mA/m^2 causes an increase of surface pH and subsequent passivation. IR-free potentials more negative than $-0.85 \text{ V}_{\text{CSE}}$ indicate an increase of the pH above 9 and the possibility of passive conditions under these circumstances.

2.5. The IR-free potential in the case of activation polarization

Most literature data can readily be explained based on the concept for concentration polarization. However, there are relevant factors affecting the corrosion behavior that are often overlooked. Pourbaix has pointed out in 1960 [26] that the cathodic polarization of steel in buffered solution can initiate or accelerate corrosion. The naturally formed protective passive film or rust layer can be cathodically dissolved and, therefore, cause an increase of corrosion rates under insufficient cathodic protection. The investigation of Schwenk [27] has indeed confirmed strongly increased corrosion rates in the range of 0.3 mm/year caused by polarization of steel to IR-free potentials of $-0.85 \text{ V}_{\text{CSE}}$ in carbonate buffers of pH 9.5. In his test IR-free potentials more positive than $-0.65 \text{ V}_{\text{CSE}}$ did not exhibit any relevant corrosion and the polarization to values more negative than $-0.95 \text{ V}_{\text{CSE}}$ limited the corrosion rate to irrelevant

levels. This effect is schematically illustrated for a solution of pH 7 in Figure 8. It is relevant to note that in the presence of carbonates the corrosion domain is further extended to higher pH values well above 10 as indicated with the blue domain for 1 M CO₂ [28]. Schwenk used concentrations in this range and confirms that no active domain is observed at pH-values of 11 [27].

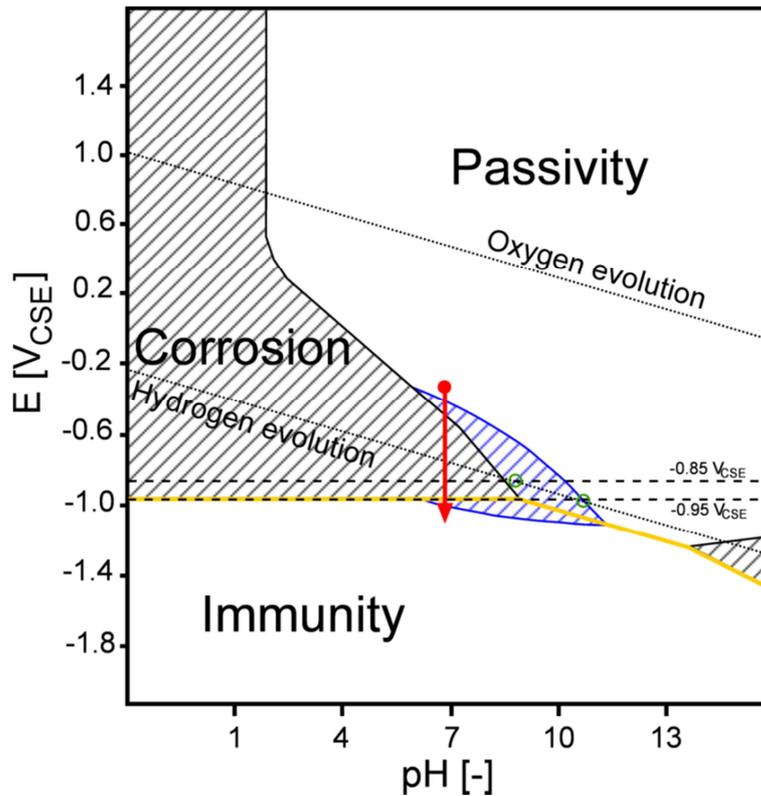


Figure 8: Possible acceleration of corrosion due to cathodic activation polarization (red arrow) from the passivity into corrosion domain in a buffered near neutral electrolyte according to [26, 27]. In yellow the pH dependent protection criteria proposed by Pourbaix are shown [13, 26]. In blue the expected additional corrosion domain in 1 M CO₂ is shown [28]. The green circles represent the expected pH values based on the IR-free potential values of -0.85 and -0.95 V_{CSE} in anaerobic conditions in the case of concentration polarization.

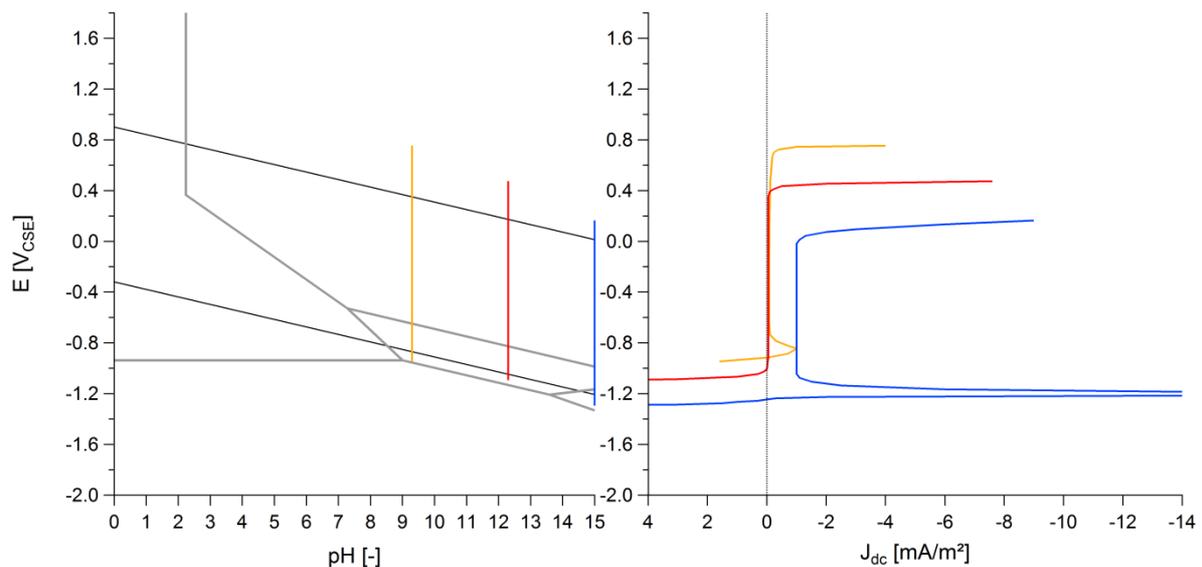


Figure 9: Polarization scans (cathodic currents with positive sign) in electrolytes with various pH values redrawn according to [29]

It must be assumed that the possible risk of corrosion acceleration due to activation polarization from the passivity into the corrosion domain has motivated Pourbaix to propose pH dependent protection criteria as indicated with the yellow line in Figure 8 [13, 26]. Pourbaix's approach is in important contrast to the requirements of EN 12954 and ISO 15589-1. Even the most negative threshold of $-0.95 V_{CSE}$ for the IR-free potential can only be accepted according to his concept, if the pH increase is limited. In case of a pH increase above values of 11, which has to be expected at typical current densities of 0.1 A/m^2 based on the data in Figure 5, a threshold of $-1.05 V_{CSE}$ would be required (according to the yellow line in Figure 8). Based on Pourbaix's concept, the application of the current standards would result in significant corrosion risks.

The absence of an active domain anodic of the immunity in the pH range of 9 to 14 is, therefore, of utmost importance for the application of cathodic protection. Based on the results in Figure 5, it has to be expected that all well bedded coating defects exhibit pH values from 9 to 13. Moreover, the EN 12954 and ISO 15589-1 require the IR-free potential to be in the range of -0.85 to $-1.2 V_{CSE}$. This happens to be the transition domain between immunity and passivity with a possible presence of an active passive transition. There is no literature presenting any relevant active dissolution in the corresponding potential and pH-domain, with the exception of carbonate solutions. Typical results from Heusler et al from 1958 [29] are presented in Figure 9. Clearly no relevant anodic dissolution is observed in the pH range from 9.5 to 13. At pH 15 however, significant anodic dissolution is observed. These results are in line with Schmuki et al. [30] for measurements at pH 13.

In contrast, active dissolution has to be expected in the case of increased carbonate concentrations as shown in Figure 8. This thermodynamically expected domain is experimentally confirmed by literature [27, 31]. A certain level of carbonates has to be expected in any soil and a consumption of the carbonates by precipitation of siderite (FeCO_3) is expected. This may contribute to the formation of covering layers that will enhance the increase of pH and contribute to a concentration polarization. Nevertheless, in the case of streaming soft and especially buffered water any threshold more positive than $-0.95 V_{CSE}$ for the IR-free potential under activation polarization cannot be justified based on the available literature.

In contrast, under mass transport limited conditions on well bedded coating defects a limited concentration of carbonates may be expected. The precipitation of siderite will rapidly decrease their concentration and favor the formation of a passive film. This is confirmed by the data of Schwenk that show a rapid decrease of the corrosion rate in his test with a limited electrolyte volume [27]. In the case of concentration polarization the application of a threshold of $-0.95 V_{CSE}$ for the IR-free potential indicates a pH increase to 11. Under these conditions protection even in increased carbonate concentration according to the green circle in Figure 8 may be expected.

2.6. Conclusion

Based on literature achieving corrosion protection by activation polarization into immunity is difficult if not impossible. In contrast, there is wide agreement that cathodic protection is achieved by an increased pH and subsequent passivation. The second edition of the standard CP textbook by Peabody [32] from 2001 nicely summarizes this observation:

"The concepts presented for CP (activation polarization) are fundamentally correct at the instant that CP is applied but are too simplistic to consider the time-dependent behavior of a cathodically protected underground structure..... This pH increase (concentration polarization) is beneficial because the corrosion rate of steel decreases with increasing pH, even under freely corroding conditions. The decrease in corrosion rate is the result of the formation of a protective

oxide film on the metal surface in the elevated pH environment, a process referred to as passivation."

This view is confirmed by more recent work [33-35]. Based on the review of literature the requirements in EN 12954 and ISO 15589-1 can only be explained by means of concentration polarization. If the cathodic protection would be based on a shift of the IR-free potential into or towards immunity, no threshold for the IR-free potential more positive than $-0.95 V_{CSE}$ could be tolerated and would represent a significant corrosion risk. The fact that the more positive threshold values -0.85 , -0.75 and $-0.65 V_{CSE}$ have been successfully applied in the past years, confirms the fact that corrosion control is readily possible at these values. Denying the relevance of the pH-increase and concentration polarization implicitly puts the technical relevance of the current standards into question.

3. The protection criteria

3.1. Introduction

Based on the above discussion of the literature, the effect of concentration polarization, the increase of pH and the subsequent passivation for the corrosion protection of steel was demonstrated. The discussion of the threshold of $-0.85 V_{CSE}$ and the relevance of the on-potential versus an IR-free potential has continued since Kuhn's original publication in 1928. The corresponding literature is revisited with the proposed concept of activation and concentration polarization. This discussion is not only relevant for the future work on the corresponding standards, but significantly affects the protection criteria for stray current corrosion. Since EN 50162 is currently under revision, an understanding of the relevant processes is of utmost interest.

3.2. The significance of the on-potential

Kuhn has proposed in 1928 [1] an on-potential (E_{on}) criterion of $-0.85 V_{CSE}$. He identified the galvanic corrosion among differently aerated coating defects as the reason for the high corrosion rates. He found that applying a sufficiently negative on-potential ensures the compensation of these galvanic couples and a strong limitation of the corrosion process. Based on the above discussion his conclusion was technically sound and correct. The work of Schwerdtfeger and McDorman [20] has clearly shown that the IR-free potential ($E_{IR-free}$) of a steel surface corroding even under anaerobic conditions is always more positive than $-0.85 V_{CSE}$ unless the pH is increased above 9. In most electrolytes such an increase of pH is sufficient for passivation. Based on equation (3) it must therefore be concluded that any on-potential more negative than $-0.85 V_{CSE}$ is bound to result in a cathodic current I on an individual coating defect. This conclusion is independent on the spread resistance R and hence the soil resistivity.

$$I = \frac{E_{IR-free} - E_{on}}{R} \quad (3)$$

Taking into account the results in Figure 5 the current density for achieving pH 9 and hence passivation is as small as 1 mA/m^2 in the case of hindered mass transport and concentration polarization. At this current density negligible ohmic drop will be obtained even with large

coating defects and increased soil resistivity. This explains the good success of Kuhn's criteria based on an on-potential and underlines its technical relevance.

It is argued that the very low soil resistivities in the Mississippi Delta, where Kuhn ran his experiment, have resulted in negligible ohmic drops [36]. This argument ignores the fact that Kuhn was working with uncoated pipelines. The high current demand required by the large metal surface area negates the effects upon the magnitude of the ohmic drop caused by the low soil resistivity in the range of 6 Ωm . However, when considering the small current densities required for protection, Kuhn's success with the on-potential criterion can readily be explained on the basis of concentration polarization. It might be relevant to consider that he performed his work on cast iron pipes. The limited mechanical properties of this material required careful bedding of the pipelines and it may be assumed that this has favored a limited mass transport and the buildup of an alkaline environment.

It follows that the on-potential is sufficient as a protection criterion in the case of a well bedded coating defect with limited mass transport allowing for concentration polarization in the case of homogeneous current distribution within the individual coating defects. This was indeed confirmed in a field test in Germany, where no relevant corrosion was found if the on-potential averaged over 24 hours was more negative than $-0.85 V_{\text{CSE}}$ in the case of coating defects of 1cm^2 surface [24]. Consequently the average current density was cathodic and the pH could increase on the specifically well bedded probes with limited mass transport allowing for pH increase and passivation.

3.3. The significance of the IR-free potential

While the on-potential is a suitable method to assure current entering into the coating defects, the IR-free potential in the case of concentration polarization corresponds to a pH measurement. This was already demonstrated by Schwerdtfeger and McDorman [20]. It could be argued based on Figure 1 that under concentration polarization (green line) an IR-free potential of $-0.85 V_{\text{CSE}}$ corresponds to a pH 9 and IR-free potential of $-0.95 V_{\text{CSE}}$ corresponds to a pH of 11. The corresponding positions in the Pourbaix diagram are shown in Figure 8 by means of the green circles. Hence, these two empirically observed criteria for the IR-free potential that were already reported by 1957 [37] can readily be explained. Within this context also the maximum negative value of $-1.2 V_{\text{CSE}}$ for the IR-free potential stated in ISO 15589-1 can be explained. This corresponds to a pH value above 13, where issues with cathodic disbondment have to be expected. It is relevant to note that this threshold has limited relevance with respect to activation polarization, since activation polarization is characterized by a lack of increase in pH. Limited issues with disbondment of the coating have to be expected in the case of activation polarization.

Within this discussion it is crucial to understand that the threshold values of -0.85 , -0.95 and $-1.2 V_{\text{CSE}}$ are only applicable for an estimation of the pH value at the steel surface, if the IR-free potential is controlled by hydrogen evolution as indicated by the green line in Figure 1. In contrast, if the IR-free potential is a result of the activation controlled oxygen reduction, as has been discussed in [6-9], significantly more positive values in the range of -0.65 or $-0.75 V_{\text{CSE}}$ may be expected as observed by Funk et al. in 1987 [19] in well aerated soils. This explains the corresponding values in EN 12954 and ISO 15589-1 for high resistive well aerated soils. However, under these conditions the IR-free potential may not be used to determine the pH with respect to protection levels or over-protection. In the case of concentration polarization, where CP is resulting in an increased pH and the formation of a passive film, it must be concluded that

the IR-free potential is irrelevant for judging the corrosion protection of a passive surface [6-9]. This is best illustrated in Figure 6: The judgement of the corrosion situation is best done based on the pH value rather than the IR-free potential. In low resistive or poorly aerated soils the IR-free potential depends on the pH and may, therefore, be used to demonstrate the protection. Under well aerated conditions the IR-free potential does no longer correlate with pH and it is, therefore, irrelevant to draw any conclusion with respect to the corrosion situation.

Whenever this buildup of an increased pH is not possible due to a high removal rate of the formed hydroxide ions, such as in soft streaming water or in presence of sulfate reducing bacteria (see **Fout! Verwijzingsbron niet gevonden.**), an activation polarization is required at significantly increased current densities. In this case only an IR-free potential of at least $-0.95 V_{CSE}$ can assure sufficient corrosion protection by polarization close to or into immunity. Not meeting this threshold in the case of activation polarization is inherently linked to corrosion.

3.4. Conclusion

The discussion of the IR-free potential (required in EN 12954 and ISO 15589-1) as well as the on-potential (required in EN 14505) demonstrates the relevance of these two criteria under the respective circumstances. Kuhn's approach with the on-potential is technically sound and valid until today in the case of concentration polarization for well bedded pipelines. However, it was bound to fail in the cases where the pH could not increase. Corrosion damages during the 1980's in Germany on a poorly bedded pipeline caused by sulfate reducing bacteria resulted in the introduction of the IR-free potential criterion in Europe in combination with a threshold value of $-0.95 V_{CSE}$. Based on the above discussion this is technically correct and justified.

While the approaches developed in the past are well justified, they lead to a key problem when it comes to determine the effectiveness of cathodic protection: As long as the bedding and the mass transport conditions of individual coating defects are not known it is very difficult to justify a protection criterion other than an IR-free potential in combination with a threshold value of $-0.95 V_{CSE}$. This assures corrosion protection in case of activation polarization to immunity or concentration polarization to a pH value of 11. However, not meeting this criterion in the case of concentration polarization does not indicate a corrosion risk, in the case of activation polarization it does. A more detailed discussion of the impact of these parameters on the protection criteria is given in [38].

4. Consequences on interference conditions

4.1. Introduction

In the above discussion the presence of ac and dc interference has been excluded. However, for the practical application their effect on the corrosion process is of utmost importance. It is beyond the scope of this paper to treat these issues in detail. For simplification, the following assumptions were made:

- The pipeline is coated with a state of the art three layer PE coating with a coating resistance of at least $1 M\Omega m^2$ exhibiting individual coating defects that are more distant than the pipeline depth

- The distance between the interfering source and the pipeline is significantly larger than the pipeline depth.

In the following only the most relevant effects of the individual parameters will be addressed. They are based on the available literature and on the proposed model concepts. In the case of time variant dc interference they are not substantiated yet.

4.2. ac interference

Based on ISO 18086 there is general agreement that ac interference is caused by increased ac and dc current densities. This is especially critical in the case of concentration polarization, since the buildup of an increased hydroxide concentration at the steel surface and its distribution into the surrounding soil causes a relevant decrease of the spread resistance of the coating defects. Under given interference conditions the increase of pH and the drop of the spread resistance leads to increased current densities and, therefore, to an increased corrosion risk. The influencing processes according to the principles given in ISO 18086 are described in [39] in more detail. In the current understanding of the process it is the alternating formation and dissolution of the passive film within the transition between immunity and passivity at pH values around 13 that are responsible for the ac corrosion process [40]. So far there is no known case of ac corrosion under activation polarization conditions, which may be explained as follows: Based on theoretical considerations a short term decrease in cathodic protection current density and especially anodic currents caused by ac interference are expected to cause relevant corrosion damage as well. The key advantage in the case of activation polarization is the lack of pH increase and the absence of a decrease in spread resistance, which limit the risk of increased ac current densities and, hence, the risk for corrosion damages. This is indeed confirmed for the rails in the humid Simplon tunnel in absence of CP and therefore lack of pH increase where the traction return current was required to cause relevant mass loss [41].

Due to the relevant effect of pH and spread resistance, the corrosion rate is strongly controlled by the on-potential. More negative on-potentials result in higher pH at the steel surface, lower spread resistance and therefore higher ac corrosion rates. This makes the ac corrosion process for unknown mass transport conditions critical in the case of both, anodic and cathodic, dc interference.

4.3. Constant dc interference

In the case of constant dc interference, as it may be caused by a foreign CP system, the gradients in the soil will, depending on the polarity of the interference, either decrease (anodic interference) or increase (cathodic interference) the protection current density on a given coating defect. In the case of an anodic interference, the above discussion allows for some conclusions depending on the mass transport conditions and the predominant type of polarization:

- In the case of concentration polarization the on-potential measured above the pipeline must be at least more negative than $-1 V_{CSE}$. Under these conditions a cathodic current will be flowing towards the coating defect, resulting in an increased pH and passivity.
- In the case of activation polarization any shift of the on-potential more positive than the minimum required value will cause an inherent risk of corrosion. With the Tafel slope of less than 100 mV/dec for the iron dissolution reaction (2) even a small shift of the on-

potential to a less negative level can result in relevant corrosion [42]. Corrosion has to be expected already in the case of a decreased protection current density in the coating defect of less than 1 A/m^2 . As a consequence, anodic interference under activation control must be compensated by shifting the on-potential more negative, with all the negative consequences on ac corrosion risk on the corresponding well bedded coating defects exhibiting concentration polarization.

In the past not much attention was paid to cathodic interference. However, in combination of ac interference a cathodic interference (e.g. caused by an anode) can dramatically increase the corrosion risk of the pipeline as follows from the requirements in ISO 18086.

4.4. Time variant dc interference

In case of interference caused by dc traction systems, typically both, anodic and cathodic potential excursions are observed when the pipeline potential is monitored against a reference electrode placed above the structure. In a first approach the time variant stray current interference could, therefore, be considered as low frequent ac interference. This has important consequences that are ignored when only focusing on anodic potential excursions as it is currently required according to EN 50162.

- In the case of concentration polarization with an increased pH in the coating defect and a subsequently formed passive film, the shift of the IR-free potential in the anodic direction does not represent an imminent corrosion risk as follows immediately from Figure 6. In the first edition of Peabody's "Control of Pipeline Corrosion" from 1967 it is stated:
"When steel is immersed in a sufficiently caustic solution with a pH around 11 and higher, it can be made to discharge current without appreciable metal loss" Similar effects are reported by [5, 21, 43-45]. Nagayama and Kawamura [46] have shown how current may be passed through a steel surface by means of the redox system $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the presence of a passive film with a very high efficiency. Schmuki et al. [30] have also shown how the repetitive and reversible $\text{Fe}^{2+}/\text{Fe}^{3+}/\text{Fe}^{2+}$ transition cycle can occur. The data demonstrates that in the presence of a passive film it is possible to observe anodic activity with no oxidation of Fe provided the potential does not become sufficiently cathodic to dissolve the passive film through electrochemical reduction.
- In chloride containing environments the initiation of pitting corrosion could in principle occur, but detailed investigations have shown that the redox system $\text{Fe}^{2+}/\text{Fe}^{3+}$ does not only consume large amounts of the passed anodic charge [3], but also limits the anodic excursion of the potential to values within the gray area in **Fout! Verwijzingsbron niet gevonden..** This makes the initiation of pitting corrosion less probable. Notably, this gray area is cathodic to the most negative possible pitting potential in solutions with pH-values above 11 even with very high chloride concentrations of 1 M [47] as shown in **Fout! Verwijzingsbron niet gevonden..** The chloride ion concentration will usually always be far less than 1 M under all practical conditions (e.g. seawater has an approximate molarity of 0.48 M) and hence the pitting potential will in most cases be more positive than the gray area. Much lower chloride ion concentrations will usually occur in soils and the pitting potential becomes more positive in **Fout! Verwijzingsbron niet gevonden.** as the chloride ion concentration decreases from 10^0 to 10^{-3} M. Hence

the anodic excursion required for the initiation of pitting at low chloride concentrations or high pH-values is often insufficient.

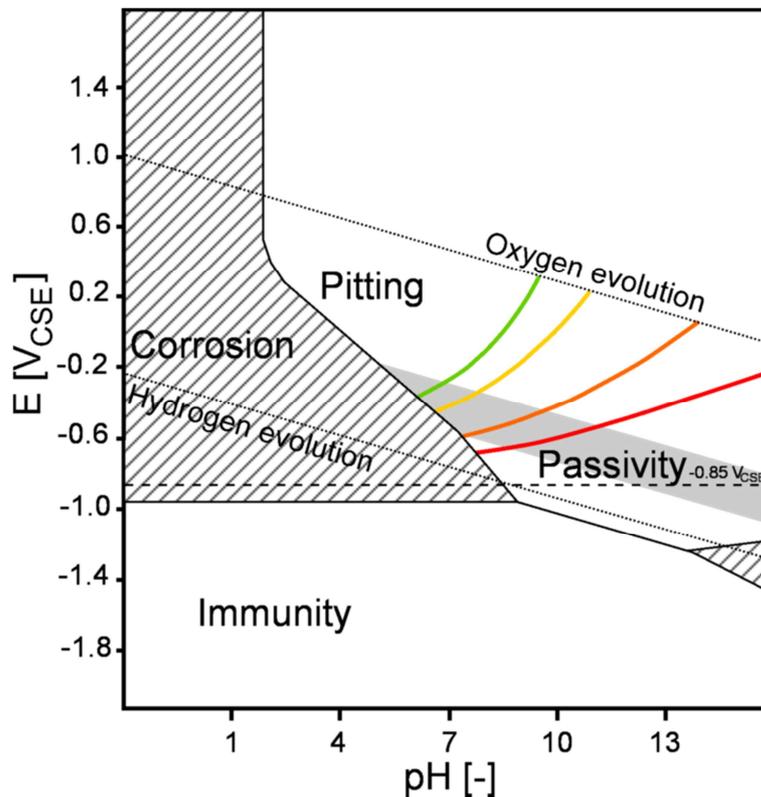


Figure 10: Influence of the chloride ion concentration on the pitting potential. Chloride concentration from 0.001 M (green), 0.01 M (yellow), 0.1 M (orange) to 1 M (red) [47].

In the case of concentration polarization the only key requirement is a sufficiently increased pH value at the steel surface. This is achieved by a current passing to the steel surface that is on average cathodic. Important anodic potential excursions can be tolerated, if their duration does not substantially decrease the surface pH. In a first approach a net cathodic current can be assured with an average on-potential that is more negative than $-1.2 V_{CSE}$. Shifting this value more cathodic will increase alkalinity and increase the tolerance with respect to prolonged anodic potential excursions.

- In the case of activation polarization cathodic excursion cannot compensate for anodic current discharge. Furthermore a rust layer containing the redox buffer Fe^{2+}/Fe^{3+} cannot form due to the solubility of Fe^{2+} . Hence, even decreasing the protection current density can cause an imminent corrosion risk and anodic current discharge is not acceptable, since this will result in iron oxidation to dissolved Fe^{2+} . Even IR-free potentials more negative than $-0.85 V_{CSE}$ and the absence of on-potentials more positive than this value can already cause relevant corrosion. Based on [42] even minor anodic shifts of the IR-free potential result in relevant acceleration of the corrosion process. In this respect anodic excursions must be strictly limited in the case of activation polarization.

In the case of time variant dc interference the expected corrosion behavior is significantly dependent on the type of polarization and the mass transport conditions at the steel surface.

4.5. Conclusions

The above discussion clearly demonstrates the importance of the bedding conditions and the resulting mass transport at the coating defect surface. In the case of concentration polarization on a well bedded coating defect severe ac and dc interference conditions are manageable and controllable. In contrast, in poor bedding conditions under activation polarization interference is critical. In the case of combined ac and dc interference, mitigation of the corrosion risk may become very challenging.

5. Consequences

The above discussion has highlighted some of the relevant processes taking place under cathodic protection. The discussion of the processes was done with a focus on individual coating defects. The presence of different coating defects with strongly different mass transport characteristics on the same pipeline has important consequences that need to be addressed. It may technically be achievable to assure that all coating defects are well bedded or at least will be covered with calcareous deposits. However, it will be difficult to assure poor bedding conditions on all coating defects. Therefore, in typical cases it has to be expected that a large number of coating defects with limited mass transport exhibiting concentration polarization and a smaller number that can only be protected by means of activation polarization are present on a pipeline. The relevant implications are discussed below:

Cathodic disbondment: Achieving sufficiently high current densities for activation polarization on the poorly bedded coating defects is inevitably going to cause over-protection on at least some of the well bedded coating defects. It is technically not possible to ensure IR-free potentials more negative than $-0.95 V_{CSE}$ on the poorly bedded ones and guarantee IR-free potentials more positive than $-1.2 V_{CSE}$ on the well bedded ones. In this respect the requirements of ISO 15589-1 cannot be fulfilled in the case of concentration and activation polarization on the same pipeline.

The IR-free potential to measure the surface pH: The above discussion has shown that the IR-free potential measurement is a suitable method for assessing the surface pH of a coating defect exhibiting concentration polarization as long as the IR-free potential is controlled by hydrogen evolution. This is explaining the relevance of this criterion. Problems occur in the case of increased aeration, increased coating defect size and increased soil resistivity, when polarization to the hydrogen evolution is not possible under typical operation conditions of CP. Often this leads to a shift of the on-potential to more negative values by increasing the current output of CP-rectifiers. This will further shift the IR-free potential to more negative values, increase current density and surface pH resulting in a risk of over-protection. This is due to the fact that the threshold of $-1.2 V_{CSE}$ represents a pH measurement as well, which is not applicable in the case of well aerated conditions. As a consequence, the IR-free potentials can be well more positive than $-0.85 V_{CSE}$, but CP has led to critical pH values at the steel surface resulting in cathodic disbondment.

The application of -0.85, -0.75 and -0.65 V_{CSE} : These values specified by EN 12954 and ISO 15589-1 are only applicable in the case of concentration polarization. They will not provide corrosion protection in the case of activation polarization. Under unknown mass transport conditions it is difficult to justify their use.

The on-potential: The on-potential does not deliver any information with respect to an individual coating defect. However, average values more negative than $-1.2 V_{CSE}$, as required by EN 14505, ensures an average cathodic current to enter every individual coating defect. This

can be considered a first minimum requirement for an effective CP. In the case of limited mass transport, buildup of an increased pH and passivation this will ensure corrosion protection in many cases. This explains the collectively good experience with CP, since most pipelines fulfill this on-potential requirement and have limited mass transport at most of their coating defects.

Interference conditions: Based on the above discussion, combined ac and dc interference can only be managed if all the coating defects can be protected by means of concentration polarization. Otherwise, severe anodic and cathodic interference in combination with high ac interference become practically impossible to mitigate.

6. Summary

Based on the historic evolution of CP, the corresponding criteria as well as threshold values lead to the conclusion that implicitly the current standards are based on an assumed concentration polarization. The thresholds for the IR-free potential of -1.20, -0.85, -0.75 and -0.65 V_{CSE} as specified in ISO 15589-1 can only be justified for well bedded coating defects, thus exhibiting limited mass transport conditions and, therefore, allow for concentration polarization. Even the IR-free potential value of -0.95 V_{CSE} could readily be explained in the case of concentration polarization, since it assures a pH increase above 11, which is sufficient for protection even in aggressive soils containing carbonates, sulfides and organic acids. However, this threshold may be applicable also in the case of activation polarization. Indeed, it was introduced based on corrosion damages on a poorly bedded pipeline with sulfate reducing bacteria where an increase of the surface pH was not possible. Hence, consideration of the mass transport and bedding conditions is crucial in assessing the effectiveness of CP. Additionally, the consideration of these aspects is of relevance when developing the EN 50162 with respect to dc interference.

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8. References standards

EN 12954:2001	Cathodic protection of buried or immersed metallic structures. General principles and application for pipelines
EN 14505:2005	Cathodic protection of complex structures
EN 50162:2004	Protection against corrosion by stray current from direct current systems
ISO 15589-1:2015	Petroleum, petrochemical and natural gas industries - Cathodic protection of pipeline systems - Part 1: On-land pipelines
ISO 18086:2015	Corrosion of metals and alloys - Determination of AC corrosion - Protection criteria

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