

CHARACTERISTICS OF POTENTIAL MEASUREMENTS IN THE FIELD OF AC CORROSION

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Abstract

The problems observed in the instantaneous off potential measurement were attributed to a non-sufficient time resolution. By increasing the data acquisition rate up to 2 MHz it was possible to determine the polarization of the metal surface within 2 μ s after disconnecting the coupon from the ac and dc power source. This increase in resolution represents an acceleration of the measurement for a factor of thousand compared to the commonly used instruments. However, it was found that the depolarization of the surface is faster than 1 μ s in calcium ion free soil solution. As a consequence, the threshold of -0.85 V CSE was not exceeded although ac corrosion occurs on the metal surface. In the presence of calcium ions, however, the threshold is exceeded due to a different depolarization behavior. As the depolarization and therefore the interpretation of the instantaneous off potential measurement depends strongly on the composition of the soil it cannot be recommended for the characterization of coupons in field applications. In order to address the influence of the soil composition and to investigate the chemical processes occurring on the coupon surface, continuous data acquisition was installed in two locations in Switzerland. The results of the first 6 months of data acquisition are presented.

Zusammenfassung

Die bei der sofortigen Ausschaltpotenzialmessung beobachteten Probleme, wurden einer nicht genügenden Zeitauflösung zugeschrieben. Indem die Datenerfassungsrate auf 2 MHz erhöht wurde, war es möglich, die Polarisation der Metalloberfläche innerhalb 2 μ s nach der Trennung der Messprobe von der AC und DC Spannungsquelle festzustellen. Diese Zunahme der Auflösung stellt eine Beschleunigung der Messung um einen Faktor von tausend verglichen mit den bisher benutzten Instrumenten dar. Es wurde jedoch gefunden, daß die Depolarisation der Oberfläche in Bodenlösungen ohne Calcium schneller als μ s 1 ist. Als Folge wurde der Grenzwert von -0,85 V CSE nicht überstiegen, obgleich Wechselstromkorrosion auf der Metalloberfläche auftrat. In Anwesenheit der Calciumionen wurde der Grenzwert jedoch, aufgrund eines anderen Depolarisationsverhaltens, überschritten. Als die Depolarisation und damit die Interpretation der sofortigen Ausschaltpotenzialmessung in starkem Mass von der Bodenzusammensetzung abhängt, kann deren Einsatz für die Charakterisierung von Messproben in Feldanwendungen aufgrund der

vorliegenden Ergebnisse nicht empfohlen werden. Um den Einfluß der Bodenzusammensetzung und der ablaufenden chemischen Prozesse zu untersuchen, wurde in der Schweiz an zwei Standorten eine kontinuierliche Datenerfassung für die relevanten Parameter installiert. Die Resultate der ersten 6 Monate der Datenerfassung werden diskutiert.

Résumé

Les problèmes observés dans la mesure de potentiel à courant coupé instantané ont été attribués à une résolution non-suffisante de temps. En augmentant le taux d'acquisition de données jusqu'à 2 mégahertz il était possible de déterminer la polarisation de la surface en métal à moins de 2 μ s après avoir déclenché l'échantillon de la source d'alimentation CA et CC. Cette augmentation de résolution représente une accélération de la mesure pour un facteur de mille comparé aux instruments généralement utilisés. Cependant, on l'a constaté que la dépolarisation de la surface est plus rapide que les μ s 1 dans la solution libre de sol d'ion de calcium. Comme conséquence la valeur limite des -0,85 V CSE n'a pas été dépassée, bien que la corrosion de courant alternatif sur la surface de métal apparaisse. En présence des ions en calcium, la valeur limite a été dépassée toutefois, sur la base d'un comportement différent de dépolarisation. Comme dépolarisation et donc l'interprétation de la mesure de potentiel à courant coupé instantané dépend fortement de la composition du sol son application pour la caractérisation des échantillons de mesure dans les applications de champ ne peut pas être recommandée sur la base des présents résultats. Pour examiner l'influence de la composition de sol et des processus chimiques écoulés, une saisie de données continue pour les paramètres pertinents a été installée en Suisse à deux emplacements. Les résultats des 6 premiers mois de la saisie de données sont examinés. Afin d'adresser l'influence de composition de sol et étudier le produit chimique traite l'occurrence sur la surface de bon, acquisition de données continue ont été installés dans deux endroits en Suisse. Les résultats des 6 premiers mois de l'acquisition de données sont présentés.

INTRODUCTION

The phenomenon "AC corrosion" was investigated very detailed since the observation of the first corrosion damages induced by AC corrosion on cathodically protected pipelines in the 1988 [1, 2]. Despite of all these investigations, the involved mechanisms are still not understood and reliable techniques for the determination of the corrosion risk are not available.

In general, it is well established that the AC corrosion can only occur if the AC current density exceeds 30 A/m^2 [3-5]. Nevertheless, corrosion attack was also observed on samples with significantly lower current density [6]. This may be caused by the formation of a chalk layer on the coupon surface, which decreases the available surface area and, as a consequence, results in an increased local current density. Moreover, it was found that also high current densities do not necessarily lead to corrosion attack. While the ac-current densities determined on coupons do provide information on the corrosion state, the ac potential measured on pipelines were found to be merely an indicator than a criterion. In extended field investigations corrosion attack was found on samples that had less than 5 V ac potential [6]. The measurement of the so-called instantaneous off potential is reported to offer access to the polarization of the metal surface due to the ac current [7]. As the information is independent on the surface area it would allow to obtain information about the corrosion state of coupons independent on the partial covering of the surface with a chalk layer. However, it was found that corrosion attack also occurs on samples where the instantaneous off potential is below the cathodic protection potential [6].

The failure of the different criteria used for the evaluation of the ac corrosion risk may be attributed to the fact that the measurements were only performed a few times a year. If the ac influence on the pipeline was not at a critical level during the measurement, the data obtained could indicate the absence of a corrosion risk. The misleading information obtained with the instantaneous off potential could be attributed to the non-sufficient measurement rate. The first potential reading was taken after 2 ms. Based on the obtained results it was concluded that this is not sufficiently fast [6].

As a consequence, the continuous monitoring of the critical parameters is required in order to get a reliable information about the development of the different parameters over time and to determine the effect of critical values. Additionally, the instrument used for the determination of the instantaneous off potential was modified in order to increase that data acquisition rate from 2 ms to 1 μs . The results obtained in these investigations are presented.

EXPERIMENTAL

Instantaneous off potential

The test coupons with a surface area of 1 cm^2 used for the characterization of the corrosion behavior by means of the instantaneous off potential measurement were exposed to two electrolytes in quartz sand. The electrolytes used where artificial soil solution with and without calcium (Table 1).

Table 1: Composition of the artificial soil solution

	solution without calcium	solution with calcium
NaHCO_3	2.5 mmol/l	2.5 mol/l
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	5 mmol/l	
NaCl	5 mmol/l	
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$		2.5 mmol/l
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$		2.5 mmol/l

CaCl ₂ *2H ₂ O		5 mmol/l
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The coupons were cathodically polarized with 3 A/m² and subjected to an ac-current load of 100 A/m². A detailed description of the experimental setup is given elsewhere [8]. In order to determine the instantaneous off-potential with high time resolution an, oscilloscope (Tektronix TDS 420) with GPIB control was used. By computer controlled switching of the REED relays and data acquisition the instantaneous off potential was determined at arbitrary times of the ac current cycle. Previous to the disconnecting of the coupon from the power source the current flowing was determined. After opening of the switch the off potential was recorded with a data acquisition rate of 2 MHz. Instantaneous off-potential measurements were performed at intervals of several weeks in order to monitor the development of the corrosion behavior.

Monitoring of the corrosion parameters in field tests

For the continuous data acquisition the coupons developed by SGK were used to install three metal samples with a surface area of 1 cm². A detailed description of the probe is given elsewhere [8]. For the data acquisition, a data logging system in combination with AC/DC converters developed by Betschen Electronics was used. A detailed description of the data logger is given elsewhere [9]. The system allowed the continuous control of the ac voltage on the pipeline and the ac current on the coupons. Additionally the soil resistivity and the temperature were monitored at different depths in the ground.

RESULTS AND DISCUSSION

Instantaneous off-potential

An example of the instantaneous off-potential measurement with high time resolution is shown in Fig. 1 for two samples exposed for 41 days to artificial soil solution with and without calcium ions in quartz sand. The ac- and the dc-current density were 100 A/m² and 3 A/m² respectively. The readings were taken 2 μs after disconnecting the coupon from the voltage source. The typical elliptic correlation between current and off-potential is observed. It is clear that the sample without calcium ions results in a maximum off potential that is below the critical value of -0.85 V CSE. Hence, even a significant increase of the detection rate and the corresponding optimization of the experimental set-up did not result in the detection of a polarization of the coupon anodic of the critical potential value. Based on this finding it has to be concluded that no ac-corrosion is expected to occur. However, the analysis of the sample after the test, clearly showed the formation of significant corrosion products.

In contrast, the same test run in artificial soil solution containing calcium ions resulted in a very different behavior (Fig. 1). Clearly, the critical value is exceeded indicating the occurrence of ac-corrosion. The characterization of the sample after the test yielded corrosion attack on the surface, as it is expected for current densities of 100 A/m².

The analysis of the potential development taken at the maximum off-potential is shown in Fig. 2. It is clear, that the sample in the solution without calcium ions resulted in a very rapid decrease of the potential within the first microsecond. Calibration measurements of the experimental setup with resistors showed an identical behavior. Hence, the values recorded in the first microsecond cannot be attributed to the depolarization of the metal surface, they are rather linked to the capacitance of the experimental set-up. Over the entire data acquisition range no further change in potential is observed. A very similar result was obtained for coupons with various exposure times, solution pH values and current densities. Moreover, the result is in good agreement with the data obtained with a time resolution of 2 ms [8]. Nevertheless, the same experiment performed with solution containing calcium ions resulted

in a very different depolarization behavior (Fig. 2). Based on the obtained results it is not possible to differentiate the end of the ir-drop and the beginning of the depolarization of the surface. Moreover, the time constants involved seem to depend strongly on the soil composition. As a consequence, the time resolution required for the measurement is affected on the soil composition and the time resolution used so far was arbitrary.

The determination of the development of the maximum off potential over time for the two different solutions is shown in Fig. 3 and 4. Visual inspection of the sample surface after the test revealed significant corrosion attack. Additionally, the samples in calcium containing soil were partly covered with a chalk layer. It is clear that the presence of the calcium ions strongly influences the off-potential. In general, the critical value of -0.85 V CSE is exceeded in the entire investigated time range in solution containing calcium ions (Fig. 3). Decreasing the ac-current density to 10 A/m² at the end of the testing period resulted in some instances in an exceeded threshold, while other samples showed off-potentials below -0.85 V CSE within 2 μ s (Fig. 5). However, the identical experiment performed with a solution free of calcium ions showed an exceeding of the critical value only once (Fig. 4).

Based on the obtained results it has to be concluded that the instantaneous off-potential measurement does not allow to detect the ac-corrosion situation even with high time resolution in solution without calcium ions. Solutions containing calcium ions strongly affect the depolarization behavior of the metal surface and show an exceeded threshold. This is presumably attributed to the formation of a chalk layer on the metal surface that alters the electrochemical behavior. Based on this finding it could be concluded that the instantaneous off-potential measurement allows the prediction of the corrosion behavior in soils containing calcium ions. However, an exceeded threshold was also observed with current densities that do not cause ac-corrosion. This observation is in agreement with the results of an extended field investigation [6] that yielded 12 coupons with exceeded threshold that did not show ac-corrosion, while the only 2 coupons with ac-corrosion did not show an exceeded threshold in the instantaneous off-potential measurement.

It has to be concluded that the depolarization of the metal surface is significantly faster than 1 μ s in calcium free electrolyte solutions, as no remaining polarization of the metal surface is found with a data acquisition rate of 2 MHz. The chalk layer forming on the sample surface affects the depolarization of the surface. The misleading results obtained in the field investigation demonstrate that it prevents a reliable detection of ac-corrosion [6].

Continuous data acquisition

Coupons with continuous data acquisition were installed at two locations in Switzerland. One is exposed primarily to ac voltage induced by high voltage power lines with 50 Hz (location A), while the other is mainly subjected to induced voltage of a railroad with 16.66 Hz (location B).

The ac-current density and the ac-induced voltage from a high voltage power line are shown in Fig. 6 and 7 (location A). It is clear that significant variations in the current density on the three different coupons are observed. So far, the critical current density of 30 A/m² is only exceeded for very short periods. It has been shown in previous work, that the current density on the coupons follows Ohms law. As a consequence, it is possible to calculate the ac-spread resistance of the coupons (Fig. 8). Based on the results obtained in laboratory investigations [8], the strong variations in the current density is primarily attributed to the formation and dissolution of a chalk layer on the metal surface. In the same location a second set of coupons has been installed in the soil where significant corrosion attack has been observed in a previous investigation [6]. The current densities measured are shown in Fig. 9. It is clear that the critical value of 30 A/m² has been exceeded from the very beginning on one coupon. It is interesting to note, that the induced ac voltage on the pipeline is below 5 V. In contrast the other coupons show only very small current density. In September an increase

is observed for one coupon while the coupon with originally high current density shows a significant decrease in November.

The obtained results demonstrate that under identical electrical conditions very different behavior can be obtained depending on the soil composition and the exposure time. Apparently, very high current densities can occur even from the very beginning when the coupons are installed. Moreover, significant variation in current density is observed over time, which demonstrates the strong variations of spread resistance.

The data obtained at location B show a different behavior. The ac-voltage on the pipeline is primarily induced by a railroad. All three coupons showed a very similar behavior. Therefore, the current density of only one coupon is shown (Fig. 10). It is clear, that the critical current density of 30 A/m^2 is only exceeded when trains are passing. The train passage results in induced voltages of up to 15 V (Fig. 11). The ac-spread resistance calculated from the current density and the ac-voltage according to Ohms law is shown in Fig. 12. It is clear that some variation in the resistance occurs. However, its absolute change is smaller and smoother than the one observed at location A. This difference may be attributed to the lack of calcium ions in the soil found in chemical analysis. Right after the installation of the coupons a relatively high resistance is observed, which readily decreases within a few weeks. This effect can be explained with the formation of hygroscopic Alkali metal salts, such as NaOH. During summer, a quite constant resistance is observed. Only after a drop of the surface temperature below freezing in fall (15th November) a significant increase in resistance is observed. In that period the current density on the coupon is generally below 30 A/m^2 .

The results obtained with continuous data acquisition clearly show various processes occurring on coupons. Soil containing calcium ions results in the formation of chalk layers, which strongly affect the observed current density. The different coupons installed at the same location show strong variation in spread resistance. This confirms the necessity of at least three coupons to be installed in parallel in such environment. In contrast, a very good reproducible behavior is found in soil that is free of calcium ions. Apparently, small differences in soil composition and calcium distribution can cause dramatic variations in the surface state of the coupon. The importance of the soil composition is additionally confirmed by the different behavior in current density in location A in the two soils. Identical electrical parameters can cause very different current densities depending on the soil composition.

Besides the chemical processes in the soil and the applied ac-voltage, the ac-current density on the coupons is influenced by climatic effects. Apparently the surface temperature seems to affect the spread resistance of the sample.

The obtained data on both locations demonstrate that the critical parameter of 30 A/m^2 is not exceeded at all times. Hence, the acquisition of single measurements can result in an erroneous judgement of the ac-corrosion risk.

CONCLUSIONS

The significant increase of the data acquisition rate in the instantaneous off-potential measurement up to 1 MHz turns out to be insufficient to detect the anodic polarization of the metal surface due to the ac-current load. No exceeding of the threshold could be observed although ac-corrosion was taking place. In presence of calcium ions the depolarization of the metal surface is altered due to the formation of a chalk layer, resulting in an exceeding of the threshold even at ac-current densities that do not cause ac-corrosion. The strong dependence of the obtained data on the soil composition and the very fast depolarization of the metal surface make the instantaneous off-potential measurement a non suitable technique for the characterization of the ac-corrosion risk of cathodically protected structures.

The continuous data acquisition of the ac-parameters on cathodically protected structures allows to differentiate the effect of chemical and physical parameters and time. The current status of the investigation allows to draw the following conclusions:

- The formation of chalk layers can cause significant variations on different coupons installed in identical locations. Hence, short measurements can cause an underestimation of the corrosion risk.
- Soil composition strongly affects the ac-corrosion risk. Identical electrical parameters can result in significantly different ac-current densities.
- Climatic conditions, such as surface temperature, seem to strongly affect the spread resistance and therefore the ac-current density on coupons.

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REFERENCES

1. G. Heim, G. Peez, "Wechselstrombeeinflussung einer kathodisch geschützten Erdgashochdruckleitung", *3R International* **27**, 345 (1988).
2. B. Meier, "Kontrollarbeiten an der Erdgasleitung Rhonetal", *GWA* **69**, 193 (1988).
3. D. Bindschedler, F. Stalder, "Wechselstrominduzierte Korrosionsangriffe auf eine Erdgasleitung", *GWA* **71**, 307 (1991).
4. G. Heim, G. Peez, "Wechselstrombeeinflussung von erdverlegten kathodisch geschützten Erdgas-Hochdruckleitungen", *gwf*, 133 (1992).
5. D. Funk, W. Prinz, H. G. Schöneich, "Untersuchungen zur Wechselstromkorrosion an kathodisch geschützten Leitungen", *3R International*, 31 (1992).
6. M. Büchler, C.-H. Voûte, J. Bieler, F. Stalder, "Korrosion durch Wechselströme: Messmethoden zur Feststellung der Gefährdung von kathodisch geschützten Rohrleitungen", *GWA* **8** (2001).
7. R. Gregoor, A. Pourbaix, paper presented at the CEOCOR 5th international conference 2000.
8. C.-H. Voûte, F. Stalder, "Einfluss der Bodenzusammensetzung auf den Ausbreitungswiderstand und die Wechselstromkorrosion von kathodisch geschützten Messproben", *GWA* **80** (2000).
9. Y. Schiegg, Dissertation Nr. 14583, ETH-Zürich (2002).

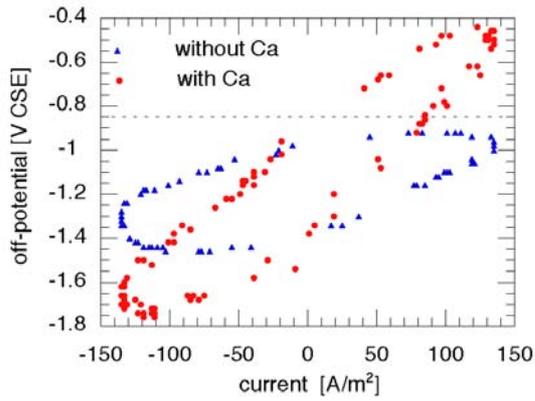


Fig. 1: Instantaneous off-potential measurement on coupons exposed to 100 A/m² ac- and 3 A/m² dc-current density for 41 days in quartz sand with two different soil solutions.

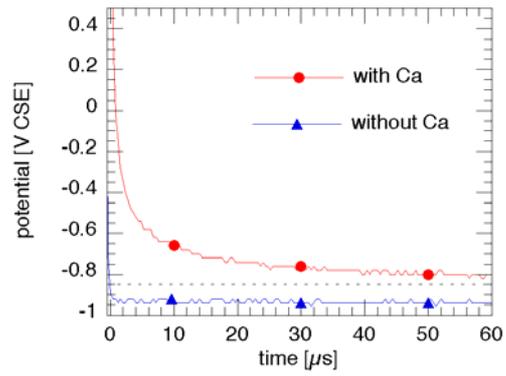


Fig. 2: Development of the off-potential over time of the readings at the maximum values shown in Fig. 1.

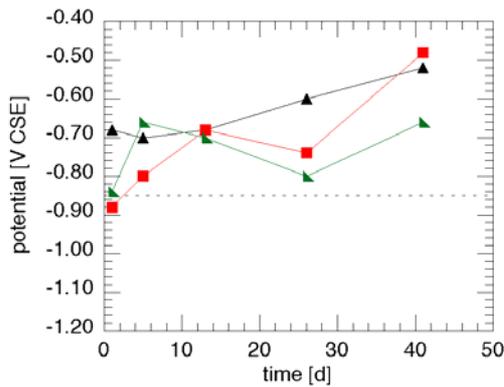


Fig. 3: Maximum off potential determined on 3 independent coupons in quartz sand and artificial soil solution with calcium ions exposed to 100 A/m² ac- and 3 A/m² dc-current density.

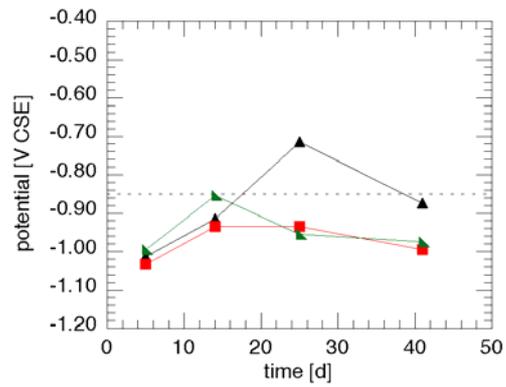


Fig. 4: Maximum off potential determined on 3 independent coupons in quartz sand and artificial soil solution without calcium ions exposed to 100 A/m² ac- and 3 A/m² dc-current density.

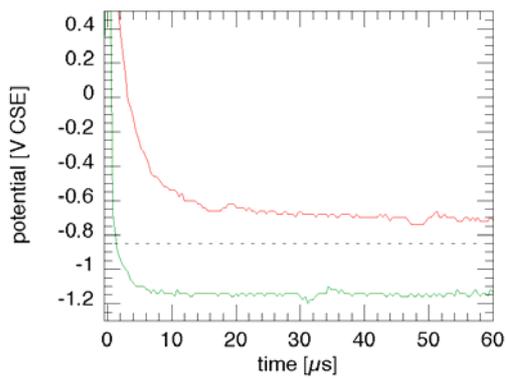


Fig. 5: Development of the off-potential of two identical samples of the readings at the maximum values. After stopping the experiment shown in Fig. 3, the current density was decreased to 10 A/m².

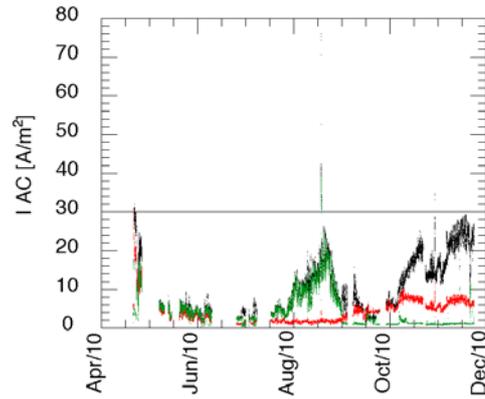


Fig. 6: AC-current density on coupons at location A under the influence of a high voltage power line.

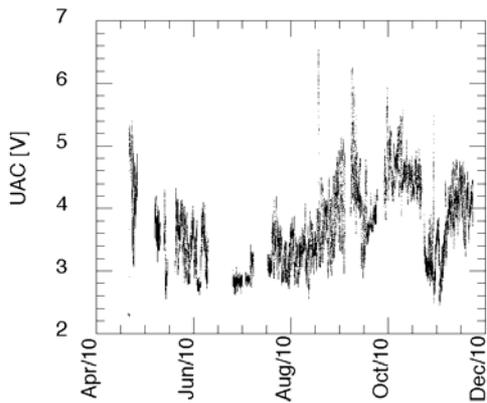


Fig. 7: AC-voltage induced on the pipeline at location A.

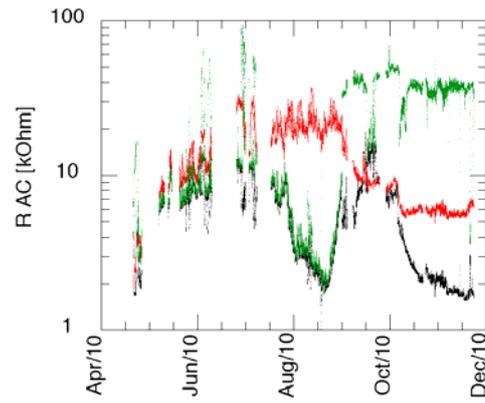


Fig. 8: AC-spread resistance of the coupons in location A calculated according to Ohms law.

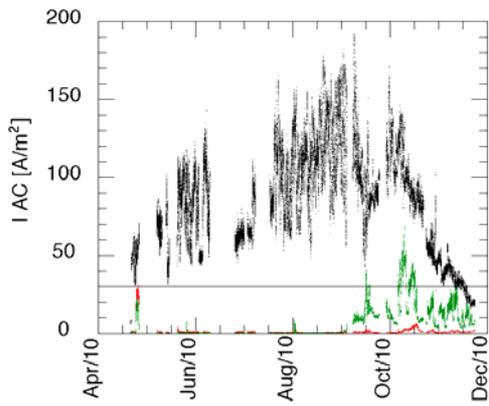


Fig. 9: AC-current density on coupons at location A. The coupons are embedded in soil that resulted in the formation of ac-corrosion in previous investigations.

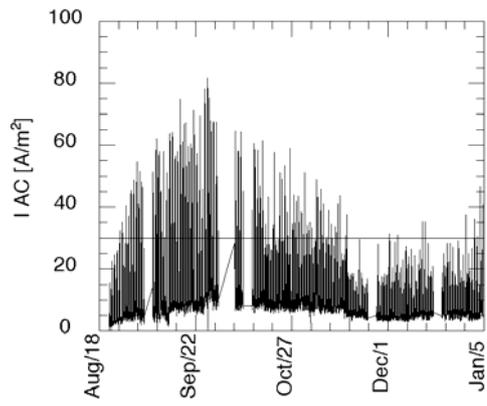


Fig. 10: AC-current density on coupons at location B under the influence of a train line with 16.66 Hz.

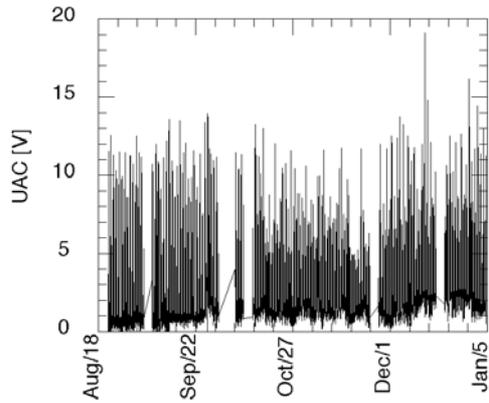


Fig. 11: AC-voltage induced on the pipeline at location B.

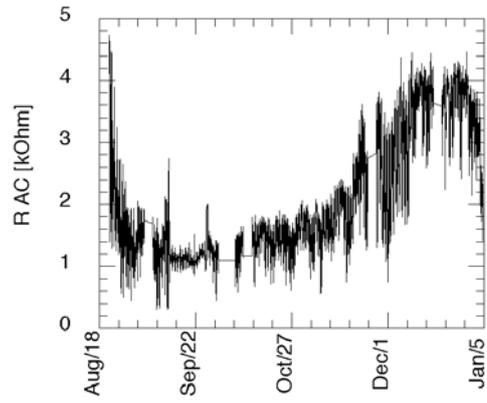


Fig. 12: AC-spread resistance of the coupons in location B calculated according to Ohms law.