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The pipeline potential: Potential measurements revisited

Das Rohrleitungspotenzial: Potenzialmessungen neu aufgegriffen

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Abstract

Since the beginning of the application of cathodic corrosion protection (CP), potential measurements and potential thresholds have been used to describe and assess the effectiveness of cathodic protection and the condition of the protected structure. While taking potential readings appears to be reasonably straightforward, there is very little discussion with respect to the relevance of these values with respect to the corrosion situation of the protected structure. Often it is erroneously assumed that this values taken at the soil surface have some relevance for the very coating defect underneath the reference electrode, the closest coating defect or even all the coating defects up to the next test post. The underlying concepts of potential measurements are presented and illustrated based on laboratory experiments. Furthermore the implications and consequences on assessing the effectiveness of CP of pipelines are discussed.

Zusammenfassung

Seit den Anfängen der Anwendung des kathodischen Korrosionsschutzes (KKS), wurden Potenzialmessungen und Potenzialgrenzwerte verwendet um die Wirksamkeit des kathodischen Schutzes und den Zustand der geschützten Struktur zu beschreiben und zu beurteilen. Während die Durchführung von Potenzialmessungen relativ einfach erscheint, wird die Relevanz dieser Werte für die Korrosionssituation der geschützten Struktur kaum diskutiert. Häufig wird fälschlicherweise angenommen, dass diese an der Bodenoberfläche gemessenen Werte eine gewisse Relevanz für die Umhüllungsfehlstelle unterhalb der Referenzelektrode, die nächstgelegene Umhüllungsfehlstelle oder sogar alle Umhüllungsfehlstellen bis zum nächsten Messpfosten haben. Die zugrundeliegenden Konzepte der Potentialmessung werden anhand von Laborexperimenten vorgestellt und veranschaulicht. Darüber hinaus werden die Auswirkungen und Konsequenzen für die Beurteilung der Wirksamkeit von KKS auf Rohrleitungen diskutiert.

1. Introduction

When working in the field of cathodic protection (CP), it is not unusual to encounter certain observations or hear from observations that don't seem to make any sense or don't seem to fit into the big picture.

One of these things for example is the discussion about if CP with galvanic anodes and CP with impressed current systems being the same or simply being not the same. The same applies for the discussion with respect to the significance of the off-potential of a pipeline and the question whether it corresponds to an IR-free potential or not.

One observation that was made a few years ago in the laboratory during extensive CP testing was one of these "don't fit into the big picture"-moments. In a box with sand and artificial soil solution a simple long term CP experiment was running. The experiment was pretty much as simple as shown in Figure 1. With a voltmeter the on-potential of the coupon was measured against a reference electrode (CSE). The measured on-potential was about -1.2 V_{CSE}.
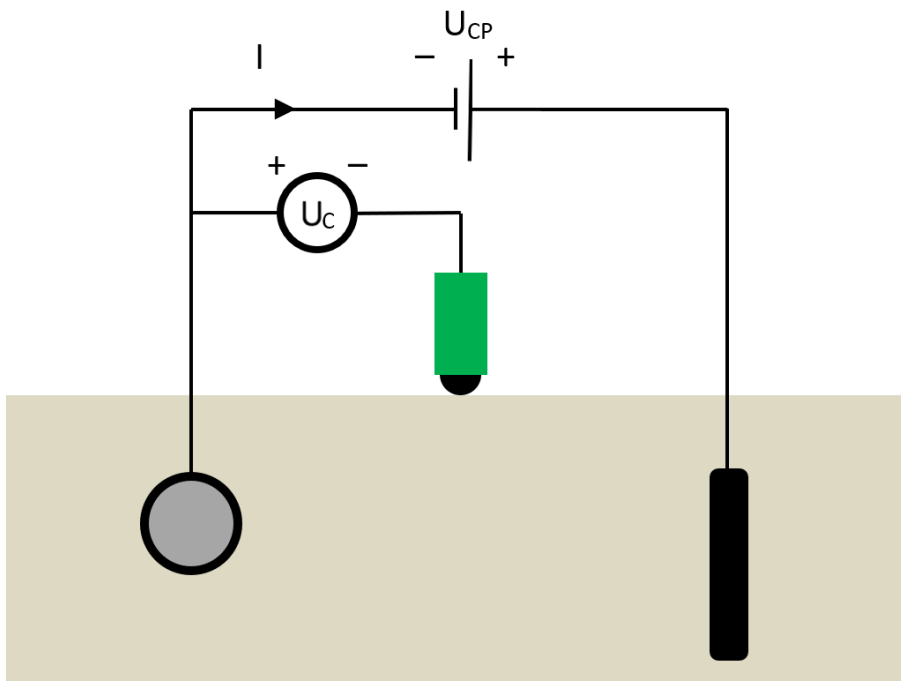

Figure 1: Simple CP experiment with a coupon (left), an anode (right), a rectifier and a voltmeter.

For visual inspection the coupon was taken out of the sand box, while everything else still was installed and running like in Figure 2 on the left-hand side. By chance it was observed, that the voltmeter still showed the same on-potential value of -1.2 V_{CSE} independent whether the coupon was in the soil or in the air. It was first assumed that this must be an error caused by a defective coupon, but it wasn't. Then it was assumed that the coupon, which was still wet and lying on the sand still had some kind of electrolytic connection to the sand, which made it possible to still measure the on-potential like during normal operation of the system. But the on-potential was still measurable after removing the coupon from the sand and after drying. In fact, the on-potential it was even measurable when disconnecting the coupon completely from the setup just leaving the anode, the rectifier and the reference electrode connected with the voltmeter to the terminal where the coupon was connected before. The current flowing in the CP circuit was indeed zero in all these measurements, with removed coupon.

Hence, the question arose how it was possible to measure an on-potential, even if obviously no coupon was installed any more, which would also represent the situation of a perfectly well

isolated pipeline in absence of a single coating defect. After some considerations it became clear, that the only thing that could still be measured was the anode potential, since this was the only metallic component in contact with the soil. But usually an anode's potential is not at -1.2 V_{CSE} during stable conditions in a longtime CP experiment. Measuring the potential of the anode on the anode's terminal, as shown in Figure 2 on the right-hand side, revealed a constant potential of about +1.1 V_{CSE}. This is indeed typical for a mixed metal oxide (MMO) coated titanium anode after interrupting the current. Measured this way, the situation seemed to be as expected. The reason for the measured on-potential on the cathode's terminal became clear, when considering that the voltage output on the rectifier was set to about 2.3 V.
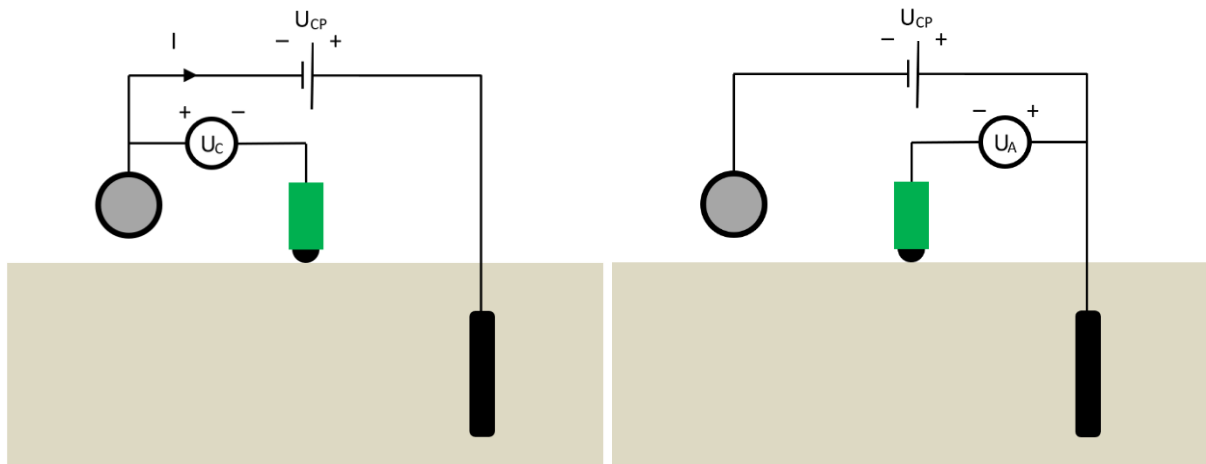

Figure 2: **Situation of the simple CP experiment with removed coupon. Voltmeter connected to the coupon (left); Voltmeter connected to the anode (right).**

This observation initiated the question of the significance of potential measurements, especially when multiple electrodes are involved. Additionally, it opened a different view on the actual function of the CP rectifier as an impressed voltage, rather than a current source.

2. Electrodes in electrolytes

For the following discussion it is necessary to make some assumptions. Some considerations are simplified, but this will help in implementing them into the proposed model concept.

Electrode potential

An electrode potential results from two or more electrochemical reactions occurring simultaneously on one electrode. Usually these are the anodic oxidation reaction of the metal and the cathodic oxygen reduction and/or hydrogen evolution.

Based on these reactions the corresponding potentials can readily be explained. For example, steel in concrete normally has a quite positive potential of about -0.2 V_{CSE} due to the kinetically hindered metal oxidation. The absence of the passive film in the case of steel in soil and the higher rate of metal oxidation causes more negative potentials for steel in soil. In the case of oxygen depletion, the cathodic reaction is dominated by hydrogen evolution, which causes a significant shift of the electrode potential in the negative direction to values as negative as -0.7 V_{CSE}.

How potentials are measured

Measuring the voltage difference of two electrodes is like measuring the output voltage of a battery. What you get is the voltage difference between the two electrode's potentials in their

respective electrolyte. The (complete) cell voltage of a battery is the result of the potential of the two electrodes (anode and cathode) often referred to as half cells. As voltages are the differences of two potentials, they can be described as shown in the following equation (1), which describes the voltage U_{12} between the two potentials E_1 and E_2.

$$U_{12} = E_1 - E_2 \tag{1}$$

The possibility to measure potentials arises if one of the two electrode's potential (one of the two half cells (e.g. E_2) is defined as a reference potential E_R. This electrode then becomes a reference electrode. This also means that the reference electrode's potential is arbitrarily defined as zero with respect to the reference potential E_R and deviations from this potential can be expressed as potential values in the form of voltages with respect to the reference electrode's potential.

With $E_2=0$, the measured voltage U_{12} between E_1 and E_2 then directly shows the potential of E_1 with respect to E_2, which is now also E_{Ref}. as follows from equation (2).

$$U_{12} = U_{1Ref} = E_1 - E_R = E_{1,Ref} \tag{2}$$

In principle every electrode can be used as a reference electrode. But there are some important properties that a reference electrode must exhibit, in order to be a good reference electrode. Its potential must be constant over time and its value may not be affected by the electrolytic contact between the reference electrode and the environment. E_1 may be changing over time and may be written as $E_1(t)$, whereas E_R shall be time independent and thus must be constant over time. Additionally, the electrolyte conditions at the reference electrode location also may not affect the reference electrode potential. Therefore, reference electrodes usually are embedded in a specific solution or solid, in order to minimize any time dependency (drift) of the reference electrode's potential.

The actual potential of the reference electrode is of minor importance as long as it is constant over time. This property makes it possible to refer to potentials, which were measured against reference electrode Ref_1 as if they were measured against reference electrode Ref_2, as long as the voltage difference between Ref_1 and Ref_2 is constant over time. This is shown in equations (3) and (4)

$$U_{Ref1Ref2} = E_{Ref1} - E_{Ref2} \tag{3}$$
$$E_{1,Ref2} = U_{1Ref1} + U_{Ref1Ref2} \tag{4}$$

The shift of electrode potentials with external DC sources

Taken an initial situation of an electrode with potential E_1, which is measured against a reference electrode with a voltage meter. If a DC voltage source is now added between the measuring device and the electrode, the voltage measured against the reference electrode will be shifted by the value of the DC voltage source (U_B). It's like measuring two batteries in series, where, depending on their polarity to each other, their voltage values will add or subtract from each other. So instead of only measuring the potential difference between an electrode with potential E_1 and a reference electrode E_R ($E_R=0$ with respect to E_R) the voltage of the battery U_B is added according to equation (5).

$$E_{1,Ref+B} = E_{1,Ref} + U_B \tag{5}$$

The described situation is shown in Figure 3 and it's the same configuration as shown in Figure 2 on the left hand side except that the electrode replaces the anode in this more general illustration. It's important to note, that in this configuration no current is flowing. Also important to note is that the electrode's potential is still E_1 but due to the DC source between the electrode and the voltage meter a shifted potential is measured. If now another electrode is connected to the side with the plus-pole of the voltmeter, it would also be affected by the shifted electrode's potential (E_1+U_B) and not only by its actual potential (E_1). This aspect will be further discussed in in a following section.
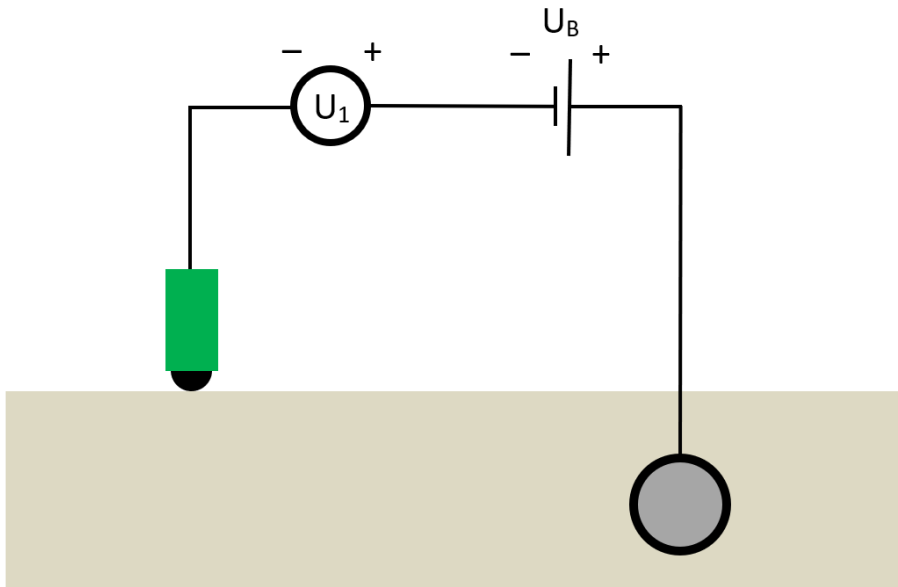

Figure 3: **Setup for measuring a shifted potential of E_1 (U_1 on the voltage meter) by U_B.**

Spread resistance of electrodes

For the further discussion it is assumed that the electrical circuit resistance is controlled by the spread resistance of the electrodes. The non-linear polarization resistances and the contribution of the electron resistivity of the metallic conductors are assumed to be negligible. In this case the spread resistance R of a hemispherical electrode with diameter d in an electrolyte with the resistivity ρ is given by equation (6).

$$R = \frac{\rho}{\pi d} \qquad (6)$$

The spread resistance gets smaller, as the electrode surface in contact with the electrolyte gets bigger. Also, it can be derived from equation (6) that the electrolyte resistivity influences directly the value of the spread resistance. The higher the soil resistivity, for example dry sand, the higher is the spread resistance of the electrode. Summarized, it can be said that the metallic surface in contact with an electrolyte, which has a certain electrolyte resistivity, determines the value of the spread resistance.

The potential of a galvanic couple

When two electrodes with different potentials E_1 and E_2 are connected to each other, a galvanic couple is formed. It is important to note, that the connection between the two electrodes must be electrically (electron conductive, metallic) and electrolytically (ion conductive) in order to generate a galvanic current. Assuming the potential E_1 is more positive than the potential E_2, then the electrode with potential E_1 will be the cathode and the electrode with potential E_2 will be the anode.

The technical current direction is against the flow of electrons, and thus from E_1 to E_2. This also means that current will flow from the anode (E_2) into the electrolyte, in the electrolyte to the cathode and again from the electrolyte into the cathode (E_1). This way, the current loop is closed.

If the potential of this structure (consisting of the combined two electrodes) is measured against a reference electrode, the potentials E_1 and E_2 will both be contributing to this newly formed structure potential E_S. E_S will be more negative than the cathode potential E_1 and be more positive than the anode potential E_2. Therefore, the following two theoretically measurable voltages U_1 and U_2 will result according to equation (7) and (8):

$$U_1 = (E_S - E_1) \tag{7}$$
$$U_2 = (E_S - E_2) \tag{8}$$

The two formulas describing the potential differences between the structure potential E_S and the contributing individual electrode potentials E_1 and E_2.

Considering Ohm's law with the prerequisites from above, these voltages can be put into relation with a corresponding current and resistance. This can be described as in the following equations (9) and (10):

$$U_1 = R_1 \cdot I_1 \tag{9}$$
$$U_2 = R_2 \cdot I_2 \tag{10}$$

Although for two electrodes it would be easier to considering Kirchhoff's 2nd law (voltage law), which describes the conservation of energy within a closed-circuit path, it is important to rather consider Kirchhoff's 1st law (current law), which describes the conservation of charge entering and leaving a junction. Either way it becomes obvious that the current leaving at the anode must be the same as the one entering at the cathode or expressed with the terminology of Kirchhoff's 1st law: The sum of all currents flowing from and to the structure has to be the zero according to equation (11).

$$I_1 + I_2 = 0 \tag{11}$$

This assumption allows to combine equations (9), (10) and (11) into equation (12):

$$\frac{U_1}{R_1} + \frac{U_2}{R_2} = 0 \tag{12}$$

And inserting formulas (7) and (8) results in equation (13):

$$\frac{(E_S - E_1)}{R_1} + \frac{(E_S - E_2)}{R_2} = 0 \tag{13}$$

This equation can now be resolved according to equation (14) for E_S:

$$E_S = \frac{E_1 R_2 + E_2 R_1}{R_1 + R_2} \tag{14}$$

E_S is the potential that can be measured between the structure and a reference electrode placed on remote earth.

The structure potential of multiple electrodes

Based on Kirchhoff's 1st law these considerations can be extended to an infinite number of electrodes by means of equation (15):

$$U_x = (E_S - E_x) \qquad (15)$$

U_X is the voltage between the structure potential E_S and the potential of the electrode X contributing to it. This potential difference will result in a current flow I_X depending on a spread resistance R_X in the galvanic circuit with each individual electrode (X = 1 to n) contributing to E_S according to equation (16).

$$U_x = R_x \cdot I_x \qquad (16)$$

Depending on whether the potential of an individual electrode is anodic or cathodic with respect to the structure potential E_S, the resulting current will enter at the electrode or leave at the electrode. Considering Kirchhoff's 1st law again, the sum of all currents flowing from and to the structure has again to be the zero according to equation (17).

$$0 = \sum_{x=1}^{n} I_x = \sum_{x=1}^{n} \frac{(E_S - E_x)}{R_x} \qquad (17)$$

Doing some mathematical substitutions will turn equation (17) into the following equation (18):

$$E_S = \frac{\sum_{x=1}^{n} \frac{E_x}{R_x}}{\sum_{x=1}^{n} \frac{1}{R_x}} \qquad (18)$$

It follows from equation (18) that a structure with a potential E_S, consisting of any amount of electrodes, with any potentials and associated spread resistances, some will have electrode potentials more positive than E_S and others will have electrode potentials more negative than E_S. It follows that E_S is an average value of all the electrodes weighed with their corresponding spread resistances and it turns out that the structure potential according to equation (18) will be dominated by those electrodes with the smallest spread resistance.

Electrical field distribution (potential gradient)

The structure potential E_S according to equation (18) will result in a current flow among the individual electrodes. The current flow will be towards the individual electrode, if the electrode potential is positive of E_S which will turn this electrode into a cathode. When the electrode potential of the individual electrode is negative of E_S a current will be leaving the electrode turning it into an anode. In both situations, an electric field is generated in the electrolyte, with potential wells and potential troughs, which are commonly called gradients or IR-drops. The generated voltage funnel depends on the geometry of each electrode and its U_X according to equation (15). The resulting electrical field is exclusively a function of U_X, the radius r_X of the electrode X and the distance r from electrode X for the assumed hemispherical electrode according to equation (19).

$$U_r = U_X \frac{r_X}{r} = \frac{I_X \rho}{2\pi r} \qquad (19)$$

This corresponds to a vector field, which describes the maximum change of the electric field for every point in the electrolyte. The commonly used term "potential gradient" describes the voltage difference of two points within the electric field.
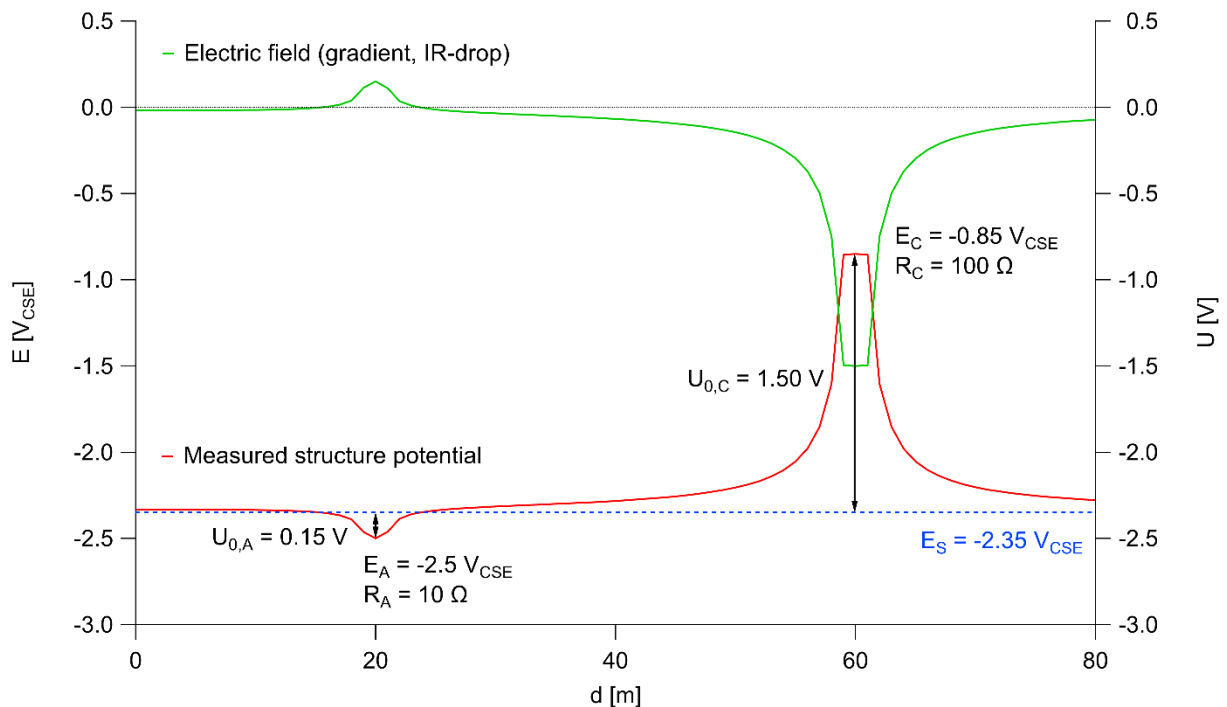
Figure 4: Spatial distribution example of the voltage funnel two hemispherical electrodes.

In Figure 4 the calculated electric field distribution between two hemispherical electrodes on an electrolyte surface are shown. The cathode has a potential of -0.85 V_{CSE} and a spread resistance of 100 Ω and the anode has a potential of -2.5 V_{CSE} and a spread resistance of 10 Ω. The calculated structure potential is therefore -2.35 V_{CSE}.

With respect to remote earth, a cathode will cause a cathodic funnel in the electrolyte and an anode will cause an anodic funnel. If the reference electrode does not stand on remote earth it will be influenced by the electric field generated by the electrodes. The closer it is placed towards one of the electrodes, the closer the measured value will be towards the effective (IR-free) potential values E_C or E_A respectively. That is because in the vicinity of an electrode the reference electrode will be influenced by the respective funnel of the electrode.

In Figure 4 the red line shows the apparent measured structure potential (voltage difference between the red line and 0 V_{CSE}) along a line between the two electrodes. The closer the reference electrode is towards one of the electrodes the closer the measured potential is to the IR-free potential of that electrode.

3. Polarization

Activation polarization

Immediately after the electrodes of a galvanic couple are connected, activation polarization builds up within milliseconds by the galvanic current entering or leaving the steel. The current entering the steel at the cathode causes a shift of the potential in negative direction. The current leaving at the anode causes a shift of the potential in positive direction . At the cathode, both, the increased oxygen reduction and the hydrogen evolution caused by the activation polarization, lead to concentration polarization due to an increase of the pH value and the decrease of oxygen concentration at the steel/electrolyte interface.

Concentration polarization

The concentration polarization is that portion of the electrode polarization produced by concentration changes resulting from passage of current exchange between the steel and the electrolyte. In the case of cathodic protection the predominant concentration effects are oxygen depletion and pH-increase. Both cause a shift of the potential in the cathodic direction

4. Cathodic protection

Galvanic anode

If an electrode with potential E_C is cathodically protected with a galvanic anode with a potential of E_A the considerations from above can be applied to calculate the resulting potential after the two electrodes are connected to each other, forming a galvanic couple, according to the following equation (20) derived from equation (14). It follows immediately that the structure potential E_S from the equation (14) consisting of the galvanic anode and the cathode corresponds to the on-potential E_{on} measured against remote earth.

$$E_{on} = \frac{E_A R_C + E_C R_A}{R_A + R_C}$$
(20)

Impressed current anode

If it is accepted, that the on-potential against remote earth in the case of CP with a galvanic anode is simply the combined potential of the anode electrode and the cathode electrode as described in equation (20) it just needs one more step to include impressed current anodes into the same model concept shown in equation (21). As illustrated in Figure 2 and explained above it is possible to shift electrode potentials with external DC sources. This is exactly what is made with impressed current anodes. Their potential, whatever it may be naturally (E_A), is shifted by means of a rectifier's voltage U_B into negative direction – as the plus-pole of the DC source is connected to the anode – until it's more negative than the cathode potential E_C.

$$E_{on} = \frac{(E_A + U_B) R_C + E_C R_A}{R_A + R_C}$$
(21)

This is illustrated by adding the output voltage (with negative polarity) of the rectifier U_B in equation (21). This results in a more negative value for E_{on} the bigger U_B is. By varying U_B, E_{on} can be adjusted to the required value. It is however important to note that E_{on} is a potential measured against the same remote reference electrode, against which also E_C and E_A are measured.

Cathodic protection of a structure

E_C is assumed to be a single electrode in the two chapters before. When protecting a pipeline, it is actually a structure that consists of many electrodes, which corresponds to the number of defects in the coating on the pipeline. In the following equation (22) the potential of the protected structure E_S is defined according to the equation (18) from above, consisting of n electrodes with n potentials and n spread resistances. The other electrode is the anode with potential E_A and resistance R_A, which is shifted by means of a rectifier by the voltage U_B into negative direction as explained in equation (21).

$$E_{on} = \frac{(E_A + U_B) R_S + E_S R_A}{R_A + R_S}$$
(22)

5. The potential of electrodes on pipelines

Multiple electrodes on a pipeline

Individual defects on a coated pipeline represent individual electrodes, of which every single one has its own (IR-free) potential. The potential of every defect is a result of its size and its surrounding electrolyte. Defects in clay will for example have a more negative potential as their aeration is poor. Defects in dry sand will have a more positive potential as their aeration is good. Depending on the soil and water composition the pH will vary along the pipeline. Also depending on the electrolyte resistivity and defect sizes, the spread resistances of individual defects will be different.

The potential of multiple electrodes under cathodic protection

Figure 5 shows the potential curves of 3 electrodes. The blue line is the potential of a stainless steel electrode (cathode 1), the green line is the potential of a steel electrode (cathode 2) and the red lines are the potential of the MMO titanium anode electrode. To better illustrate how different potentials of different electrodes are combined into one structure potential, the connection between the electrodes was set to be only 1 second every 5 seconds. The anode potential was measured on both sides of the rectifier. The dotted line shows a common anode potential of about +0.6 V_{CSE} as it is usually measured. The solid red line shows the anode potential measured at the cathode (minus) side of the rectifier, the side on which also the other two electrodes are measured and connected. The chosen time frame additionally shows two different impressed DC voltages (U_B of 1.4 V and 2.0 V), which demonstrates the potential shift effect of the rectifier.
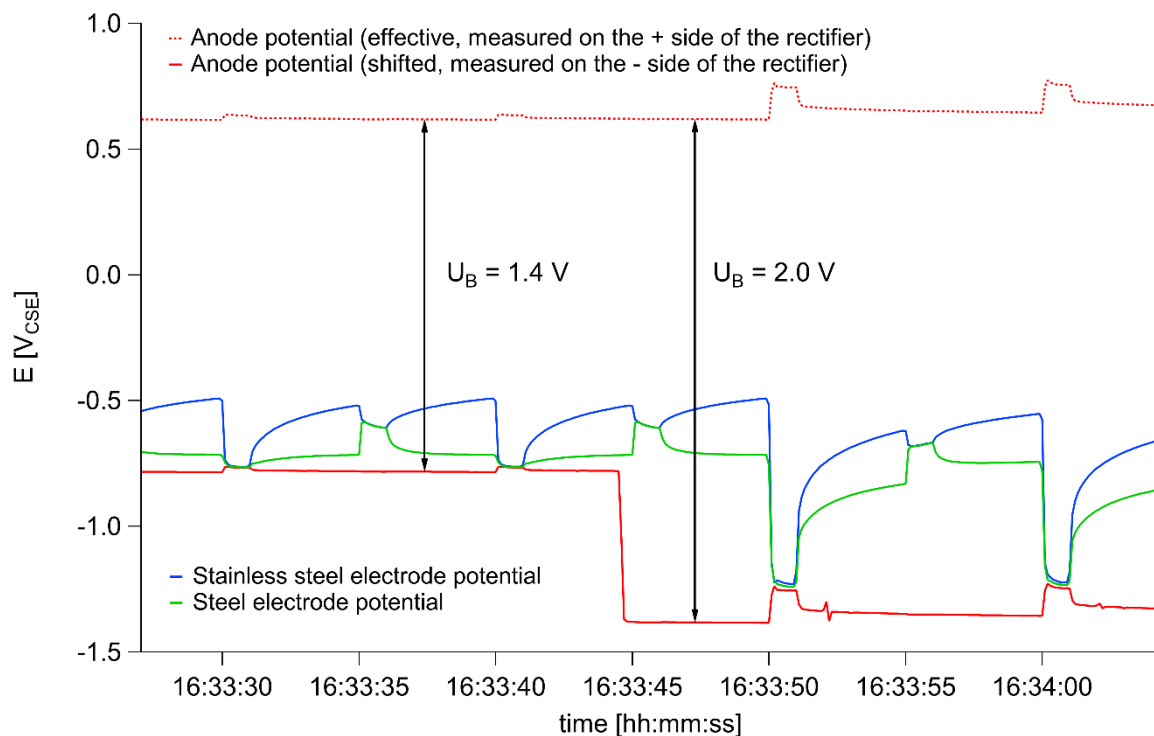

Figure 5: Potential measurement of 2 steel coupons (cathodes) and an anode connected to a rectifier with output voltage U_B.

In the case where only the two cathodes are connected with each other, the resulting combined potential curve lies between the blue and the green curve. It is closer to the blue potential because the stainless steel electrode was bigger and thus had a lower resistance. This combined structure potential can be interpreted as the off-potential of a pipeline having only 2 defects with different

aeration. In this galvanic couple the steel electrode is the anode, which experiences an anodic shift, whereas the stainless steel electrode is the cathode that experienced a cathodic shift. In the case where the two cathodes of the CP system were connected to the anode both experienced a cathodic potential shift and only the anode potential experienced a shift in the anodic direction. This effect is more dominant in the case of U_B=2.0 V as had to be expected as a result of the increased voltage shift of the rectifier.

Even during this very short period of 1 second, where the electrodes were connected, a concentration polarization occurred. This can clearly be seen by the depolarization during the 4 seconds after disconnecting the electrodes. After the first connection with U_B=2.0 V the potential of the steel electrode was already more negative than -0.85 V_{CSE} short after disconnecting the anode. It is assumed that this shows the quick removal of oxygen in the soil solution saturated quartz sand at the steel surfaces. The relatively fast depolarization is then a result of the oxygen in the vicinity that diffuses back to the steel surfaces.

Shifted electrodes are still bound to physical boundaries. The potential of MMO coated titanium anodes will be bound to the oxygen evolution. Connecting a rectifier with output voltage U_B between such anodes and cathodes will mainly cause a shift of the cathodes in negative direction because the effective anode potential is controlled by the oxygen evolution and will hardly be shifted anodically.

6. Conclusion

With respect to the discussed points above, the following conclusions are possible.

Measuring the potential of a structure means measuring every single electrode connected electrically and electrolytically with respect to the location of the reference electrode. This is true for all pipelines irrespective of the coating system applied.

Under normal operating conditions it is always possible to measure an on-potential. This also applies for the theoretical case of a perfectly isolated pipeline in absence of any current flow. As soon as the first coating defects forms the current will flow and cause cathodic protection to the steel surface. The structure potential, meaning the on-potential, however will not be influenced by this newly formed electrode at the coating defect. The formation of the coating defect will only be detected by the current supplied.

With unlimited power it is theoretically possible to setup any on-potential. As in equation (22) E_{on} is getting always more negative, when E_A is shifted more negative by higher values of U_B. Hence, a potential controlled rectifier with sufficient power is always able to control a given on-potential. This controlled potential however is only valid at the location of the piloting electrode. If that electrode is influenced for example by the nearby anode funnel the effective set on-potential will be different when measured with respect to remote earth.

The on-potential is the combined potential of all electrodes on the pipeline and the voltage-shifted anode potential. It is the potential an electrode will be polarized to with respect to remote earth. Electrodes with potentials cathodic to the on-potential will experience cathodic polarization and current entering. Electrodes with potentials anodic to the on-potential will experience anodic polarization and current leaving.

Based on the discussion of the structure potential it becomes clear that the off-potential of a pipeline only corresponds to the IR-free of every single coating defect, if there is only one defect or every defect has exactly the same IR-free potential. Otherwise the off-potential will always be

a structure potential that is a function of the individual coating defect potentials and spread resistances. If some of the electrodes will have a potential anodic to the structure potential, then others must have a potential cathodic to the structure potential. The ones being more positive to the off-potential will be cathodes and will receive cathodic current. The defects being more negative with respect to the off-potential will receive anodic current. All electrodes exhibit their own IR-free potential but none of them is measurable against remote earth or a reference electrode placed above the coating defect.

In the theoretical case of an instant off-potential of -0.85 V_{CSE} on a pipeline with n coating defects of equal size it must be assumed from equation (18) that about n/2 of them do not meet the protection criterion. This is due to the fact that the least resistive ones dominate the value of E_S, which corresponds to the instant-off-potential.