Corrosion protection through cathodic polarization: A discussion of the relevant effects and comparison with literature

M. Büchler

SGK Swiss Society for Corrosion Protection
Technoparkstr. 1, CH-8005 Zürich,
markus.buechler@sgk.ch

Abstract

There is general agreement on the fact that cathodic protection is achieved through polarisation. However, it is often ignored that ISO 8044 specifies that polarization is achieved through activation as well as concentration polarization. Cathodic protection (CP) industry has failed to appreciate these different types of polarization and to consider their implications on measurement techniques. These aspects are discussed and the implications on the assessment of the effectiveness of CP are presented with respect to the various protection criteria in the standards. The failure to distinguish activation and concentration polarization has also made it impossible to appreciate two apparently opposed concept for corrosion protection: The achievement of corrosion protection through polarization of the cathode to the anode as proposed by Mears and Brown in contrast to the protection through polarization of the anode to the cathode as presented by LaQue. The understanding of the mechanisms associated with cathodic polarization provides insight in the underlying principles of the corrosion protection mechanisms and can contribute to the ongoing discussion on protection criteria.

Zusammenfassung

Es besteht Einigkeit darüber, dass der kathodische Schutz durch Polarisation erreicht wird. Es wird jedoch oft ignoriert, dass die ISO 8044 spezifiziert, dass die Polarisation sowohl durch Aktivierungs- als auch durch Konzentrationspolarisation erreicht wird. Die kathodische Korrosionsschutz (KKS) Industrie hat es versäumt, sich dieser verschiedenen Polarisationsarten bewusst zu sein und ihre Auswirkungen auf die Messtechnik zu berücksichtigen. Diese Aspekte werden diskutiert und die Auswirkungen auf die Beurteilung der Wirksamkeit des KKS im Hinblick auf die verschiedenen Schutzkriterien in den Normen dargestellt. Die fehlende Unterscheidung von Aktivierungs- und Konzentrationspolarisation hat es auch unmöglich gemacht, zwei scheinbar gegensätzliche Konzepte für den Korrosionsschutz zu verstehen: Die Erreichung des Korrosionsschutzes durch Polarisation der Kathode zur Anode, wie von Mears und Brown vorgeschlagen, im Gegensatz zum Schutz durch Polarisation der Anode zur Kathode, wie von LaQue dargestellt. Das Verständnis der mit der kathodischen Polarisation verbundenen Mechanismen gibt Einblick in die zugrunde liegenden Prinzipien der Korrosionsschutzmechanismen und kann zur laufenden Diskussion über Schutzkriterien beitragen.

1. Introduction

While there is wide agreement with respect to the effectiveness of cathodic protection (CP) with respect to ensuring the integrity of pipelines, there are a number of key aspects associated with CP that are commonly ignored. They will be summarized in this paper in order to facilitate the future discussion with respect to protection criteria. Addressing these aspects is only possible when some of the associated key aspects are sufficiently clarified, which requires the underlying fundamental aspects to be presented. This includes the effects associated with homogeneous and heterogeneous electrodes.
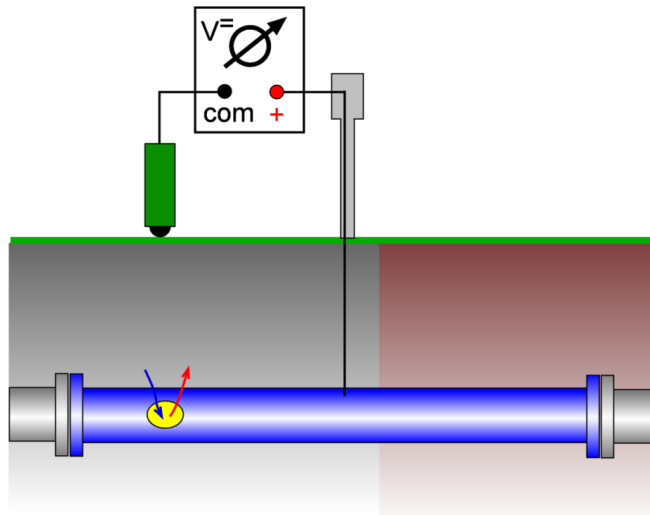

Figure 1: **Situation of a galvanically separated pipe section (blue) with a single coating defect. The potential measurement is performed with a reference electrode (green) placed above the coating defect.**

In Figure 1 the situation of a pipeline with the hypothetical case of an individual coating defect is shown. In this configuration (no cathodic current applied and no stray current interference) the potential measurement will provide the IR-free potential of the coating defect consisting of a single electrode (according to the definition of the IR-free potential in ISO 15589-1). The anodic iron oxidation is shown with the red arrow and the cathodic oxygen reduction is shown with blue arrow. Since the amount of electrons transferred must be identical for cathodic and anodic reactions the length of the arrows is correspondingly identical.
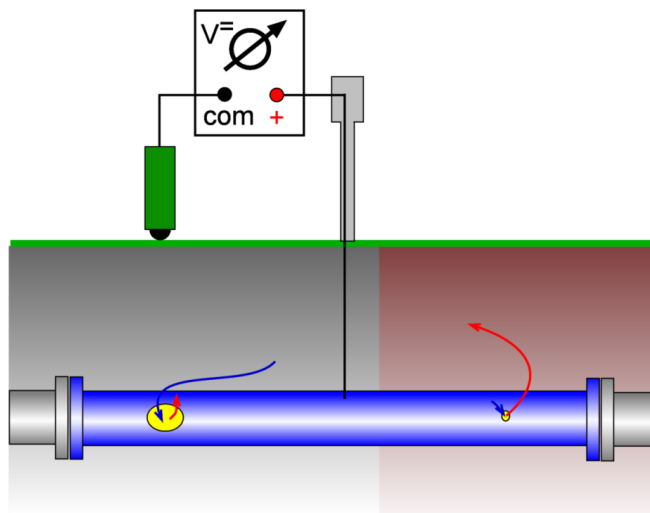

Figure 2: **Situation of a galvanically separated pipe section (blue) with two individual coating defects. The large one is in well aerated sand and the small one in poorly aerated clay.**

In Figure 2 the situation for a pipeline exhibiting two coating defects with different geometry (size) in different soil is shown. The difference in aeration results in a difference of the IR-free potential and, as a consequence, in a galvanic current flow between them. The potential measurement according to Figure 2 will not provide an IR-free potential (even in absence of a CP current and in absence of stray current interference), since there is a galvanic current flowing between the two coating defects. Again the total length (amount of electrons) of all the blue arrows is identical to the total length of all the red arrows. However, the large coating defect receives a net cathodic current (cathodic protection) and the small coating defect in clay experiences an anodic interference and an acceleration of corrosion. There is no net current flowing into the structure, but there is a relevant corrosion process taking place as a result of the galvanic corrosion. As a consequence, the potential measurement corresponds to an off potential (E_{off}), since all external current sources are interrupted. This E_{off} is a result of the IR-free potentials of the two coating defects as well as their corresponding spread resistances. It is relevant to note that IR-free potentials of steel within the coating defects can readily be between -0.8 to -0.4 V_{CSE}, depending on soil conditions and especially its aeration. As a consequence, the E_{off} of a pipeline with two coating defects with the individual IR-free potentials ($E_{IR-free}1$ and $E_{IR-free}2$) as well as the spread resistances (R1 and R2) can be calculated according to equation (1) [1-4].

$$E_{off} = \frac{E_{IR-free}1 \cdot R2 + E_{IR-free}2 \cdot R1}{R1 + R2}$$

(1)

Equation (1) clearly shows that the structure potential will never correspond to the IR-free potential of an individual coating defect, unless both coating defects happen to have exactly the same IR-free potential. This is correspondingly stated in EN 13509 as the precondition for using the instant-off potential as an approximation of the IR-free potential. This is however highly unlikely due to the fact that under normal conditions every coating defect has a different IR-free potential as a result of different sizes and soil conditions. This results in galvanic currents and mutual polarization as shown in Figure 2.

This galvanic corrosion on the pipeline was identified by Kuhn in 1928 [5] as the main reason for the significant number of leaks in pipeline systems. 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 this concept all coating defects would receive a net cathodic current as shown on the left side of Figure 3. In this configuration there is a net current flowing to the structure. This approach can readily be justified based on Ohm's law with the following formula with respect to a single coating defect with a potential $E_{IR-free}$ (2):

$$I = \frac{E_{IR-free} - E_{on}}{R}$$

(2)

Under the assumption that -0.85 V_{CSE} is the most negative naturally possible potential (as confirmed in 1951 by Schwerdtfeger and McDorman [6]), it can be concluded that any on-potential more negative than -0.85 V_{CSE} is bound to result in a cathodic current I on any individual coating defect. This conclusion is independent of the spread resistance R and hence the soil resistivity. This is the very basis for the on-potential criterion of -0.85 V_{CSE} proposed by Kuhn as discussed in [7]. This concept is further fully in line with the model proposed by Mears and Brown [8]. They explained the mechanism of cathodic protection based on bringing the potential of the cathodes to the potential of the anodes. This will effectively eliminate all galvanic current.
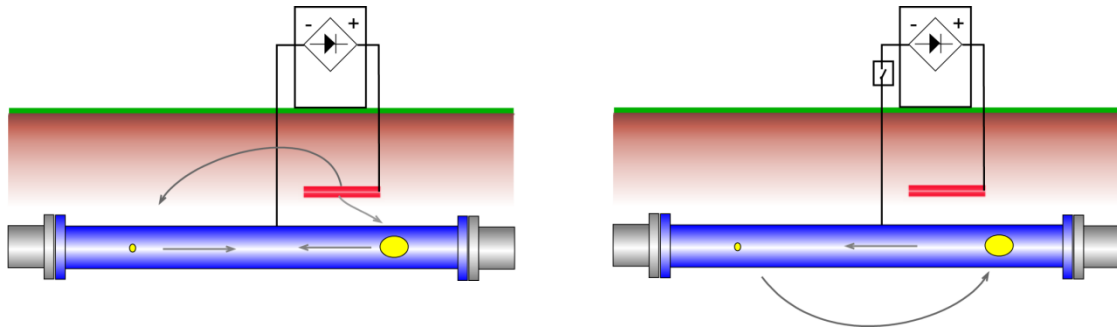
Figure 3: Effect of coating defect size and heterogeneous polarization on the off-potential. The situations with (left) and without (right) protection current are shown.

It is undisputed that the on-potential will only demonstrate the direction of the current flow but will not allow any demonstration of effective cathodic protection according to ISO 15589-1:2015.

This consideration needs to be completed by a discussion of the instant-off measurement. Interrupting the current at the rectifier (Figure 3 right) will result in a net current flow of zero on and off the structure, but there will still be relevant equalizing currents between the different coating defects. As a consequence, the instant off potential will correspond to a structure potential according to equation (1). The only cases where an instant off-potential corresponds to an IR-free potential according to EN 13509 are:

- There is only one coating defect on the pipeline (cf. Figure 1)

- All coating defects have identical IR-free potentials

Both cases are well known to be non-realistic. Despite this implication the CP industry uses instant-off potentials in order to demonstrate compliance with ISO 15589-1:2015.

The fact that the single coating defects IR-free potential is not measurable in most real applications is therefore addressed by an approximation that can lead to severe misjudgement as a careful consideration of equation (1) readily shows based on the most commonly misinterpreted situation of pipelines coated with three layer polyethylene (3LPE) and fusion bonded epoxy (FBE). The consequences of these effects of equation (1) are illustrated in Table 1 for 3LPE and Table 2 for FBE. The only difference between the two coating systems is the assumption that the FBE coated pipeline has a significantly larger number of small coating defects with 1 mm diameter coating defects than the 3LPE.

It is evident based on equation (1) that the instant-off potential is dominated by the IR-free potential of the defect with the smallest spread resistance. As a consequence, having a coating systems that exhibits a very large number of very small coating defects (that will have higher current densities and are hence will be better polarized) will generate the impression of being easier to polarize and easier to cathodically protect. The comparison illustrated in Table 1 (3LPE) and Table 2 (FBE) clearly demonstrates that this is an artefact generated by the large amount of small and well polarized coating defects. In fact, the larger coating defects on both pipelines have the same level of polarization and hence corrosion protection. The large number of small coating defects simply generates the illusion of higher protection on the FBE coated pipeline compared to the 3LPE coated one.

Table 1: Instant off potentials calculated according to equation (1) for a pipeline with 3LPE coating and assumed IR-free potentials in soil with a resistivity of 60 Ωm and 10 coating defects with diameter of 1 mm diameter and 10 coating defects with diameter of 100 mm.

ρ [Ωm]	60	Number	$E_{\text{IR-free}}$ [V_{CSE}]	E_{off} [V_{CSE}]
d1 [mm]	1	10	-1	-0.60
R1 [Ω]	30000			
d2 [mm]	100	10	-0.6	
R2 [Ω]	300			

Table 2: Instant off potentials calculated according to equation (1) for a pipeline with FBE coating and assumed IR-free potentials in soil with a resistivity of 60 Ωm and 10000 coating defects with diameter of 1 mm diameter and 10 coating defects with diameter of 100 mm.

ρ [Ωm]	60	Number	$E_{\text{IR-free}}$ [V_{CSE}]	E_{off} [V_{CSE}]
d1 [mm]	1	10000	-1	-0.96
R1 [Ω]	30000			
d2 [mm]	100	10	-0.6	
R2 [Ω]	300			

It is key to understand that the instant off-potential measurement will for sure never provide the IR-free potential of a whole structure and, hence, will never allow demonstrating compliance with ISO 15589-1:2015 in realistic configurations (i.e. not all coating defects have the same level of polarization). Correspondingly it was concluded in the panel discussion during the 2015 Ceocor congress that an instant-off potential of -0.95 V_{CSE} only allows for concluding that many coating defects are protected [7].

It is relevant to note that the understanding of cathodic protection has substantially changed in recent decades. This is primarily due to the understanding of the relevance of pH increase and passivation associated with concentration polarization. This was first indicated by Schwerdtfeger and McDorman in 1951 [6] and Kobayashi in 1974 [9]. Thompson and Barlo [10] demonstrated the relation between cathodic current, pH increase and a possible passivation in 1983. While there is general agreement in literature that the protection is achieved through electrochemical polarization, there was only limited consideration given to the type of polarization and the respective characteristics. While the application of a cathodic current will instantaneously cause a certain shift of the IR-free potential in the negative direction as a result of activation polarization, the reaction products consisting of hydroxide ions will, over time, result in concentration polarization. Freiman emphasized the relevance of pH and passivation in 1988 [11] and his concept is today best illustrated by the standard text book on cathodic protection: *Peabody's Control of Pipeline Corrosion*, second edition 2001 [12]:

"The concepts (activation polarization) presented for CP are fundamentally correct at the instant that CP is applied but are too simplistic to consider the time-dependant behaviour 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 concept allows for explaining all threshold values, the small protection current densities required for polarization according to ISO 15589-1:2015 in the range of 0.1 to 1 A/m^2, the relevance of averaged current and on-potential values over time according to ISO 18086:2015 and the irrelevance of temporary loss of protection during surveys or due to anodic interference caused by stray current interference [10, 13-16]. All these effects are a result of the comparably slow processes associated with the build-up up of concentration polarization. Once concentration polarization is achieved it usually takes time for depolarization. Von Baeckmann has emphasized this in 1996 [17]:

"The electrical polarization and the ohmic drop in soil exhibit different time constants. The ohmic drop in the soil has a time constant of $t_B = 10^{-7}$ s, the activation polarization has $t_P = 10^{-4}$ s and the concentration polarization $t_K > 10^{-2}$ s up to seconds, hours or days."

This view is confirmed by Cherry in 2006 [18]. To physically explain this: The cathodic current consumes oxygen at the steel surface and increases the surface pH value. After sufficient time of polarization a far reaching increase of the pH and oxygen depletion (several decimetres) has built up into the adjacent soil. This explains the generally accepted observation that the polarization takes time. After loss of cathodic protection, it takes minutes, hours or even days to equilibrate this local change of soil composition at the coating defect with the surrounding soil due to the slow diffusion processes. In other words: CP generates a high pH in the soil comparable to the values observed in concrete. In concrete the corrosion protection of steel is ensured by the high pH value and the resulting passivity. As a consequence, the effect of CP can be interpreted as electrically generating the conditions of concrete and hence providing the very same kind of corrosion protection. While these aspects are well described since 1988 [11], their implications are still not entirely appreciated by many CP specialists today.

The delay after interrupting the external current sources for measuring the instant-off potential according to ISO 15589-1:2015 is >0.3 seconds. Based on the above discussion it is clear that this will only allow for measuring concentration polarization, hence depletion of oxygen and increase of pH and the slow diffusion processes associated with it.

the transport of accumulated OH^- and depleted O_2 result in a significant inertia in the system. Once polarization is built up (i.e. once the conditions for the formation of a passive film are present) the system becomes very tolerant with respect to short term interference.

This discussion reveals that the beneficial effects of CP in the past 90 years can only be associated with concentration polarization for the very simple reason that CP assessment, even when misinterpreted as activation polarisation, was actually based on concentration polarisation as activation polarization was never possible to be measured on buried pipelines due to very fast depolarization.

2.   Implications of concentration polarization

2.1.   Introduction

The introduction has revealed the relevance of the galvanic currents that flow between the coating defects with different IR-free potentials. The illustration in Figure 3 on the right side demonstrates that a coating defect that exhibits a more negative IR-free potential will result in a current discharge on those coating defects that have more negative IR-free potentials. For the example in Table 1 (3LPE) and Table 2 (FBE) the coating defects with an IR-free potential of -1 V_{CSE} will

result in an inversion of the polarity of voltage gradients after disconnecting the pipeline from the rectifier. They will appear as anodic sites after interruption of the cathodic current.

This inversion of the voltage gradient is used in the so called "intensive measurement" according the EN 13509 as basis for calculating the IR-free potential. Consequently, all anodic currents measured as an inversion of the voltage gradient in DCVG are the indication of a high level of protection based on EN 13509. This is in clear contrast to the Anglo Saxon approach, where those sites with an inversion of the current direction are described as anodic sites and correspondingly as corrosion sites. To highlight this: There is not only a small discrepancy in the interpretation of the data. There is the complete opposite in the conclusion. In Central Europe these sites are considered well polarized and hence protected and in the Anglo Saxon CP community these sites are considered to be at a corrosion risk. The larger the voltage gradient the higher the level of protection or corrosion in these respective countries. In a world that defines the competence of CP persons based on the same ISO 15257 this is bound to result in problems and puts the credibility of the industry in question.

Interestingly there is another key discrepancy within the discussion of cathodic protection which is best illustrated in the work of Dexter et al. [19]. Mears and Brown demonstrated that CP is achieved by polarizing the cathode to the potential of the anode [8]. In contrast, LaQue concluded in 1963 (reprinted in 1982 [20]) that cathodic protection is achieved through polarization of the anode to the cathode. Similarly to the discussed interpretation of the polarity of the voltage gradient this understanding of the processes associated with cathodic protection are completely opposed. The careful analysis reveals that all of these statements and conclusion are correct under the specific conditions. This will be illustrated in the following.

2.2.   Corrosion of steel in near neural soil

In Figure 4 the configuration of steel in a near neutral soil is shown in absence of any external polarization. The anodic and cathodic current is identical, which results in a corrosion potential at the intersection between the blue and the red line in the Evans diagram (right). In this configuration an exchange current density of about 0.4 A/m^2 is obtained, which corresponds to a corrosion rate of about 0.4 mm/year.

The data in Figure 4 are calculated under the assumption of a poorly aerated soil with a diffusion limited oxygen reduction rate (J_{O2}) of 0.01 A/m^2. This results in a corrosion potential of about -0.78 V_{CSE} in the given configuration. Applying a cathodic current to this coating defect will result in a significant change in the corrosion rate. The associated effects will be discussed in the following.

2.3.   The polarization of the cathode to the anode

Polarizing the cathode to the anode will ensure a current entering in all the steel surface in line with the concept proposed by Kuhn. Since current densities as small as 1 mA/m^2 are sufficient to provide an increase of the pH and subsequent passivation [10], a current entering in the steel surface is bound to result in corrosion protection.
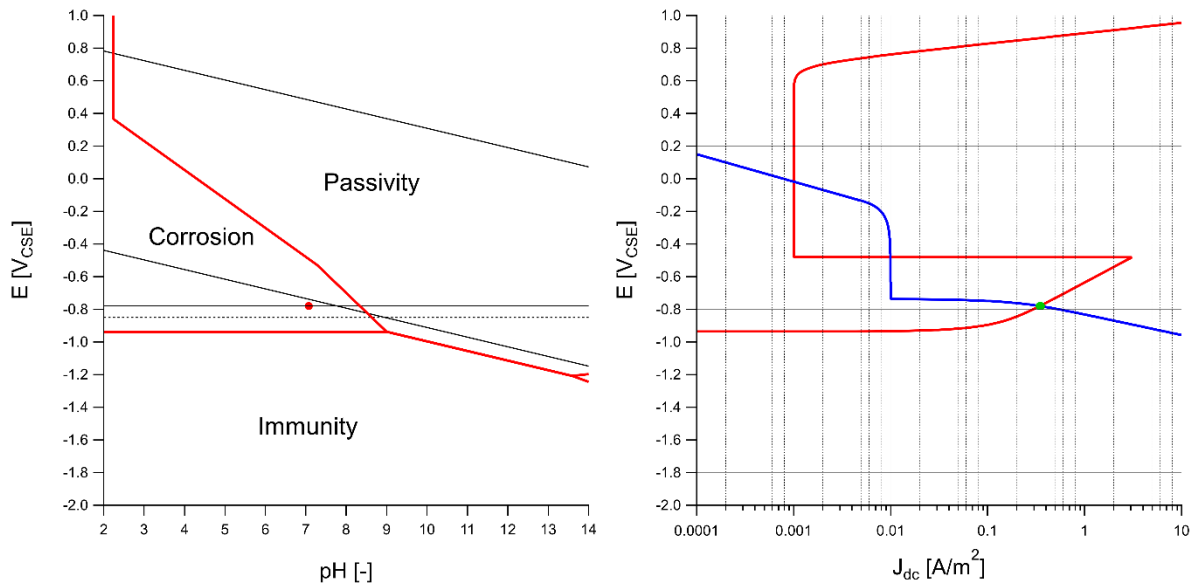
Figure 4: $E_{IR\text{-free}}$ **calculated for steel with a surface of 100 cm^2 in a neutral soil with 100 Ωm with poor aeration (J$_{O2}$ 0.01 A/m^2) and a Fe^{2+} concentration of 10^{-6} M. Left: Pourbaix diagram with the red dot showing the corrosion conditions at the corrosion potential at the steel surface. The dashed horizontal line represents the protection criterion of -0.85 V$_{CSE}$ according to ISO 15589-1 and the solid horizontal line the corrosion potential of -0.78 V$_{CSE}$ that is expected under the given circumstances. Right: Polarization curves for anodic (red) and cathodic reactions (blue) on steel at the corresponding pH value of 7. Based on the exchange current density at the corrosion potential a corrosion rate of about 0.4 mm/year is expected.**
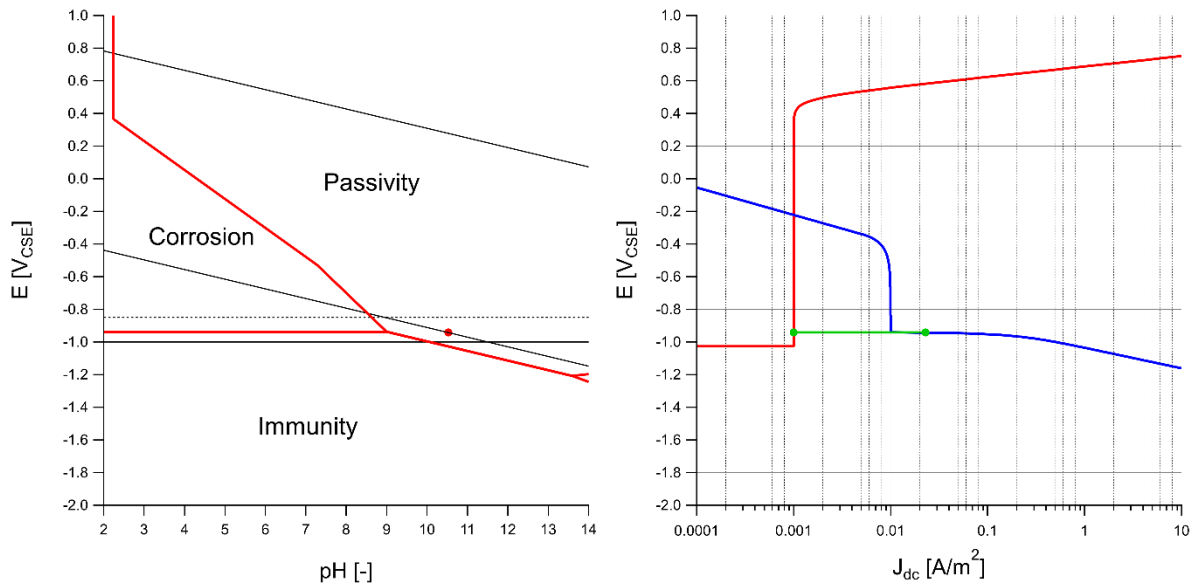

Figure 5: $E_{IR\text{-free}}$ **calculated for steel with a surface of 100 cm^2 in a neutral soil with 100 Ωm with poor aeration (J$_{O2}$ 0.01 A/m^2) at an on-potential of -1 V$_{CSE}$ (solid horizontal line). The current density is about 20 mA/m^2 (length of green line). More details are given in the caption of Figure 4. Based on the current density a corrosion rate of about 0.001 mm/year is expected.**

Therefore, the application of an on-potential of -1 V$_{CSE}$ results in corrosion protection as a result of an increase of the pH and subsequent passivation as shown in Figure 5. Based on equation 2 a current will enter the steel surface, since the on potential is more negative than the corrosion potential in Figure 4. This current entering the steel surface will result in an increase of the pH and passivation. In the present case this is achieved by means of the current density of about 0.01 mA/m^2 that causes an IR-free potential of about -0.95 V$_{CSE}$. This IR-free potential in controlled by the hydrogen evolution as can be concluded from Figure 5. As expected based on the

protection criteria of ISO 15589-1 corrosion protection is achieved, which is confirmed by the corrosion rate of 0.001 mm/year based on Figure 5. This effect is fully in line with the mechanism proposed by Mears and Brown of polarizing the cathodes to the potential of the anodes and therefore ensuring a current to enter into all steel surfaces. This current provides an increase of pH, passivation and corrosion protection on all steel surfaces. It is immediately clear that the protection criteria of -0.85 and -0.95 V_{CSE} are directly associated with an increase of pH and passivation. As detailed in [7] the measurement of the IR-free potential corresponds to a pH measurement, where -0.85 and -0.95 V_{CSE} correspond to pH values of about 9 and 10.4 respectively. This effect is a direct result of the pH dependence of the hydrogen evolution as shown by means of the tilted line in Figure 5.

2.4.   The polarization of the anode to the cathode

The effect of polarizing the anode to the potential of the cathode by means of a cathodic current appears to be in conflict with the practical experience and the conventional concepts of cathodic protection. Correspondingly the model of LaQue has received various criticism. However, a more careful consideration of the conditions that led to the physical observation of a shift of the IR-free potential of the anode in positive direction to the one of the cathode as a result of a cathodic current reveals that this effect indeed is expected to occur. It is relevant to note that these tests were run in aerated electrolyte solutions. By changing the diffusion limited oxygen reduction current density (J_{O2}) of 0.01 A/m^2 to 1 A/m^2 the results in Figure 6 are obtained for an on-potential of -1 V_{CSE}.
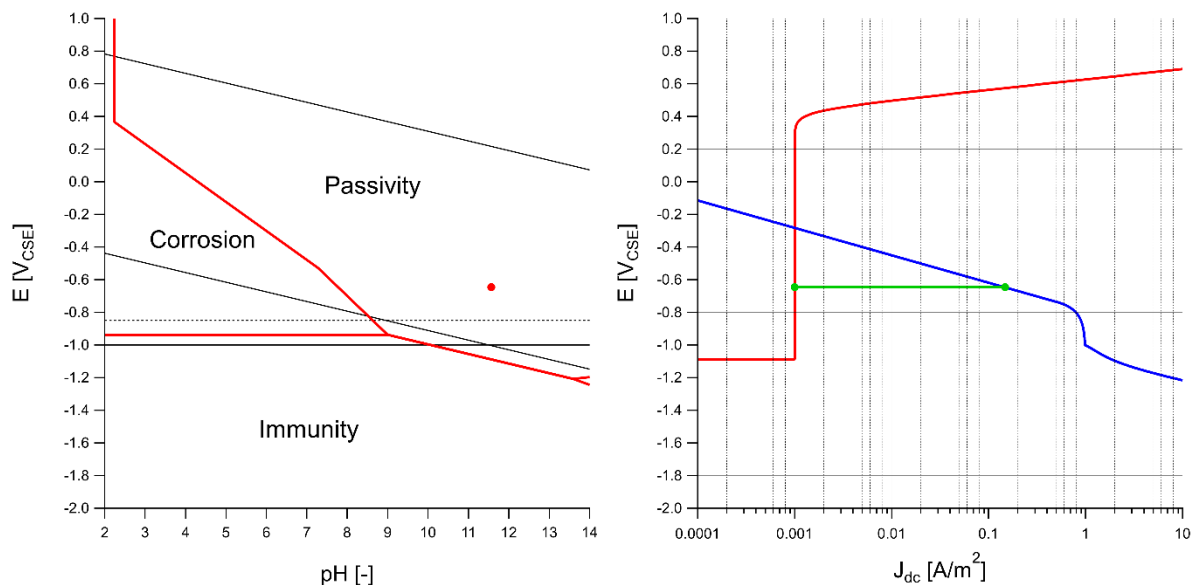

Figure 6:   **$E_{IR-free}$ calculated for steel with a surface of 100 cm^2 in a neutral soil with 100 Ωm with good aeration (J_{O2} 1 A/m^2) at an on-potential of -1 V (solid horizontal line). The current density is about 100 mA/m^2 (length of green line). More details are given in the caption of Figure 4. Based on the current density a corrosion rate of about 0.001 mm/year is expected.**

It is evident that in well aerated conditions the application of cathodic protection results in a shift of the IR-free potential of the corroding steel surface in the range of -0.78 V_{CSE} in the positive direction to about -0.65 V_{CSE}. The potential moved in the positive direction into the range of a passive cathode as a result of the application of a cathodic current. This is fully in line with the concept proposed by LaQue: The passivation of the anode resulted in its polarization to the potential of the cathode. After passivation, cathode and anode exhibit the same potential.

2.5.   Conclusion

The above considerations clearly demonstrate that both concepts proposed in literature for achieving cathodic protection are valid. It turns out that in limited aeration increase of pH and passivation under cathodic current flow results in a shift of the IR-free potential of the cathode in negative direction to about -0.95 V_{CSE}. In contrast, under well aerated conditions a shift of the IR-free potential in positive direction to -0.65 V_{CSE} is observed. Both cases result in corrosion protection as a result of passivation, which is perfectly reflected by the protection criteria of -0.95 V_{CSE} for anaerobic conditions and -0.65 V_{CSE} for aerated conditions. Hence, both concepts are covered by ISO 15589-1. A careful examination of the potential controlling reactions reveals that in the case of the polarization of the cathode to the anode potential according to Mears and Brown (Figure 5) the IR-free potential is controlled by the hydrogen evolution. In the case of polarizing the potential of the anode to the cathode according to LaQue (Figure 6) the IR-free potential is controlled by the oxygen reduction. The underlying mechanism of corrosion protection is identical: The cathodic current results in an increase of the surface pH and subsequent passivation. The only difference is the potential controlling cathodic reaction. Correspondingly, the two apparently different concepts do not exclude each other as is best illustrated by means of the associated threshold values of -0.95 and -0.65 V_{CSE} in ISO 15589-1.

At first view this conclusion is in contradiction to the analysis of Dexter et al. [19]. Their experiments were performed in aerated sea water similar to those of LaQue. However, in their case the steel surface was covered with a gel that contained a pH indicator. The experiments confirm nicely that the pH at the steel surface increased very rapidly as a result of cathodic protection. These data are perfectly in line with Figure 5. However, they could not confirm the model of LaQue based on a polarization of the anode to the potential of the cathode, since they were run under diffusion limited oxygen reduction resulting in a polarization of the cathode to the anode. Based on the above discussion this is a direct result of the experimental procedure that implies the coating of the steel surface with a gel. The water saturated gel effectively blocked convection at the steel surface and increased the diffusion length of oxygen from the electrolyte to the steel surface. This increase of diffusion length for oxygen significantly decreases the diffusion limited oxygen reduction current density. Correspondingly, a behavior according to Figure 5 based on the concept of Mears and Brown is expected. This was indeed confirmed by the investigation of Dexter et al. However, without considering the relevant effect of mass transport and oxygen diffusion this observation may not be generalized to a well aerated condition. In this context is has to be emphasized that the model of LaQue predicts the occurrence of heterogeneous corrosion prior to full polarization of all anodes to the potential of the cathode. It has to be noted that the protection criterial of -0.65 V_{CSE} is based on the work of Funk et al. [21]. They ran tests in well aerated soil with a J_{O2} of 1 A/m^2 (as in Figure 6). They reported relevant localized corrosion, which they attributed to so called "microelements" as they were predicted by LaQue. This confirms the relevance of the concepts proposed by LaQue for the case of well aerated conditions.

3.   Consequences on the assessment of effectiveness of CP

3.1.   Introduction

The above discussion clearly demonstrates that the concepts of Mears and Brown as well as LaQue do not exclude each other. Instead they are the result of special cases of cathodic protection in poor and well aerated conditions. The presented discussion resolves the apparent

contradiction and emphasizes the identical underlying concepts that are reflected in the protection criteria of -0.65 and -0.95 V_{CSE} in ISO 15589-1.

3.2. Discussion

While these aspects are to some degree academic and may have limited relevance to the practical application, there is a similar apparent contradiction in the case of the assessment of the effectiveness of cathodic protection. This involves the interpretation of voltage gradient data with respect to the effectiveness of CP. For this consideration DCVG measurements on a pipeline section were considered in an area with two passive coating defects in Figure 5 and Figure 6. Additionally it was assumed that another coating defect as shown in Figure 4 could not increase the pH due to poor bedding in rocky stones and streaming soft water. It is known that under such conditions the increase of the surface pH and passivation is not possible [7]. As, a consequence the application of an on-potential of -1 V_{CSE} and the resulting cathodic current of 50 mA/m^2 will not relevantly decrease the corrosion rate.

Table 3: **Polarity of the voltage gradient measured over three coating defects in the case of the on-potential of -1 V_{CSE} as well as in the case of different instant-off potentials.**

Potential	Corroding defect without pH increase	Passive poorly aerated coating defect	Passive well aerated coating defect
$E_{IR\text{-}free}$	-0.78 V_{CSE}	-0.95 V_{CSE}	-0.65 V_{CSE}
E_{on} -1 V_{CSE}	Positive	Positive	Positive
E_{off} -0.96 V_{CSE}	Positive	Positive	Positive
E_{off} -0.86 V_{CSE}	Positive	Negative	Positive
E_{off} -0.76 V_{CSE}	Negative	Negative	Positive
E_{off} -0.60 V_{CSE}	Negative	Negative	Negative

In Table 3 the polarity of the voltage gradients measured between a reference electrode placed above the coating defect (connected to the com of the voltmeter) and a reference electrode on remote earth (connected to the + of the voltmeter) is shown. It is evident that at an on-potential of -1 V_{CSE} a current is entering all coating defects (as shown in Figure 3 left) resulting in a positive polarity of the voltage gradient on all coating defects. In the case of an off-potential of -0.86 V_{CSE} the passive coating defect (according to Figure 5) in poor aeration shows an inversion of the polarity. This corresponds to the situation Figure 3 right, where the higher level of polarization as a result of depletion of oxygen and the associated more negative IR-free potential results in a current discharge when the rectifier is disconnected from the pipeline. This current discharge on the well polarized coating defects results in cathodic current on the corroding (according to Figure 4) coating defect as well as on the passive coating defect in well aerated soil (according to Figure 6). In contrast, at an instant-off potential of -0.6 V_{CSE} all coating defects show current discharge, the corroding as well as the passive ones.

This discussion leads to the conclusion that it is impossible to draw any conclusion with respect to the level of corrosion protection based on both, the IR-free potential as well as the polarity of the voltage gradient measured at individual coating defects, if the aeration is not known. This is due to the fact that depending on the mechanism associated with cathodic protection (i.e. polarizing the cathode to the anode or polarizing the anode to the cathode) a significant shift of the IR-free potential in the positive direction and an inversion of the voltage gradient is obtained. The

careful analysis of the data in Table 3, however, reveals that it would indeed be possible to determine effectiveness of CP, if all coating defects would achieve corrosion protection through the same mechanism. This is discussed in the following based on the theoretical case of two pipelines where all coating defects have the same size and are either well, or poorly aerated.
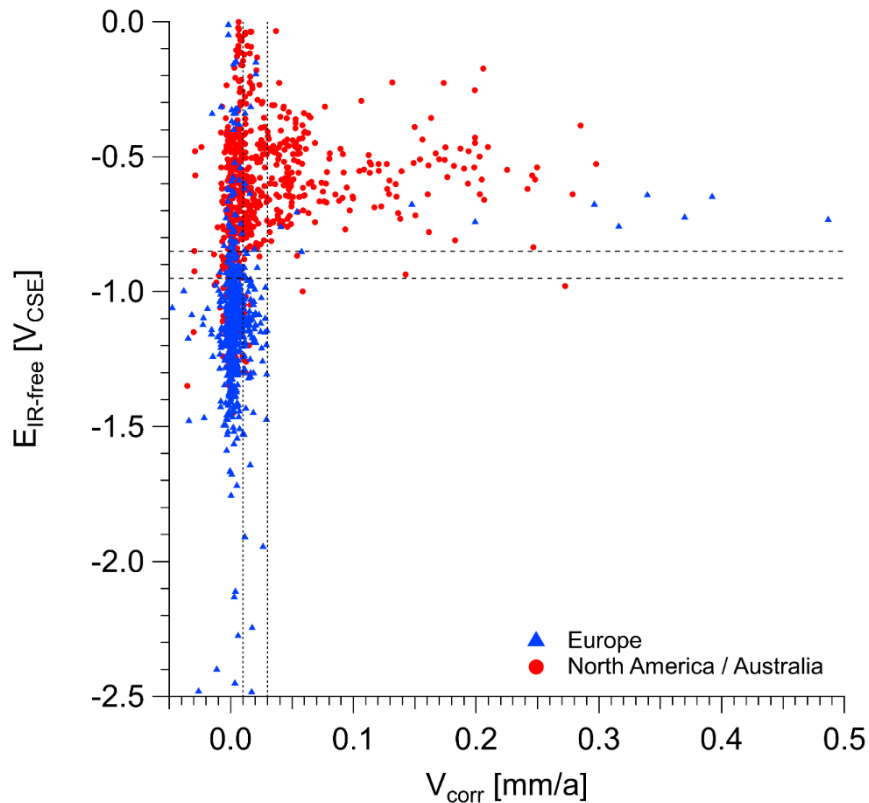

Figure 7: Correlation between corrosion rate and IR-free potential based extensive field investigations discussed in [22].

Poorly aerated coating defects: In this case corrosion protection would be achieved on all coating defects based on the concept of Mears and Brown by polarizing the cathode to the anode, resulting in current entering all steel surfaces, increase of pH and passivation. In this case corrosion protection is associated with a shift of the IR-free potential in the negative direction. The large number of coating defects exhibiting corrosion protection as a result of oxygen depletion, increase of pH and subsequent passivation will ensure that the instant off-potential according to equation (1) will be more negative than -0.85 V_{CSE}. Correspondingly, all coating defects that did not experience sufficient concentration polarization and associated increase of pH will exhibit IR-free potentials more positive than -0.85 V_{CSE}. They are, therefore, characterized by a positive voltage gradient and cathodic current flow into these coating defects after interrupting the connection of the pipeline to the rectifier.

Well aerated coating defects: In the this case corrosion protection is achieved on all coating defects according to the concept of LaQue by polarizing the anode to the cathode. Again corrosion protection is achieved through increase of pH and subsequent passivation. However, since the IR-free potential is controlled by the oxygen reduction rather than the hydrogen evolution, this passivation will cause a shift of the IR-free potential in the positive direction as a result of cathodic protection. The large number of coating defects exhibiting corrosion protection as a result of pH-increase and subsequent passivation will result in an instant off potential more positive than -0.7 V_{CSE} according to equation (1). Correspondingly, all coating defects that did not experience sufficient concentration polarization and associated increase of pH will exhibit IR-free potentials more

negative than -0.7 V_{CSE}. Hence, corrosion sites are indicated by an anodic current discharge indicated by a negative voltage gradient after disconnecting the pipeline from the rectifier.

Unfortunately, pipelines do hardly ever exhibit only either well or poorly aerated conditions on all the coating defects. Furthermore the coating defects have never the same size. Instead, there is any given sequence of aeration, size and bedding conditions of coating defects along the pipeline. Correspondingly, applying the above concept of IR-free potential and polarity of the voltage gradient is bound to result in a misjudgment of the corrosion situation in the case of unknown aeration at the steel surface of coating defects. This is best illustrated based on the evaluation of the correlation between the IR-free potential and the corrosion rate of the two largest field tests ever performed in North America and Australia [23] as well as Europe [24] shown in Figure 7 reported in [22]. It is evident that there is no correlation between the IR-free potential and the corrosion rate. Instead, corrosion protection is observed over the entire potential range, while instances with increased corrosion rates are only observed in the potential range between -0.2 and -1 V_{CSE}. Based on the above discussion it is possible to attribute individual domains in Figure 7 to different scenarios:

- No relevant corrosion at IR-free potentials more negative than -0.85 V_{CSE}: In these instances the corrosion protection was achieved by polarizing the cathode to the anode according to the concept of Mears and Brown. The increase of pH and the subsequent passivation resulted in effective corrosion protection. The IR-free potential is controlled by the hydrogen evolution as shown in Figure 5. Typically this protection mechanism is observed in soil with poor aeration, on small coating defects or low soil resistivity as well as a combination of these parameters. This situation is addressed by the protection criteria of -0.85 and -0.95 V_{CSE} in ISO 15589-1.

- No relevant corrosion at IR-free potentials more positive than -0.85 V_{CSE}: In these instances the corrosion protection was achieved by polarizing the anode to the cathode according to the concept of LaQue. The increase of pH at the steel surface resulted in passivation and a shift of the potential in positive direction. The IR-free potential is controlled by the oxygen reduction as shown in Figure 6. Typically this protection mechanism is observed in well aeration soils, on large coating defects or high soil resistivity as well as a combination of these parameters. This situation is addressed by the protection criteria of -0.75 and -0.65 V_{CSE} in ISO 15589-1.

- Relevant corrosion at IR-free potentials in the range between -0.95 and -0.6 V_{CSE}: The insufficient concentration polarization of the steel surface with respect to pH increase did not result in passivation. The IR-free potential is controlled by iron dissolution and hydrogen evolution as shown in Figure 4. Typically this lack of protection is observed in poor bedding conditions in rough bedding material in combination with streaming water. This corrosion is particularly pronounced in the case of poorly aerated soft, buffered or acidic soil water as well as a combination of these parameters. The cathode was not polarized sufficiently negative in these cases to provide sufficient cathodic current densities on the anode. Correspondingly, concentration polarization was not possible because the generated hydroxide ions were removed by flowing water or neutralized by the acidic soil conditions. This effect is especially pronounced in the case of microbial activity under anaerobic conditions. Typically this corrosion is observed in poorly aerated or anaerobic soils in combination with organic acids and carbon dioxide. Their mitigation requires IR-free potentials more negative than -0.95 VCSE as specified in ISO 15589-1.

- Relevant corrosion in IR-free potentials in the range between -0.7 and -0.2 V_{CSE}: The insufficient concentration polarization of the steel surface with respect to pH increase did not result in complete passivation. This partial passivation of the steel surface (as discussed in [25]) results in pitting corrosion within a passive surface. This configuration cannot be described as a homogeneous electrode. Instead it is a heterogeneous electrode consisting of a large passive surface acting as cathode (according to Figure 6) in well aerated soil and a local anode (according to Figure 4). This situation is fully in line with the concept proposed by LaQue as detailed in [19] and will result in locally accelerated corrosion. The IR-free potential measured at the corresponding coating defects is an average of the IR-free potentials of anode and cathode as described by equation (1). The corrosion is a result of insufficient polarization of the anode to the cathode (lack of complete passivation). Typically this lack of protection is observed on larger coating defects in well aerated soils in rough and heterogeneous bedding material in combination with increased soil resistivity. The insufficient increase of the pH did not provide passivation of the anode and hence failed to polarize the anode to the cathode.

It is readily possible to explain the field data based on the two concepts of Mears and Brown as well as LaQue. Failure to acknowledge these aspects will not allow to further advance the understanding of the underlying mechanisms of CP. At first glance it could be argued that this discussion is purely academic. However, a more careful analysis reveals that it clearly has severe implications on the assessment of effectiveness of CP.

3.3.   Implications of the protection mechanism

It is relevant to note that the pipeline industry has failed to distinguish these two mechanisms of corrosion protection. In the Anglo Saxon CP industry the current discharge and the so called "anodic sites" are considered to be insufficiently protected and at corrosion risk. In contrast, the central European approach has the exact opposite view: The current discharge is a demonstration of a high level of corrosion protection and the so called "cathodic sites" are considered to be insufficiently protected and at corrosion risk. This view is backed by EN 13509 and the measurement method called "intensive measurement".

Of course it is inacceptable that the CP industry evaluates the same physical effect not only different, but exactly opposite depending on the continent the reading has been taken. The fact that this is indeed the case raises the question with respect to credibility especially in the light of ISO 15257 that describes the competence of CP persons on a global level.

4.   Conclusions

The presented discussion of the underlying mechanisms of cathodic protection as proposed by Mears and Brown (polarizing the cathode to the anode) as well as LaQue (polarizing the anode to the cathode) confirms again the relevance of concentration polarization and passivation. Furthermore it allows for explaining a number of key aspects in cathodic protection and assessment of effectiveness:

- The protection criteria in ISO 15589-1 of -0.85 and -0.95 V_{CSE} are based on polarizing the cathode to the potential of the anode resulting in pH increase and passivation. The IR-free potential is controlled by hydrogen evolution. This process is typically observed on small coating defects in electrolytes with limited aeration or in low resistivity soil.

- The protection criteria in ISO 15589-1 of -0.75 and -0.65 V_{CSE} are based on polarizing the anode to the potential of the cathode as a result of a pH increase and passivation. The IR-free potential is controlled by oxygen reduction. This process is typically observed on large coating defects, in well aerated soil or soil with high resistivity.

- The relevance of aeration and soil resistivity is emphasized in Table 1 in ISO 15589-1. However, without further knowledge of the underlying mechanism of protection it is not possible to demonstrate effectiveness of CP according ISO 15589-1 even it if is assumed that the IR-free potential is actually measurable.

- Effectiveness of CP can only be demonstrated based on an IR-free potential of -0.95 V_{CSE}. However, such negative potentials cannot be assured on all coating defects especially in increased aerated soils. Correspondingly it leads to the erroneous conclusion that these coating defects are corroding. In fact they are cathodically protected based on the mechanism described by LaQue.

- Corroding sites cannot be reliably identified based on "anodic sites" during DCVG surveys, since this procedure assumes that all coating defects are protected according to the mechanism proposed by LaQue. On poorly aerated coating defects this procedure results in the erroneous conclusion that they are corroding. In fact they are well polarized and protected by the mechanism proposed by Mears and Brown.

- The discussion of the instant off-potential reveals that it only represents an average of the IR-free potentials of all coating defects on the pipeline. If some of them are protected according to the mechanism of Mears and Brown and some others are protected according to the mechanism of LaQue the obtained average value is entirely arbitrary and meaningless. This consideration immediately explains the paradox effect that polarizing a pipeline with a high resistive coating system (e.g. 3LPE) to an instant-off potential of -0.85 V_{CSE} requires more negative on-potentials than polarizing a pipeline with less resistive coating (e.g. FBE). This artefact is a result of the larger number very small coating defects that are polarized according to the concept of Mears and Brown. After disconnecting the pipeline form the rectifier these well polarized coating defects provide cathodic protection to the larger coating defects that are protected according to the concept of LaQue. This discussion reveals that using an instant-off potential for assessment of effectiveness of CP is entirely arbitrary. It confirms once more that the statement in EN 13509 is correct: The instant-off potential may only be used as an approximation of the IR-free potential in absence of compensation currents. The above discussion reveals that this is only possible if all coating defects are protected according to the mechanism of Mears and Brown. Unfortunately it is impossible to ensure this.

- It might be concluded that considering the problems associated with the demonstration of effectiveness of CP based on the IR-free potential would favor the use of the 100 mV depolarization criterion as an alternative approach. This is wrong for the following reasons: the 100 mV criterion is based on activation polarization of a homogeneous electrode, while cathodic protection of buried structures is based on concentration polarization and subsequent passivation (see [12]) of a structure consisting of numerous electrodes with different IR-free potentials (hence a heterogeneous electrode). The key assumption of an actively corroding homogeneous steel surface is hardly ever fulfilled. This is correctly reflected in ISO 15589-1: The 100 mV criterion may only be used in the absence of compensation currents (i.e. on a homogeneous electrode). While the presence of a homogeneous electrode must be technically excluded, there is another key issue in association with the 100

mV criterion: Since the depolarization of activation polarization occurs according to von Baeckmann within milliseconds, it is simply impossible to measure on a pipeline. ISO 15589-1 suggest waiting time before taking the first reading to be at least 0.3 seconds after disconnecting the rectifier from the pipeline. It is clear that all activation polarization has long disappeared before the first reading even has been taken. Correspondingly the 100 mV criterion taken on any pipeline was never associated with the Tafel slope and a decrease of the corrosion rate caused by the shift of the IR-free potential in the negative direction based on activation polarization. This readily explains the poor correlation between predicted corrosion protection and actual corrosion behavior [22] of the 100 mV criterion. The use of the 100 mV criterion can, therefore, not be justified based on theoretical, practical and empirical basis.

This discussion emphasizes the relevance of the discussion on CP criteria. While it is out of question, that CP represents a key technology that ensures the integrity of pipelines, the currently used protection criteria have fundamental problems. First they are not measurable on modern pipelines due to high coating quality and the associated small voltage gradients. The only available technology for determining the IR-free potential according to EN 13509 is the "intensive measurement" that requires voltage gradients of at least 100 mV in order to allow for reliable determination of the IR-free potential. More importantly the obtained IR-free potential cannot be evaluated in the case of well aerated soil conditions, since the IR-free potential of $-0.75V_{CSE}$ can be associated with both, corrosion as well as passivity.

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