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Assessing the risk of stray current induced corrosion: Protection criteria developed based on the present understanding of the involved processes

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Abstract

Based on the present understanding with respect to the mechanisms associated with cathodic protection of buried structures new criteria for the assessment of the stray current corrosion risk were developed. These are confirmed by extensive laboratory investigations as well as the available literature. All this information clearly demonstrates that the protection against stray current induced corrosion is achieved by the increased pH at the steel surface and the associated passivity that prevents relevant corrosion even under extended anodic polarisation. Based on this model concept corrosion will not occur as long as the anodic charge is compensated in the by a sufficient cathodic charge. This results in a requirement of a time averaged cathodic charge. For the first time this model allows for explaining the effects occurring during AC interference as well as time variant DC interference can be explained with a single approach. Based on present directives, todays concept of cathodic protection as well as various laboratory investigations technically correct, reproducible and simple accessible parameters are defined. These form the basis for a simple assessment of the corrosion risk of buried cathodically protected pipelines under stray current interference. Furthermore, these concepts readily allow for the identification of protection measures with respect to stray current corrosion as well the determination of their effectiveness.

Zusammenfassung

Basierend auf den aktuellen Erkenntnissen zur Wirkungsweise des kathodischen Korrosionsschutzes von erdverlegten Anlagen wurden neue Kriterien zur Bewertung der Gefährdung durch Streuströme entwickelt. Diese werden von umfangreichen Laboruntersuchungen und der verfügbaren Literatur bestätigt. Der wesentliche Aspekt ist dabei die Erhöhung des pH-Werts an der Stahloberfläche und die daraus resultierende Passivierung als Folge des kathodischen Korrosionsschutzes. Aus dem Modellansatz wird deutlich, dass auch grössere anodische Ladungen nicht zu Korrosion führen, solange sie im zeitlichen Mittel durch ausreichende kathodische Ladungen kompensiert werden. So können erstmals sowohl die Effekte bei Wechselspannungsbeeinflussung als auch die bei zeitlich veränderlicher Beeinflussung einheitlich beschrieben werden. Damit wird es möglich auf der Basis von aktuell vorliegenden Regelwerken, neusten Erkenntnissen zur Wirkungsweise des KKS sowie verschiedenen Laboruntersuchungen technisch korrekte, nachvollziehbare und mess-technisch einfach zugängliche Messgrößen festzulegen. Damit sind die Grundlagen für eine einfache Bewertung der Gefährdung von erdverlegten Anlagen durch Streuströme geschaffen. Zudem wird es basierend auf diesen neuen Ansätzen einfach möglich Schutzmassnahmen zu treffen und deren Wirksamkeit zu bewerten.

1. Introduction

The application of the cathodic protection (CP) technique is generally statutory for high pressure gas- and oil-pipelines. Moreover, CP is frequently used for water pipelines and buried containers. The relevant basic principles and protection criteria are stated in EN ISO 15589-1:2017. Based on the standard EN 50162:2004 coupons are generally required for the assessment of these structures with regard to the protection against stray current corrosion. These coupons had been installed in certain cases. The mutual interaction of electric field distribution and geometrical design, however, had generally not been considered, resulting in a limited significance of the measured data. It was, therefore, frequently neither possible to provide an assessment of the corrosion risk due to stray currents conforming to the above-mentioned standards nor to verify the effectiveness of cathodic protection under DC interference.

In the past the understanding of stray current interference was based on the concept that a reversion of the CP current was inevitably related to a corrosive dissolution of the metal following Faradays Law, i.e. an anodic current always forces corrosion to occur. According to this view even a short term anodic current, leaving the steel surface of a buried structure stringently represents a corrosion risk.

Based on the present model conceptions according to the effect of CP a clearly more differentiated understanding is generally accepted today with regard to the electrochemical processes: It is nowadays widely accepted that the effectiveness of cathodic protection is primarily based on the increase of the pH-value on the steel surface. The alteration of ionic concentrations at the steel surface due to the CP current changes the composition of the soil not only in the immediate vicinity of the steel surface but also in the surrounding environment. This effect, named concentration polarization, provokes a shift of both the pH-value and the potential along the hydrogen equilibrium line (blue line in Figure 1). The enhancement of the pH-value at the steel surface and in the surrounding soil as well as the passivation are illustrated in Figure 3a. Since the hydrogen equilibrium potential, which correlates with the cathodic limit of water stability, depends on the pH-value, the pH-value at the steel surface can directly be concluded from the IR-free potential. This has been discussed in detail by Angst et al [1]. For this reason, the protection potentials according to EN ISO 15589-1:2017 can readily be explained:

- $E_{IR-free} = -0.85 \text{ V}_{CSE}$ corresponds to pH = 9, which is, according to Figure 1, even sufficient for achieving passivity
- $E_{IR-free} = -0.95 \text{ V}_{CSE}$ corresponds to pH = 10,5 (yellow circle in the middle of Figure 1), which allows for passivity even in aggressive soils
- On the other hand, $E_{IR-free} = -1.2 \text{ V}_{CSE}$ corresponds to pH = 13 (yellow circle to the right in Figure 1), which, according to EN ISO 15589-1:2017, may cause problems with the adhesion of coatings.

It should be noted in this context, that a pH level of 13 is typical for concrete, provoking the formation of a protecting passive film, thus providing an effective corrosion protection for the steel reinforcement.

The dependence of the pH-value at the steel surface on the CP current density had been investigated by several authors and the results are shown in Figure 2. It can be concluded that cathodic current densities in the range from 20 to 1000mA/m², which are typical for the CP of coating defects on buried pipelines, result in pH-values from 10.5 to 12.5. According to Figure 1 these levels correlate with IR-free potentials in the range from -0.95 to -1.2V_{CSE}. This considera-

tion shows the relevance of the preceding argumentation for the practical implementation of the CP technique for buried pipelines.

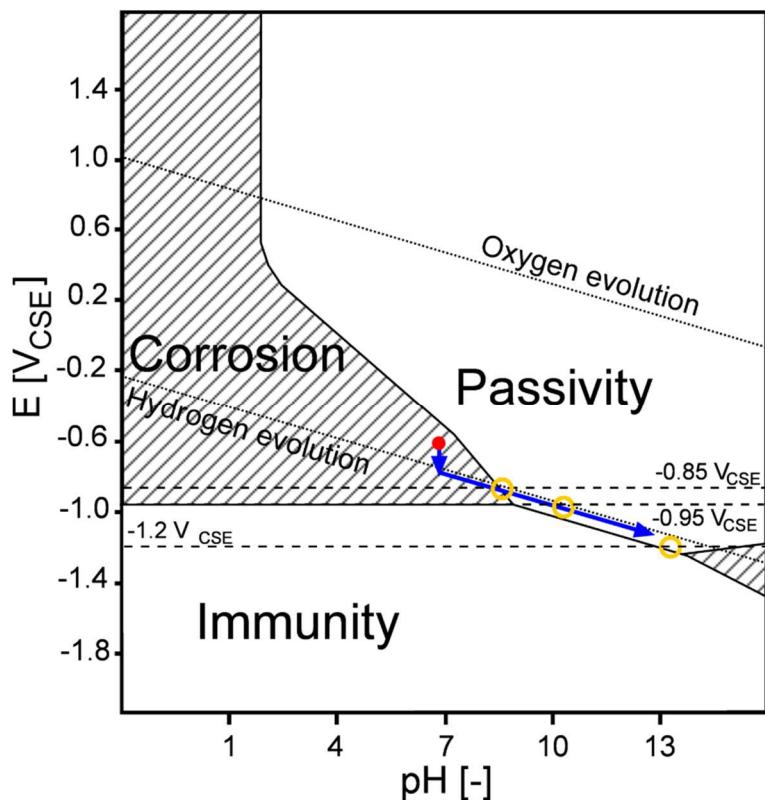


Figure 1: Pourbaix-diagram ($\text{Fe}/\text{H}_2\text{O}$) illustrating the cathodic polarization of steel [2]. The blue arrow shows the effect of concentration polarization and the resulting enhancement of the pH-value as well as the passivation. The yellow circles indicate the position of the protection potentials according to ISO 15589-1.

It follows from this consideration that the cathodic protection of steel is based on the increase of the pH-value and the resulting passivity. This observation has far reaching consequences for the assessment of time variant stray current interference (e.g. of a cathodically protected pipeline) as it is caused by DC-operated railways or trams. It is evident that a time limited anodic current cannot result in corrosion. In fact, the anodic polarization will only shift the potential within the passive domain, which does not result in corrosion. The anodic charge will rather be consumed for the oxidation of ferrous ions (Fe^{2+}) within the oxide layers on the steel surface. As a consequence, the repeated cathodic and anodic interference caused by DC-operated railways or trams will indeed cause a relevant charge transfer through the steel surface, the electric charge however will not be consumed by the corrosion reaction, but will be used for the redox system $\text{Fe}(\text{II})/\text{Fe}(\text{III})/\text{Fe}(\text{II})$. Bette observed this phenomenon already in 2005 [3] and described it with capacitive charging effects. In fact, the above-mentioned redox system acts as a pseudo-capacity and may absolutely be compared with the charging/discharging of an accumulator. Consequently, the combination of passivity with the redox system explains the empirical observation that a temporal limited anodic current will neither result in important anodic potential shifts nor in corrosion. All more recent investigations of stray current induced corrosion confirm that the electric charge will not be consumed for the corrosion reaction as long as the steel surface is passive [4-9].

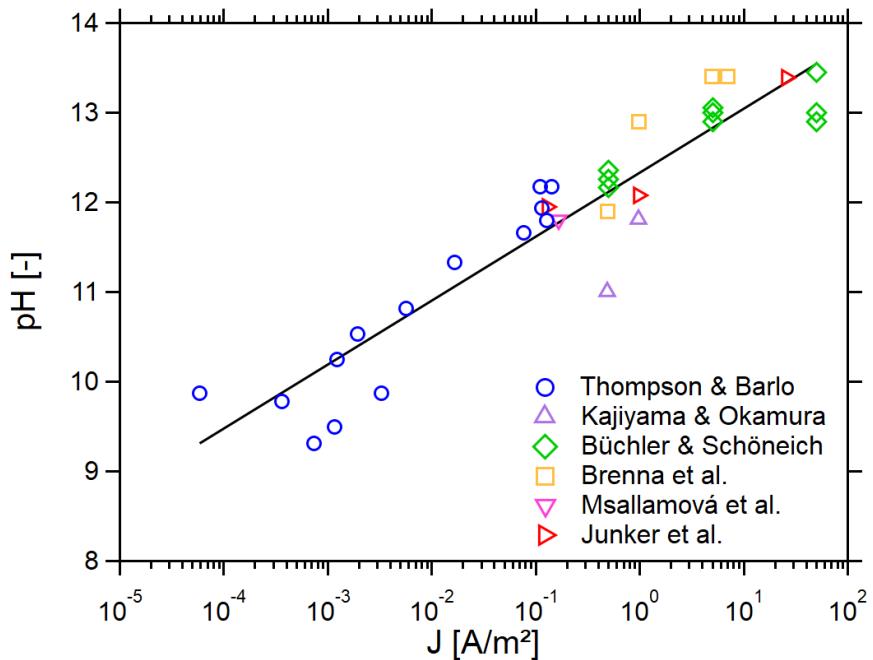


Figure 2: The pH-value at the steel surface as a function of the cathodic current density according to different literature sources summarized in [10].

This discussion illustrates that the assessment of stray current interference of cathodically protected pipelines needs to be reassessed in the light of today's knowledge. The present mechanistic models, the available literature as well as available empirical data allow to develop new interference assessment concepts and the corresponding thresholds. These will be discussed in the following.

2. Normative Preconditions

The criteria specified in EN 50162:2004 are based on the assumption of a time constant anodic stray current load. Hence it is required to discuss the effects of a time constant anodic current on the corrosion processes. In case of a time constant anodic current it is not possible to achieve an increase of the pH at the steel surface. In fact, a time constant anodic current results in a decreasing pH-value and thus in an acidification at the steel surface leading to corrosion according to Figure 3b. Moreover, the effect of a decreasing pH-value is illustrated with a red arrow in Figure 4. The formation of an acidic electrolyte provokes aggressive conditions and passivation will be impossible. Under such circumstances it is to be expected, that 100% of the anodic current is consumed by the redox system $\text{Fe}(0)/\text{Fe}(\text{II})$, i.e. for the corrosion reaction. This underlines, that EN 50162:2004, which had been elaborated for time variant interference from DC-operated railways or trams, is based on incorrect assumptions: The relevant increase of the pH-value as a result of effective CP, which is crucial for the effectiveness of cathodic protection, the resulting passivation, the importance of the redox system $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ and also the consequences of a CP current, that is cathodic when averaged over a representative period of time, are ignored.

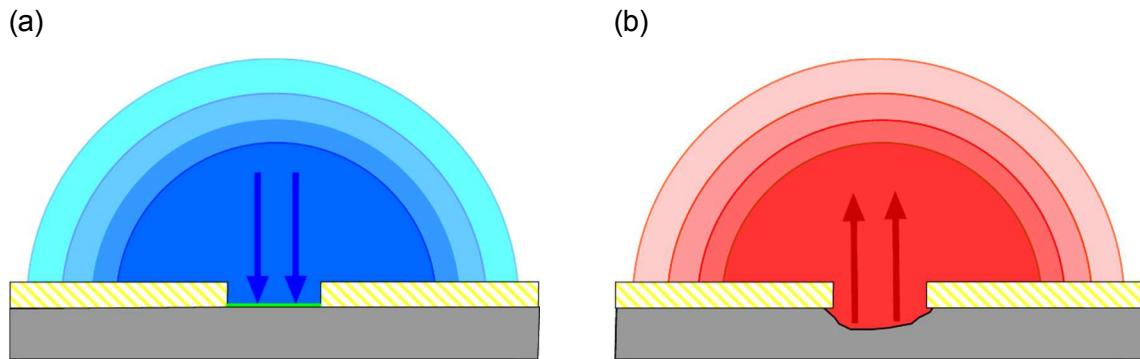


Figure 3: Schematic illustration of cathodic concentration polarization (a) and anodic concentration polarization (b). The cathodic current entering the steel surface, results in a depletion of oxygen, an increase of the pH-value in the soil and passivation (a). The anodic current leaving the steel surface results in a lowering of the pH-value and provokes corrosion (b). The intensity of colouring indicates the extent of pH change.

3. Influencing factors

Based on the above discussed aspects various influencing factors can be identified, which relevantly control the corrosion under time variant stray current interference.

Anodic current will decrease the pH, while cathodic current will result in an increase of pH at the steel surface. It immediately follows that the average current over a full interference cycle (e.g. 24 hours) represents a relevant parameter. This is due to the fact that the current efficiency for alkalinity formation is at least as good as the one for acidity formation in the case of steel. An average cathodic current is therefore bound to result in a pH increase over time irrespective of temporary anodic excursions. Hence the polarity of the average electrical charge controls the direction of pH change at the steel surface. This effect of concentration polarization can best be illustrated based on an analogy: In absence of anodic current discharge or in case of cathodic interference a reservoir of alkalinity is accumulated at the steel surface. This reservoir will be consumed during anodic current discharge. Saving alkalinity provides, therefore, corrosion protection during anodic interference intervals. As long as more alkalinity is saved than consumed an increased surface pH and hence corrosion protection is ensured even under severe time variant anodic stray current interference.

This analogy reveals important implications: The duration of the anodic interference is bound to be relevant, since the decrease of pH is not only a result of anodic current discharge. Diffusion and migration into the surrounding soil, neutralisation with carbon dioxide as well as convection and streaming water will contribute to a loss of the accumulated alkalinity. These effects are negligible with respect to the pH at the steel surface in the case of short anodic interference during AC interference of 50 Hz or short telluric interference of up to 3 seconds. This is illustrated by means of the green arrows in Figure 4. Indeed, experience confirms that there is no detrimental effect with respect to corrosion caused by loss of surface pH under such conditions. However, based on the argumentation in EN 50162 they would have to result in relevant metal loss as a result of Faradays law.

In contrast, a duration of the anodic interference of 30 seconds causes a relevant change of the surface pH during the anodic excursion, although the time averaged current is cathodic. (blue

arrows in Figure 4). Such durations are typical for tram operation. A further increase of the duration of the anodic interference to 300 seconds, as they are characteristic for DC train operation, can cause a major loss of surface pH resulting in temporary initiation of corrosion (orange arrows in Figure 4). While the subsequent cathodic interference will re-establish passivating conditions according to Figure 4, a non-negligible corrosion rate will be observed under these conditions. Based on the above discussion the current efficiency based on the reaction $\text{Fe}(0)/\text{Fe}(\text{II})$ will not be 100 %, which is indeed experimentally confirmed.

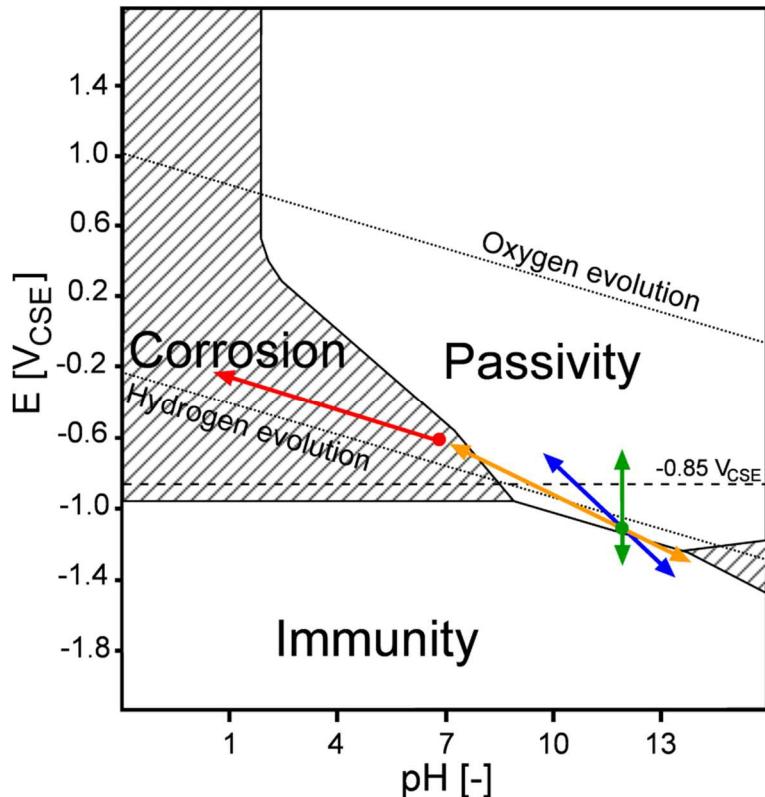


Figure 4: Polarisation of steel under stray current interference illustrated in the Pourbaix diagram [2]. The red arrow shows the concentration polarization under time constant anodic interference (in case of ineffective CP). A time variant interference in case of effective CP is illustrated with the green, blue and orange double arrows. The different duration of the anodic interference of 3 (green), 30 (blue) and 300 (orange) seconds results in different levels of concentration polarisation at a given cathodic charge.

Theoretically, the duration of the anodic interference is expected to be relevant with respect to the corrosion behaviour. However, there are additional aspects that require consideration in the practical application. The current will flow through individual coating defects as illustrated in Figure 3, which typically have various sizes and geometries and are in contact with various soils with different aeration and resistivities. It is therefore necessary to consider these aspects in the case of the practical application of these concepts.

4. Application of these concepts

Based on the above discussion the current density is relevant with respect to the surface pH that is established (see Figure 2). With decreasing defect size and decreasing soil resistivity increased current densities are expected. As a consequence, in case of a time constant interference (red arrow in Figure 4) highest corrosion rates have to be expected on smallest coating

defects in least resistive soil. However, in the case of time variant interference (e.g. caused by a DC traction system) it is observed that also the cathodic current densities are increased. It follows that the effect of defect size during time variant interference is essentially eliminated.

Based on this consideration only the following influencing parameters need to be considered:

- A reference current density for establishing effective CP at the steel surface in accordance with ISO 15589-1 is required. Typical values are between 20 to 200 mA/m².
- The cathodic charge must be larger than the anodic charge resulting in a time averaged pH increase at the steel surface.
- With increasing duration of the anodic excursion, the cathodic charge needs to be proportionally larger compared to the anodic charge. The excess in alkalinity is required to compensate for the contribution of migration and diffusion. This will ensure a durably increased pH at the steel surface and prevents the conditions shown with the orange arrows in Figure 4.

This consideration is illustrated in Figure 5 by means of schematic measuring data collected on a coupon on a cathodically protected pipeline under DC traction interference. The reference current density J_{ref} is required to establish effective CP. This J_{ref} is measured in the non-interfered situation, for example during the night in absence of train operation. During the day the train operation is causing anodic and cathodic current densities on the coupon, which are often a multiple of J_{ref} .

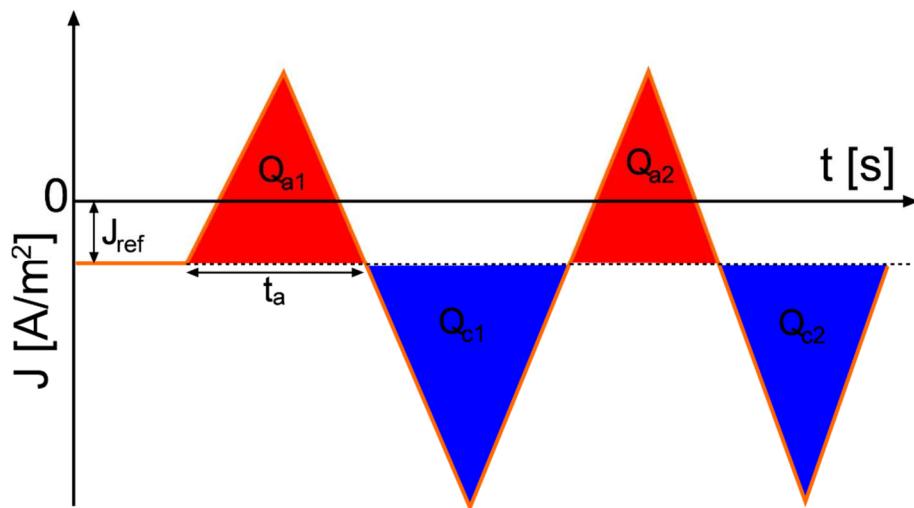


Figure 5: Schematic evolution of the current density in the coating defect (or a coupon) on a stray current interfered pipeline. The cathodic (blue) and anodic (red) charges are obtained based on the surface integral of the respective current densities. The duration t_a corresponds to the longest anodic excursion.

The ratio of the anodic and cathodic charge is relevant with respect to concentration polarization and hence the pH at the steel surface. The assessment of the corrosion risk can, therefore, be performed based on the equation (1) with the anodic interference charge Q_a (total red surface) and cathodic interference charge Q_c (total blue surface) over the representative period.

$$Q \leq (|Q_c| - |Q_a|) / |Q_a| \quad (1)$$

The value on the right-hand side of equation (1) describes the ratio of anodic and cathodic charge. For identical charges a value of zero is obtained. When the cathodic charge is double the anodic charge, it equals 1. Experimentally it was found that for artificial soil and artificial soil solutions the dependence of Q from t_a can be described by equation (2):

$$Q = t_a * 0.004 \text{ s}^{-1} \leq (|Q_c| - |Q_a|) / |Q_a| \quad (2)$$

This dependency is shown in Figure 6 based on laboratory measurements of SGK. These measurements were performed in artificial soils as described in [11] and in hard water with the calcium containing electrolyte given in [12]. A galvanostatic saw tooth shaped (according to Figure 5) current was applied. The current variation (anodic peak/ cathodic peak) was 2 A/m². Various values for J_{ref} and t_a were applied. It is evident that for typical DC traction interference with t_a of about 4 minutes Q has a value of 1. In this case the anodic stray current charge is twice the cathodic stray current charge.

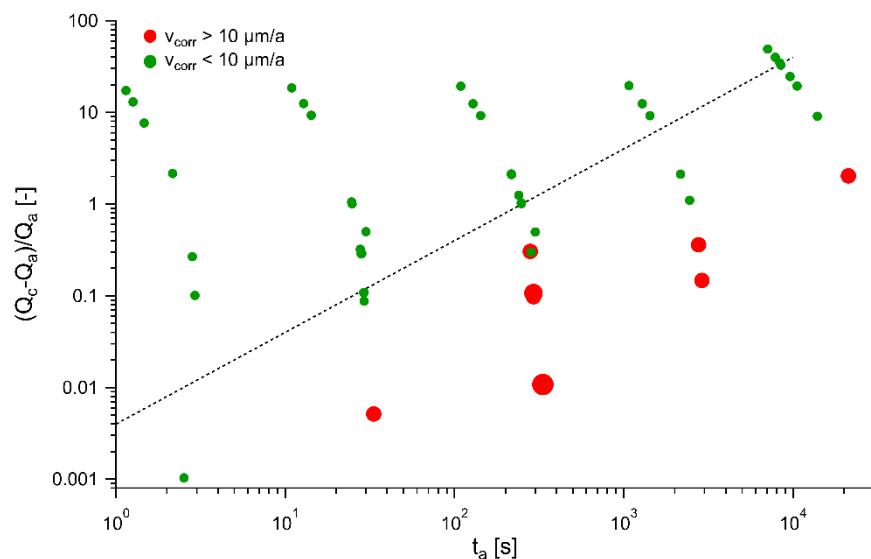


Figure 6: Experimental determination of Q as a function of t_a in artificial soil and hard water. The dotted line represents the minimum requirement for protection against stray current corrosion, i.e. $(|Q_c| - |Q_a|) / |Q_a| = t_a * 0.004 \text{ s}^{-1}$.

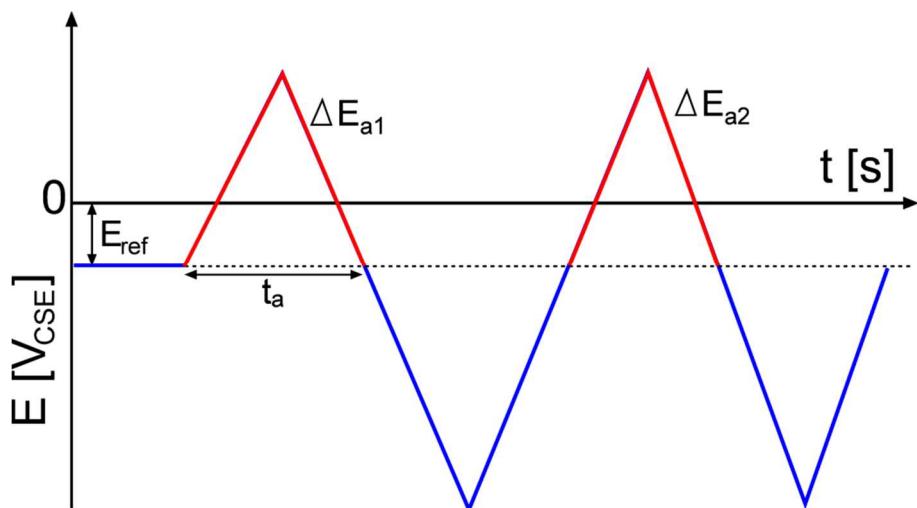


Figure 7: Schematic potential evolution of a cathodically protected pipeline. The anodic interference $\Delta E_{a,\text{avg}}$ is the result of the average anodic shift of the potential relative to E_{ref} . The duration t_a corresponds to the largest anodic excursion.

This discussion emphasizes the relevance of the current density for the assessment of the stray current risk. This is fully in line with the generally accepted behaviour shown in Figure 2. However, a criterion based on current densities has significant limitations in the practical application, since current densities cannot be directly measured on the pipeline. Based on Ohm's law it is, however, possible to translate the current density consideration into a potential consideration under the following assumptions:

- The polarization resistances for anodic and cathodic reactions are small compared to the spread resistance. This is indeed the case for both the hydrogen evolution as well as the redox system Fe(II)/Fe(III).
- The spread resistance does not relevantly change during the cathodic and anodic interference. This might not be the case during extended interference durations, but the cathodic interference will always result in lower spread resistance (and hence smaller potential change) compared to the anodic interference. This assumption is, therefore, conservative.

Under these conditions for a typical DC traction interference DVGW GW 21 [13] states equation (3) as the minimum requirement with respect to stray current protection:

$$E_{on,avg} \leq E_{ref} - \Delta E_{a,avg} \quad (3)$$

The on-potential averaged over 24 hours ($E_{on,avg}$) must accordingly be more negative than the reference potential (E_{ref}) minus the average anodic interference ($\Delta E_{a,avg}$). Similarly to the charge consideration in equation (1), a stronger anodic interference can hence be compensated by larger cathodic charge, which is obtained at a more negative average on-potential. In Figure 7 the analogy between the current density (see Figure 5) and the potential evolution is evident. E_{ref} corresponds to the minimal required on-potential in absence of DC interference required for establishing effective CP. E_{ref} correspondingly ensures J_{ref} . $E_{on,avg}$ is the time average of all on-potential values recorded over a representative period of time. $\Delta E_{a,avg}$ corresponds to the average of all red potential values minus E_{ref} . Equation (3) was first published in 2009 and has today the status of a recognized state of the art in Germany. It is applicable for DC-traction interference where typical maximum values of t_a of about 250 seconds are observed, which results in a value for Q of 1. Indeed it can be demonstrated based on the Annex that equation (1) and equation (3) are mathematically identical. It is hence readily possible to extend the application range of equation (3) based on the conditions in equation (2) and consider the effect of various values of t_a according to equation (4).

$$E_{on,avg} \leq E_{ref} - Q * \Delta E_{a,avg} = E_{ref} - 0.004s^{-1} * t_a * \Delta E_{a,avg} \quad (4)$$

According to the Annex and equation (4) the equivalence of the charge and potential consideration is evident as shown in equation (5):

$$Q \leq (|Q_c| - |Q_a|) / |Q_a| = (E_{ref} - E_{on,avg}) / \Delta E_{a,avg} \quad (5)$$

The relevance and the correctness of the requirements of DVGW GW 21 and the underlying concepts are confirmed by the independent validation in Figure 6 based on an electrical charge consideration. The crucial advantage of equation (4) is the expansion of the application range of the DVGW GW 21 to the entire frequency domain of stray current interference. This domain ranges from AC frequencies ($t_a=0.01$ s) over DC traction interference ($t_a=300$ s) and tidal interference ($t_a=22'000$ s) to time constant interference ($t_a=\infty$).

The validity of equation (4) and (5) is confirmed by Figure 6 as well as the requirement of DVGW GW 21 for values of t_a in the range of a few minutes. For infinitely small values of t_a Q is approaching zero according to equation (2). Hence the anodic charge (or potential excursion) may be approximately identical to the cathodic charge (or potential excursion). Based on equation (4) $E_{on,avg}$ must only be more negative than E_{ref} . This is indeed confirmed by extensive field investigations in Germany [14]. Based on these data no corrosion is expected even in the case of AC current densities as high as several hundred A/m² at sufficiently negative average on-potentials (e.g. more negative than -1 V_{CSE}).

In Annex D of EN 50162 a method for assessing the stray current corrosion risk caused by DC traction systems is presented. This method was developed in the Netherlands and was successfully used during the last 25 years. It is based on the limitation of the current discharge from a steel coupon to only 3.6 seconds during the hour with the highest stray current interference. Considering a typical cycle duration of about 10 minutes during DC traction interference, the acceptable duration t_a of the anodic interference during this period is less than 1 second. While the duration is strictly limited, the level of the anodic current discharge during this 1 second is not restricted based on Annex D in EN 50162 and it could theoretically reach very high values. This significant limitation of t_a to values of less than 1 second generates at first glance the impression that this successfully used methodology is significantly more conservative than the one in equation (4). However, the Annex D and equation (4) are in fact in very good agreement, when the operation conditions of CP in the Netherlands during the last decades is considered. The effectiveness of CP was usually assessed based on an on-potential that was controlled in the range between -0.85 and -1.2 V_{CSE}. Hence $E_{on,avg}$ was very close (or even identical) to E_{ref} . Without strict limitation of $\Delta E_{a,avg}$ equation (4) can only be satisfied at almost identical $E_{on,avg}$ and E_{ref} , if t_a is extremely small. Indeed Annex D of EN 50162 does not limit $\Delta E_{a,avg}$ and t_a is extremely small (e.g. less than 1 second). There is wide consensus in Europe that these requirements in Annex D are very conservative, which is confirmed by laboratory and field investigations. This conclusion is plausible, since most CP systems in Europe are operated at $E_{on,avg}$ more negative than -1.6 V_{CSE}. As a consequence, significantly higher values of t_a can be tolerated according to equation (4). The example of AC interference as well the very small values of t_a in Holland (reported in Annex D of EN 50162) are therefore fully in line with the presented methodology.

Equation (4) is also confirmed for very large values of t_a , as they are observed in case of time constant stray current interference. In this case Q becomes infinite and equation (5) can only be satisfied when the anodic charge (or $\Delta E_{a,avg}$) approaches zero. This is indeed only possible if equation (6) is fulfilled:

$$E_{on} \leq E_{ref} - \Delta E_{a,max} \quad (6)$$

The on-potential must be shifted in the cathodic direction by the maximum anodic shift ($\Delta E_{a,max}$). This eliminates any anodic interference and Q_a becomes zero satisfying equation (1). Indeed, this is a common procedure for mitigation of time constant stray current interference.

This consideration confirms the relevance of equation (4). It is well established by practical application in the last 10 years in Germany and can be expanded to cover the entire frequency domain of anodic stray current interference ranging from AC interference to time constant anodic DC interference. It allows for an assessment of the stray current corrosion risk as well the identification and control of mitigation measures.

5. Conclusions

Based on the described concepts the specifications of German technical rule DVGW GW 21 can be explained for the first time. Even since 2009 this document permits relevant anodic currents without considering the IR-free potential – in clear conflict with EN 50162. The above discussed phenomena and presented results are able to explain the experiments on which DVGW GW 21 is based and also the positive experiences with its application over the last 10 years. It follows from the specifications of this technical rule that the anodic interference (and hence anodic charge) is only half of the cathodic one. Due to this excess of cathodic charge a continuous increase of the pH-value at the steel surface and thus its passivity will be assured. From the described concepts and investigations, it follows that increased duration of anodic interference, as it may be expected from solar activity (tellurics) or tidal effects, can readily be compensated by accordingly increasing the cathodic polarization. Based on these findings it is now possible to extend the scope and specifications of DVGW GW 21 from DC-operated railways and trams to the complete spectrum of interference frequencies. The new concept allows for assessing the risk of stray current interference based on easy measurable potential data followed by an averaging process.

6. Literature

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Annex

Electric charge is the product of current and time.

$$Q = I \cdot t$$

The voltage is the product of current and resistance, and as is the difference between potentials.

$$U = R \cdot I = \Delta E$$

Averaged values are divided by the total time, which is the sum of all anodic and all cathodic times.

$$t = t_a + t_c = a + c$$

The following formulas combine the above ones into anodic and cathodic interference.

Anodic interference	Cathodic interference
Total anodic charge $Q_a = \frac{\Delta E_{a,avg} \cdot t}{R}$	Total cathodic charge $Q_c = \frac{\Delta E_{k,avg} \cdot t}{R}$
Averaged total anodic deviations $\Delta E_{a,avg} = \frac{1}{t} \sum_{x=1}^a \Delta E_{a,x}$	Averaged total cathodic deviations $\Delta E_{c,avg} = \frac{1}{t} \sum_{x=1}^c \Delta E_{c,x}$
Individual potential differences to E_{Ref} $\Delta E_{a,x} = E_{a,x} - E_{Ref}$	Individual potential differences to E_{Ref} (positive) $\Delta E_{c,x} = E_{Ref} - E_{c,x}$
Averaged potential differences to E_{Ref} $\Delta E_{a,avg} = E_{a,avg} - E_{Ref}$	Averaged potential differences to E_{Ref} (positive) $\Delta E_{c,avg} = E_{Ref} - E_{c,avg}$

The formula for the Q-requirement writes as follows.

$$\frac{Q_c - Q_a}{Q_a} = 0.004 \cdot t_a = 1$$

For $t_a = 250$, the Q's ratio becomes 1 and can therefore be transformed into the following equation.

$$Q_c - Q_a = Q_a$$

Replacing the total charges with the respective formulas including ΔE results in the following equation.

$$\frac{\Delta E_{c,avg} \cdot t}{R} - \frac{\Delta E_{a,avg} \cdot t}{R} = \frac{\Delta E_{a,avg} \cdot t}{R}$$

As t and R are assumed to be constant, they can be eliminated

$$\Delta E_{c,avg} - \Delta E_{a,avg} = \Delta E_{a,avg}$$

Replacing with the two averaged potential differences on the left side with the respective sum terms the formula can be written as follows, when multiplied with -1.

$$-\frac{1}{t} \sum_{x=1}^c \Delta E_{c,x} + \frac{1}{t} \sum_{x=1}^a \Delta E_{a,x} = -\Delta E_{a,avg}$$

Inserting the potential differences within the sums brings back E_{Ref} into the formula.

$$\frac{1}{t} \sum_{x=1}^c (E_{c,x} - E_{Ref}) + \frac{1}{t} \sum_{x=1}^a (E_{a,x} - E_{Ref}) = -\Delta E_{a,avg}$$

Taking E_{Ref} out of the sums result in two remaining sum parts which can be written in this way.

$$\frac{1}{t} \left(\sum_{x=1}^c E_{c,x} + \sum_{x=1}^a E_{a,x} \right) - \frac{a+c}{t} E_{Ref} = -\Delta E_{a,avg}$$

The sum over all cathodic potentials added to the sum over all anodic potentials and divided by the total time results in the mean value over all potential values E_{avg} .

$$E_{avg} = E_{Ref} - \Delta E_{a,avg}$$

This finally is the formula that can be found in the DVGW GW 21. The following two requirements are therefore exactly the same:

$$E_{avg} = E_{Ref} - \Delta E_{a,avg} \leftrightarrow \frac{Q_c - Q_a}{Q_a} = 1$$