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Corrosion of metals and alloys — Multielectrode arrays for corrosion measurement

Corrosion des métaux et alliages — Assemblages multi-électrodes pour la mesure de la corrosion

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Foreword

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This document was prepared by Technical Committee ISO/TC 156, *Corrosion of metals and alloys*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Multielectrode array technology has been used to study electrochemical behaviours and the localized corrosion of metals and alloys since the 1970s[1] to [5]. It has been demonstrated that multielectrode arrays are highly powerful tools for studying the spatiotemporal behaviour of metals in laboratories[2] to [16] and for monitoring non-uniform corrosion, especially localized corrosion in laboratories and plants[17]. Multielectrode arrays are also used as high throughput probes for studying the statistical behaviour of metal corrosion[1][18] and for the evaluation of inhibitors[19].

This document is designed to outline the requirements and procedures for conducting corrosion measurements using multielectrode arrays.

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Corrosion of metals and alloys — Multielectrode arrays for corrosion measurement

1 Scope

This document specifies the methodology of using multielectrode arrays for the measurement of the corrosion, especially localized corrosion, of metals and alloys. It can be used as a powerful tool for studying the initiation and propagation processes of localized corrosion. It is also a useful tool for long-term corrosion monitoring in the field, especially for localized corrosion, and for obtaining high throughput results for the evaluation of metals with different compositions and/or physical properties in different environments and the screening of a large number of inhibitors. Additionally, the galvanic coupling current and potential distribution of dissimilar metal pairings can be assessed by multielectrode arrays. Multielectrode arrays can be implemented in full-immersion, thin-film, spray and alternating wet–dry cycle exposures.

This document is not intended to be used for measurements of corrosion caused by a non-electrochemical mechanism.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 8407, *Corrosion of metals and alloys — Removal of corrosion products from corrosion test specimens*

ISO 8044, *Corrosion of metals and alloys — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 8044 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
uneven general corrosion
corrosion that occurs over the whole exposed area of a metal at different rates across the exposed area

Note 1 to entry: It is a type of general corrosion, as defined in ISO 8044, that produces an uneven or wave-like surface[20][21] where the thickness reduction at the more corroded areas is significantly larger than the thickness reduction at the less corroded areas or the average corroded areas.

3.2
non-uniform corrosion
corrosion that occurs at different rates over a metal surface where there is a localized surplus of net anodic or net cathodic rates such that a localized area does not exhibit charge neutrality and electrons flow within the metal from the anodic-dominant areas to the cathodic-dominant areas

Note 1 to entry: Non-uniform corrosion includes both localized corrosion, as defined in ISO 8044, and *uneven general corrosion* (3.1). Non-uniform corrosion also includes the type of general corrosion that produces even surfaces at the end of a large time interval, but uneven surfaces within small time intervals.

3.3
multielectrode array
device consisting of multiple electrodes for corrosion studies and corrosion monitoring

Note 1 to entry: The electrodes in a multielectrode array can either be arranged in an organized pattern on a 2D plane or packed randomly on a 2D plane or in a 3D space. When the electrodes are randomly packed, the word "array" in the term means that there are many electrodes in the device.

3.4
zero-voltage ammeter
ZVA
ammeter that imposes a negligibly low voltage drop when inserted into a circuit for measurement of current

Note 1 to entry: When a ZVA is used to measure the coupling current between two electrodes, the two electrodes are essentially at the same potential.

Note 2 to entry: Both a *zero-resistance ammeter* (3.5) and a simple device formed with a shunt resistor and a voltmeter can be used as the ZVA providing they do not impose a significant voltage drop (< 2 mV) in the current-measuring circuit.

3.5
zero-resistance ammeter
ZRA
zero-voltage ammeter (3.4) that has a near zero dynamic resistance when inserted into a circuit for measurement of current

Note 1 to entry: ZRA is usually built with operational amplifiers and may impose a voltage between 50 µV and 2 mV in the current-measuring circuit.

Note 2 to entry: When the measured current is in the nanoampere range or lower as often found in the *multielectrode arrays* (3.3), the ZRA's static resistance determined with Ohm's Law (ratio of voltage to current) is usually higher than 50 000 ohm, even though its dynamic resistance (derivative of voltage to current) is near zero ohm.

3.6
coupled multielectrode array
CMA
multielectrode array (3.3) whose electrodes are coupled together by wires or through the use of a multichannel *zero-voltage ammeter* (3.4) between the electrodes and the coupling joint so that all the electrodes connected to the coupling joint are essentially at the same potential

3.7
coupled multielectrode array sensor
CMAS
coupled multielectrode array (CMA) (3.6) that is used as a sensor for corrosion monitoring

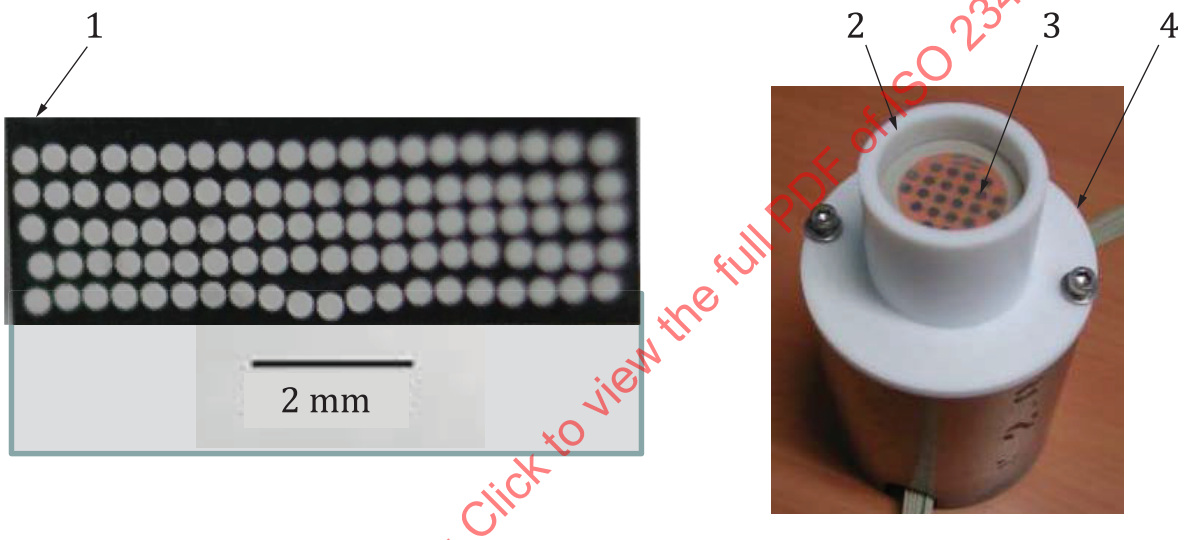
Note 1 to entry: The outputs of a typical CMAS are usually simple parameters such as maximum corrosion rate and maximum penetration depth, while the outputs of a typical CMA are usually the large number of currents and/or potentials from all the electrodes.

3.8
cathodic protection effectiveness margin
cathodic protection margin of effectiveness
CPEM
degree of cathodic protection derived from the current of a *coupled multielectrode array sensor* (3.7) that has a value of 0 % when the cathodic protection starts to be adequate in terms of acceptable corrosion rate (e.g. 0,01 mm/a or 0,0 mm/a), and a value of 100 % when excessive hydrogen evolution starts

4 Principle

4.1 Multielectrode arrays

One of the characteristics of non-uniform corrosion, especially localized corrosion, on a metal surface is that there are some small areas that are more anodic and some small areas that are less anodic or that are cathodic. Multielectrode arrays, as shown in Figure 1, are highly effective tools for studying non-uniform corrosion. In Figure 1 a), the electrodes of the multielectrode array were closely packed in a 5 × 20 pattern to simulate the metal surface for studying the spatiotemporal behaviour of corrosion[10]. In Figure 1 b), the multielectrode array was buried under sands in a cup to evaluate under deposit corrosion[22]. In general, the electrodes in a multielectrode array for spatial-temporal studies are arranged in regular patterns on a 2D plane, such as those shown in Figures 1 and 2, and this type of multielectrode arrays are also called "wire beam electrodes"[2][13]. The multielectrode arrays may also be arranged randomly on a 2D plane or 3D space [1][18]. In this case, the word "array" in the term means that there are many electrodes in the device.



a) With closely packed electrodes for spatial-temporal corrosion studies[10]

b) With a sand cup for evaluation of under-deposit corrosion[22]

Key

1 5 × 20 electrodes flush-mounted in epoxy
2 sand-holding cup
3 24 electrodes
4 heating device

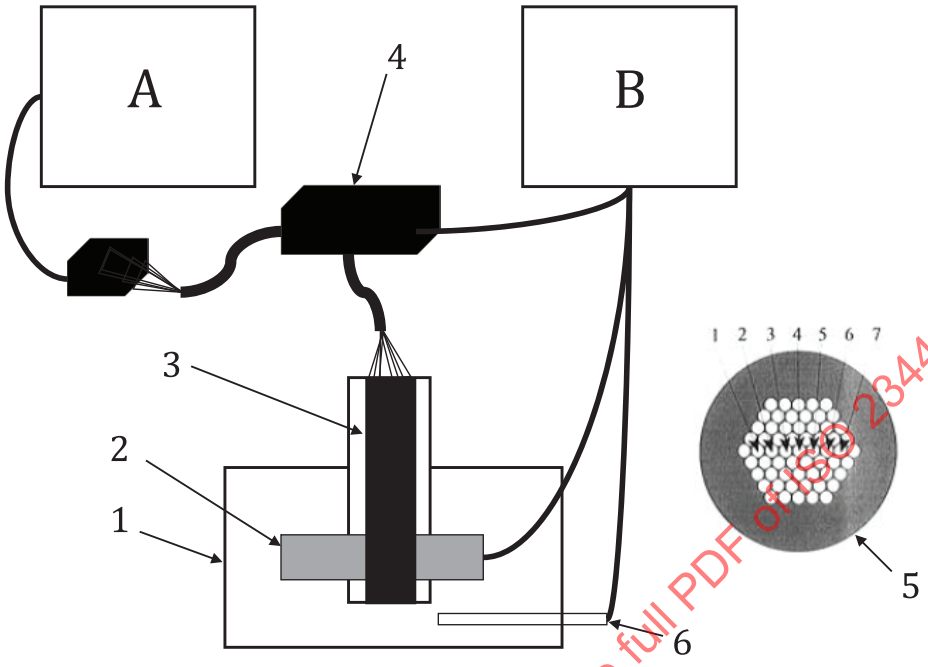
Figure 1 — Typical multielectrode arrays

The currents of the electrodes composing the array can be measured individually. It is possible to measure the potentials of each individual electrode, of a selected group of electrodes, or the totality of the electrodes if they are coupled (see below). It is at times technically feasible to polarize one or more electrodes using a single-channel potentiostat or a multi-channel potentiostat in order to evaluate the effects of polarization on the neighbouring electrodes[10]. Because of the small size of the electrodes in the array, the polarization currents are usually very small (less than 1 μA) and their effects on the measurements of the potential of the neighbouring electrodes due to the IR drop can be ignored.

4.2 Coupled multielectrode array (CMA)

If all the electrodes or a selected number of electrodes in a multielectrode array are coupled together by wires or through the use of multichannel ammeters that impose near-zero voltages between the electrodes and the coupling joint so that all the electrodes connected to the coupling joint are essentially at the same potential, such multielectrode array is called a "coupled multielectrode array (CMA)". The ammeters that impose near zero voltage are called "zero-voltage ammeters (ZVAs)" and are described

in 5.2. Figure 2 shows a typical CMA system where all the electrodes are controlled at the same potential by the potentiostat through a multichannel ZVA box[3].



Key

A	multichannel data acquisition system	4	multichannel ZVA
B	potentiostat	5	bottom view and electrode ID of the array
1	electrochemical cell	6	reference electrode
2	counter electrode		
3	CMA		

NOTE 1 All electrodes are at the same potential.

NOTE 2 The counter electrode is electrically separated from the multielectrode array.

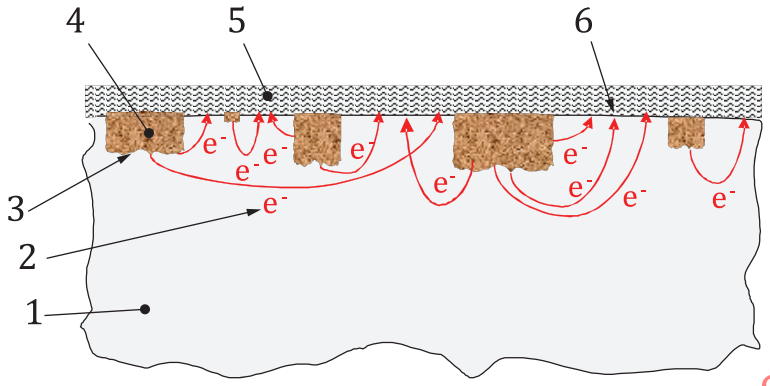
Figure 2 — Typical CMA system for electrochemical studies under polarization conditions[3]

4.3 Multielectrode array with closely packed electrodes for studying spatiotemporal behaviour of localized corrosion

4.3.1 If the electrodes are arranged in an organized pattern such as 4 × 4, 5 × 20 or 10 × 10 and the electrodes are closely packed and their size are small (typically < 1 mm in diameter), such multielectrode array may be used to study the spatial and temporal behaviour of corrosion on a metal surface, e.g. when and where localized corrosion first initiates and how the localized corrosion propagates on the metal surface. Annex A shows a typical use of the CMA for studying the spatial and temporal behaviour of corrosion.

4.3.2 The CMA may also be used at its corrosion potential without any polarization. In a typical case of localized corrosion where there is clear separation of anodes and cathodes, the array simulates a one-piece metal section for which the electrodes that have net anodic currents simulate the anodic areas and the electrodes that have net cathodic currents simulate the cathodic areas on the metal surface as shown in Figure 3. By measuring the electron flow from the anodic electrodes to the cathodic electrodes on the

array as a function of time, the information of the initiation and propagation of localized corrosion that takes place on the metal under freely corroding conditions can be obtained.



Key

1	metal	4	corrosion products and electrolyte
2	electrons	5	corrosive electrolyte (liquid, thin, film or wet deposits)
3	anodic sites	6	cathodic sites

NOTE The electrons flow randomly in metal from anodic sites to cathodic sites. Cathodic reactions such as $O_2+4e^-+2H_2O = 4OH^-$ occur at the cathodic sites. Anodic reactions such as $Fe-2e^-+2H_2O = Fe(OH)_2 + 2H^+$ occur at the anodic sites.

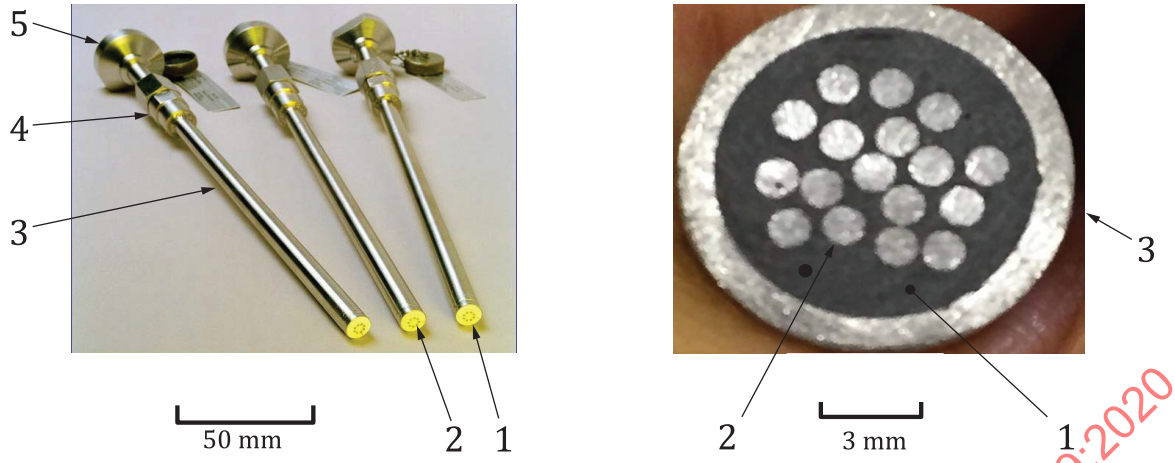
Figure 3 — Typical characteristics of localized corrosion on a metal surface at its corrosion potential — Electrons flow from anodic areas to the cathodic areas within the metal[4]

In a typical non-uniform general corrosion case, there is no clear separation of anodes and cathodes, but some areas corrode more and some areas corrode less and all areas are anodic, at least for a short duration during corrosion process. The electrodes on the array that have net anodic currents simulate the more corroding areas and the electrodes that have net cathodic currents simulate the less corroding areas.

4.4 Coupled multielectrode array sensor (CMAS)

4.4.1 CMAS for corrosion monitoring

If a CMA is used as a sensor for corrosion monitoring, such a CMA is called a "coupled multielectrode array sensor (CMAS)". Figure 4 shows some typical CMASs. Unlike a CMA for spatial studies, a CMAS for field applications usually has fewer electrodes [see Figure 4 a)] and the electrodes can be randomly packed [see Figure 4 b)]. There is no need for a plant operator to know all the individual currents and create a corrosion map for a sensor in the fields. It often suffices for the operator to know the maximum corrosion rate, at the worst corroding area, and the associated maximum penetration depth, without needing to know where exactly these worst areas are. The outputs of the CMAS probes are often those two simple parameters: maximum corrosion rate (calculated from the most anodic current, which is from the worst or most corroding electrode) and maximum penetration depth (calculated from the most corroded electrode). The operators can apply their corrosion mitigation measures (e.g. by adding a corrosion inhibitor) based on the maximum corrosion rate. On the other hand, the engineers may decide how often the plant equipment should be inspected based on the maximum penetration depth (see ASTM G217-16 for additional information[36]).



a) CMAS with 8 electrodes for high-temperature and high-pressure systems[4]

b) CMAS 16 electrodes packed randomly[31]

Key

1 insulator
2 electrodes
3 probe body
4 fitting for mounting to pressure vessel
5 electrical connector

Figure 4 — Typical CMAS with randomly packed electrodes for field applications

4.4.2 CMAS used without polarization to measure corrosion rate at free corrosion potential

CMAS probes are often used without any polarization. In this case, all the electrodes that are coupled together simulate the behaviour of a one-piece metal section at the free corrosion potential. The non-uniform corrosion rates measured from the CMAS probe corresponds to the non-uniform corrosion occurring at the different anodic sites under the freely corroding condition. B.1 shows some typical corrosion rates in different environments measured with a CMAS probe made of 16 carbon steel electrodes.

Because of the existence of local cathodes (see Figure 5) on each electrode when the CMAS is not sufficiently polarized, the corrosion current measured by the ZVA in the external circuit may underestimate the corrosion rate on each electrode. This is especially true for the case of uniform corrosion, therefore the non-polarized CMAS probe is not suitable for uniform corrosion. For non-uniform corrosion cases, however, the worst corroding electrode, when its potential is raised significantly by the other less corroding electrodes, usually does not have significant local cathodic current, and the maximum corrosion rate of a CMAS probe that is calculated from the worst corroding electrode is often close to the corrosion rate occurring on this electrode. When the CMAS electrodes are sufficiently polarized, such as the case when monitoring corrosion of cathodically protected systems or stray-current affected systems (see 4.4.3), the local cathode effect is less important because all the electrodes are sufficiently polarized from their corrosion potentials.

4.4.3 CMAS used to evaluate the effectiveness of cathodic protection and the effect of stray current

As mentioned in 4.3.2, a CMA can be used with or without polarization. When the coupling joint where all the electrodes are coupled to is connected to a metal structure under cathodic protection (CP), all the electrodes are polarized to essentially the same CP potential as the metal structure (see Figure 5). Then, the CMAS measures the corrosion under CP conditions. When the CP is insufficient, one or more of the electrodes will undergo corrosion and the maximum corrosion rate calculated from the most corroding electrode is a good indicator for the insufficiency of the CP. When the corrosion rate as indicated from the most corroding electrode is near zero, all the electrodes are protected by the CP.

Because the lowest corrosion rate is zero, it cannot be used to indicate the degree of protection by the CP, except for showing that the CP is effective, when the corrosion rate from the most corroding electrode is zero. Another parameter, the "cathodic protection margin of effectiveness" or "cathodic protection effectiveness margin (CPEM)", which is defined as the ratio of the cathodic current from the most corroding electrode to a maximum allowable cathodic current that corresponds to excessive hydrogen evolution, can be used to indicate the degree of CP[23].

When the CPEM is larger than zero, the current from the most corroding electrode is cathodic (has the same sign as the maximum allowable cathodic current) and there is no corrosion from any of the electrodes on the CMAS. Therefore, all of the electrodes are fully protected. When the CPEM is 100 %, however, the most anodic electrode starts to experience excessive hydrogen evolution, which should be avoided. Therefore, the CPEM should be controlled above zero and below 100 %. B.2 shows the typical responses of the corrosion rate and CPEM from a CMAS when the CP potential varies from the corrosion potential (about −0,7 V versus $Cu/CuSO_4$) to a large negative potential (lower than −1,25 V versus $Cu/CuSO_4$).

If the CP is considered adequate when the corrosion rate is lower than a predetermined acceptable level (e.g. 0,01 mm/a), the CPEM may also be defined such that its value is 0 % when the corrosion rate from the CMAS is at this acceptable level and 100 % when excessive hydrogen evolution occurs. Because the CPEM is related to how safely a CP system protects the metal structure, it is also called "cathodic protection safe margin (CPSM)"[23].

Compared with the CP criteria based on the instant-off potential measurements, the method provided by the CMAS does not require the use of the reference electrode. The reference electrode usually requires regular maintenance and has a shorter life than the CMAS probe, which has only solid components and can last for 10 to 50 years under dry or wet conditions.

4.5 Multielectrode arrays for high throughput measurements

Corrosion behaviours, especially localized corrosion behaviours, of metals are usually stochastic. For example, localized corrosion rates for carbon steel may vary by 200 % to 600 % in seawater[24]. Therefore, a statistical approach should be used to characterize the corrosion behaviour of metals and a large number of samples tested in the same solution under the same environmental conditions are required to derive a statistical conclusion. Multielectrode arrays are highly efficient for such statistical studies[18]. The development of inhibitors requires the evaluation of the performance of a large number of formulations and multielectrode arrays can also be useful for such evaluations[19].

4.6 Multielectrode arrays for other applications

Multielectrode arrays can also be used in many other applications, including the following.

— Assessing the electrochemical behaviour of a material across various weld zones. As a material is welded, various zones are created that differ in properties due to the differences in cooling rates and heat treatment from welding. These differences in properties are spatially dependant and can be assessed with multielectrode arrays[25].

— Understanding the galvanic throwing power of sacrificial anodes by measuring the coupling current and potential distributions between the sacrificial anode and the surrounding electrodes being cathodically protected[26].

— Studying the effect of corrosion inhibitors on reducing the anodic or cathodic reaction rates at an electrode interface, especially for spatial-temporal release from inhibitor containing coatings.

5 Instrumentation

5.1 Potential measurement

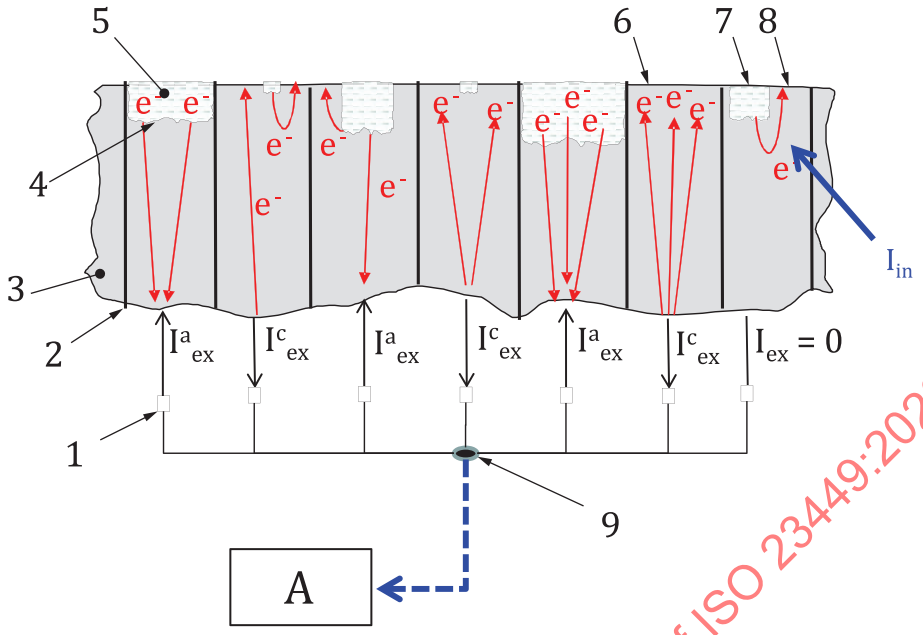
When the multielectrode array operates in an uncoupled configuration, the open-circuit potential of each electrode should be measured individually against a reference electrode. When the multielectrode array is used in a laboratory as a CMA, the coupling joint potential that is a mixed potential for all the coupled electrodes should be measured against the reference electrode. This is essential when the array is polarized or one or more groups of selected electrodes are polarized to different potentials. Because the potential is not needed to derive the corrosion rate, it is not necessary to measure the potential of the array when the array is used as a CMAS probe for corrosion monitoring.

A multichannel voltammeter or a single channel voltmeter with a multichannel switching mechanism may be used for measuring the open-circuit potential of the individual electrodes or one or more groups of selected electrodes against a reference electrode immersed in the same solution. Because the single electrode surface area of a typical multielectrode array is small (usually less than 1 cm^2), the input impedance of the voltmeter must be high enough so that it does not withdraw a significant amount of current that would cause the unwanted polarization of the electrodes. Input impedance of more than 100 GΩ is usually acceptable, unless the solution conductivity is extremely low or the kinetics of the electrode is extremely slow.

5.2 Coupling current measurement

Figure 5 shows a typical schematic diagram for the measurements of the coupling currents from the coupled electrodes with or without the polarization. The working electrode (WE) of a potentiostat or a metal structure under CP can be connected to the coupling joint to polarize the CMA. According to 4.2, the ZVAs in Figure 5 impose near-zero voltage, so all the electrodes are at the same potential[27]. A simple device formed with a shunt resistor and a voltmeter for the measurement of current by applying Ohm's Law is one type of ZVA, as long as they do not impose a significant voltage drop in the current-measuring circuit. The zero-resistance ammeter (ZRA) as defined in ASTM 199 for electrochemical noise measurements (see ISO 17093[35]) is another type of ZVA.

Regardless of the type of ZVAs, they all impose a small voltage in the measuring circuit. The effect of the voltage imposed by the ZVA on the measurement of current depends on the open-circuit potential between the measured electrode and the coupling joint after the measured electrode is decoupled. The variation in the open-circuit potentials of the identical electrodes in the CMAs is usually large (e.g. 20 mV to 300 mV[13]) in corrosive environments, which causes uneven general corrosion or localized corrosion.



Key

A	WE of potentiostat or metal under CP	7	local anodic site
1	ZVA	8	local cathodic site
2	insulator between electrodes	9	coupling joint
3	metal	I^a_{ex}	external anodic current that flows through the ZVAs
4	anodic site	I^c_{ex}	external cathodic current that flows through the ZVAs
5	corrosion products	I_{in}	internal current that flows within an electrode
6	cathodic site		

Figure 5 — Schematic diagram for the measurement of coupling currents with or without the polarization by a potentiostat or metal under CP

When the open-circuit potential of an electrode is 20 mV away from the coupling potential, the error in measured current caused by a voltage of 0,5 mV is less than 5 % of the theoretical value[28]. In general, the maximum voltage imposed by the ZVAs for use with a CMA should not exceed ±1 mV.

5.3 Effective coupling of individual electrodes

5.3.1 Coupling with multichannel ZVA

When multiple ZVAs or a multichannel ZVA are used to measure the coupling currents as shown in Figure 5, the individual electrodes are also permanently coupled to the coupling joint by the ZVAs. Because all areas of a one-piece metal have the same potential, the voltages imposed by the multiple ZVAs may also affect the ability for the multiple electrodes to simulate the behaviour of the one-piece metal. For example, if one of the ZVAs imposes a significant positive voltage between an anodic electrode and the coupling joint, the potential of this anodic electrode is lower than the potential of the coupling joint and this electrode would corrode at a lower rate than at the coupling potential. Therefore, the voltage imposed by the worst ZVA (or the worst channel of the multichannel ZVA) shall be as small as possible and should not exceed ±1 mV for most applications.

The advantage for using the ZVA to couple all individual electrodes is that both the coupling of the individual electrodes and measurement of the coupling current are achieved by using the same ZVA and there is no need for switching on and off the electrode being measured, which may produce transient noises and affect the electrochemical processes on the electrode (see 5.3.2 for more information).

5.3.2 Coupling with wires and measuring current with a single ZVA

When the ZVAs as shown in Figure 5 are replaced by a conductor or a wire and all the electrodes are short-circuited to the coupling joint, all electrodes are coupled to the same coupling joint without any components that would impose a non-zero voltage. Obviously, this is the ideal way for coupling the multiple electrodes in a CMA so that the individual electrode on the array can better simulate the behaviour of an anodic or a cathodic site in a piece of metal. However, there shall be a switching mechanism that allows a ZVA to be temporarily inserted between each electrode and the coupling joint for the measurement of the current flowing through the electrode. Because a ZVA will always introduce a small voltage between the electrode and the coupling joint, the effect of the ZVA on the measurement of the coupling current cannot be avoided. In addition, the on-and-off switching may introduce some transient response, which may alter the steady-state behaviour of the electrode. Therefore, the coupling-by-wire approach should be applied when the measurement is relatively slow and sufficient settling time is allowed between the switching and measurement to avoid the transient effect by switching. The minimum settling time may be determined by increase the settling time until the measured coupling currents do not vary significantly with the settling time.

6 Fabrication of multielectrode array

6.1 Electrode preparation

For corrosion studies of a particular metal or corrosion monitoring of a particular metal or piece of equipment in a given environment, all electrodes of a multielectrode array should have the chemical and metallurgical properties that closely match those of the metal or alloys of interest. As the electrodes of a multielectrode array are usually small (less than 2 mm in diameter), metal wires are often used to make the electrodes. Special care shall be taken when using extruded or drawn wires for the reason that the microstructure of the drawn or extruded wire may not accurately reflect the microstructure of the bulk material of interest. For example, extrusion processing can result in elongated grain structures and "stringer" configurations of constituent particles in the direction of extrusion (along the length of the wire).

When working with some metals, especially the cast alloys, where the wires for these types of metals are not available, the electrodes should be cut from a plate or bar stock or from a piece of the equipment material such as a pipe wall and machined to the required diameter (by electric discharge machining or water jet, for instance). Enough cooling should be provided during the cutting to maintain the original metallurgical structure. If it is not avoidable to cause some heating to the surface during cutting, the diameter of the initial cut should be large and the excess material should be removed by wet grinding (e.g. by centreless grinding) to the required diameter of the electrodes without the effect of heating on the surface.

For corrosion studies of galvanic coupling between dissimilar metals, two (or more) types of metals can be used as microelectrodes in the array to simulate the couple. For example, the galvanic interactions between stainless steel and an aluminium alloy (as with a stainless steel fastener in an aluminium alloy airframe structure) can be observed with respect to spatiotemporal current and potential distribution. In this example, a concentric ring of aluminium alloy wires would be arranged around a ring of stainless steel wires to simulate the morphology of the stainless steel fastener in the aluminium alloy. Adapted multielectrode arrays can even be constructed for non-planar geometric considerations, such as might simulate a crevice formed by a fastener and a plate along the length of the fastener.

6.2 Number of electrodes

For the purpose of spatiotemporal studies, the number of electrodes should be large. The number of electrodes reported in the literature for spatial studies was between 24 and 100[3][9][13][22]. For corrosion monitoring in the field, the number of electrodes can be small due to the cost associated with the increase of number of electrodes in the probe and the increase of the ZVA channels. The number of electrodes reported in the literature was between 8 and 25 for laboratory applications, and between 8 and 16 for plant applications[4].

6.3 Mounting of electrodes

The electrodes in a multielectrode array for spatiotemporal studies are usually flush mounted in an epoxy or a high-temperature insulator. The probe's sensing surface can be polished and reused until the limit of the depth that corresponds to the length of the electrodes embedded in the insulator is reached. The electrodes in a multielectrode array for corrosion monitoring or high throughput measurements may be individually sealed and separated from each other because they do need to be close to each other on the same sensing surface.

Adapted arrays can also be constructed in which multielectrode wires are embedded within the same metal of interest to better simulate the chemical-electrochemical environment of exposure. For this application, each multielectrode wire shall be coated with a thin insulating layer (see also 6.4) such that the wire is not short-circuited with the matrix metal, which would disable the multielectrode wire current and potential from being measured.

6.4 Surface coating on electrodes for preventing crevice corrosion

The electrode side surfaces of the multielectrode array should be precoated before being imbedded in the insulator to minimize crevice corrosion taking place between the side surface of the electrodes and the insulator. The coating material should be compatible with the process environments. For example, epoxy coating may be used if the application temperature is below 100 °C and diamond-like carbon (DLC) coating may be used when the system temperature is beyond 100 °C[29]. The DLC is an amorphous carbon material that displays some of the typical properties of diamond and has excellent corrosion resistance in many corrosive environments at high temperatures.

6.5 Electrode configuration

For spatiotemporal studies of non-uniform corrosion on a metal surface, the electrodes of the multielectrode array should be packed in a regular pattern such as 10 x 10, or 5 x 20, depending on what is being studied. The 5 x 20 configuration is more suitable for the studies of one-dimensional problems such as the impact of crevice corrosion or local polarization on the nearby electrodes[7]. The 10 x 10 configuration is more suitable for the studies of two-dimensional problems.

For corrosion monitoring and high throughput studies, the electrodes can be randomly packed because the spatial configuration is not important in these applications.

6.6 Size of electrodes

For the evaluation of localized corrosion rate, the size of the electrodes of the multielectrode array should be such that its surface area is as close to the area of localized corrosion site as possible. This is because the whole exposed surface area of the electrode is usually used in the calculation of the corrosion rate for each electrode. In reality, the size of a pit may be only a few micrometres in diameter in the initiation stage, but it may not be practical to make an electrode of this size. The size of the electrode should be as small as reasonably achievable and not larger than 1 mm in diameter. Although the area of a 1-mm-diameter electrode is much larger than the initial size of a pit, it may reasonably represent the pit site after the pit has fully developed at a later stage in corrosion monitoring.

A downside of using small electrodes is the realistic representation of the microstructure on such small areas. This is especially relevant when localized corrosion is linked to the presence of specific microstructure (such as pitting corrosion of aluminium alloy 2024 initiating on copper-rich S-phase). If the size of the electrode is small enough that it is not statistically representative of a bulk material, then the array shall contain a large number of electrodes or testing may be inaccurate. Using electrodes of different composition may be a suitable alternatively (e.g. pure copper and pure aluminium electrodes to replicate Cu-rich S-phase in Al-rich matrix in the case of alloy 2024).

6.7 Spacing of electrodes for spatiotemporal studies

For spatiotemporal studies of non-uniform corrosion or localized corrosion on a metal surface, the CMAs with closely packed electrodes should be used. The spacing between the electrodes in a closely packed CMA should be as close as possible to achieve an effective coupling of electrode through potential field and an effective coupling of electrode through chemical interactions[9]. The effective coupling through potential field requires that the potential drop caused by the solution resistance for a given current must be low. The effective coupling through chemical interaction requires that the distance between the adjacent electrodes must be small so that the aggressive chemical species produced at one electrode can be transported to the adjacent electrodes within a reasonable time period. Therefore, both types of couplings require that the spacing be as small as possible. Some researchers have successfully used CMAs with a spacing of 30 μm[9]. In general, the spacing should not be more than the size of the diameter of the electrode.

6.8 Spacing of electrodes for corrosion monitoring in oil and gas application

During corrosion monitoring in the crude oil and natural gas pipelines, H_2S is often present, which reacts with steel and forms electronic-conducting iron-based corrosion products[30]. Hence, the CMAS with far-spaced electrodes should be used, which prevents the effect of the short circuiting of adjacent electrodes by the electronic-conducting products. Because the currents in a CMAS probe are usually small (< 1 μA) and the conductivity of the electrolyte in the water-bearing pipelines is usually high (> 10 mS/cm), the effect of the spacing in terms of coupling through potential may not be significant. It has been demonstrated that a spacing of 8 mm is acceptable for monitoring carbon steel corrosion in simulated seawater[31]. There is no literature data available on the minimum spacing for the electrodes in the CMAS probes that prevents the effect of short-circuiting; the spacing should be as large as reasonably achievable, but not greater than the value that would affect the coupling through potential.

6.9 Size and spacing of the electrodes for high throughput studies

For high throughput studies of the independent corrosion behaviour of a metal or alloy in a certain environment, the spacing between the adjacent electrodes should be as large as possible to avoid the effect by the adjacent electrodes, but not to exceed the value that causes significant solution IR drop. The size of the electrode is not important in this case.

7 Test procedure

7.1 The test surface of the multielectrode arrays shall be ground to at least 150 grit finish. A documented cleaning procedure, typically the application of a degreasing agent and rinsing with an appropriate solvent, shall be used to ensure that the test specimens, as well as specimen supports are free of all contaminants, including particulates, oils, greases, or other residual surface films, prior to testing. The cleaning method shall be verified using an appropriate method, e.g. ISO 8407, ASTM-G1[37] or a similar standard. The device shall then be stored to avoid contamination or atmospheric degradation prior to use.

7.2 A reference electrode shall be immersed in the test solution if the study involves measurement of the open-circuit potential of the individual electrodes or the potential of the coupled array.

7.3 For laboratory applications, the temperature of the test solution shall be kept constant during the test with an accuracy of ±1 °C. Depending on the nature of the study, stirring may or may not be required. For example, if the objective is to study the corrosion behaviour in a stagnant solution, no stirring is required.

7.4 Whenever possible coupons should be exposed to the same environment to validate the results from the multielectrode arrays if the coupon data are not already available.

7.5 The results from the multielectrode arrays should be validated against the data from the coupon exposed to the same environments or compared to the literature data obtained with different methods for the same conditions.

7.6 If pitting is the dominant mode of corrosion, ISO 11463[33] should be followed to evaluate pitting corrosion.

7.7 For high throughput studies, ISO 14802[34] should be followed to apply the statistical principle in the analysis of the data.

8 Test report

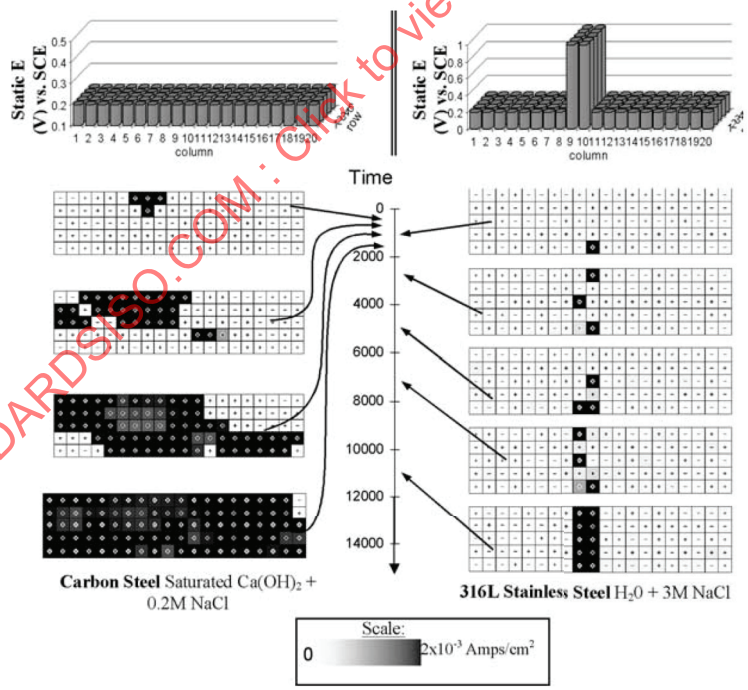
8.1 A detailed description about the multielectrode arrays used, the testing environment and the duration shall be included in the report.

8.2 For spatiotemporal studies, pictures shall be taken of the array surface before and after the corrosion deposits have been removed following the procedures described in ISO 8407 (see Annex C). The pictures allow direct visualization of the degree of non-uniform corrosion and whether the CMAS method is effective. Laser profilometry may be used to probe the depth of each electrode of the multielectrode array and compare with the corrosion rate calculated based on the measured corrosion current from the electrode.

Annex A
(informative)

Typical results from multielectrode array with closely packed electrodes for studying spatiotemporal behaviour of localized corrosion

Figure A.1 shows a typical use of the CMA for studying the spatial and temporal behaviour of corrosion. Figure A.1 a) shows the spreading of depassivated surface when all the coupled electrodes were held at an elevated potential. Figure A.1 b) shows the spreading of the depassivated surface when only a group of the coupled electrodes were held at an elevated potential. The array used to obtain these results was a 5 x 20 array. The potential of each electrode is presented as a 3D cylinder chart. The currents measured on the array are presented as a grid with each square representing a single electrode. The current value is monochromatically colour-coded in shades of grey (from 0 mA/cm^2 to 2 mA/cm^2). The sign in each square indicates if the current is anodic or cathodic. The time scale is in seconds. The results show that corrosion spreads rapidly across the surface from active sites on carbon steel electrodes held at 0,2 V_{SCE}, while stainless steel demonstrated complete resistance to spreading from preferentially initiated sites held at 1 V_{SCE} onto surrounding electrodes. Moreover, the preferentially active sites resisted initiation and did not fully activate until approximately 11 000 s. It can be seen from these results that the spreading of corrosion along the electrode surface is greatly influenced by the material composition.



a) When all electrodes were held at an elevated potential

b) When only the middle columns are held at an elevated potential

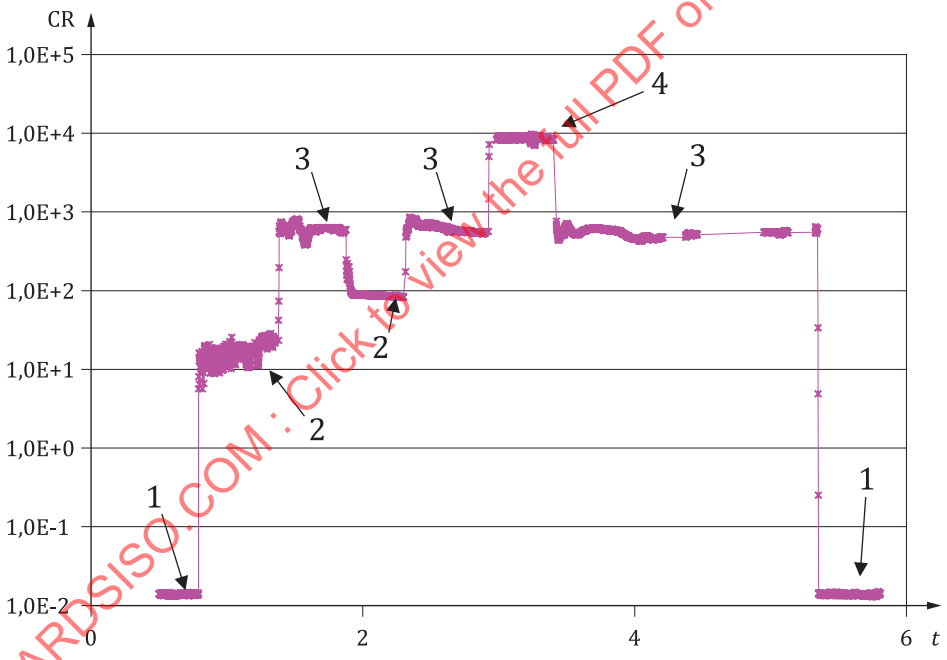
Figure A.1 — CMA with closely-packed electrodes for studying the spreading of depassivated surface[10]

Annex B
(informative)

Typical results from a CMAS for corrosion monitoring

B.1 Typical response of the CMAS to different environments

Figure B.1 shows typical responses of the maximum localized corrosion rate (derived from the most anodic current) of a low carbon steel CMAS probe[4]. The maximum localized corrosion rate in air was close to the instrument theoretical detection limit (10 nm/a). The initial maximum localized corrosion rate was 10 µm/a in distilled water, but continued to increase as the water absorbs CO_2 from the air. The maximum localized corrosion rate in simulated seawater was approximately 1 mm/a. When 10 mM H_2O_2 was added to the simulated seawater, the corrosion rate was 10 mm/a.



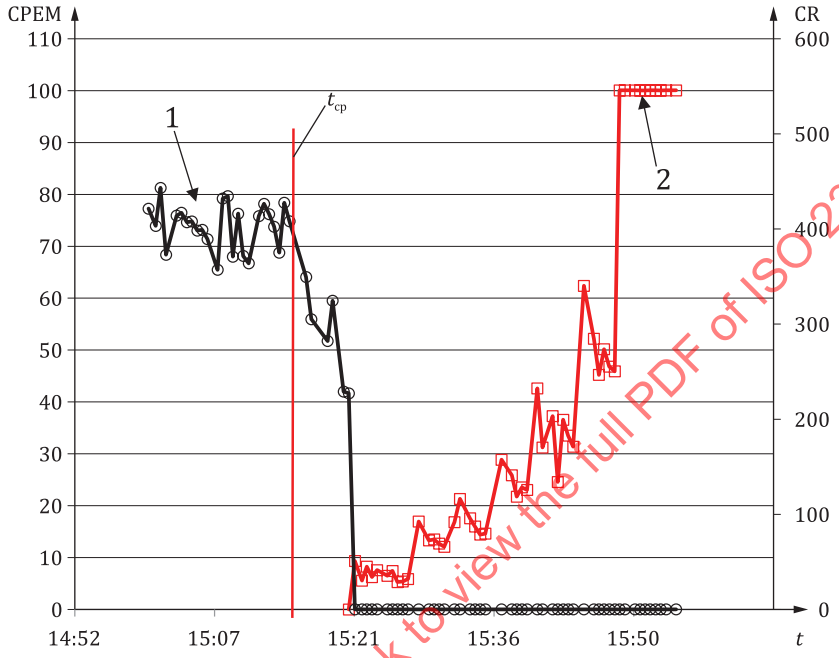
Key

1	exposed to dry air	*t*	time (day)
2	exposed to distilled water	CR	non-uniform corrosion rate (µm/a)
3	exposed to seawater (3 % mass sea salt)		
4	exposed to seawater +10 mM H_2O_2		

Figure B.1 — Typical maximum localized corrosion rate CMAS probe with 16 carbon steel electrodes[4]

B.2 Typical results from CMAS under cathodic protection conditions

Figure B.2 shows typical corrosion rate calculated from the current on the most corroding electrodes and the CPEM when the CP potential varied step by step from the free corrosion potential (about −0,7 V versus Cu/$CuSO_4$ before 15:10) to a large negative potential (lower than −1,25 V versus Cu/$CuSO_4$ at 15:50)[23]. The CMAS probe effectively measures the corrosion rate when the CP is insufficient. As the CP potential becomes more negative and reached the minimum adequate CP potential, the corrosion rate is near zero, indicating that the metal was fully protected.



Key

1	before the start of CP	t	time (hour:min)
t_{cp}	time when CP was applied	CPEM	CP effectiveness margin (%)
2	current from the most corroding electrode reached maximum allowable current	CR	non-uniform corrosion rate (µm/a)
			CPEM
			corrosion rate

Figure B.2 — Typical parameters from a carbon steel CMAS probe in simulated seawater for CP evaluations when the CP potential varied step by step from the free corrosion potential (about −0,7 V versus Cu/$CuSO_4$ before 15:10) to a large negative potential (lower than −1,25 V versus Cu/$CuSO_4$ at 15:50)[23]

At the time the corrosion rate reached zero, the CPEM was zero and started to increase as the CP potential decreased. When the CP potential reached the maximum threshold potential (about −1,25 V versus $CuSO_4$ electrode), the CPEM reached 100 % (the threshold CPEM for excessive hydrogen generation), indicating that even the most anodic electrodes starts to experience significant hydrogen evolution. Therefore, the CPEM should be controlled above zero and below 100 % and it is a quantitative indicator for the degree of CP when the CP is adequate.

Together, the CPEM and the corrosion rate can be used to effectively monitor the effectiveness of CP. When the CP is insufficient, the CPEM is less than zero, and the degree of corrosion is shown by the corrosion rate. When the CP is adequate, the corrosion rate reaches zero and loses its effectiveness as an indicator for the degree of protection. However, the CPEM can be used to guide the operator as to how to control the CP to the optimum condition when the CP is adequate.