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Corrosion of metals and alloys — Electrochemical measurement of ion transfer resistance to characterize the protective rust layer on weathering steel

Corrosion des métaux et alliages — Mesurage électrochimique de la résistance au transfert d'ions pour caractériser la couche de rouille protectrice sur l'acier autopatinable

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Contents

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

Weathering steel containing Cu, Ni, P, etc., is widely used for bridges, buildings, towers and other structures because of its maintenance-free characteristics resulting from the formation of a protective and adhesive rust layer when exposed to the atmosphere.

This feature makes it possible for weathering steel to be used without any surface treatment. It requires, however, several years of exposure to form the protective rust on untreated surfaces. During this period, quite complicated reactions occur within the rust layer affected by local environmental factors[1][2]. Therefore, there is a strong need for a quantitative and non-destructive monitoring method for the assessment of the protective rust layer condition on weathering steel structures[3].

INTERNATIONAL STANDARD **ISO 22410:2020(E)**

Corrosion of metals and alloys — Electrochemical measurement of ion transfer resistance to characterize the protective rust layer on weathering steel

1 Scope

This document specifies a method for the electrochemical measurement of ion transfer resistance of the rust layer formed on weathering steel alloys in order to assess their protective properties against corrosion thereafter[3]. This method uses an electrochemical AC impedance measurement[4][5][6][7][8], together with harmonic analysis, to identify the ion transfer resistance, and a rust thickness measurement to characterize the stability of the protective rust layer in terms of corrosion protection under used environments.

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 2178, *Non-magnetic coatings on magnetic substrates — Measurement of coating thickness — Magnetic method*

ISO 9223, *Corrosion of metals and alloys — Corrosivity of atmospheres — Classification, determination and estimation*

3 Terms and definitions

For the purposes of this document, the following terms and definitions 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

ion transfer resistance

resistance against an ionic current migrated by the voltage difference through media

Note 1 to entry: In this document, “media” means the rust layer and electrolyte.

3.2

protective rust layer

layer formed on *weathering steel* (3.3) after long-time exposure to the atmosphere that enables corrosion resistance

EXAMPLE Patina on Cu alloys.

Note 1 to entry: The protective rust layer usually consists of a double-layered structure comprising a dense protective rust layer (a-Rust) underneath a crystalline FeOOH rust layer.

3.3

weathering steel

low-alloyed steel containing Cu, Ni, P, etc. that allows for a *protective rust layer* (3.2)

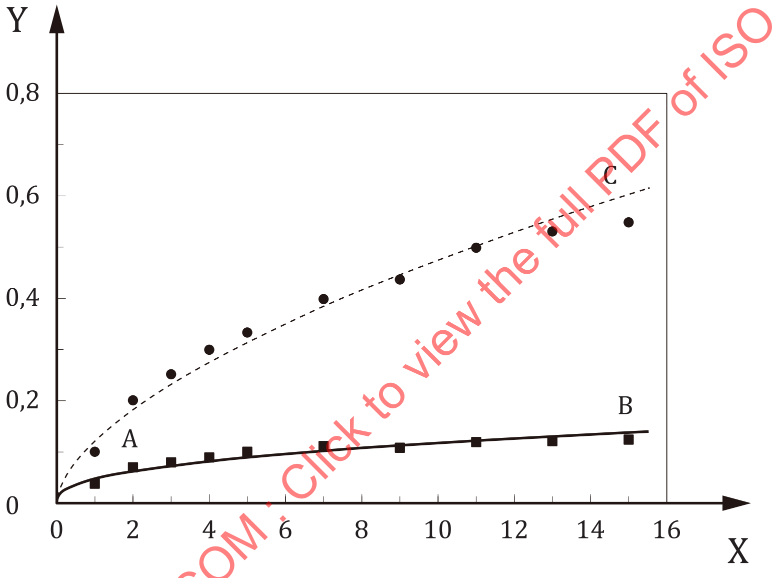
3.4
harmonic current
current with a frequency that is a multiple of the primary current

Note 1 to entry: A higher-order harmonic current means a nonlinear component of frequency current response under regular frequency voltage to a system.

4 Corrosion resistance by weathering steel

4.1 Formation of rust

Generally, weathering steel exhibits a good corrosion resistance after long-time exposure to the atmosphere, as shown in Figure 1. This is because it forms a protective rust layer adhered to the substrate steel. However, the formation of the protective rust layer depends on the atmospheric environment and the time elapsed. Sometimes, severe corrosion can occur because there is no protective rust layer, in particular when chloride ion hinders the formation of such rust.



Key

X	elapsed time, in years	A	initial rust
Y	corrosion depth, in mm	B	protective rust
		C	unprotective rust

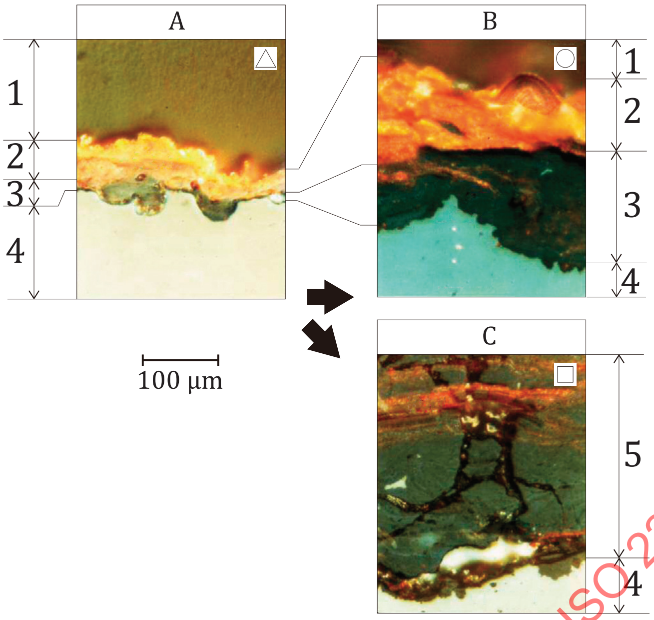
Figure 1 — General effect of atmospheric corrosion on weathering steel over time

The protective rust usually consists of a double-layered structure, as shown in Figure 2. It can be seen whether or not the rust has grown by examining a cross-sectional view of the whole rust under a microscope, as shown in Figure 2. The expected features of the corrosion resistant rust are:

a) an outer layer consisting mainly of crystalline FeOOH;

b) an inner layer consisting mainly of amorphous or very fine crystalline iron oxyhydroxides with an enrichment of Cu, Ni, P, etc.

In initial rust and protective rust, the outer bright rust layer consists of crystalline FeOOH, whereas the inner dark rust layer has amorphous rust (very fine crystal).



Key

A	initial rust	1	resin
B	protective rust	2	FeOOH
C	unprotective (anomalous) rust	3	a-Rust
		4	metal (steel)
		5	thick Fe_3O_4

NOTE 1 “a-Rust” means amorphous or very fine crystalline iron oxyhydroxides with an enrichment of Cu, Ni, P, etc.

NOTE 2 “Anomalous rust” means anomalously grown rust.

Figure 2 — Classification of typical rust layers based on cross-sectional observations made using a polarized light microscope

4.2 Typical types of rust by cross-sectional view

Based on the cross-sectional microscopic observations of numerous rust layers on weathering steels exposed to various locations for various periods (see Figure 2 and Reference [3]), the rust layers can be typically classified into three types: initial rust (unknown), protective rust and anomalous rust (unprotective).

a) Initial rust: Islands of thin amorphous (very fine crystals) rust are visible at the steel-rust interface under a crystalline rust layer. The total thickness is usually less than 400 µm. The rust layer can be observed either at the initial stage of service or after long-term exposure to a mildly corrosive environment. The corrosion loss of the steel is very small.

b) Protective rust: An amorphous or very fine crystalline rust layer covers the whole surface area under the crystalline rust layer (FeOOH). The total thickness is usually between 40 µm and 400 µm. This is the ideal protective rust layer for weathering steel.

c) Anomalous rust: FeOOH exists both at the external surface and along crack surfaces. The rest of the rust consists of crystalline Fe_3O_4 (usually confirmed by X-ray analysis). The total thickness is more than 400 µm. The rust contains numerous cracks, sometimes bearing sea salt. It tends to form when the wetting period is excessive and/or accumulated salt is present.

The initial rust or protective rust can be identified by observing the cut samples under a microscope, although this type of characterization is destructive. The anomalous rust can be identified by observing a thickness measurement of rust of > 400 µm.

A non-destructive monitoring method to identify the rust layer on weathering steel is to take electrochemical measurements of the ion transfer resistance.

5 Measurement of ion transfer resistance

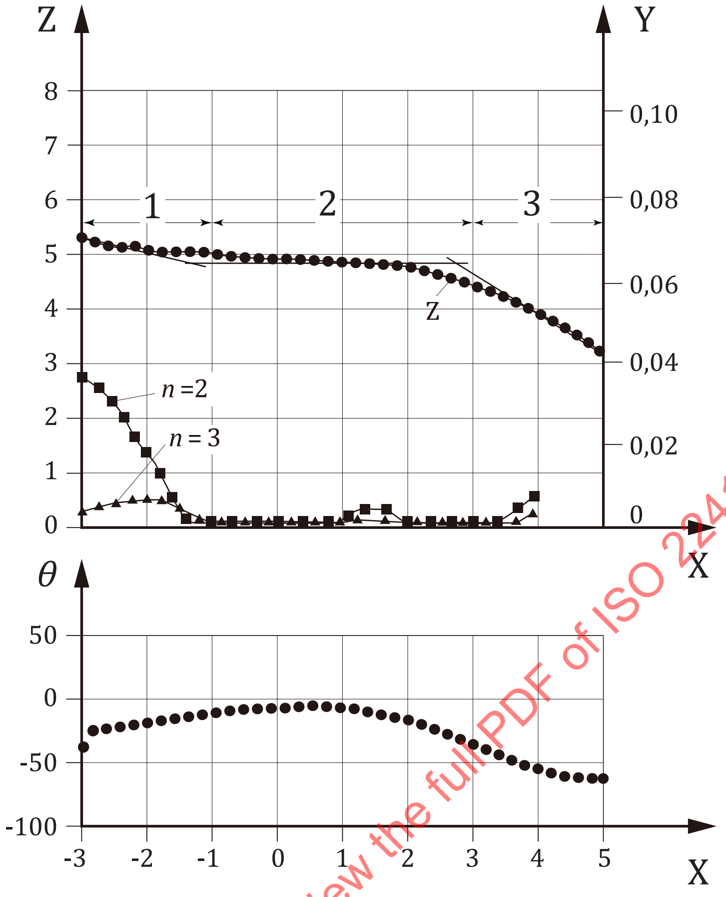
5.1 General

The protective properties of rust can be determined by measuring the ion transfer resistance through the dense and adhesive rust layer. This technique consists of using electrochemical impedance together with harmonic current measurements to identify the ion transfer resistance from the rust layer and its thickness measurement. In this case, the current is linear to potential, meaning there is almost no higher-order harmonic current. Many existing steel structures made of weathering steel under various atmospheres and periods are measured using a double-probe type of portable monitoring instrument. The thickness of the rust is measured, usually by using an electromagnetic device, and the gathered data provide a criterion map by which to characterize the property of the rust layer formed on the weathering steel, and therefore to determine whether the existing rust layer is effective as a corrosion protective barrier.

5.2 Electrochemical impedance and harmonic current measurements

In order to obtain the ion transfer resistance as a measure of the protective properties of the rust layer, the electrochemical impedance and harmonic current measurements are taken in a laboratory on various kinds of rusted low-alloyed steels exposed to the actual atmosphere over a long period. A conventional three-electrodes measurement is adopted with an Ag-AgCl reference electrode. For a standard impedance measurement, the system consists of a potentiostat and a frequency response analyser, which are controlled by a computer. An aqueous solution of 0,1 M Na_2SO_4 opened to the air is usually used as an electrolyte because the impedance parameters of the rust layer exhibit little change when this solution is used. This solution generally does not cause degradation or changes in the rust layer in a relatively short time. All the measurements are performed at room temperature (about 25 °C), which simulates the measurement practice as used in the field.

A typical impedance and second and tertiary harmonic current response for a weathering steel covered with protective rust is shown in Figure 3, where three distinct regions of frequency exist.



Key

X	frequency, in log hertz (Hz)		1	impedance region 1
Y	harmonic current, in × 10^{-6} amperes per square centimetre (A/cm^2)		2	impedance region 2
Z	impedance, in log ohms per square centimetre (Ω/cm^2)		3	impedance region 3
θ	phase shift, in degree			

NOTE $n = 2$ and $n = 3$ represent the second and the third harmonic currents, respectively.

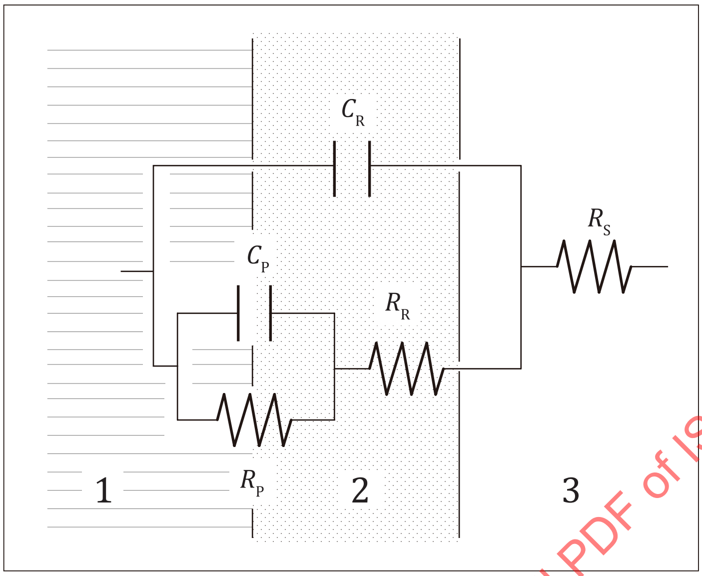
Figure 3 — Typical impedance and the higher-order harmonic current spectra for a dense protective rust layer on weathering steel (0,1 M Na_2SO_4 solution)

Region 1 is the frequency region of less than approximately 10^{-1} Hz, where the phase shift deviates negatively from zero and the impedance is dependent on the frequency to some extent. This is called the "pseudo-capacitive impedance" since the slope of log Z/log f is not equal to −1, which would be exhibited in an ideal capacitor. The second and third harmonic currents are also observed, thereby indicating corrosion resistance resulting from charge transfer reactions. The higher order harmonic current is observed only when the current-potential relationship is nonlinear, e.g. the current-potential relationship depicted by the Butler-Volmer equation, on which the charge transfer reaction is based. Pseudo-capacitance in this region, of which the electrical connection should be theoretically parallel to the corrosion resistance, can be attributed to the double-layer capacitance at the steel-rust interface.

Region 2 is the frequency region between approximately 10^{-1} and 10^3 Hz, where the phase shift is nearly zero and the frequency dependence of the impedance can be almost disregarded. This is called the "pseudo-resistive impedance" since the slope of log Z/log f is not perfectly zero. The current response in this pseudo-resistive impedance region is judged to be linear because the higher-order harmonic currents are nearly zero. Therefore, this resistance can be attributed to ion migration, which normally exhibits a linear current-potential relationship, i.e. follows Ohm's law, through the tightly adherent inner protective rust layer. This resistance is called the "rust layer resistance" (the ion transfer resistance through the rust).

Region 3 is the frequency region higher than approximately 103 Hz, where pseudo-capacitive impedance is also observed. This pseudo-capacitance is considered to be attributed to the rust layer capacitance that corresponds to the charge accumulated by the large electric field across the high-impedance rust layer.

Based on the above analysis, an equivalent circuit for rusted steel can be derived, as shown in Figure 4.



Key

R_s	solution resistance	1	steel
R_R	ion transfer resistance	2	rust
R_p	polarization resistance	3	solution
C_R	rust layer capacitance		
C_p	double-layer capacitance		

Figure 4 — An equivalent circuit for rusted weathering steel

Here, a variable resistance, R_R, and two variable capacitances, C_R and C_p, exhibit a frequency dependence that is known as the "dispersion phenomenon". Weathering steel generally exhibits a higher ion transfer resistance and a lower corrosion rate than plain carbon steel when both types of steel are exposed to the same chronological and environmental conditions. It can be deduced that the density, i.e. the crack and pore-free structure, of the rust layer is what provides the protection. The more protective the rust layer, the higher the value for the ion transfer resistance. Therefore, the ion transfer resistance, R_R is the key measurable parameter for evaluating the protective properties of the rust.

6 Measurements in the field

Many existing steel structures made of weathering steel under various atmospheres and periods are measured using a double-probe type of portable monitoring instrument.

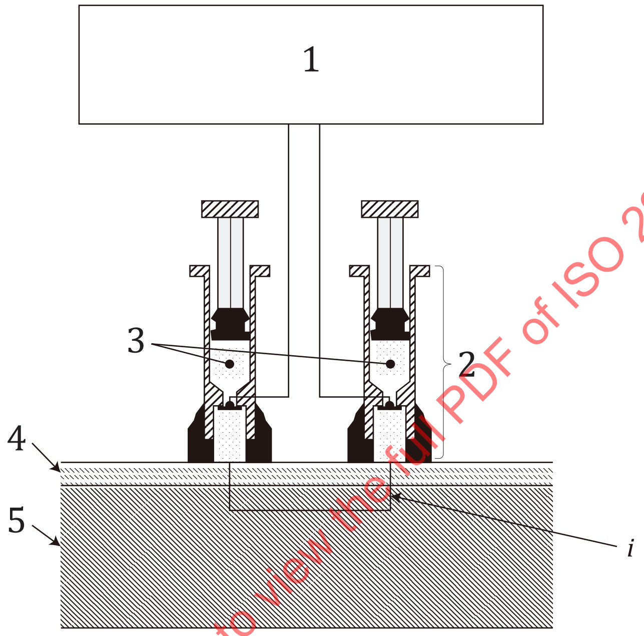
A schematic illustration of a portable measuring instrument for taking measurements in the field is shown in Figure 5.

Generally, electrochemical impedance measurements use a three-electrodes system or a two-electrodes system. A three-electrodes system requires a reference electrode, a sample electrode and a counter electrode. A two-electrodes system only uses a sample electrode and a counter electrode in order to simply investigate the current under defined voltage, eventually obtaining the electrochemical impedance.

A single-probe sensor system can be used by either the three-electrodes or two-electrodes system. However, it needs to have a direct electrical connection to the sample substrate, leading to a destructive measurement. Alternatively, a double-probe sensor system, as shown in Figure 5, does not require a destructive electrical connection to substrate.

In addition, the reference electrode of the three-electrodes system cannot be located close to the sample substrate due to thick rust.

As a result, a double-probe sensor system of two-electrodes, as shown in Figure 5, gives the most simplified and convenient system for field measurement.



Key

1 electrochemical impedance measurement system (with harmonic analysis)
2 sensor
3 electrolyte
4 rust
5 steel
i electric current

Figure 5 — Portable measuring instrument

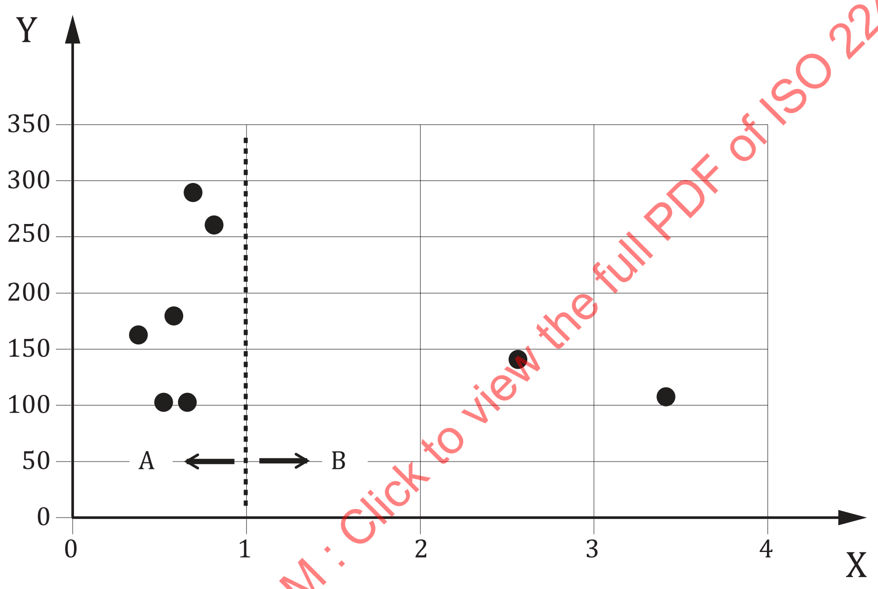
This instrument comprises a pair of sensors and a set of electrical circuits. The sensors consist of platinum electrodes within open-ended compartments, which are filled with an absorbent polymer that includes an electrolyte (0,1 M Na_2SO_4) and cylindrical reservoirs from which the absorbent polymer is supplied to the open-ended compartments. An alternating current is applied to measure the rust film resistance by way of indirect electrolysis through the sensors. The mouths of the open-ended compartments are made of silicone rubber and this area has to be normalized (e.g. to 1,2 cm^2). The compact electrical instrument comprises:

- a standard impedance measuring system such as a current pulse generator;
- an electrometer;
- a phase-sensitive detector with an integrator;
- an AC/DC converter;
- a central processing unit as the system controller.

The frequency range in which the rust layer resistance (ion transfer resistance) appears depends on the quality of the rust layer. Normally, the higher the quality, the lower the frequency range shifts (see Annex A). In addition, the amplitude of the applied AC current pulse should be adjusted with respect to the resistances in order to prevent deterioration of the rust caused by an unexpectedly large overpolarization.

Therefore, the frequency and amplitude of alternating current pulses are controlled by the computer to give the optimal measurement condition on the basis of a feedback method detecting over- or under-polarization in a predetermined voltage range, 20 mV to 200 mV (peak to peak voltage) in which no deterioration of the rust may occur. The measuring frequencies are predetermined intermittently from 10^{-1} Hz to 1 kHz with respect to every range of the rust layer resistance (ion transfer resistance). The best measuring frequency can be selected automatically.

Plotting a graph between the obtained R_R values and the rust thickness (or the actual corrosion depth of steel) exposed in the same environmental atmosphere for the same period shows that the higher R_R tends to be the lower corrosion, as shown in Figure 6.



Key

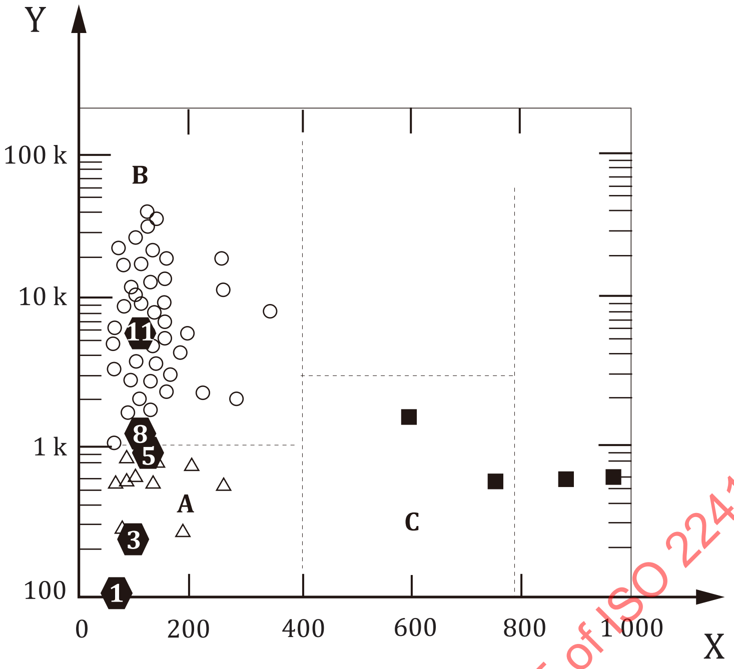
X ion transfer resistance (R_R), in kiloohms (kΩ)
Y rust thickness, in micrometres (correspondent to corrosion depth)
A initial rust
B protective rust

Figure 6 — Correlation between ion transfer resistance, R_R, and rust thickness of various low alloyed steels weathered for 13 years in a semi-industrial atmosphere (category C3 by ISO 9223)

Therefore, ion transfer resistance is the essential parameter, not only for distinguishing the protective rust layer, but also for estimating the protective properties of the rust layers. However, this measurement is limited to the ion transfer resistance only, i.e. barrier effect of the rust layers. It cannot measure the corrosion rate itself.

7 Evaluation of the corrosion protective property of the rust layer

The data of the ion transfer resistance are important for a quantitative evaluation of the rust layer for corrosion protection. Actual data taken from the field are summarized in Figure 7. These data can be classified into three types of rust, see 4.2. This figure may be used as an empirical criterion for the assessment of the rust layer formation.



Key

X	thickness of rust, in micrometres
Y	ion transfer resistance (R_R), in ohms (Ω)
A	initial rust formation
B	protective rust formation
C	unprotective (anomalous) rust formation

○	protective rusts
△	initial rusts
■	anomalous rusts

NOTE The ion transfer resistance was measured. The hexagonal mark denotes an example of the measured R_R of a real bridge at different exposure times up to 11 years (category C3 by ISO 9223).

Figure 7 — Quantitative classification of rust conditions formed on weathering steel based on measuring rust layer resistances and rust thicknesses

8 Practical method of measurement for ion transfer resistance and thickness

8.1 For rusted steel structures made of weathering steel, both an electrochemical measurement of ion transfer resistance through the rust layer and a measurement of the rust thickness provide the condition and status of the rust layer in terms of corrosion protection. The measurements may be done for existing structures in the field or for samples cut from a structure in a laboratory in accordance with the procedure given in 8.2 to 8.7.

8.2 Before taking an electrochemical measurement in the field, the resistance of the sensor probes (which can be a cause of inaccuracy) is first measured then stored in the memory installed in the instrument by attaching the sensor to an abraded stainless-steel plate as calibration. This should then be automatically subtracted from each measured value to obtain an accurate value of the rust layer resistance (the subtraction of R_s as shown in Figure 4).

In addition, it is recommended that the resistance between the double-probe sensors is checked by standard 1 kΩ and 1 MΩ resistors.

8.3 The measured surface is cleaned to avoid contamination such as oil, dust and other material.

8.4 The rust thickness measurement shall be taken by using an electromagnetic thickness gage in accordance with ISO 2178.

About 10 measurements of thickness should be taken, measured randomly within approximately 10 cm × 10 cm after the removal of the outer non-adhesive rust.

NOTE Anomalously large or small values compared with the other values can be neglected from the data, since they can be considered as measurement errors due to the porosity of the rust.

If there is any indication that the rust scale has detached from the surface of the weathering steel due to anomalous corrosion, the empirical value 400 µm should at least be added to the measured value of the rust thickness for compensation.

8.5 The non-adhesive outer rust scale can be removed, as it has nothing to do with corrosion protection and can be a cause of error in the precise measurement of the rust film resistance. The adhesive rust layer should not be removed.

NOTE Usually the rust layer consists of two or more layers (see Figure 2) and the outer rust scale sometimes detaches when the rust grown to be large.

8.6 The ion transfer resistance (R_R) is measured by the double-probe sensors together with harmonic analysis. A couple of measurements shall be repeated within approximately a 10 cm × 10 cm area.

NOTE 1 The harmonic analysis is not always needed, since the appropriate frequency range to measure the ion transfer resistance for the rust layer on weathering steel is often already know. An example is shown in Annex A.

NOTE 2 In the field, the electrochemical measurement can take 0,5 min to 2 min depending on the condition of the rust layer. The solution uses 0,1 M Na_2SO_4, which makes almost no harm to the protective rust layer. The measured impedance sometimes decreases up to 20 % in a slow and stable manner after wetting by the probes. In this case, the data are taken after a predetermined time has passed.

NOTE 3 The spacing of the probe sensors is arbitrary provided that the electrical resistance of the substrate steel between them can be regarded as zero.

8.7 Photographs should be taken of the surface of the rust layer on the weathering steel, since they can demonstrate the condition of the rust layer.

9 Test report

The test report shall provide at least the following information.

a) For the steel structure:

1) location (e.g. corrosivity category by ISO 9223, if obvious);

2) type, history (e.g. manufacturer, time elapsed) and details of the structure (e.g. open or sheltered);

3) materials (e.g. with or without coating, steel grades);

4) present manner of corrosion.

b) For the test and investigation:

1) date, time and duration of the test;

2) test operator and instruments;

3) test schedule and plan (e.g. data format, data collection rates);

4) testing condition (e.g. surface preparation);

    5) testing results.

c) For the environmental conditions:

    1) time and weather;
    2) rainfall;
    3) temperature and relative humidity (RH);
    4) surface temperature of the structure;
    5) contamination deposition (e.g. chloride deposition and SO_2 deposition by ISO 9225);
    6) corrosivity category by ISO 9223, if obvious.

10 Application of the method of measurement

The measurement method given in Clause 8 can be done once a year or once every couple of years. This enables a check of whether the rust layer formed on the weathering steel is going to be more protective, more stabilized, or less protective with higher, the same or lower ion transfer resistance (R_R)[9]. In cases where it is unknown whether the initial rust (see Figure 7) is in protective or unprotective region, the ion transfer resistance of the rust should be checked frequently. An example of a data set taken from a real structure with the number of the time passed for exposure[10] is given in Figure 7.

Atmospheric environments around the steel structure can sometimes change even after long-time exposure, which can have an influence on the protective properties of the rust even if it has already been formed. The ion transfer resistance of the rust should therefore be checked intermittently. If there is a detrimental change to the rust where the ion transfer resistance lowers to below a threshold value (approximately around 1 kΩ), corrosion protective treatments may be applied, e.g. conversion coatings or painting, to prolong the use of structures.