HUNGARIAN JOURNAL OF
INDUSTRY AND CHEMISTRY
Vol. 54(2) pp. 141–152 (2026)
hjic.mk.uni-pannon.hu
DOI: 10.33927/hjic-2026-36

INVESTIGATION OF SWITCH-OFF TRANSIENTS OF CATHODIC PROTECTION IN HIGH-TEMPERATURE MEDIA

PÉTER JANKOVICS[1], TAMÁS KRISTÓF[1]* AND ZOLTÁN LUKÁCS[1]

1 Faculty of Engineering, University of Pannonia, Egyetem u. 10, Veszprém, 8200, HUNGARY

Corrosion is the undesirable physicochemical transformation and degradation of structural materials caused by environmental factors. Cathodic protection is a widely used method to mitigate corrosion of steel structures, but its applicability is limited by specific operational conditions, such as extreme temperatures. This study investigates the effectiveness of cathodic protection at elevated temperatures, utilizing a novel experimental methodology to evaluate switch-off transients. Measurements were carried out in liquid and sand media at 80 °C with varying concentrations of NaCl, Na_2CO_3, and Na_2S. The results indicate that a system remains cathodically protected even at elevated temperatures if the ohmically compensated polarization is at least -100 mV relative to the calculated corrosion potential. Furthermore, the calculated corrosion current drops by orders of magnitude when the cathodic Tafel slope decreases below 20 mV, providing another control parameter for the effectiveness of the protection.

Keywords: cathodic protection, transient depolarization, elevated temperature, soil corrosion, potential criterion

1. Introduction

Corrosion is the undesirable physicochemical transformation and degradation of structural materials, typically metals, caused by environmental factors. During this process, mechanical and chemical effects typically act synergistically on the metal surface. As a result of technological development, numerous procedures are currently available for the mitigation of corrosion damage. Cathodic protection (CP) is one of the most important methods for metal structures in soil. Although CP is known as a generally robust and reliable corrosion protection technology, the mechanism of CP is not fully understood and the criteria for adequate operation remain unclear. These problems become even more serious when CP is applied at elevated temperatures, e.g. in hot water tanks, on gas pipelines after the booster stations, on gas and oil flowlines and well casings. In the latter case, temperatures can exceed 200 °C, and pressures can reach up to 500 bar. Under such conditions, the standard criteria for cathodic protection are unlikely to be applicable; nevertheless, in general practice, the conventional -850 mV potential criterion is routinely applied even in the cathodic protection of well bottoms. References to high-temperature cathodic protection are rare in the literature [1], and a systematic investigation of the topic is largely lacking. In this paper a novel methodology is used for the assessment of the protection level at elevated temperatures.

2. Theoretical background and methodology

The theoretical foundations of high-temperature cathodic protection are unsettled. The primary source of this problem is that the absolute potential of any single electrode is unknown, and consequently, the temperature coefficient of its absolute potential is also unknown. As a consequence, the temperature coefficients of reference electrodes can only be specified relative to the temperature coefficient of the standard hydrogen electrode (SHE). Furthermore, if the reference electrode is maintained at a normal temperature, the emerging thermodiffusion potential can introduce an unknown degree of error into the determination of potential values [2]-[6]. A further practical obstacle to the cathodic protection of high-temperature systems is that Pourbaix diagrams (upon which, for instance, the thermodynamic foundation of the potential criterion rests) are only available to a limited extent for those specific conditions (elevated temperature, high pressure, and high chloride, carbon dioxide, and hydrogen sulfide content). Given the uncertainties in thermodynamic data and the conclusions that can be drawn from them, the conventional -850 mV (or any other fixed-threshold) potential criterion cannot

Received: 1 July 2026; Revised: 12 July 2026;
Accepted: 13 July 2026
*Correspondence: kristof.tamas@mk.uni-pannon.hu

be applied. In its absence, to determine a suitable kinetic criterion, the applicability of the depolarization criterion derived from switch-off transients warrants consideration.

The corrosion processes of metal structures placed in soil or in deeper geological formations are fundamentally electrochemical by nature [7]. Although theories and equations developed for the description of conventional, liquid-phase electrolytes serve as a starting point, the specifics of natural media, i.e., soils and formation waters, result in numerous significant deviations. Near-surface soil is an extremely complex, heterogeneous, and capillary-porous (colloidal) system, whereas in deep oil and gas wells, pipe structures are already in contact with variously composed solid rock layers and the fluids filling them. These characteristics – which differ from those of liquids and homogeneous electrolytes, particularly in terms of their modified kinetic constants – markedly influence electrochemical corrosion processes. In near-surface structures, the gas permeability and aeration of the soil directly determine the oxygen content. In media with higher oxygen concentrations, spontaneous passivation can occur on the surface of steel structures. Conversely, for structures located in deeper rock layers, e.g. well casings, the primary corrosive medium consists of formation water present in porous rocks. These fluids typically possess high salt concentrations (especially chloride ions), as well as significant amounts of dissolved, aggressive gases (carbon dioxide and hydrogen sulfide). Under the anoxic conditions prevailing at such great depths, alongside differential oxygen supply, the presence of acidic gases and high ionic strength becomes a key factor in corrosivity [7].

This complex picture is further nuanced by the strong temperature and pressure dependence of electrochemical processes, which are critically important in the case of deep wells and pipelines transporting high-temperature production fluids to the surface. Since the geothermal gradient increases with depth, the elevated temperature not only shifts thermodynamic equilibria but also, in accordance with the Arrhenius equation, exponentially accelerates reaction kinetics, and increases the rates of diffusion and charge transfer processes as well. The exact field determination of these altered parameters and the verification of protection, however, face serious theoretical and technical limitations.

2.1. Fundamentals and mechanism of cathodic protection

Corrosion is an electrochemical process in which the anodic dissolution of the metal is accompanied by a complementary cathodic reduction (typically the reduction of hydrogen ions or dissolved oxygen molecules). The objective of cathodic protection is the suppression of this anodic metal dissolution through the negative polarization of the metal structure. The mechanism of action of the protection is fundamentally described by two models [8].

1. The kinetic model states that cathodic polarization directly reduces the rate of anodic processes.
2. According to the thermodynamic model, during the accelerated cathodic reactions, an increase in pH occurs on the metal surface, altering the thermodynamics of the ongoing processes. The stability range of metallic iron in the alkaline pH range approaches that of water, which inherently inhibits corrosion [9].

In practice, the two mechanisms operate together. At the initiation of protection, kinetic control dominates (which requires current densities orders of magnitude higher to maintain protection [10]), and as polarization continues, thermodynamic effects also engage due to alkalization. This is supported by the observation that in soils with high buffer capacities – where surface pH increase is hindered – protection often proves insufficient [11].

The root cause of the problem associated with elevated temperature conditions lies partially in the limitations of field diagnostics. Since the size of the active reaction surfaces is unknown, extensive parameters (e.g., the current delivered by cathodic protection) cannot be used to qualify the system. Measurements are limited to recording the pipe-to-soil potential and switching the protective current on and off (switch-off transients). The most widely used -850 mV potential criterion is basically thermodynamic in nature, but by definition, it also incorporates ohmically compensated polarization; thus, it is encumbered with confounding kinetic factors.

Given the mixed mechanism of protection, a reliable protection criterion – one that remains functional even under extreme temperature conditions – should theoretically consider both the temperature dependence of thermodynamic and kinetic parameters. For this, the separate determination of the corrosion potential and the actual polarization (i.e., the difference of the ohmically compensated potential and the corrosion potential) is necessary. In what follows, we present a measurement and evaluation procedure to meet this requirement.

2.2. The OFF-potential and depolarization

The so-called OFF-potential can be determined by briefly interrupting the cathodic protection system. Following the decay of the ohmic potential drop resulting from soil resistance and the inductive peak transient (if any) – the time constants of which are typically no greater than 10 microseconds – the value settles at the ohmically compensated structure potential. When appropriate measurement technology is applied, this closely approximates the potential difference existing in the ON state of the interfacial double layer between the structure and the soil [11].

However, the measurement is significantly complicated by the relatively rapid potential decrease occurring as a result of transient depolarization. Although transient depolarization is a complex and partially unknown phenomenon, at least three main

phases can be distinguished. In the first phase, charge transfer is described by the Butler-Volmer (BV) equation. The second phase corresponds to the linear approximation of the BV equation in the vicinity of the corrosion potential (Linear Polarization Resistance, LPR range). In the third phase, the slow concentration equalization between the electrode surface and the bulk phase commences. During this slow process, depolarization continues, but its rate cannot be expressed in terms of the discharge of the electrochemical double layer as it is controlled by transport processes. Since these phases are not sharply distinct and under real field conditions the process is accompanied by further inherent disturbing factors (e.g., the presence of equalization currents), the first and second phases of transient depolarization appear suitable for estimating kinetic parameters, as the significance of these disturbing effects is smaller there.

2.3. The potential criterion and the thermodynamic and kinetic protection mechanisms

The -850 mV criterion (the so-called potential criterion) was introduced by Kuhn to assess the effectiveness of cathodic protection, particularly for the corrosion protection of pipelines [12]. According to the potential criterion, cathodic protection is effective if the OFF (ohmically compensated) structure potential is more negative than -850 mV relative to the saturated Copper Sulfate Electrode (CSE). In poorly aerated, aggressive (contaminated), acidic, swampy soils, containing hydrogen sulfide, the limit is -950 mV. This criterion is the most widely used protection criterion, applied in the case of buried pipelines, casing pipes of oil and gas production wells, the internal side of tanks, and rarely, the external protection of tank bottoms [11]. It is not applicable to structural materials embedded in concrete or to non-carbon steel materials, such as stainless steels or lead. According to thermodynamic theory, the -850 mV threshold value is based on the premise that even a minimal current density (in the magnitude of 1-10 mA/m^2) may be sufficient to maintain the pH value above 9 on the protected steel surface. At such high pH levels, the electrode potential more negative than the potential criterion falls in, or very near to the domain of immunity, therefore a strong suppression of anodic processes is expected. This reduces the rate of corrosion processes [9], therefore this state is called the state of thermodynamic protection. As an alternative interpretation of the protection mechanism, according to kinetic theory, a negative polarization of at least 200 mV from the free corrosion potential of the system (typically from -450 mV to -600 mV) suppresses the anodic sub-process to such an extent that its rate decreases by at least an order of magnitude.

The potential criterion does not provide an exact parameter for determining overprotection, and operators define the state of overprotection only by specifying highly empirical, theoretically unjustifiable, and essentially arbitrary parameters. In the majority of cases, this falls to an OFF-potential value between -1200 mV and -1300 mV and/or an ON-potential limit is also specified. This situation is far from reassuring because overprotection can have severe consequences, too, particularly if the system also contains stainless steel (e.g., production tubing of wells) or lead (shielding of petroleum industry telephone and data cables) (*Table 1*).

Table 1: The value of protection potential for different metals [13]

Metals or alloys	Free corrosion potential: E_0 [V]	Protection potential: Ep [V] (IR-free)
Carbon steels (General soils)	between -0.65 and -0.40	-0.85
Carbon steels (T > 60 °C)	between -0.80 and -0.50	-0.95
Carbon steels (Aerobic conditions, 100 Ω·m - 1000 Ω·m resistivity)	between -0.50 and -0.30	-0.75
Carbon steels (Aerobic conditions, over 1000 Ω·m resistivity)	between -0.40 and -0.20	-0.65
Austenitic stainless steels Pitting Resistance Equivalent < 40	between -0.10 and +0.20	-0.50
Austenitic stainless steels Pitting Resistance Equivalent > 40	between -0.10 and +0.20	-0.30
Martensitic or duplex (austenitic-ferritic) stainless steels	between -0.10 and +0.20	-0.50
Stainless steels	between -0.10 and +0.20	to be determined
Copper or copper alloys	between -0.20 and 0.00	-0.20
Lead	between -0.50 and -0.40	-0.65
Aluminum alloys	between -0.70 and -0.50	-0.80
Galvanized steel	between -1.10 and -0.90	-1.20

In certain cases, when the application of the potential criterion is not expedient – for example, in evaluating the external protection of tank bottoms – the so-called -100 mV potential shift criterion is preferred, which, according to the literature and broader practical experience, can be considered appropriate [9,10,13].

2.4. Standards pertaining to the potential criterion

Standards provide the legal and technical frameworks for industrial activities. Although standards typically reflect the recent findings of a given scientific field, in contradictory or knowledge-deficient cases it can be difficult to reconcile scientific findings, practical expectations, and standards, and sometimes even clarity between or within the standards themselves. In the European Union, the European Standards (EN) are authoritative for cathodic protection as well; however, in the oil and gas industry, US standards are typically utilized. For the detailed discussion of the topic, three widely applied standards were considered: BS EN 12954:2019 [14]; DIN EN 13509:2003 [15]; NACE Standard TM0497-2012 [16].

From the perspective of measuring the potential criteria applied by the standards – which also vary as a function of environmental factors – the so-called OFF-potential or instant OFF-potential, to which the potential criterion is referenced, is of central significance.

The OFF-potential measurement procedure specified in BS EN 12954:2019 is as follows. A few microseconds after the synchronized interruption of the protective current, when the transient decay of the soil's RC circuit has already concluded, the ohmically compensated switch-off potential can be measured (*Figure 1*). The measurement must take place as soon as possible after the interruption, before significant depolarization occurs in the system due to the relaxation of the polarization resistance and the interfacial double layer's RC circuit (see Figure B2 of [14]). This ensures that the measured potential reflects, with a good approximation, the actual IR-free (instant OFF) electrode potential of the protected structure's surface. High-temperature media have a fundamental impact on the criteria for cathodic protection. As temperature increases, the rate of corrosion processes increases, too, which necessitates more rigorous control. Accordingly, while under normal conditions the generally accepted protection potential for carbon steels is -0.85 V (CSE), at operating temperatures above 60 °C, this threshold value is modified to -0.95 V [14]. Furthermore, the standard requires the omission of the 100 mV potential shift criterion in media above 40 °C. In the standard there is no further advice on the quality control of setting of CP at higher temperatures.

The OFF-potential measurement procedure specified in DIN EN 13509:2003 is as follows. The reference electrode must be placed in the soil, as close as possible to the structure under investigation, while simultaneously ensuring that it does not come into direct contact with the metal. In practice, the reference electrode is placed on the soil surface, except when a so-called permanently installed electrode is utilized. To measure the switch-off potential, the cathodic protection system must be briefly switched off. This can be accomplished manually or via an automatic timer. The potential measurement must be executed immediately following the disconnection to avoid rapidly changing

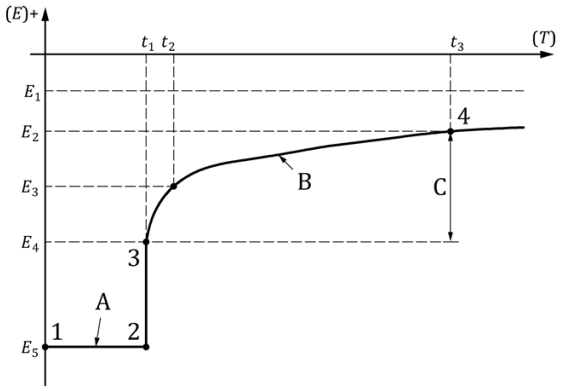


Figure 1: Transient decay according to the BS EN 12954:2019 standard [14]

t_1: Time of switching off the protection
t_2: Time of potential measurement
t_3: Time of potential measurement required for depolarization calculation
E_2: Potential difference between the protected structure and the electrolyte at time t_3
E_3: OFF- (measured) potential
E_4: Instant OFF-potential
E_5: ON potential

depolarization effects. This value is termed the instant OFF-potential.

Although the standard comprehensively discusses the measurement techniques of cathodic protection and mentions ambient temperature as a potential source of measurement error, it does not provide sufficient guidance for the investigation of high-temperature systems. While the document lists the theoretical potentials of the most common reference electrodes, it does not specify definite temperature coefficients for them. Consequently, this standard alone cannot be applied for the precise quantification and compensation of potential shifts occurring under extreme operational conditions.

The measurement of the OFF-potential according to NACE Standard TM0497-2012 [16] prescribes measurement conditions similar to the others. These include, for instance, the use of a saturated calomel electrode (SCE) and the synchronized interruption of the protective current. Furthermore, it emphasizes that a voltmeter of appropriate resolution or an oscilloscope should be utilized so that the voltage spikes generated during the voltage drop (*Figure 2*) can be disregarded, thereby preventing them from interfering with the measurement and the reading.

According to this standard, considering environmental factors, particularly temperature, is indispensable when measuring the effectiveness of cathodic protection. It stipulates that one possible cause of inaccurate measurements is the failure of the measuring personnel to apply the necessary temperature correction. According to the regulation, if the temperature of the reference electrode deviates significantly from the 25 °C (77 °F) reference value, appropriate correction factors must be applied to the measured values. Specific guidance is also available for

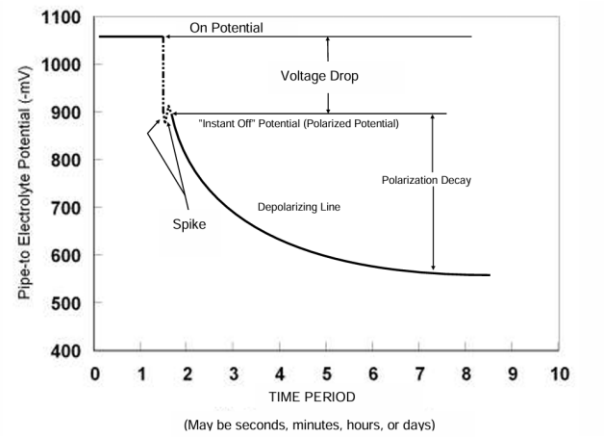


Figure 2: Transient decay according to the NACE Standard TM0497-2012 [16]

this: based on the calibration table, the temperature coefficient of the SCE is 0.97 mV/°C, that of the Ag/AgCl electrode is 1.0 mV/°C, the saturated calomel electrode's is 0.65 mV/°C, and the 1 M calomel electrode's is 0.24 mV/°C. The knowledge and practical application of these coefficients are critical for systems operating under extreme conditions, where without compensating for the voltage shift resulting from the temperature difference, the protection criteria and system effectiveness cannot be reliably evaluated. However, there is no indication also in this standard on the applicable potential criteria for different temperatures.

Figure 2 was taken from page 19 of the standard. Note the depicted transient voltage spikes, which make the reading of the instant OFF-potential uncertain even when it is otherwise technically feasible (e.g., via oscilloscope reading); in practice, these spikes can reach the magnitude of hundreds of millivolts.

2.5. Evaluation and mathematical analysis of the standard specifications

The standards mentioned in the previous section unambiguously prescribe the measurement method of the instant OFF-potential; however, they do not provide a reliable guideline on how this can be carried out under field conditions. During the measurement of the instant OFF-potential, the potential should be read immediately following the moment of disconnection to minimize the effect of depolarization. Precise timing is critical to achieving reliable results. The general practice is to read the potential 0.5–1.5 seconds after the current is switched off, simply because the applied multimeters (and human sensing) are too slow to catch the potential in the appropriate point immediately after the relaxation of the solution RC circuit and the subsequent inductive loop (if any). Obviously, this delay can introduce errors of up to several hundred millivolts, distorting the potential data and can lead to erroneous assessment.

Although a type of transient decay curve appears in the standards, none discuss this in detail. DIN EN 13509:2003 does not account for this transient, and its section 4.4.2.1 recommends reading the potential at approximately 1 second, asserting that the voltage is stable at this point. This strongly contradicts the definition of the instant OFF-potential. Consequently, a reading taken at an incorrect time significantly influences the measurement results and does not necessarily reflect reality. From the BS EN 12954:2019 standard, it emerges that the measurement must be performed somewhere within the transient, where the potential value is more stable. Executing this step encounters difficulties, as there is no truly stable, barely changing potential value on the curve of the transient decay. At the same time, this procedure deviates from the potential measurement method prescribed by the definition. According to NACE Standard TM0497-2012, voltage spikes frequently appear in the decay curve, which interfere with the measurement. As shown in *Figure 2* of the subject standard, it recommends reading the switch-off potential at a time instantly after the spike has decayed, but this can significantly differ from the true value. The standards all contain these inherent contradictions between the definition of the instant OFF-potential and its method of determination.

To resolve the contradictions within and between these standards, it is necessary to determine what can be measured and evaluated physically and how these measurements relate to the protection state. For precise evaluation, the IR-free potential must be used, as the voltage drop caused by the electrical resistance of the soil can cause distortion in the potential measurable on the surface [14]. Based on currently applied measurement practices, it cannot be known what the difference is between the instant OFF-potential and the corrosion potential valid under the given conditions.

The transient presented in the NACE Standard TM0497-2012 clearly shows that the curve has a well-defined, easily measurable intermediate section. It is important to investigate this section so that a true instant OFF-potential, and, if possible, the corresponding corrosion potential value, can be derived from its data. For this, the physical properties of the interfacial double layer must be considered, as well as the decay transients of the RC circuits present in the system, since this model best explains the physical content of the measured decay curves.

The lack of unified guidance for assessing high-temperature media is particularly striking. While the BS EN 12954:2019 standard recognizes the effect of temperature on electrochemical processes and prescribes a more stringent protection potential above 60 °C, it does not provide any provisions for the temperature correction of the reference electrodes, which is indispensable for the measurement. This practical deficiency is compensated for by the NACE TM0497-2012 standard, which assigns exact temperature coefficients to the measuring instruments, while DIN EN 13509:2003 merely mentions temperature as a general source of measurement error without specifying concrete compensation values or criterion modifications. It is thus clearly visible that these standards do not form a perfectly coherent system in the handling of extreme operational conditions, which

complicates the unambiguous qualification of measurement results.

Based on the equivalent circuit of the interfacial double layer (*Figure 3*), two parallel RC circuits connected in series with each other are distinguished in the system. When measuring the instant OFF-potential, the objective is to measure an IR-free potential, which means that the current is interrupted but the depolarization of the charge transfer RC circuit does not start yet. The decay transients of the RC circuits are shown in *Figure 4*.

The transient depolarization of the parallel charge-transfer RC circuit can be described using the laws of classical electricity. In the case of significant polarization (in the initial section of the curve), where the processes are dominated by charge transfer kinetics (BV equation):

$$J = J_0 \left(\exp\left[\frac{\eta}{b_A}\right] - \exp\left[-\frac{\eta}{b_C}\right] \right) \quad (1),$$

where b_A is the anodic and b_C is the cathodic Tafel slope, J_0 is the corrosion current density and η is the polarization, i.e., the difference of the ohmically compensated electrode potential and the corrosion potential. In the case of significant cathodic polarization (in the initial section of the depolarization curve), the system can be described by the following equation (see the details in Supplementary Material which is available in the Editorial Office of HJIC):

$$\frac{t}{E} = \frac{1}{b_C}\frac{\int_0^t E\,d\tau}{E} + (dE/dt)^{-1}|_{t=0} \quad (2),$$

where t is the time elapsed since switching the current off, E is the electrode potential – considering that at the onset of transient depolarization $t = 0$ and $E = 0$ (the potential values can be shifted with a constant value, provided that it is done consequently). In the later stage of the transient decay, approaching the corrosion potential, the behavior is determined by the time constant (t_0) of a classical RC circuit (cf. *Figure 3*). The equation derivable from this is formally analogous to *Equation 2*:

$$\frac{t}{E} = \frac{1}{E_0}\frac{\int_0^t E\,d\tau}{E} + \frac{t_0}{E_{corr}} \quad (3),$$

where E and E_0 are the electrode potential and the corrosion potential, respectively. Both equations utilize a transformed potential, where, due to the choice of scale, $E(t = 0) = 0$. Subsequently, the corrosion current calculable from the transient depolarization curve of cathodic polarization was determined. It is assumed that after the current is switched off, the sum of the current arising from the discharge of the double-layer capacitance and the Faradaic current of the system is zero:

$$J_F = -J_C = -\frac{dE}{dt} C_{DL} \quad (4),$$

where J_F is the Faradaic current, J_C is the capacitive current, and C_{DL} is the double-layer capacitance. Based on the BV equation, if the Faradaic current is substituted into the right side of the above equation, it yields:

$$\frac{dE}{dt} C_{DL} = J_0 \exp\left[-\frac{E-E_0}{b_C}\right] \quad (5),$$

where J_0 is the corrosion current density under the conditions of cathodic polarization, from which C_{DL} can be determined based on the initial conditions (cf. *Equation 4*):

$$J_{F,0} = -(dE/dt)^{-1}|_{t=0} C_{DL} \quad (6),$$

where $J_{F,0}$ is the current density measured at the end of the polarization phase preceding depolarization. Since the numerical determination of the time derivative of the potential from highly scattered measurement data is encumbered with high uncertainty, in practice, it is expedient to apply the time integral of *Equation 5*:

$$\int_0^t \frac{dE}{d\tau} d\tau = \frac{J_0}{C_{DL}} \int_0^t \exp\left[-\frac{E-E_0}{b_C}\right] d\tau \quad (7).$$

All the above derivations can be found in detail in the Supplementary Material. The practical significance of the above relationships lies in the fact that different physical parameters can be determined from different ranges of the measurement curve. From the initial points of the curve, based on the slope and intercept of

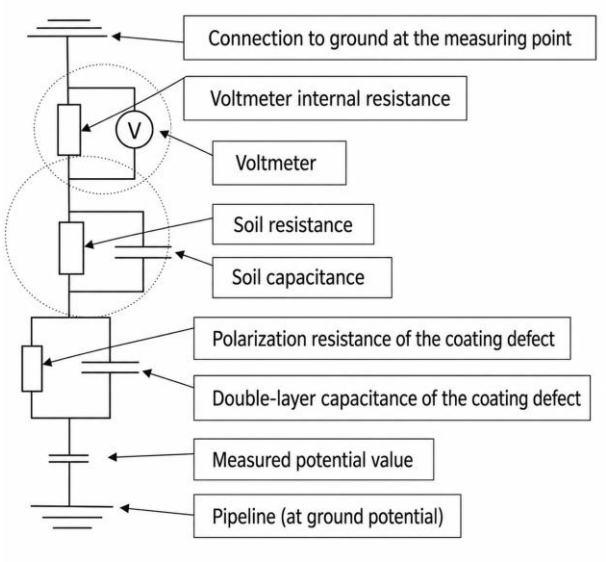


Figure 3: Schematic diagram of the interfacial double layer

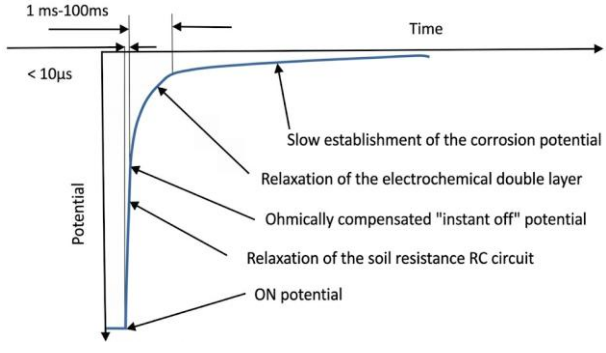


Figure 4: Sub-processes of transient depolarization

Equation 1, the kinetic characteristics ($1/b_C$ and the inverse of the initial derivative) can be obtained, whereas from *Equation 3*, fitted to the later section of the curve, values associated with the corrosion potential ($1/E_0$ and t_0/E_0) can be extracted and *Equation 6* provides the value of the corrosion current.

3. Experimental

When designing the experimental apparatus, a simple, clear configuration was prioritized. Two glass electrochemical cells, each with a volume of slightly more than 1 L, were used as experimental vessels; these were filled with liquid in five instances, and with washed sand in one instance. Different salt concentrations were prepared in the cells; the composition and temperature of the experimental series are shown in *Table 2*. With the exception of the soil-based test, the volume of the solution used was 1.2 dm^3 in all cases. The measurements were carried out using solutions containing 500 mg/dm^3 NaCl, and 500 mg/dm^3 NaCl combined with 100 mg/dm^3 Na_2CO_3, and/or 1000 ppm of Na_2S (see *Table 2*). In both the control and the soil-based measurements, 500 mg/dm^3 NaCl in the solution ensured the appropriate corrosive medium. These compositions simulated soils and formation waters of varying aggressiveness, to test cathodic protection at elevated temperatures under different corrosion rates. The experimental setup is shown in *Figures 5 and 6*.

To protect the reference electrode from the adverse effects of high temperature, the unpolarized electrode served as the reference electrode in each cell. During the relatively short measurement period, the potential of the unpolarized second test electrode was assumed to be unchanged or changed only slowly. Before and after each measurement, and also frequently during the experiment, the potential of the unprotected electrode was verified against an Ag/AgCl electrode. Since the potential of the Ag/AgCl electrode is approximately 100 mV more negative than that of the saturated Cu/$CuSO_4$ electrode, all reported data were converted to reflect the values measured with the Cu/$CuSO_4$ electrode.

Table 2: Data of the applied media

Series No.	Medium	Temp. [°C]	Composition
1.	Liquid	80	500 mg/dm^3 NaCl
2.	Liquid	80	500 mg/dm^3 NaCl + 100 mg/dm^3 Na_2CO_3
3.	Liquid	80	500 mg/dm^3 NaCl + 1000 ppm Na_2S
4.	Liquid	80	500 mg/dm^3 NaCl + 100 mg/dm^3 Na_2CO_3 + 1000 ppm Na_2S
5.	Sand	80	500 mg/dm^3 NaCl
6.	Liquid	25	500 mg/dm^3 NaCl



Figure 5: The assembled measurement cells and the thermostat



Figure 6: The measurement setup with the potentiostats and the controlling computers

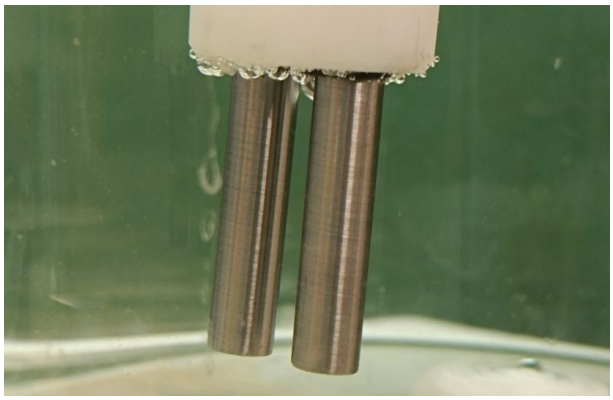


Figure 7: Protected and unprotected electrodes at the beginning of a measurement

Two test electrodes of identical material quality and geometry were placed into each cell. These electrodes had a diameter of 6 mm and a length of 30 mm (see *Figure 7*). The material of both the working electrode (modelling the cathodically protected structure)

and the unpolarized second test electrode in all series was DIN ST-52 type carbon steel, while a platinum mesh with a relatively large surface area served as the counter electrode.

The potential of the working electrode relative to the reference electrode in each cell was controlled by a PguEducation type laboratory potentiostat manufactured by IPS Elektroniklabor GmbH & Co. KG. A PICOSCOPE 4824 type instrument was used as the oscilloscope for recording the fast potential decays during the transient depolarization tests. The power supply was interrupted using a custom-built, adjustable, fast FET switch, which toggled the current on and off in response to the potential signal emitted by the oscilloscope within 1 µs. The FET switch was driven by the signal generator output of the oscilloscope (see the drawing of *Figure 8*). The oscilloscope was connected to a computer, which stored and visualized the data during the measurements. Throughout the experiment, the temperature of the glass reactors was controlled with an accuracy of ±1.5 K using an MTA KUTESZ 227 type ultrathermostat.

At the beginning of the measurement, the electrodes were inserted into the electrochemical cells, and the protective current was applied immediately after the electrical connections were established. Following the application of the current, the initial measurement was performed using a pre-configured program. This program also controlled the switching unit via the built-in signal generator of the oscilloscope. The program was used to record the transient curves on the protected electrode during each measurement. The ON-potential setpoints on the potentiostats were maintained throughout the experiment to ensure that the expected initial polarization value for the subsequent measurement was approximately 100 mV. In *Figures 9 and 10*, the horizontal axis represents time in seconds, while the vertical axis represents voltage in volts; the blue and red curves represent the potential difference measured at the working electrode relative to the reference electrode and the control signal generated by the oscilloscope, respectively. A practically imperceptible, minor ohmic potential drop can be noted at the moment the circuit is opened (*Figure 9*), and *Figure 10* shows a visibly significant ohmic potential drop.

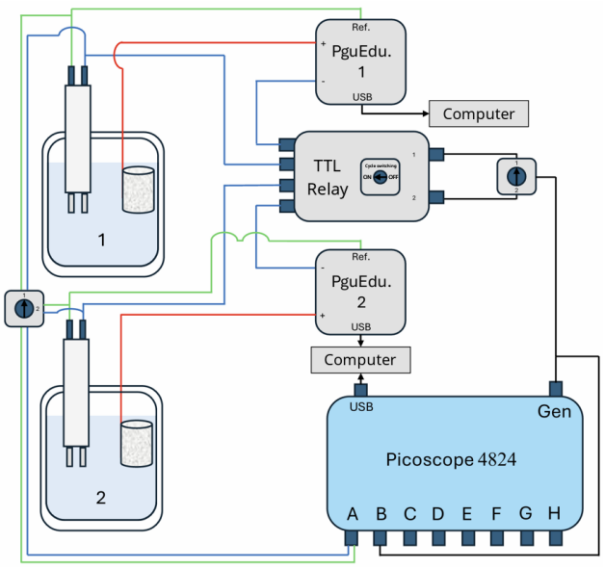


Figure 8: Circuit diagram of the system

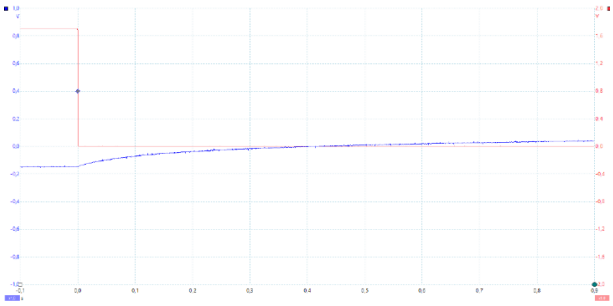


Figure 9: Decay transient of a cathodically protected system in an aqueous solution

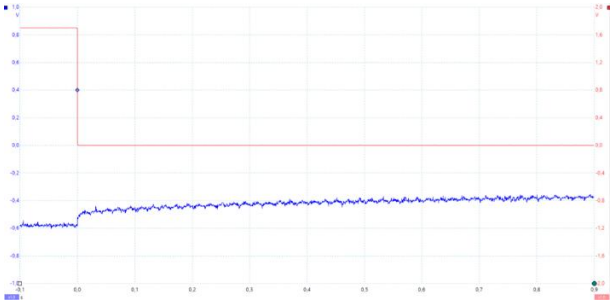


Figure 10: Decay transient of a cathodically protected system in soil

4. Results and discussion

Excluding the preparation phase, the total duration of the experimental series was 19 days (481 hours). During this period, a total of 25 measurements were conducted, during which the decay transients of the protected electrodes were recorded. The characteristic parameters of all measurements are summarized in tables, whereas the data for the solution containing 500 mg/dm³ NaCl were processed and plotted in the figures.

The raw measurement data sets were noticeably noisy (*Figure 11*); however, this situation accurately reflects real-world field conditions (field measurements of cathodic protection are invariably highly noisy). To prevent offsets during integration that could cause numerical and evaluation errors, transformations were applied to the measurement data. The curves in *Figure 12* were shifted by a constant value so that the first plotted potential data point, namely the OFF-potential, coincided with the origin of the coordinate system. Since a constant shift of the potentials does not affect the evaluation (analogous to potential values measured against

reference electrodes of different potentials), the parameters obtained from the transient depolarization curves will remain invariant under these shifts, provided that an appropriate inverse transformation is applied (if necessary). Evaluations according to *Equations 1, 2, and 4-6* were performed on these transformed curves.

The curves consist of three sections. The initial steep section cannot be described by a simple negative exponential equation, but it approximates the behavior of the BV equation. The cathodic slope value was determined from this region (cf. *Equation 1* and the related comments). The middle section can be approximated well by a negative exponential equation; therefore, the regular transient decay of an RC circuit can be accurately fitted in this region. This region roughly corresponds to the potential range of the LPR determination, from which the corrosion potential value was derived. Note that the corrosion potential can be assessed from this section according to *Equation 2*. The final, prolonged, and slowly changing section of the curve represents the slow depolarization phase, which is presumably controlled by relatively slow transport processes (e.g., diffusion) and not by kinetic depolarization.

The OFF-potential specified in the standards must be read from the first point of the curves following the current interruption (these correspond to the potential values at time $t = 0$ in *Figure 11*). Because of the potential shift required for more accurate evaluation, the OFF-potential is always 0 V in the applied coordinate system by definition; the corrosion potential, calculated according to *Equation 2*, is expressed as a positive value; its negative is the electrode's maximum polarization. In field practice, the OFF-potential is often read incorrectly because typically slow, inaccurate multimeters are used; thus, measurements frequently capture the final section of the curve, which increases the uncertainty in the measurement results and may lead to false decisions by the Operator.

The result of the linear transformation applied to the measurement data (based on *Equations 1 and 2*) is presented in *Figure 12*.

The value of the cathodic slope can be determined from the initial section of the dataset obtained through linear transformation, in accordance with *Equation 1*. The quadratic polynomial fitted to the measurement data is presented in *Figure 13*. The initial slope (i.e., the reciprocal of the cathodic slope according to *Equation 1*) can be obtained from the fitting parameters of the quadratic polynomial.

The question arises as to why the dataset in this region can be fitted with a quadratic polynomial rather than a linear function, as would be expected from *Equation 1*. It must be considered that, according to *Equation 1*, the polarization curve was assumed to be within the Tafel region. However, based on the values of the maximum polarization and the cathodic slope, it can be concluded that at this polarization level this assumption does not necessarily reflect reality with the expected accuracy. Nevertheless, it is certain that the slope and intercept data determined at the initial time

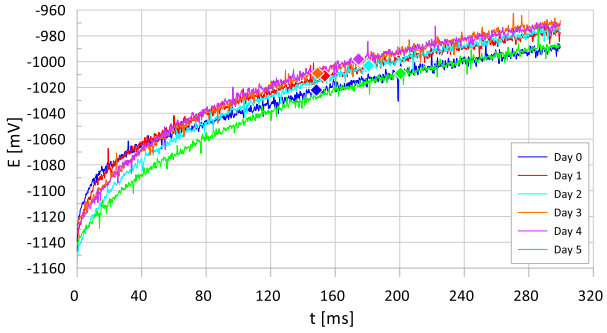


Figure 11: Measurement data from the solution containing 500 mg/dm^3 NaCl at 80 °C

*The colored diamonds indicate the corresponding corrosion potentials

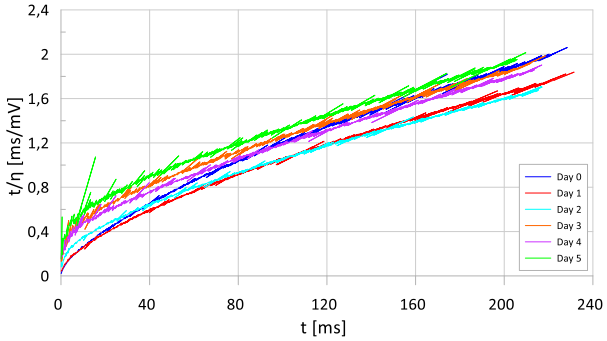


Figure 12: The linear transformation defined by *Equations 1 and 2*

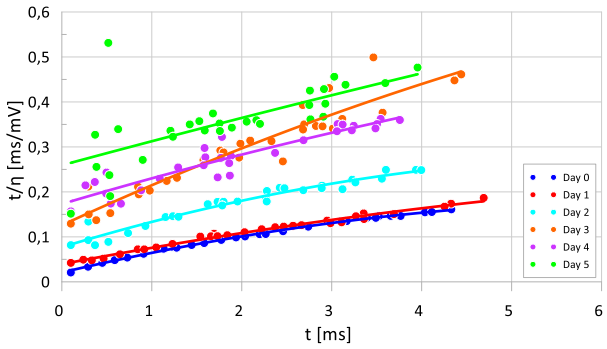


Figure 13: The first 30 points of *Figure 12* with the fitted quadratic polynomial

point reflect the value of the cathodic slope most accurately, as these points provide the best approximation of *Equation 1*.

From the medium section of the transformed curve (i.e., where the original curves are strictly negative exponential), the corrosion potential of the system can be determined in accordance with *Equation 2*. The corresponding linear fit is presented in *Figure 14*.

Utilizing the aforementioned equations and curve fittings, the cathodic slope, maximum polarization, and corrosion potential were determined for all 25 datasets. The data demonstrated similar fitting characteristics

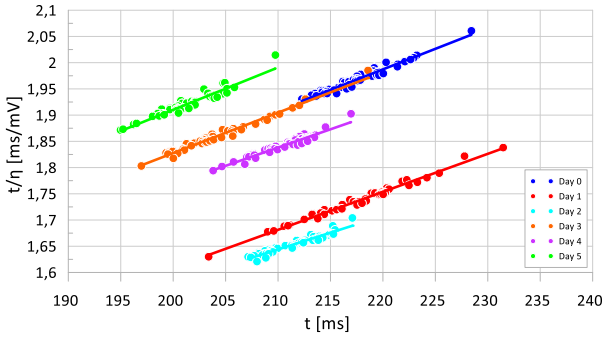


Figure 14: The last 30 points of *Figure 12* with the linear fit

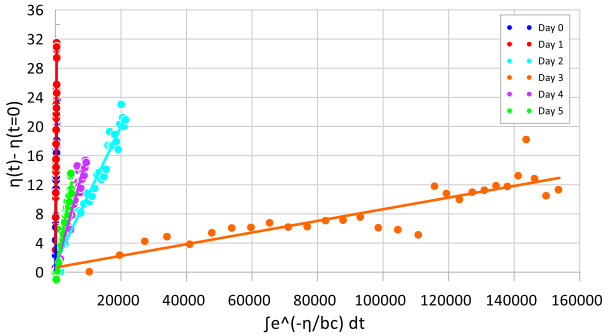


Figure 15: Lines used for determining the corrosion current

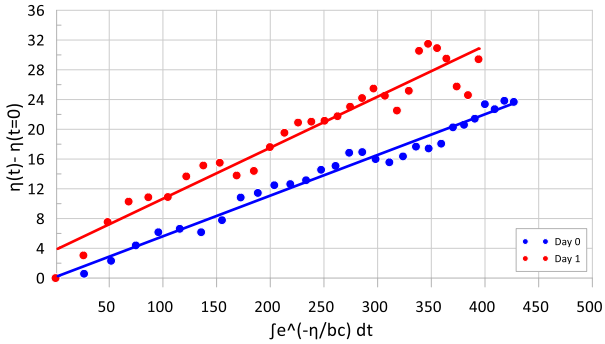


Figure 16: Lines used for determining the corrosion current (highlighting the first two lines)

across all measurement datasets. *Figures 15 and 16* present the corrosion current density values determined according to *Equation 4*. The data span a very wide range, which justified presenting them across two separate diagrams. This aspect will be specifically addressed during the discussion of the tables.

The photographs of the electrodes (*Figures 17 and 18*) demonstrate that the methodology is applicable for assessing the state of protection and that the protection was effective in all instances. Significant corrosion on the protected electrode is observable only in Series 5; however, in this configuration, the unprotected electrode suffered particularly severe corrosion damage, as clearly demonstrated by the photographs in *Figure 18*. The

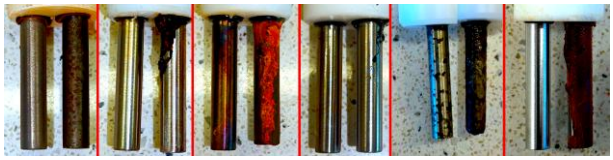


Figure 17: Electrodes after the measurements (the electrodes tested in different media, progressing from left to right from Series 1 to Series 6)



Figure 18: Series 5, 5% NaCl in sea sand (80 °C)

extensive corrosion on all high-temperature, unprotected electrodes is consistent with the theoretical conclusion that an increase in temperature dramatically elevates the corrosion rate in soil. Furthermore, this provides experimental evidence that protection criteria utilized at standard temperatures cannot be applied in these cases.

Regarding *Figure 18,* one can note the particularly significant corrosion damage on the unprotected electrode on the left side in both images (the protected electrode is placed in the middle). The electrode on the right is an additional "unpolarized" electrode used for reference purposes only.

In Series 5, the protected electrode also suffered mild corrosion, which may be related to the fact that the polarization did not reach the -100 mV value throughout the entire duration of the experiment (consistent with the observation that for electrodes without observable damage, the -100 mV polarization was maintained in all cases). This finding indicates that the extent of polarization of -100 mV is both necessary and sufficient for effective corrosion protection, even at the elevated temperatures applied during the measurement. Previous room-temperature measurements also indicated that a polarization of -100 mV is sufficient to maintain protection (these results have not yet been published).

In Series 3, the electrode became discolored. Although the exact cause is unknown, the surface remained smooth and uniform; therefore, there is no reason to assume significant corrosion.

Based on the tabulated results (*Tables 3-8*), the results indicate that if the calculated cathodic slope is below approximately 20 mV, the corrosion current can decrease by orders of magnitude. This phenomenon may correspond to the theoretical expectation that kinetic protection, following an adequate degree of surface polarization, can turn into thermodynamic protection. According to literature data, current densities several orders of magnitude lower are sufficient for adequate protection in this state [10].

Table 3: Results of Series 1 (80 °C, 500 mg/dm^3 NaCl solution)

Time [day]	b_C [mV]	η_0 [mV]	E_0 [mV]	E_{off} [mV]	I_{be} [mA]	J_0 [μA/cm^2]
0	21.3	-118.4	-1022	-1140	-14.9	2.86
1	26.2	-136.1	-1011	-1147	-11.1	5.96
2	16.5	-151.2	-1003	-1154	-2.00	0.03
3	10.8	-119.8	-1009	-1129	-1.33	0.01
4	16.9	-135.2	-998	-1133	-1.33	0.06
5	18.5	-133.1	-1009	-1142	-1.55	0.17

Table 4: Results of Series 2 (80 °C, 500 mg/dm^3 NaCl + 100 mg/dm^3 Na_2CO_3 solution)

Time [day]	b_C [mV]	η_0 [mV]	E_0 [mV]	E_{off} [mV]	I_{be} [mA]	J_0 [μA/cm^2]
0	23.2	-123.2	-1054	-1177	-5.6	3.61
1	8.6	-81.3	-1069	-1150	-3.1	0.01
2	39.8	-207.2	-1038	-1245	-9.3	4.89
3	15.0	-129.7	-1065	-1195	-3.18	0.08
4	11.8	-113.4	-1082	-1195	-2.5	0.02
5	15.1	-141.6	-1059	-1201	-2.35	0.03

Table 5: Results of Series 3 (80 °C, 500 mg/dm^3 NaCl + 1000 ppm Na_2S solution)

Time [day]	b_C [mV]	η_0 [mV]	E_0 [mV]	E_{off} [mV]	I_{be} [mA]	J_0 [μA/cm^2]
0	97.5	-231.7	-1068	-1299	-40	469
1	26.9	-161.5	-1172	-1333	-13.1	4.01
2	13.4	-123.6	-1149	-1272	-6	0.08
3	44.6	-212.5	-1087	-1299	-30	35.9
5	16.6	-136.6	-1008	-1145	-17	0.20
6	11.7	-114.7	-990	-1105	-15	0.02
7	9.7	-80.7	-939	-1020	-7.3	0.03

Table 6: Results of Series 4 (80 °C, 500 mg/dm^3 NaCl + 100 mg/dm^3 Na_2CO_3 + 1000 ppm Na_2S solution)

Time [day]	b_C [mV]	η_0 [mV]	E_0 [mV]	E_{off} [mV]	I_{be} [mA]	J_0 [μA/cm^2]
0	20.3	-122.0	-1190	-1312	-10	4.27
1	17.8	-139.5	-1166	-1305	-5.95	0.19
2	11.8	-113.3	-1153	-1266	-3.4	0.03
3	17.2	-154.1	-1145	-1299	-5.2	0.08
5	4.8	-101.7	-1060	-1161	-1	2.5E-08
6	6.3	-95.1	-1078	-1173	-1	2.0E-05
7	4.1	-72.0	-1102	-1174	-0.9	5.3E-07

Table 7: Results of Series 5 (80 °C, 500 mg/dm^3 NaCl solution in sand)

Time [day]	b_C [mV]	η_0 [mV]	E_0 [mV]	E_{off} [mV]	I_{be} [mA]	J_0 [μA/cm^2]
0	38.5	-128.3	-1224	-1353	-7.4	13.4
1	40.4	-163.6	-1175	-1338	-9.0	9.88
2	19.9	-91.2	-1217	-1308	-5.7	2.32
3	16.7	-94.6	-1185	-1279	-4.8	0.08
4	25.1	-92.9	-1270	-1363	-3.6	3.53
10	32.5	-52.6	-1141	-1194	-0.8	8.38

Table 8: Results of Series 6 (25°C, 500 mg/dm^3 NaCl solution) (control).

Time [day]	b_C [mV]	η_0 [mV]	E_0 [mV]	E_{off} [mV]	I_{be} [mA]	J_0 [μA/cm^2]
0	50.1	-194.6	-1023	-1218	-7.6	24.5
1	35.1	-209.8	-922	-1132	-3.3	1.40
2	13.6	-208.9	-831	-1040	-1.9	4.6E-05
3	6.4	-160.4	-782	-942	-1.1	5.7E-10
4	5.9	-95.3	-780	-875	-0.7	1.7E-06
10	6.0	-119.8	-733	-853	-0.6	8.5E-08

5. Conclusion

Using the previously developed experimental methodology, polarization measurements were conducted at 80 °C on cathodically protected test specimens.

The results indicate that the protection criterion (-850 mV versus CSE) is not applicable under such conditions. In contrast, by evaluating the depolarization transients, the cathodic slope, the corrosion potential, and the corrosion current in the polarized state can be determined.

Based on the results of the proposed new evaluation procedure, the system remains cathodically protected even at elevated temperatures when the ohmically compensated polarization is at least −100 mV relative to the calculated corrosion potential.

With adequate polarization, the calculated corrosion current and the calculated Tafel slope steeply decrease after a while; if the value of the cathodic Tafel slope decreases to below approximately 20 mV the calculated corrosion current can decrease by orders of magnitude. This state may correspond to the "thermodynamic protection," discussed in the corrosion literature, which requires a protective current roughly two orders of magnitude lower than that required for so-called "kinetic protection."

Acknowledgements

Project no. 2025-2.1.1-EKÖP-2025-00029/81 has been implemented with the support provided by the Ministry of Culture and Innovation of Hungary from the National Research, Development and Innovation Fund, financed under the 2025-2.1.1-EKÖP funding scheme.

REFERENCES

[1] Ani, M. H., Azman, M. A. F., Musa, M., Anhar, Z., & Hamid, M. (2020). High temperature cathodic protection of Fe-Cr alloy. *IOP Conference Series: Materials Science and Engineering, 864*(1), Article 012031. https://doi.org/10.1088/1757-899X/864/1/012031

[2] Lukacs, Z. (2012). Application of the remote earth potential in cathodic protection measurements. *Hungarian Journal of Industry and Chemistry, 40*(2), 77–82, https://doi.org/10.1515/345

[3] Macdonald, D. D. (1978). Reference electrodes for high temperature aqueous systems—A Review and assessment. *Corrosion, 34*(3), 75–84. https://doi.org/10.5006/0010-9312-34.3.75

[4] Trasatti, S. (1980). The electrode potential. In J. O. Bockris, B. E. Conway, & E. Yeager (Eds.) *Comprehensive treatise of electrochemistry* (pp. 45–81). Springer. https://doi.org/10.1007/978-1-4615-6684-7_2

[5] Trasatti, S. (1986). The absolute electrode potential: an explanatory note (Recommendations 1986). *Pure and Applied Chemistry*, 58(7), 955–966. https://doi.org/10.1351/pac198658070955

[6] Beverskog, B., & Puigdomenech, I. (1996). Revised Pourbaix diagrams for iron at 25-300 °C. *Corrosion Science, 38*(12), 2121–2135. https://doi.org/10.1016/S0010-938X(96)00067-4

[7] Bácskai, Gy. (1967). *Soil-induced corrosion* (in Hungarian). Tankönyvkiadó

[8] Büchler, M., Angst, U., & Ackland, B. (2017). Cathodic protection criteria: A discussion of their historic evolution. In *European Corrosion Congress (EUROCORR 2017) and 20th International Corrosion Congress and Process Safety Congress 2017* (Vol. 1, pp. 428–451). Curran Associates, Inc.

[9] Angst, U. M. (2019). A critical review of the science and engineering of cathodic protection of steel in soil and concrete. *Corrosion, 75*(12), 1420–1433. https://doi.org/10.5006/3355

[10] Joint EFC/CEOCOR Working Goup. (2021). *Cathodic protection criteria for buried carbon steel structures.* [Report]. https://ceocor.lu/wp-content/uploads/2022/12/Cathodic-protection-criteria-for-buried-carbon-steel-structures-joint-WG-EFC-CEOCOR-202105-resized2.pdf

[11] von Baeckmann, W., Schwenk, W., & Prinz, W. (1997). *Handbook of cathodic corrosion protection*. (3rd ed.). Gulf Professional Publishing.

[12] Kuhn, R. J. (1933). Cathodic protection of underground pipelines from soil corrosion. *API Proceedings, 14*, p. 157.

[13] Attarchi, M., Mohamad, S., Mirghafourian, S., & Karladani, M. N. (2015). Selecting appropriate cathodic protection criteria for tank bottom using polarization method. In *European Corrosion Congress (EUROCORR 2015)* (Vol. 1, pp. 1611–1617). Curran Associates, Inc.

[14] British Standards Institution. (2019). *General principles of cathodic protection of buried or immersed onshore metallic structures* (Standard No. BS EN 12954:2019).

[15] Deutsches Institut für Normung. (2003). *Cathodic protection measurement techniques* (Standard No. DIN EN 13509:2003).

[16] NACE International (2012). *Measurement techniques related to criteria for cathodic protection on underground or submerged metallic piping systems* (NACE Standard TM0497-2012).