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Paper A01 - **The effect of variation of ac-interference over time on the corrosion of cathodically protected pipelines**

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The effect of variation of ac-interference over time on the corrosion of cathodically protected pipelines

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Summary

In recent investigations it was found that the level of cathodic protection has an influence on the a.c. corrosion rate observed on coupons. In order to obtain data for optimizing the cathodic protection parameters, the corrosion rate was investigated at various On potentials and interfering a.c. voltages. Based on the obtained results it was possible to demonstrate that the corrosion rate can significantly be decreased if the Off potential is more negative than -0.85 V CSE and the On potential is in the range of -1.2 V CSE. Under these optimized cathodic protection conditions various interfering ac voltages and different time dependences were investigated. In addition, the effect of defect geometry, soil composition and soil resistivity were considered. The contribution of these parameters for the durability of the pipeline and their consequence for interference thresholds are discussed. Based on the obtained understanding of the mechanism of a.c. corrosion a new approach to use the cathodic protection technique in order to mitigate a.c. corrosion is proposed.

1. Introduction

The phenomenon "a.c. corrosion" has been investigated very detailed since the observation of the first corrosion damages induced by a.c. corrosion on cathodically protected pipelines in the year 1988 [1, 2]. Soon the a.c. current density was identified as a critical parameter [3-5]. Later the contribution of the d.c. current density to the corrosion rate was reported [6-9]. However, a profound understanding of the detailed mechanism was lacking for years. Only in recent investigations it was possible to develop a model capable of explaining the empirically obtained experimental data [10, 11].

Based on this concept a.c. corrosion rate can be decreased to insignificantly low values, if the d.c. current density is limited [7][12]. Preferably the value should be below 1 A/m^2. This should be achievable if the on potential is in the range of -1.2 V CSE and the off potential is below the required protection potential according to EN 12954 [13]. Under these conditions, the driving force for d.c. current flow is minimized resulting in minimal possible d.c. current densities.

While general agreement is obtained regarding the adjustment of the d.c. current density as a critical parameter, only limited information is available regarding the threshold for the interfering a.c. voltage. Especially information regarding the influence of variation of a.c. voltage over time is lacking.

In the present work the results of various time dependent a.c. interference levels in artificial soil solution of various conductivities are presented. Additionally the effect of defect geometry and soil composition on the corrosion rate was investigated. Based on the obtained results possible consequences regarding threshold levels and a new approach to use the cathodic protection technique in order to mitigate a.c. corrosion are discussed.

2. Experimental setup

Artificial soil solutions were prepared from reagent grade chemicals and de-ionized water. For the simulation of the behavior in soil, coupons were exposed to artificial soil solution in quartz sand. The composition of the electrolyte is given in Table 1. Solutions with and without Calcium ions were used in order to investigate the effect of chalk layer formation. Additionally, pure sodium chloride solution and solutions without any chlorides were investigated to characterize the effect of chlorides on the corrosion rate. All potentials are referred to saturated Copper/Copper sulfate electrode (CSE).

Table 1:   Composition of the artificial soil solution in quartz sand

Electrolyte	1	2	3	4	5
	no Calcium [mM]	no Calcium [mM]	Calcium [mM]	Chloride [mM]	Sulfate [mM]
NaHCO$_3$	2.5	0.5	2.5		2.5
Na$_2$SO$_4$*10H$_2$O	5	1			
NaCl	5	1		15	
MgSO$_4$*7H$_2$O			2.5		7.5
CaSO$_4$*2H$_2$O			2.5		
CaCl$_2$*2H$_2$O			2.5		
ρ [Ωm]*	17	70	15	17	18

In order to characterize the effect of defect geometry, two types of defect were used. Type 1 had a remaining coating of 7 mm thickness simulating a punctuation through the coating, while type 2 was planar with surface of the surrounding polymer coating simulating an open defect excluding the pore resistance in the coating (Fig. 1). Both situations represent extreme cases of coating defects.
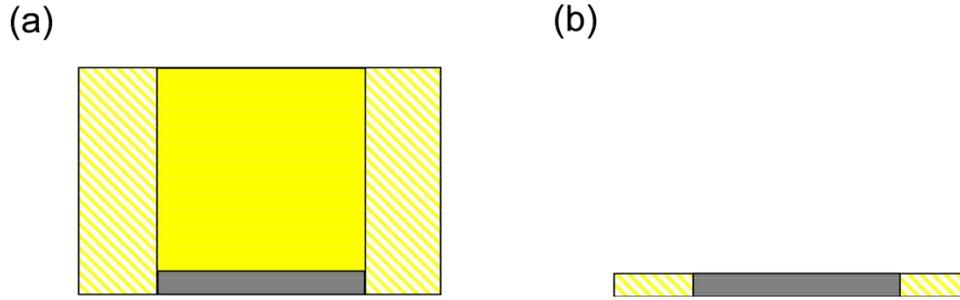
(a)   (b)

*Fig. 1:   Geometry of the two types of defects used in the investigations. a) Type 1 with 7 mm punctuation; b) Type 2 planar to the surface. The steel plate had a surface of 1 cm². *

For the investigation of the influence of varying a.c. voltages with time two approaches were used. In the first series the a.c. voltage was applied for a certain time and then switched off completely. In the second series the a.c. voltage was switched between a high and a low level resulting in an average a.c. voltage of about 14 V. The parameters used are shown in Table 2.

Table 2:   Parameters used for time dependent a.c. interference. Each conditions was investigated with type 1 and type 2 geometry

	Experiment	Electrolyte		Series [Vac]				
				1	2	3	4	5
2 min Uac, 4 min off (long)	long	1	Uac max	14	26	40	60	80
			Uac avg	5	9	14	20	26
20 s Uac, 40s off (short)	short	1	Uac max	14	26	40	60	80
			Uac avg	5	9	14	20	26
20 s high, 80s low	Low (ρ=17Ωm)	1	Uac max	14	26	40	60	80
			Uac min	14	11	7.5	2.5	0
			Uac avg	14	14	14	14	14
20 s high, 80s low	Low (ρ=70Ωm)	2	Uac max	14	26	40	60	80
			Uac min	14	11	7.5	2.5	0
			Uac avg	14	14	14	14	14

The corrosion rate was either determined by mass loss or by determination of the change of electrical resistivity of the coupon due to corrosion (ER Coupons). The a.c. and d.c. voltages were applied by transformers connected in series on the coupons and a counter electrode made of activated titanium or stainless steel 1.4435. Any interference of d.c. and a.c. currents was avoided by shortening the d.c. source with a capacitor of 10 mF. The frequency of the a.c. voltage was 50 Hz in all cases.

3. Results and discussion

In order to simplify the discussion of the obtained results the current understanding of the a.c. corrosion mechanism is shortly summarized. In the following the effect of variation of a.c. interference levels over time, the effect of soil composition and a new approach to cathodic protection will be discussed.

Mechanism of a.c. corrosion

The cathodic protection of pipelines forces current to enter the pipeline through the metal surface in contact with soil where the coating is damaged. This current prevents corrosion from taking place by removing oxygen from soil and eliminating potential differences along

the pipeline. Moreover, the cathodic current results in the increase of the alkalinity on the steel surface.

When an a.c. voltage is present on the cathodically protected pipeline, current will flow through the metal surface at defects in the coating. The amount of current flowing depends on the a.c. voltage and the impedance of the system. During the cathodic half wave the amount of current entering the steel surface and therefore the reduction reactions are generally increased. During the positive half wave of the a.c. voltage, the current will leave the metal surface if the a.c. voltage is sufficiently large. A current leaving the metal surface is associated with oxidation reactions and can, therefore, cause corrosion.

The current leaving the metal surface can cause charging of the double layer capacitance, oxidation of hydrogen and corrosion products reduced by the cathodic protection current, and oxidation of the pipeline steel. Since the pH-value is typically sufficiently high (above 10) this oxidation of the pipeline can result in the formation of a passive film. In contrast, current entering in the metal surface can result in the charging of the double layer capacitance, reduction of oxygen, formation of hydrogen, and reduction of oxidized corrosion products. Furthermore, the passive film formed during the anodic half wave can be electrochemically reduced.

Empirically it is observed that, very high and low d.c. current densities allow preventing a.c. corrosion. This effect may be associated with the increase of the pH at the steel surface, the resulting decrease of the spread resistance, the change of the time constant of the system, and the increased electrochemical reduction reactions taking place on the steel surface. These effects result in increased a.c. and d.c.current densities, larger charges passed during the anodic and cathodic half wave, change of the solubility of oxidation products of iron and their oxidation state.

A simplified description of the process taking place during a.c. corrosion is shown in Fig. 2a. During the positive half wave the bare metal surface is oxidized resulting in the formation of a passive film. This is due to the current that leaves the metal surface. During the negative half wave, when the current enters the metal surface this passive film is reduced and, therefore, converted in a non protective rust layer. In the following anodic cycle a new passive film grows. Upon reduction of the passive film the amount of rust is increased [14, 15]. If this process would result in the formation and dissolution of a single oxide layer during every anodic half wave, corrosion rates in the range of 70 mm/year would be obtained. Since such high corrosion rates were only achieved under extreme laboratory conditions, it may be concluded that the formation and/or reduction of the passive film is in most cases only partially taking place.

Based on this concept it is possible to discuss several empirical observations. The a.c. corrosion process only takes place if the passive film is formed (at least partly) and dissolved (at least partly). If the formation of a passive film is prevented by sufficiently high d.c. current densities at sufficiently low a.c. current densities the a.c. corrosion can be stopped (Fig. 2b).

Similarly, the a.c. corrosion can be stopped if the cathodic reduction (dissolution) of the once formed passive film is prevented (Fig. 2c). This is possible by sufficiently limiting the cathodic current density. It is found that under these conditions even a.c. current densities of up to 1500 A/m^2 do not cause corrosion. This is possible since the anodic and cathodic charge passing through the metal surface during an a.c. cycle can be consumed by oxidizing and reducing the iron ions in the rust layer [10, 11]. As a consequence, the a.c. corrosion can be stopped if the pH is sufficiently high and a rust layer is formed capable of consuming anodic and cathodic charge.

Based on this consideration it is clear that both, high and low d.c. current densities allow preventing a.c. corrosion. This has to be taken into account in the discussion of threshold since these are two fundamentally different concepts of preventing a.c. corrosion. The above

mentioned model allows explaining the relevance of the various thresholds, such as the existence of a critical ratio between a.c. and d.c. current density and the existence of a critical a.c. current density.

In the further discussions in this paper we will focus on the investigation of the situation under optimized cathodic protection at low d.c. current levels according to Fig. 2c.
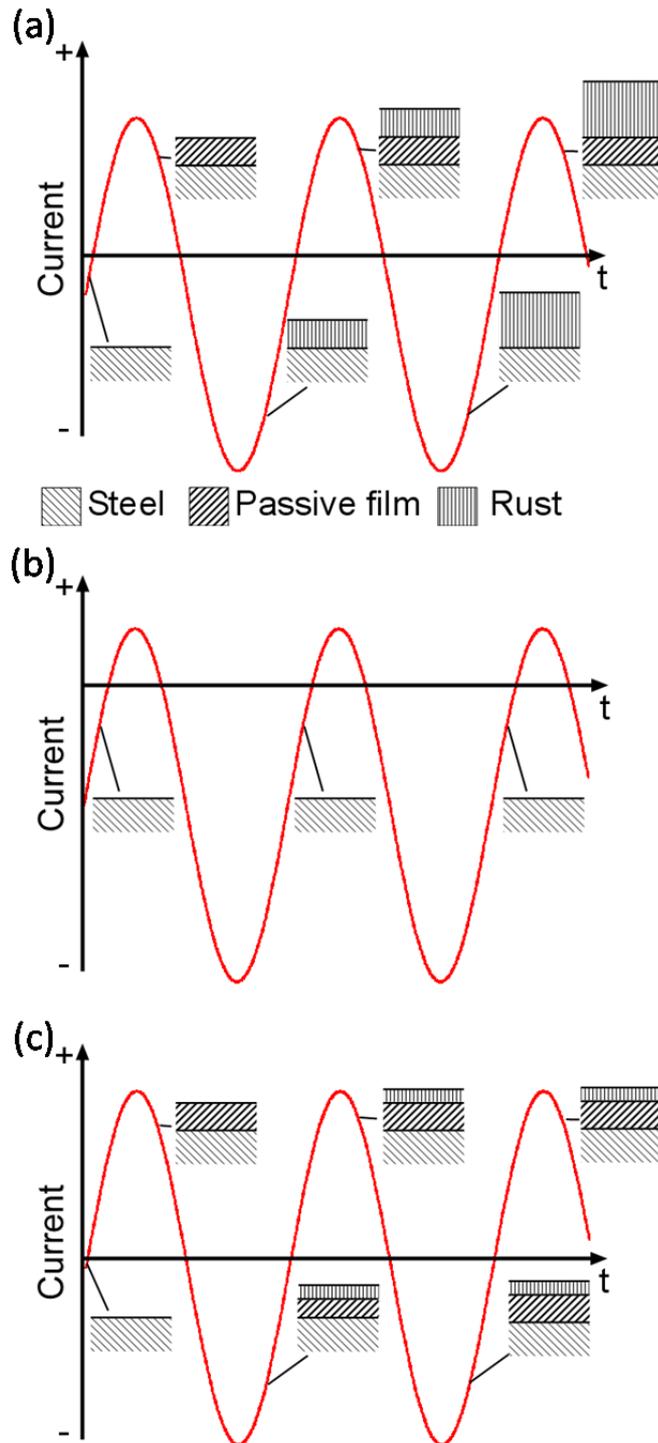

Fig. 2: *Schematic representation of the processes taking place on steel under a.c.-interference on at various d.c. current densities: a) high d.c. current density, b) very high cathodic d.c. current density, c) low cathodic d.c. current density*

Effect of variation of a.c. interference

In Fig. 3 the coupons of type 2 are shown after 3 months test in the series of 14 V avg a.c. voltage in soil solution with 17 Ωm. The results are typical for all investigations shown in Table 2. Although all coupons exhibit identical average a.c. voltage, clearly a difference in the amount of rust layer formation is observed. Microscopic analysis shows that no corrosion has taken place in the central area of the coupons. Even the traces from machining the coupons are still visible in all cases. Although no serious a.c. corrosion has taken place, the amount of rust layer formation appears to be related to the higher maximum a.c. voltage applied. According to the proposed mechanism of a.c. corrosion, extremely high a.c. current densities can be passed through the metal surface without causing corrosion, if the charge can be consumed by oxidation and reduction of the rust layer formed on the metal surface. Hence, higher a.c. current densities require thicker rust layers, which indeed is experimentally concluded in all cases from the increasing blackening of the samples. The amount of anodic charge that can be consumed by the rust layer was determined at the end of the test by coulometric oxidation. The results are shown in Fig. 4. Additionally the amount of charge flowing during an anodic half wave is displayed.

Fig. 3: Coupons of type 2 (after removing the surrounding polymer) after 3 months test in the series of 14 V avg a.c. voltage in soil solution with 17 Ωm. The coupons correspond from left to right to the series 1 to 5.
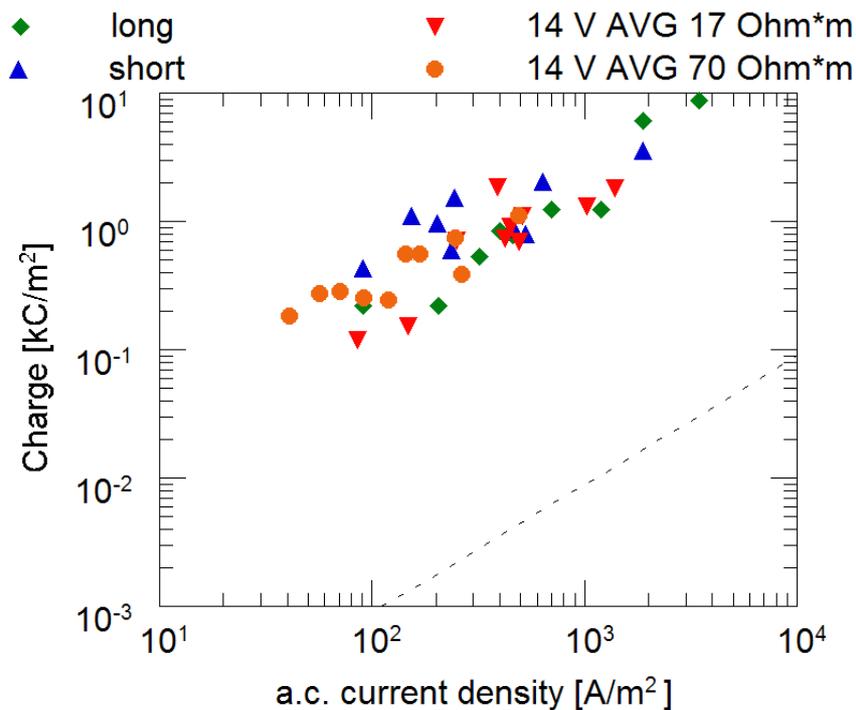

Fig. 4: Charge available in the rust layer for anodic polarization compared to the maximum a.c. current density for coupons type 1 and 2. The dotted line represents the charge flowing during a half wave of the a.c. cycle.
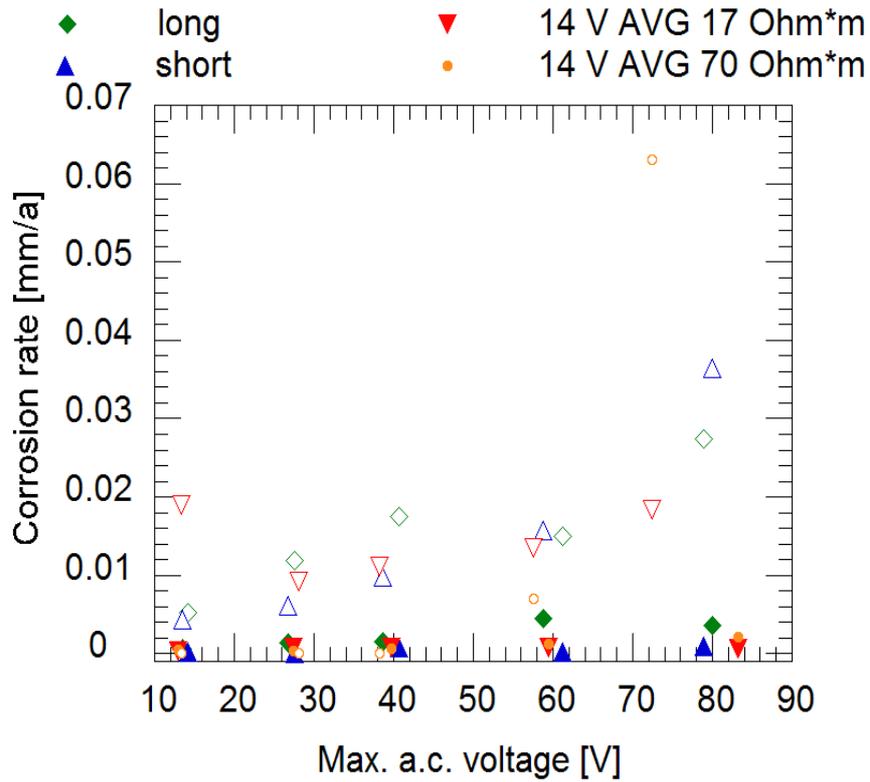
Fig. 5: *Effect of the maximum a.c. voltage applied on the coupons. The closed symbols correspond to coupons with geometry of type 1 and the open symbols correspond to coupons with geometry of type 2.*
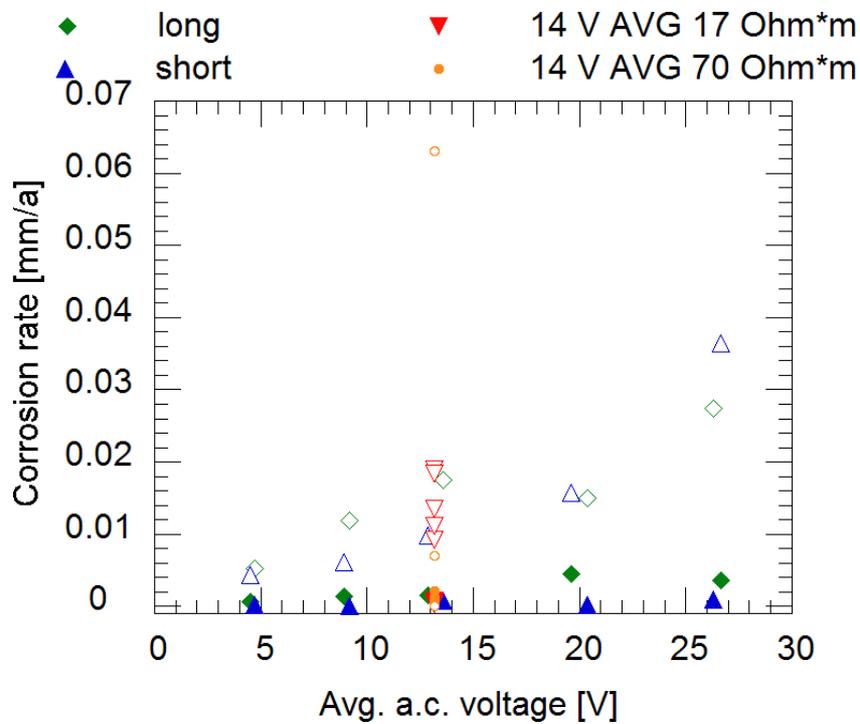

Fig. 6: *Effect of the average a.c. voltage applied on the coupons. The closed symbols correspond to coupons with geometry of type 1 and the open symbols correspond to coupons with geometry of type 2.*

Based on these data it becomes clear that higher a.c. current densities indeed are related to thicker rust layers providing higher capacity for consuming anodic and cathodic charge during the a.c. current cycle. There is significantly more capacity available than theoretically required. Based on these data no charge has to be consumed due to capacitive effects or alternative electrochemical reactions, since all can be consumed for oxidation and reduction of the rust layer. The excess of charge is rather an indicator that not all of this charge is electrochemically accessible during the a.c. cycle. This could be attributed to the fact that prior to the coulometric oxidation the rust layer was electrochemically reduced at increased d.c. current densities. Possibly part of the rust layer was oxidized due to oxygen present in the soil solution and was hence not capable of being oxidized by the anodic component of the a.c. current. Nevertheless the result demonstrates clearly a correlation between rust layer thickness and a.c. current density.

The correlation of the corrosion rate with the a.c. voltage is shown in Fig. 5 and 6. Interestingly, no corrosion is observed for the coupons of type 1, while a certain corrosion rate occurs for the coupons of type 2. There is some increase of corrosion rate with higher maximum a.c. voltage but also at lowest values corrosion is observed in some cases. Since corrosion occurs exclusively on the coupons with geometry type 2 a microscopic inspection was performed (Fig. 7). The result is typical for all coupons of type 2. Most of them showed more or less pronounced corrosion on the very edge of the coupon. A few micrometers away from the edge no corrosion can be seen. Even the traces from the machining are still visible.
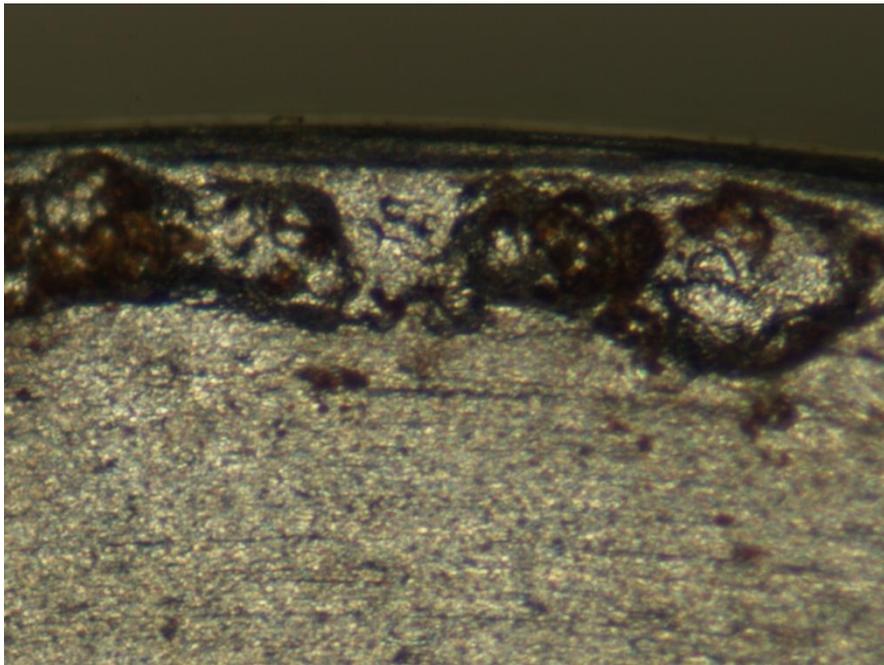

Fig. 7:   Corrosion attack on the very edge of coupon of type 2. A few micrometers away from the edge no corrosion can be seen at all. The traces from machining are still visible.

These data demonstrate that for defects of type 1 a maximum a.c. voltage of up to 80 V is acceptable (under optimized d.c. current levels) while for type 2 geometry even 15 V may be too high. Hence, a critical a.c. interference level can only be defined based on known defect geometry. Even soil conductivity has only limited influence compared to the contribution of the defect geometry. When defining limiting interference values and operation levels it is crucial to understand the reason for the strong influence of the defect geometry.

All data collected in Fig. 5 and 6 had on potentials in the range of -1.2 V CSE. Despite of the identical soil solution and the well defined experimental set-up some of these coupons of type 2 resulted in increased corrosion rate. The reason for the strongly localized corrosion on the edges of the coupon may be explained with the heterogeneous current distribution. This effect is qualitatively demonstrated in Fig. 8. For coupon type 1 an almost perfect homogeneous current distribution is obtained. In this case the current density can readily be determined by dividing the current by the exposed surface. In contrast, for coupon geometry of type 2 a heterogeneous current densitiy distribution which is characterized by maxima at the sample edges and a minimum in the center is obtained. This causes strongly increased current densities at the edges of the coupon. When dividing the current flowing through the coupon by the surface area, an averaged current density is obtained. This, however, has nothing to do with the local current density that may occur at the edges of the coupon. As a consequence, the calculation of the maximum current density is not possible in the case of coupon of type 2. Generally it is accepted that a d.c. current density below of 1 A/m^2 does not result in a.c. corrosion. Unfortunately the averaged current density may well be below this value, but the local current density on the edges may significantly exceed. Since an increased current density results in a local increase of the pH value the spread resistance on the edges will decrease. This causes an even higher d.c. current density with even stronger decrease of spread resistance. Due to this autocatalytic effect the system may result in a.c. corrosion even under optimized on potentials and at low a.c. current density.
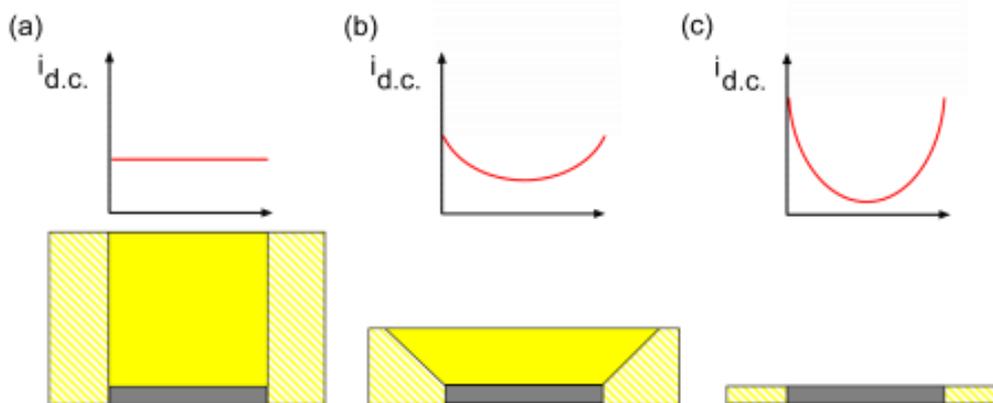

Fig. 8: *Geometry of the different types of defects and schematic representation of the expected current distribution. a) Type 1 with 7 mm punctuation; b) Type 3 with intermediate geometry; c) Type 2 planar to the surface.*

Based on this discussion the question rises regarding the realistic defect geometry. It is clear that type 1 and type 2 represent extreme cases. While type 2 is very conservative, type 1 is probably too optimistic. This discussion has led to a coupon geometry of type 3 (Fig. 8 b) which is an intermediate of the two extremes. This geometry has been used in Switzerland since 2006 on so called "perforation coupons" that allow the detection of a local perforation depth of 0.75 mm.

Effect of soil composition
It was observed that soil composition has a strong effect of the formation of chalk layers on cathodically protected pipelines [16]. Additionally, the proposed mechanism according to Fig. 2c suggests that chloride content might affect the formation of a protective passive film as well. The effect of soil composition on the corrosion rate is shown in Fig. 9. The results confirm that in general current densities below 1 A/m^2 do not result in severe corrosion. Comparable to the results in Fig. 5 and 6, increased corrosion rates were observed in the case of coupon type 2. Even at optimized d.c. protection levels no negative effect of an increased

chloride content compared to the chloride free electrolyte (i.e. the "sulfate" electrolyte, see table 1) could be observed.

In the case of the calcium containing electrolyte, the formation of solid chalk deposits was observed. This caused a local concentration of the current density and a locally increased corrosion rate. While the averaged corrosion rate was in the range of 20-30 µm the local depth was exceeding 150 µm even in the case of coupon type 1.
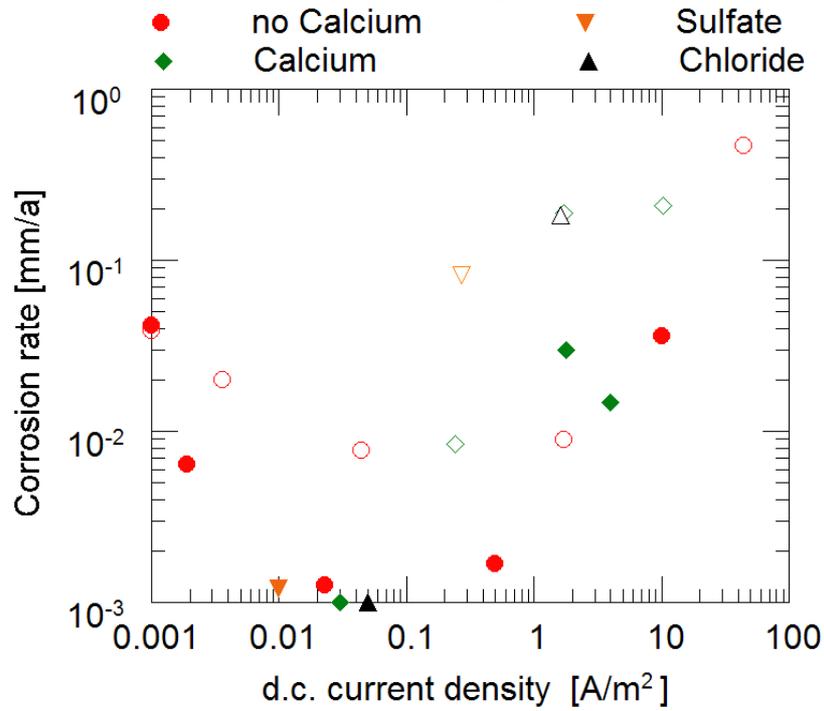

Fig. 9: *Effect of the soil composition (Electrolyte 1: no calcium; 3: Calcium; 4: Chloride; 5: Sulfate) with specific resistivity of about 17 Ωm at constant 14 V a.c. voltage and on the corrosion rat. The closed symbols correspond to coupons with geometry of type 1 and the open symbols correspond to coupons with geometry of type 2.*

Threshold values

Based on the obtained results it can be concluded that - under a given a.c. interference - the d.c. current density is the primarily controlling parameter in a.c. corrosion. The proposed model is readily capable of explaining its detrimental effect. Clearly, the a.c. current density, the a.c. voltage, the spread resistance of the coupon, soil conductivity, and soil composition also contribute to a.c. corrosion rate but their effect is of minor significance compared to the local d.c. current density controlled by the cp-level and by the geometry of an individual coating defect.

While the obtained information provides a profound understanding of the involved processes, they also demonstrate the difficulty in solving the a.c. corrosion problem. While shifting the on-potential to more positive values will in general decrease the risk of high d.c. current densities, the local decrease of spread resistance especially on defects with heterogeneous current distribution can locally cause increased current densities. As a consequence, a low cathodic protection level decreases the risk of a.c. corrosion but cannot guarantee its absence. Similarly, lowering the a.c. voltage on the pipeline can only lower the risk for damages. Based on the present information a reasonable protection against a.c. corrosion risk should be obtainable if the on-potential is in the range of -1.2 V CSE and the average a.c. voltage is below 15 V.

When discussing alternative thresholds often the off potential as a possible control parameter is mentioned. Especially an off potential between -1 and -0.85 V CSE is considered to be safe. The evaluation of the off-potential versus the corrosion rate of all tests is shown in Fig. 10b. Surprisingly, highest corrosion rates are observed with off potentials between -1 and -0.85 V CSE. This effect can readily be explained with the fact that a more negative on potential does not necessarily decrease the off potential. This is partly due to the fact, that the off potential is primarily determined by the hydrogen evolution on the metal surface. Even strong increase in d.c. current density will therefore only cause a minor shift of the off potential. Additionally, the decrease in spread resistance due to the formation of high pH value in front of the metal surface increases the a.c. current density that will cause an increased faradaique rectification (Fig. 10a). The result is a shift of the off potential in anodic direction. As a consequence, the off potential is not only ill suited for judging the a.c. corrosion risk. It may even result in a high risk for the integrity of the pipeline especially when used in combination with off potential controlled rectifiers.
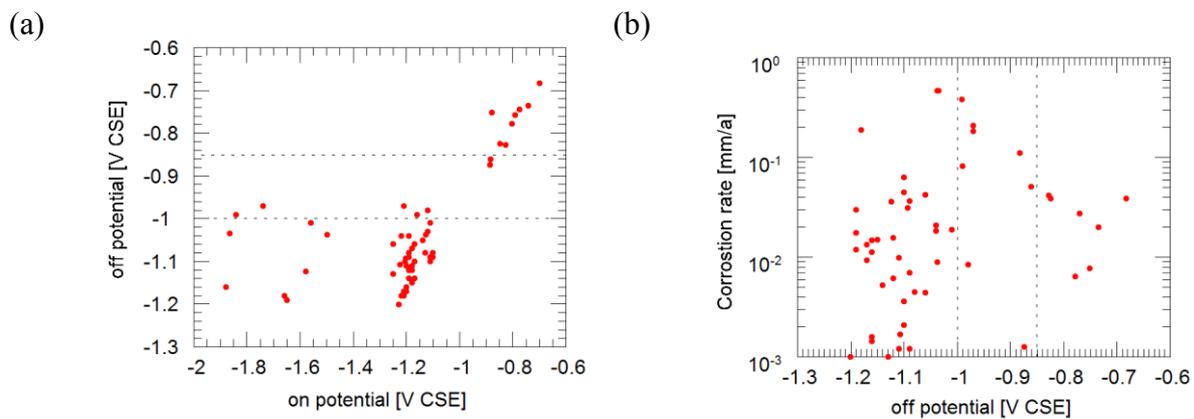
(a)   (b)

Fig. 10: Test results of the experiments in table 2 and previous publication [10, 11]a) Correlation between off potential and on potential. b) Correlation between corrosion rate and off potential

Alternatively the direct determination of the current density on coupons may represent a more reliable tool for judging the a.c. corrosion risk. However, the possibly heterogeneous current distribution, as a result of chalk layer formation or adverse defect geometry, makes it typically impossible to reliably determine the maximum current density present on the coupon.

New approach to a.c. corrosion mitigation
Since the local increase of current density as a result of increased pH or decreased metallic surface as a result of chalk layer formation cannot be avoided or controlled over the entire length of a pipeline a new approach is proposed. Clearly, the cathodic d.c. current density is minimal when the cathodic protection is switched off. This represents an extreme case of the situation demonstrated in Fig. 2c. Under this condition a.c. current densities of up to 1500 A/m^2 do not cause a.c. corrosion as long as the pH value is sufficiently high for passivity and a rust layer is present that can consume the anodic and cathodic charge of the a.c. current. While this condition may be fulfilled for a certain time after switching off the cathodic protection, the pH will decrease due to diffusion and reaction with carbon dioxide in the soil and both, galvanic and a.c. corrosion will take place in the long run.
Based on Fig. 2a, protection against a.c. corrosion should also be possible in the case of very high d.c. current density. In this case, the high pH generated at the metal surface may damage the coating of the pipeline. As a consequence the protection mode in Fig. 2a is not suited for

high a.c. voltages since the required d.c. voltages would endanger the integrity of the pipeline due to delamination of the coating.

Nevertheless, the combination of protection mode in Fig. 2a and Fig. 2c could represent a solution to the a.c. corrosion problem. This could be operated as follows:

1. At first a high d.c. potential is applied preventing a.c. corrosion by eliminating any anodic faradaique charge transfer through the metal. During this period, oxygen is depleted and a high pH is built up in front of the metal surface. After a certain time the rectifier is switched off.

2. When the rectifier is switched off exchange currents in the pipeline will cause the passivation of the steel and the oxidation of the rust layer in the case of the strongly polarized defects that exhibited high current densities. On the other hand the less polarized defects will receive some cathodic protection. Meanwhile the pH value will decrease and oxygen will diffuse to the defects causing a shift of the potential to more positive values and even above -0.85 V CSE. As soon as this is the case, the rectifier is switched on again.

This alternating switching between two protection modes prevents the decrease of the spread resistance of defects over time and should allow for sustainable long term protection of the pipeline. In the laboratory a test was run over 3 months at 15 V a.c. voltage in soil solution 1 according to table 1. The on potential of -7.5 V CSE was applied for 1 minute and the rectifier was then switched off for 59 minutes. The corrosion rate was clearly below 10 μm per year. Moreover the spread resistance did not significantly change over time.

Based on the promising laboratory data an extensive field study is planned. When successful, this would offer a method for reliably mitigating a.c. corrosion.

4. Conclusions

Under optimized cathodic protection at on potentials of -1.2 V CSE the a.c. voltage present on the pipeline is only of minor significance for a.c. corrosion. A.c. voltages of up to 80 V do not cause corrosion even in low resistant soil as long as the d.c. current density is not locally higher than 1 A/m^2. Unfortunately the local current density can readily exceed this value even under optimized cathodic protection in the case of certain defect geometries. Hence, the defect geometry represents a crucial parameter when defining interference thresholds and operation conditions for the cathodic protection. Compared to the local d.c. current density on worst case defects all other contributing parameters such as a.c. current density, soil composition, soil conductivity, and a.c. voltage are of minor significance. Based on this consideration a new coupon geometry is proposed.

Possible interference levels and criteria for judging the risk for a.c. corrosion are discussed under consideration of the significant effect of the defect geometry. This results in the conclusion that the measuring of the current density on coupons may represent a risk. Moreover it is demonstrated that the off potential is not suitable for judging the a.c. corrosion and even represents a risk for the integrity of the pipeline.

All currently available thresholds only decrease the risk for a.c. corrosion, but are not capable to guarantee the protection of the pipeline. As a consequence, a new approach and preliminary results for using the cathodic protection technique in order to mitigate a.c. corrosion is discussed.

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