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Paper 19

**Effect of variation of cathodic protection level over time on the a.c.  
corrosion process**

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## **Abstract**

The use of alternating cathodic protection levels could offer interesting possibilities in optimizing the corrosion behavior under a.c. interference. The effect of pulsed cathodic protection on the a.c. corrosion process is discussed and the relevant physical chemical effects are discussed.

## **Zusammenfassung**

Die Anwendung eines alternierenden kathodischen Schutzniveaus könnte eine interessante Möglichkeit für die Optimierung des Korrosionsverhaltens unter Wechselfspannungsbeeinflussung bieten. Die Auswirkung eines gepulsten Schutzstroms auf den Wechselstromkorrosionsprozess werden diskutiert und die relevanten physikalischen und chemischen Effekte werden diskutiert.

## **Résumé**

L'utilisation de niveaux de protection cathodique alternants pourrait offrir des possibilités intéressantes pour l'optimisation du comportement de corrosion en cas d'interférence du courant alternatif. L'effet de la protection cathodique à impulsions sur le processus de corrosion CA est examiné, ainsi que les effets physiques et chimiques concernés.

## 1. Introduction

In 1988, the first damages by alternating current (a.c.) corrosion of cathodic protected pipelines have been observed [1, 2]. As a result, this type of corrosion was investigated and soon the a.c. current density was identified as the critical parameter [3-5]. Later the influence of the protection current density on the corrosion rate was reported [6-9]. A deeper understanding of the processes involved has been missing for a long time though. Only in recent studies it was possible to develop a model that was able to explain all empirical observations [10-12].

Based on this concept, the corrosion rate can be reduced to a negligible level when the protection current density is limited [7, 13]. Preferably, it should be less than  $1 \text{ A/m}^2$ . This should be achieved if the on-potential more positive than  $-1.2 V_{\text{CSE}}$  and the average a.c. voltage is below  $15 \text{ V}$  [14, 15]. Additionally, the off-potential must be more negative than the required criterion of protection according to EN 12954. Under these conditions, the driving voltage for the direct current flow is minimized, which reduces the risk of a.c. corrosion to a significant extent.

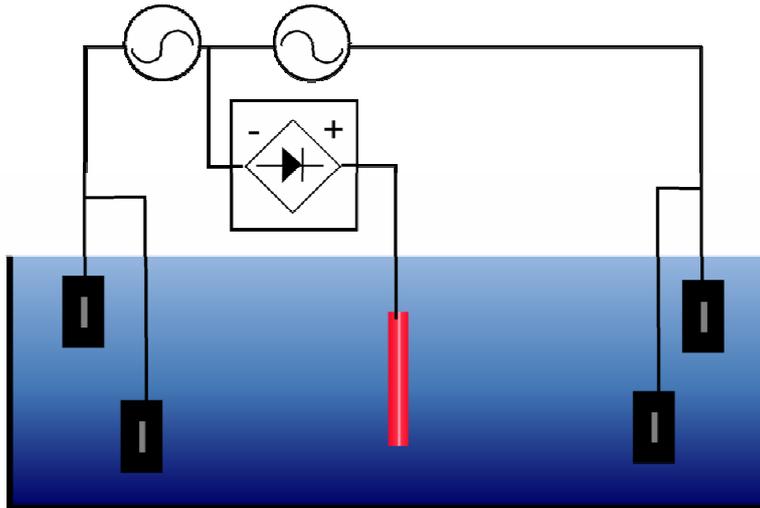
Based on the model concepts and experimental data it is likely that a.c. corrosion can be prevented even at high protection current densities. Based on laboratory tests it is probable that this is possible when the protection current density is larger than one third of the a.c. current density [6, 14].

Based on laboratory studies and model concepts, there is a profound understanding of the involved processes in a.c. corrosion and the required limits. In field studies it was further shown, that an implementation on pipelines [16] is possible.

The problem now is that there is no easy possibility to apply these limits to all existing pipelines. This is due to the sometimes very heterogeneous bedding of the pipe, the bad quality of the coating or the at least temporarily very high AC voltage interference. Given these external constraints, the question arose, if by the periodic alternation between the two protection options – very high and very low protection current – it might be possible to optimize the cathodic corrosion protection.

## 2. Experimental Methods

The experiments were run in gravel, loam, peat, and quartz sand soaked with an artificial soil solution [17] without calcium ions. Every soil was soaked with deionized water to obtain reproducible moisture conditions. For all measurements Metricorr coupons (ER probes with a thickness of  $500 \mu\text{m}$  and a surface area of  $1 \text{ cm}^2$ ) together with a data logger ILC-02 were installed. The ER probes are strip-shaped and have a length of  $3 \text{ cm}$ . The schematic experimental setup is shown in Figure 1. The AC voltage was applied by two transformers on the coupons, while a DC voltage source provided the protection current. The temporal variation of the protective current was generated by a relay. Compensation currents between anode and cathode were prevented by a diode in the anode lead.



**Figure 1:** Schematic experimental setup for the laboratory experiments. The AC voltage from the ER coupons was applied over two transformers.

For the investigation of the electrochemical processes at the steel surface during temporary alternating protection current, two different types of test coupons with a circular area of 1 cm<sup>2</sup> were used. Type 1 was covered with a surrounding layer of 7 mm thickness, thus simulating a pore in the coating. In type 2, the surface of the metal sample was even with the surrounding coating, thus simulating an "open" defect, where the resistance in the coating is eliminated. Both types of geometries characterize extreme defects. For the electrochemical study of coupons a Jaisle potentiostat/galvanostat PCT 1002 in combination with a computer was used. All potentials refer to the saturated copper/copper-sulphate electrode (CSE).

### 3. Situation

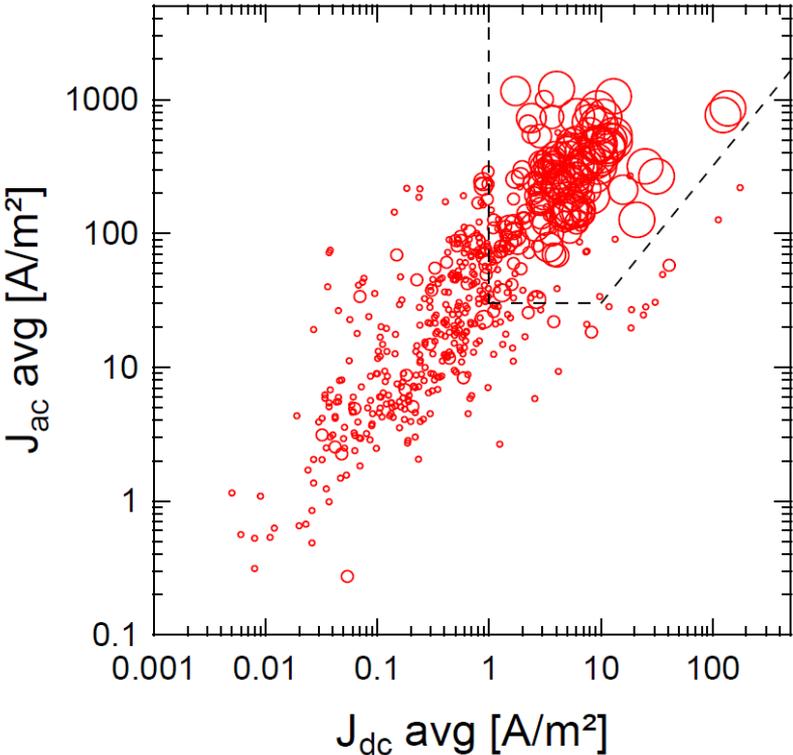
The limits for the occurrence of AC corrosion developed in laboratory studies [14, 15] have been confirmed in an extensive field study with seven pipeline operators in Germany. Influence criteria as current densities and on-potentials as well as AC voltages were determined. For current density values determined for coupons in accordance with these studies, one of the criteria below must be met:

- Average AC current density <30 A/m<sup>2</sup>
- Average protection current density <1 A/m<sup>2</sup>
- AC- to protection current density ratio <3

The results of all current density values of the field experiment are shown in Figure 2 together with those limits. Referring to the determined current densities it should be mentioned that there is a certain correlation between the DC and AC current densities. This would mean that high protection current densities as well as a high AC current density lead to AC corrosion. Accordingly, negative on-potentials and high AC voltages can lead to AC corrosion. The analysis of the data shows clearly that a high protective current density with a constant AC voltage result in most cases in an increase in AC current density, because the spread resistance of the defects decreases by increasing the pH. The electrical resistivity of the ground is therefore altered by the protection current density. On the other hand increasing the AC current density leads to an increase in the protection current density due to the Faraday rectification. This mutual influence of the parameters soil resistance, AC and DC current density

is clearly shown in Figure 2. Generally, high AC currents are associated with high DC currents, and even with increased specific soil resistivity it is possible to obtain high current densities due to a reduced spread resistance based on the increase in pH.

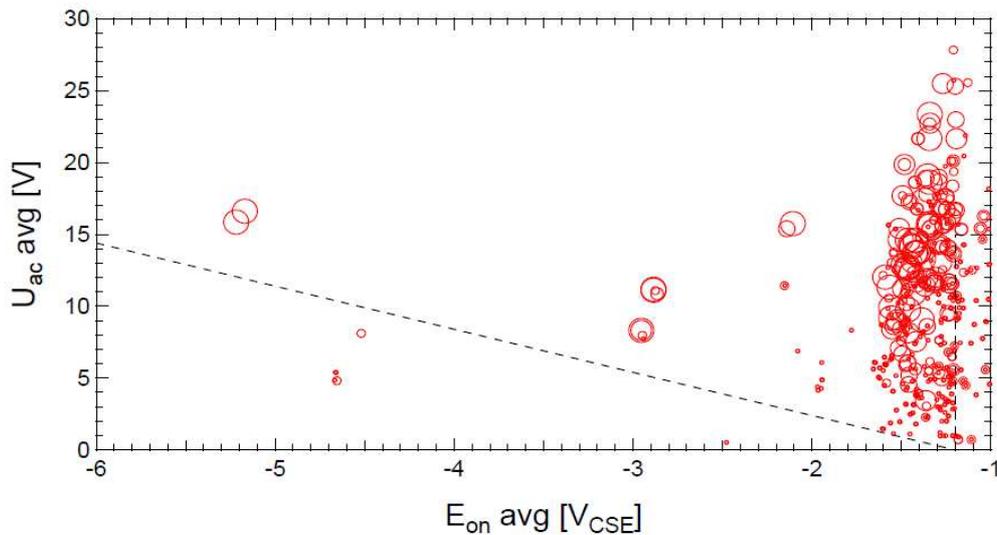
- < 0.01 mm/a
- 0.01 - 0.03 mm/a
- 0.03 - 0.1 mm/a
- 0.1 - 0.3 mm/a
- 0.3 - 1 mm/a
- > 1 mm/a



**Figure 2:** Current density values of all measured data. According to the proposed limits a corrosion risk exists above the boundary line.

The boundary values based on current density values measured at coupons allow assessing the corrosion risk. The discussion of the mechanism [18] of AC corrosion clearly shows that the current densities are responsible for the corrosion process. Insofar the determination of current density values for the assessment of the corrosion risk is justified. However, the use of coupons is fraught with some problems, since the results are highly determined by the local soil conditions, the coupon installation and the defect geometry.

The use of AC voltage and potential values to assess the corrosion risk offers significant advantages, as the evaluation of the AC corrosion risk can be made at all potential measuring points on the pipeline.



**Figure 3: Potential values of all measured data. According to the proposed limits a corrosion risk exists above the boundary line**

The evaluation of the field data in terms of potential values is shown in Figure 3. Additionally, the determined limits in laboratory experiments are shown. A good agreement between field and laboratory data is found. Based on the available findings one of the criteria below must be respected for potential values:

- Average AC voltage <15 V and average on-potential more positive than -1.2 V<sub>CSE</sub>
- $\frac{U_{ac}}{|E_{on}| - 1.2} < 3$

Concerning the limits at very negative on-potentials is important to remember that there is no theoretical justification for the ratio of 3. So in principle it is possible that the value may be even smaller. Please also note that in case of potential values; in principle a lower value should be used, since the calculation for the second criterion is based on the assumption that the spread resistance for AC current and DC current is equal. Experience shows that this condition is not always fulfilled.

Based on the available evidence is clear that AC corrosion can be prevented at very negative and at relatively positive on-potentials. In this context, the associated processes will be explained briefly.

The cathodic protection of a pipe leads at the defects of the coating, where the steel is in direct contact with the surrounding soil, to a current entry into steel. This causes a reduction of oxygen, which is lowering the potential of the steel surface and also leads to an increase in pH in the adjacent soil. If the cathodic protection current is sufficiently high, the potential of the steel surface reaches the equilibrium potential for hydrogen evolution. A further lowering of the potential is hindered by the hydrogen evolution and is only possible with high current densities. With increasing polarization time, the potential of the steel surface is moving parallel to the equilibrium line for the hydrogen evolution due to the increasing pH value (Figure 4). Once the protection criterion of -0.85 V<sub>CSE</sub> is under run, the pH-value is so high that a stable protective passive layer can form on the steel surface. This protective passive layer prevents the occurrence of corrosion. If the protective current density is high enough (> 1 A/m<sup>2</sup>), the potential of the steel surface can be polarized into the area of immunity. In this case, the protective

passive layer is lost, but the corrosion protection is ensured by the immunity present at these low potentials.

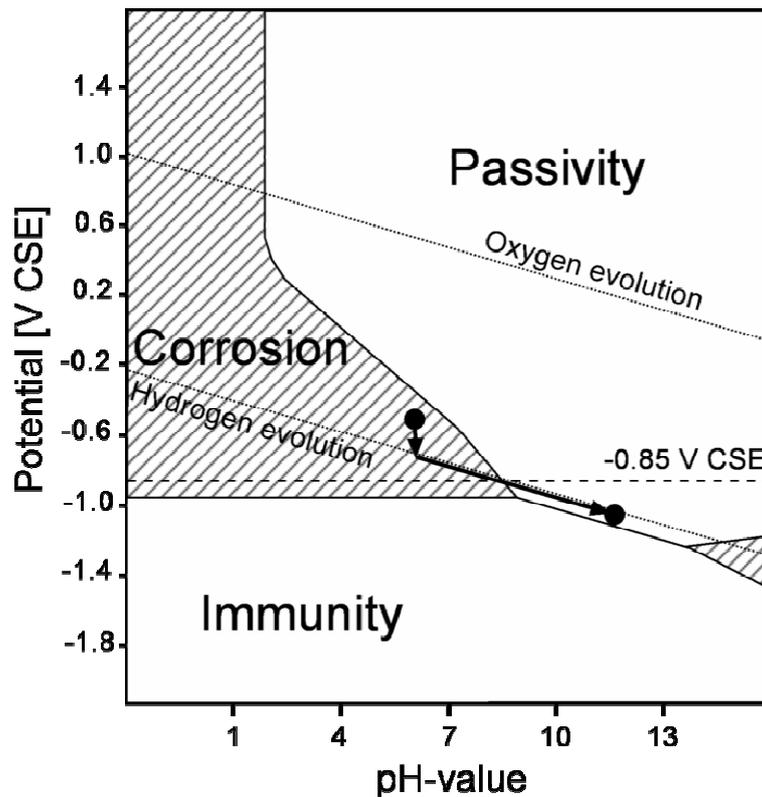


Figure 4: Effect of cathodic protection current density of  $0.1 \text{ A/m}^2$  on potential and pH value on a steel surface in the ground shown using the Pourbaix diagram.

According to this description of the processes it is clear that the change of pH in the soil at the steel surface is required for cathodic protection, and pH values of more than 13 can be achieved at sufficiently high current densities. This increase in pH generally leads to a lowering of the spread resistance. In the case of increased total hardness in the soil, in certain cases it is possible that by increasing the pH an electrically insulating layer of calcium carbonates on the coating defects is formed. Instead of an insulating calcium carbonate layer also hard porous deposits can form in front of the defect, which also lead to very low spread resistances even in soils with very high total hardness. The other soil parameters are typically of secondary importance for the cathodic protection.

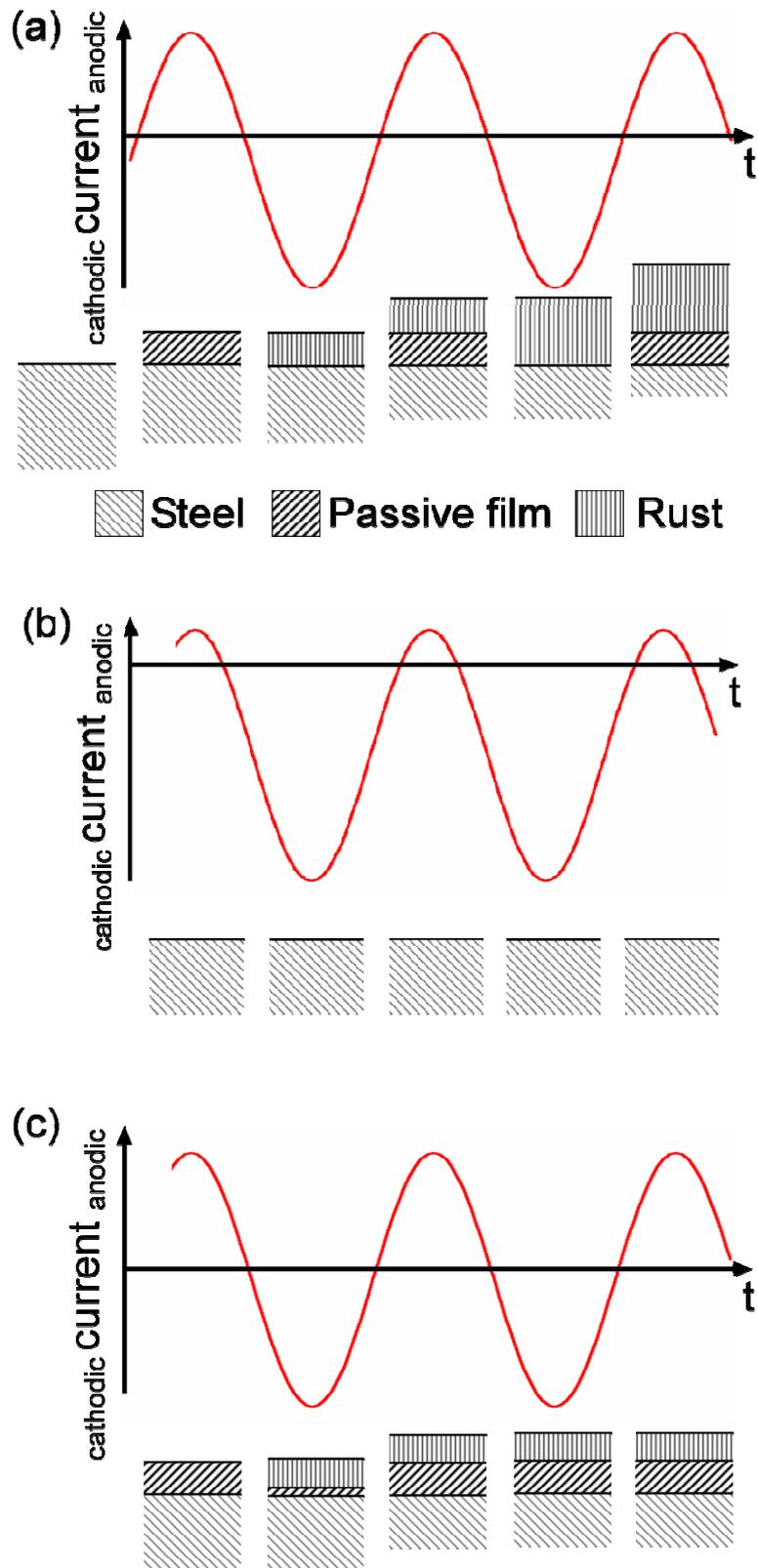


Figure 5: Schematic illustration of the processes, which happen on the steel surface at different protection current: a) high cathodic protection current ( $I_{dc} > 1 \text{ A/m}^2$ ), b) very high cathodic protection current ( $I_{ac}/I_{dc} < 3$ ), c) low cathodic protection current ( $I_{dc} < 1 \text{ A/m}^2$ ).

When an AC voltage is induced in a cathodically protected pipeline, an AC current flows through the steel surface at the coating defects of the pipeline. The AC current density depends on the AC voltage and the spread resistance of the defect. During the cathodic half cycle, the cathodic

reduction reactions at the metal surface are increased and thus enhance the cathodic protection. Depending on the amount of AC voltage, a current may exit from the steel surface during the anodic half cycle. The charge during the anodic cycle can lead to capacitive charging of the double layer, the oxidation of hydrogen, the oxidation of corrosion products, and oxidation of iron. Since the pH at the metal surface of the steel is typically high enough (over 10) the oxidation of iron leads to the formation of a passive film.

In contrast, the charge in the cathodic half-cycle is consumed by the recharging of the double layer capacitance, the reduction of oxygen, the formation of hydrogen, and the reduction of oxidized corrosion products. In addition, the cathodic charge can polarize the passive film, which was formed in the anodic half-wave, into the area of immunity and thus dissolve it electrochemically, if the protection current density is greater than  $1 \text{ A/m}^2$ .

A simplified description of the processes involved in the AC corrosion processes is shown in Figure 5a for the case of a high protection current density ( $> 1 \text{ A/m}^2$ ). During the anodic half-wave the steel surface is oxidized by the current leaving the steel surface, leading to the formation of a protective passive film. After the formation of the passive film, larger anodic charges can be absorbed by oxidation of the rust layer, without causing any corrosion. During the cathodic half-wave the steel surface gets polarized into the immunity area, the passive film is electrochemically reduced and converted into a porous rust layer. In the subsequent anodic cycle, a new passive film is formed below the non-protective rust layer. During the subsequent cathodic reduction of the passive film the amount of porous rust is increased. With each new formation of the passive film, a small amount of the steel is oxidized. Corrosion is therefore not a result of anodic metal dissolution but of repeated passive film formation. Assuming that this process leads to the formation and dissolution of a passive film with a thickness of one atomic layer of oxide with each half-wave, corrosion rates in the range of  $70 \text{ mm/yr}$  would be expected. Since such high corrosion rates occur only under extreme conditions, it can be concluded that only parts of the passive film are formed and/or dissolved during a period of the AC voltage in most cases.

As is shown in Figure 5a, AC corrosion is the result of the electrochemical formation and dissolution of the passive film. Therefore, the corrosion process can be stopped by either preventing the formation or the dissolution of the passive film. These two methods against AC corrosion are discussed below.

The formation of the passive film can be prevented by applying a sufficiently high protective currents that the remaining anodic charge is used for reversing the capacitive charge of the double layer (Figure 5b). In this case it does not lead to the formation of a passive layer. The required protection current density depends on the present AC current density. Experience shows that the AC current density must be no larger than three times the protective current density when AC corrosion should be prevented.

AC corrosion can also be prevented if the reductive dissolution of the once formed passive film is prevented (Figure 5c). This is possible if the protective current density is limited to values smaller than  $1 \text{ A/m}^2$ . Under these circumstances, it is observed that even very high AC current densities of over  $1000 \text{ A/m}^2$  do not lead to corrosion. The anodic and cathodic charge of the AC current is used for the oxidation and reduction of the rust layer.

All the empirical observations of laboratory and field studies can be explained by the conceptual model in Figure 5. The problem now is that with a cathodic protection at high current densities, the pH at the steel surface can be strongly increased. This can lead to delamination of the coating. On the other hand it is possible that with low protection currents the criterion of  $-0.85$

$V_{CSE}$  according to EN 12954 may not always be met. Moreover, it can be difficult to control the on-potential at the pipeline in the narrow range between  $-1.2$  and  $-1.1 V_{CSE}$ . As a possible solution to this problem, the periodical change between the two protection methods as shown in Figure 5b and Figure 5c is imaginable. Therefore the disadvantages of the respective protective methods could compensate each other.

## 4. Results and Discussion

### 4.1. Effect of a pulsed cathodic protection

The original concept idea in connection with the pulsed CCP, respectively, the changing between the protective methods as shown in Figure 5b and Figure 5c consisted in switching the cathodic corrosion protection alternately on and off. Therefore, investigations were carried out on the corrosion behavior of coupons in relation to different cathodic protection current densities and durations. A typical result is shown in Figure 6. After switching off the cathodic protection current a relatively rapid rise of the potential is observed. Depending on soil composition, the potential rises to values more positive than  $-0.85 V_{CSE}$ . The protection criterion for cathodic protection according to EN 12954 is lost within short time. In all cases, the potential rise flattens off within a few hours until a rapid drop of the potential occurs. In connection with the pulsed CP, it is important to understand the processes after turning off the CP in detail.

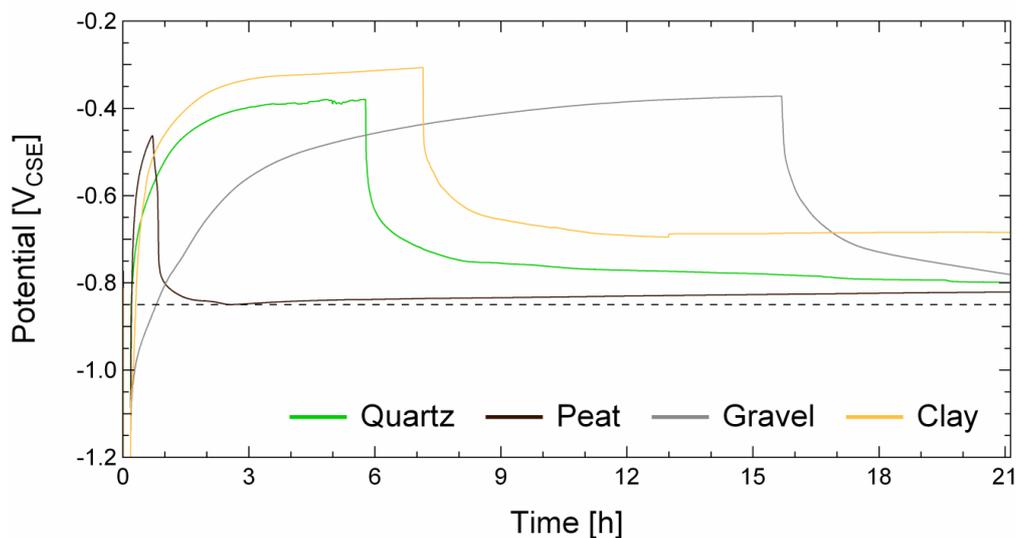
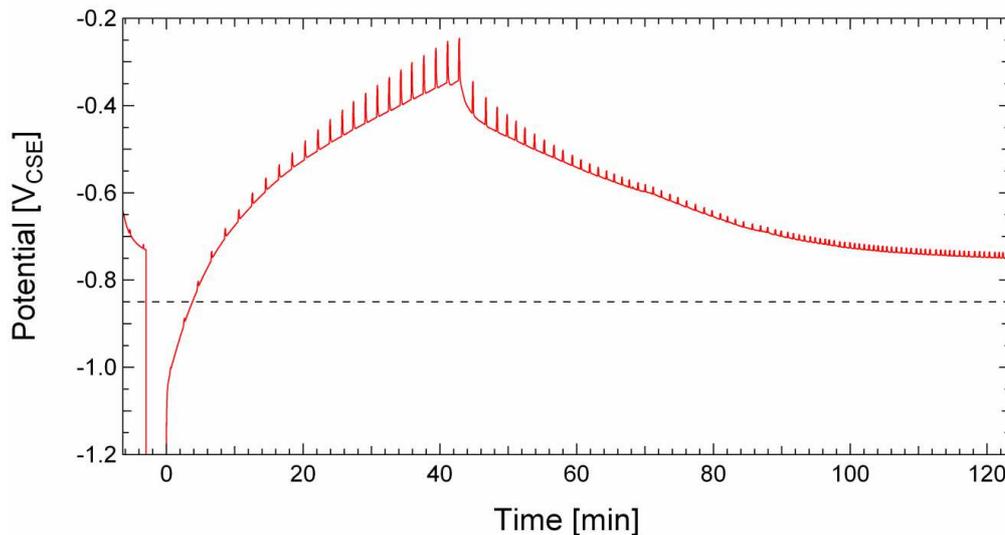


Figure 6: Potential of circular type 2 coupons with  $1\text{cm}^2$  surface after a cathodic polarization at  $40\text{ A/m}^2$  for 10 minutes.



**Figure 7:** Potential of a round coupon with a surface of  $0.031 \text{ cm}^2$  after a cathodic polarization at  $32 \text{ A/m}^2$  for 3 minutes. At periodic intervals, a of anodic current pulse with  $0.032 \text{ A/m}^2$  was applied.

Further tests were therefore carried out, in which at periodic intervals an anodic pulse of  $0.032 \text{ A/m}^2$  was applied. Turning off the protective current of  $32 \text{ A/m}^2$  after 3 minutes showed qualitatively the same potential behavior as in Figure 6. Additionally, it can be seen, that the current pulses lead to larger anodic potential shifts with increased potential. After the drop of the potential the anodic potential shifts get smaller. The potential shift is primarily caused by the current flow through the polarization resistance of the steel surface and the resistance of the electrolyte. If a constant electrolyte resistance is assumed, the potential shift is primarily caused by the polarization resistance of the steel. The polarization resistance of steel is typically increased by the formation of a passive layer on the steel surface. Taking into consideration the effects of cathodic corrosion protection (Figure 4) the protective current will lead to a depletion of oxygen and an increase of the pH value at the steel surface. These changes in the soil composition in the immediate vicinity of the steel surface are shown in Figure 8a and b. After turning off the CP, oxygen from the environment will diffuse to the steel surface. The increase in oxygen concentration leads to a positive shift of the potential. According to the Pourbaix diagram (Figure 4) this potential shift moves the steel surface into a region of passivity. Due to the high pH value corrosion is not expected even if the potential is more positive than  $-0.85 \text{ V}_{\text{CSE}}$ .

This effect was discussed in detail in [18] for the case of stray current interference. The increase of the potential is associated with an increase of the thickness of the passive layer, which again is shown in the rising potential shifts during the anodic current pulses. The increase in oxygen concentration at the steel surface will therefore not directly lead to increased in corrosion. Since the cathodic protection was applied only for a short time, the zone with an increased pH value has only a small spatial extension into the electrolyte. Therefore, the pH at the steel surface will decrease over time (Figure 8c). The decrease in pH and the increase of the potential by the diffusion of oxygen increase the risk for the local destruction of the passive layer. With the decreasing of the ratio between hydroxyl ions and chlorides in the electrolyte and the increasing potential of the steel surface the risk for the initiation of pitting corrosion increases over time. As soon as the passive film is locally destroyed and corrosion is initiated, oxygen is again consumed at the steel surface and the potential of the coupon starts decreasing. The initiation of corrosion can also be traced by the decreasing potential shifts of the anodic current pulses

under the influence of anodic. These experiments clearly show the close interaction between the electrochemical reactions, the mass transport in soil and the soil properties. Based on these results it is clear that a complete elimination of the cathodic protection can create a significant risk due to local activation of corrosion.

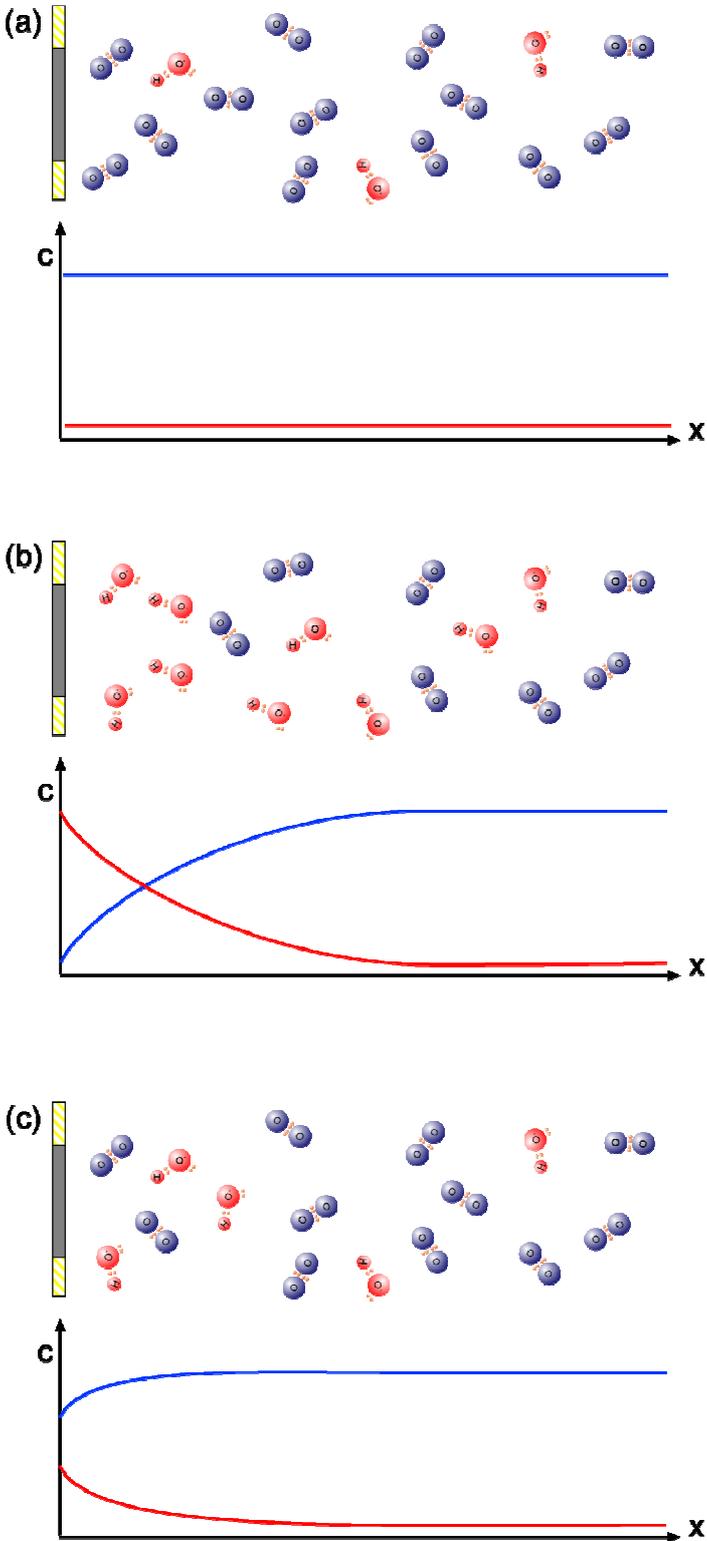


Figure 8: Concentration distribution of oxygen ( $O_2$ ) and hydroxyl ions ( $OH^-$ ) in soil: a) homogeneous distribution before the start of the CP, b) Reduced oxygen and increased hydroxyl ion concentration on the steel surface with CP, c) increase in the oxygen and lowering of hydroxyl ion concentration by diffusion processes over time.

## 4.2. Optimization of a CP system with pulsed protection current

The possibilities of a cathodic protection under temporally varying protection current were subsequently investigated systematically. In all experiments, the AC voltage was set to values in the range of 16 volts. The on-potential was set to  $-16 V_{CSE}$  ( $E_1$ ) for a certain time  $t_1$  and subsequently set to a potential  $E_2$  during a period of time  $t_2$ .

An example of a representative series of experiments in quartz sand with an artificial soil solution is shown in Figure 9. The lower coupons are in constantly soaked sand, while the upper coupons are in drier sand. The associated operating parameters are listed in table 1. In a first series of experiments A, the time  $t_1$  was one minute and  $t_2$  about 5 hours. The measurements show that the corrosion rate is negligible in this case. Time  $t_2$  was then reduced to 11 min (test series B). Subsequently, heavy corrosion started immediately, which again immediately stopped as  $t_1$  was reduced to 2.4 seconds (test series C). This clearly shows that the time periods  $t_1$  and  $t_2$  cannot be chosen arbitrarily and must be coordinated. A similar effect occurs when  $t_1$  is one minute and  $t_2$  about one hour (test series D). In this case, there is slight corrosion, but it also stops completely if  $t_1$  is reduced to 12 seconds (test series E). Interestingly, it is found that corrosion occurs whenever the average on-potential over time is more negative than  $-1.2 V_{CSE}$  (Figure 10). This result is in good correlation with the results from the field trial. It also shows that the calculation of the average value also applies in the case of on-potentials more positive than  $-1.2 V_{CSE}$ . Furthermore it can be concluded immediately that a pulsed cathodic corrosion protection can actually prevent corrosion by switching between the case in Figure 5b and Figure 5c. However, it should be noted that the operating parameters must be precisely adjusted on each other.

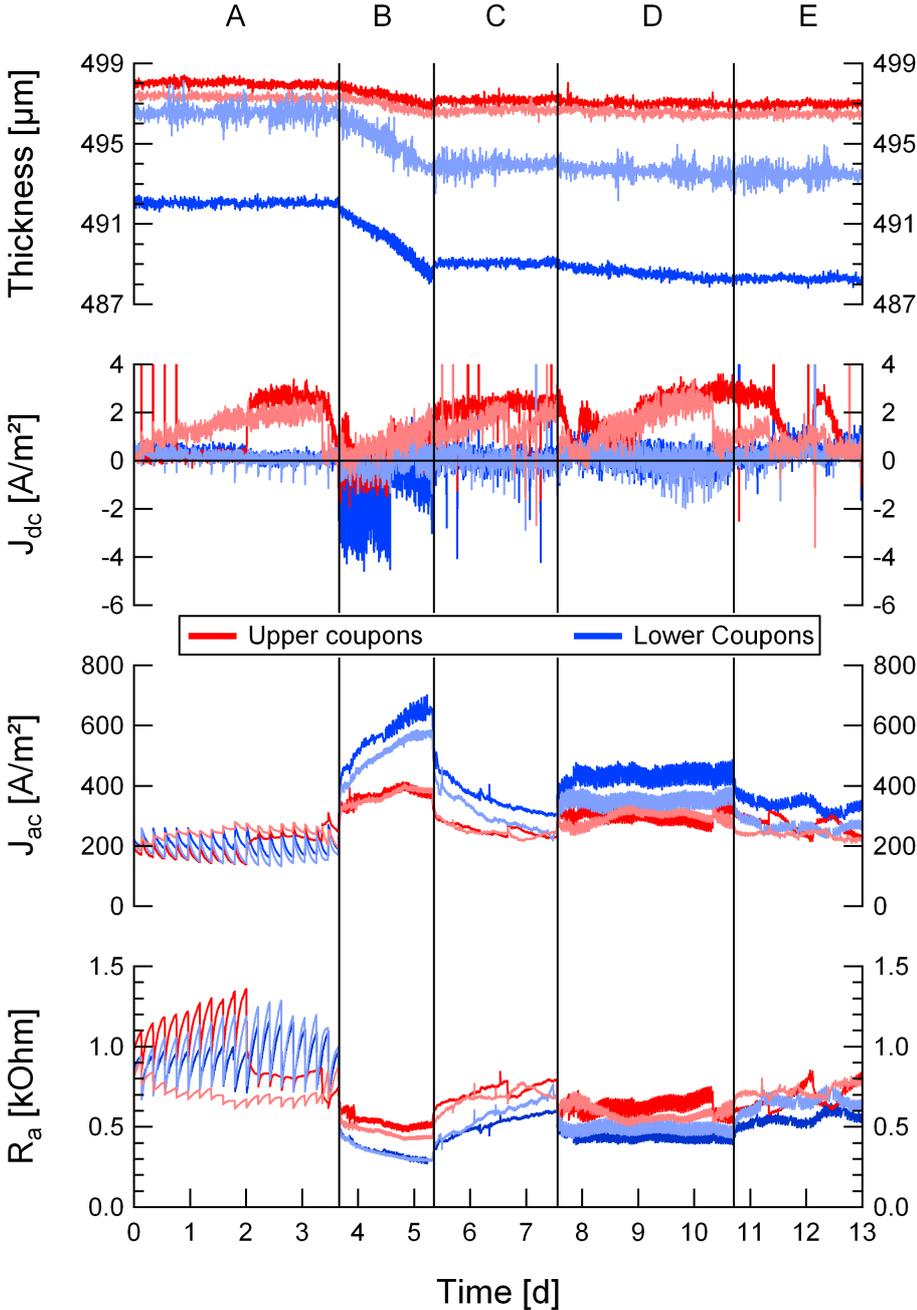
**Tabelle 1: Operating parameters of the test series in quartz sand**

Phase	Time [hh:mm:ss.0]		Eon [ $V_{CSE}$ ]		Average [ $V_{CSE}$ ]
	$t_1$	$t_2$	$E_1$	$E_2$	
A	00:01:00	04:59:00	-16.00	-1.00	-1.05
B	00:01:00	00:11:00	-16.00	-1.00	-2.25
C	00:00:02.4	00:11:00	-16.00	-1.00	-1.05
D	00:01:00	00:59:00	-16.00	-1.00	-1.25
E	00:00:12	00:59:00	-16.00	-1.00	-1.05

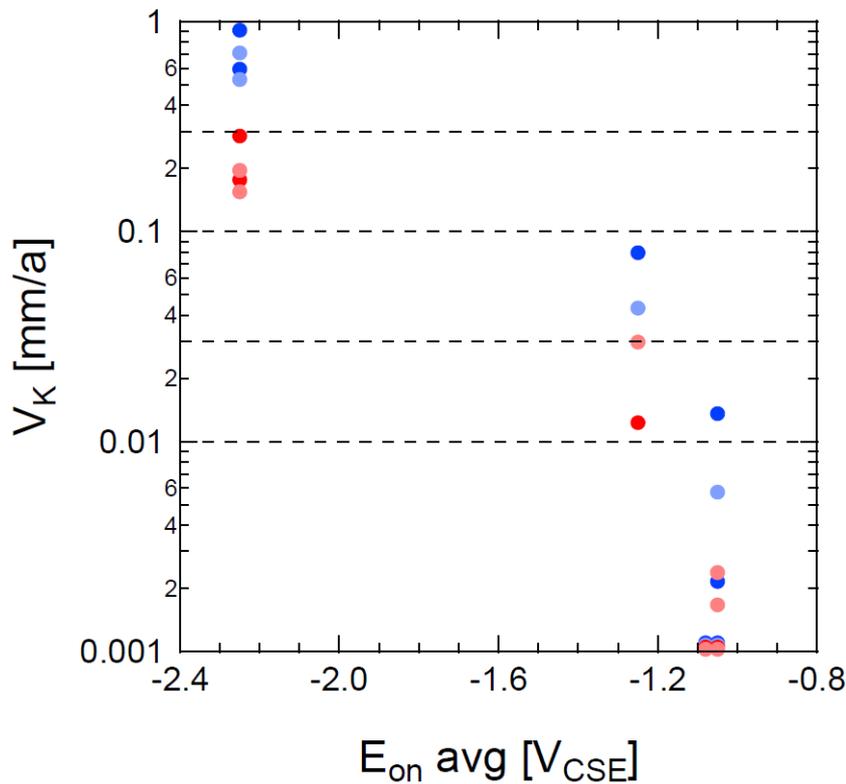
The question rises why the temporal sequences  $t_1$  and  $t_2$  have to match one another so exactly. The answer may lie in the processes shown in Figure 8. It turns out that the alkalis formed at high protection current must have sufficient time at low protection current in order to diffuse away from the surface. Otherwise, the pH at the steel surface increases over time and the pH-increase will extend further into the soil, leading more and more to lower spread resistances. Consequently with the same driving potential differences higher current densities are obtained. The problem can be demonstrated with the variation of the spread resistance of the coupons over time (Figure 9). In the test series A, the reduction of the spread resistance can be traced during one minute at  $-16 V_{CSE}$  and the subsequent increase during the following 5 hours by the diffusion of the alkalis. In the test series B there is not enough time for the diffusion of the alkalis and the spread resistance is reduced over time. In the test series C, the trend is reversed,

because there is less time for the formation of hydroxyl ions. Generalized may therefore be concluded that corrosion occurs whenever the spread resistance decreases over time.

This discussion illustrates the problem when switching between the two protective systems. As discussed above, the AC corrosion is controlled by the present current densities. From the perspective of the pipe operator, it is though only possible to adjust the on-potential. However, since the driving potential differences are linked to the effective corrosion-relevant current densities by the time-varying spread resistance, the switching between the two protection-systems "negative" ( $E_1$ ) and "positive" ( $E_2$ ) on-potential is only possible under consideration of the processes which control the spread resistance.

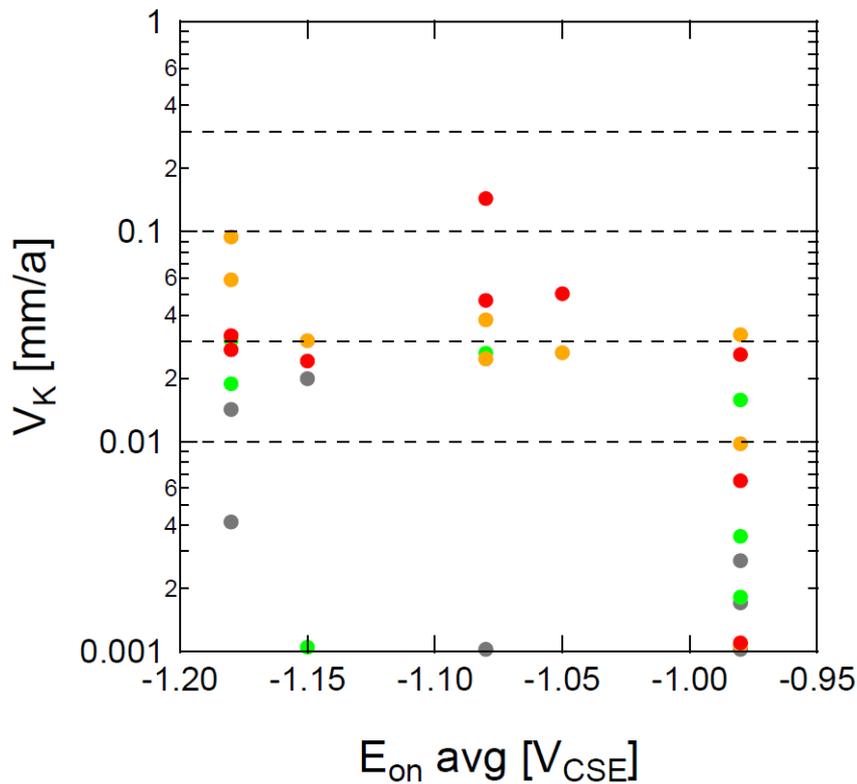


**Figure 9:** Results of a series of experiments in quartz sand, soaked with artificial soil solution with different operating parameters according to Table 1. The lower coupons are in constantly wet sand, while the upper coupons are in drier sand conditions.



**Figure 10:** Corrosion rate as a function of the on-potentials mean values for all experiments carried out in quartz sand

Furthermore, a similar series of experiments were performed in four different soils (clay, peat, gravel and sand with artificial soil solution). Generally, the same effects were observed as in Figure 9. However, it appeared that the problem is significantly increased in clay and especially in peat. In these soils, the average on-potential had to be more positive than  $-1 V_{CSE}$ , in order to prevent AC corrosion efficiently. In the case of peat, the risk of corrosion arises due to the increased protection current density, which is probably caused by the relatively positive off-potential of about  $-0.95 V_{CSE}$ . In contrast, the increased corrosion rate in clay should be primarily based on the significant anodic currents, which occur during  $t_2$ . They are a result of the exchange currents with the poorly polarized coupons in peat.



**Figure 11:** Corrosion rate as a function of the mean values of on-potentials for experiments in clay (yellow), peat (red), gravel (gray) and quartz sand (green).

Given the results, the question of the appropriateness of a pulsed cathodic corrosion protection raises. The observed effects can indeed be largely explained with the existing conceptual models but from the tests it's also clear that the maintenance of the required protection condition demands a sophisticated control of the pipeline potential.

An analysis of the data has shown that with optimized pulsed cathodic corrosion protection, the corrosion rates tend to be slightly lower than at comparable constant on-potential. At the same time it was found that the total sum of consumed protective current on average is higher in pulsed cathodic corrosion protection than with constant on-potential. Qualitatively, this effect could be explained as follows:

For the maintenance of passivity, an increased pH at the steel surface is required. With regard to corrosion protection, it is therefore desirable that the pH value directly at the steel surface is in the range of 13. But if zone with increased pH extends far into the surrounding soil, there is a significant reduction in the spread resistance. As a result, the AC current density increases at constant AC voltage, which in turn increases the protection current density, because of the Faraday rectification. Thus the corrosion process is enhanced by the increase of pH. However, the increase of pH is required in order to provide the conditions for passivity. The pulsed CP would therefore generate an increased pH directly at the steel surface but could prevent the decrease the spread resistance over time.

## 5. Conclusion

The investigation of the corrosion behavior of steel surfaces after switching off the cathodic protection clearly shows the importance of pH increase and oxygen depletion on the corrosion

process. The results confirm that the formation of a passive layer may have an important function for the efficiency of cathodic protection.

The presented results show that using a pulsed cathodic corrosion protection can prevent the occurrence of AC corrosion. The problem is that the on-potentials and the durations of the pulses must be coordinated in a precise.

The results clearly show that it is acceptable to use the average of the on-potential values for assessing the risk of corrosion. This finding agrees well with the results of the field trial. The effect can be explained by the lowering of the spread resistance by the protecting current and the rectified AC current. The change in the spread resistance is based on the formation of hydroxyl ions at the steel surface as well as their diffusion and migration into the surrounding soil. During a short-term increase in DC current density (either by a more negative on-potential or by a higher AC voltage) indeed more hydroxyl ions are formed. The spread resistance of the defect is though only significantly reduced, if the concentration of hydroxyl ions is sufficiently increased in the surrounding soil. Short-term current increases are therefore not of importance for the corrosion behavior.

Based on the results it may be concluded that the same principle applies for stray current interfered pipelines. As a consequence, the average potential must be at least more positive than  $-1.2 V_{CSE}$ . Hence, in areas with significant cathodic interference it may be critical to achieve this requirement.

## 6. Acknowledgement

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## 7. Literature

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