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Corrosion of metals and alloys — Electrochemical potentiokinetic reactivation measurement using the double loop method (based on Čihal's method)

Corrosion des métaux et alliages — Mesurage de la réactivation électrochimique potentiocinétique par la méthode de la double boucle (dérivée de la méthode de Čihal)

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 12732 was prepared by Technical Committee ISO/TC 156, *Corrosion of metals and alloys*.

Corrosion of metals and alloys — Electrochemical potentiokinetic reactivation measurement using the double loop method (based on Čihal's method)

WARNING — This International Standard may involve hazardous materials, operations and equipment. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices, and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies the method for measuring the degree of sensitization (DOS) in stainless steel and nickel-based alloys using the Double Loop Electrochemical Potentiokinetic Reactivation (DL-EPR) test (based on Čihal's method).

The method may be used for the quantitative assessment of deleterious thermal effects resulting in the formation of alloy-element-depleted zones at grain boundaries or in the matrix. However, attention should be paid when testing heat-affected weld zones, due to possible non-uniform distribution of sensitized zones along the fusion lines.

The results of the test can be used as an index to identify the potential susceptibility of stainless steel and nickel-based alloys to intergranular corrosion, pitting corrosion, and intergranular-stress corrosion cracking, but prediction of these corrosion modes depends on complementary specific testing.

This International Standard describes the general methodology and, in Annex C, gives examples of suitable test exposure conditions for specific alloys.

2 Normative references

The following referenced documents are indispensable for the application 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 8044:1999, *Corrosion of metals and alloys — Basic terms and definitions*

ISO 643:2003, *Steels — Micrographic determination of the apparent grain size*

3 Terms and definitions

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

3.1
integrated charge
Q
charge measured during passivation (Q_p) and reactivation (Q_r), given by the time integral of current below the passivation and reactivation peak of the curve

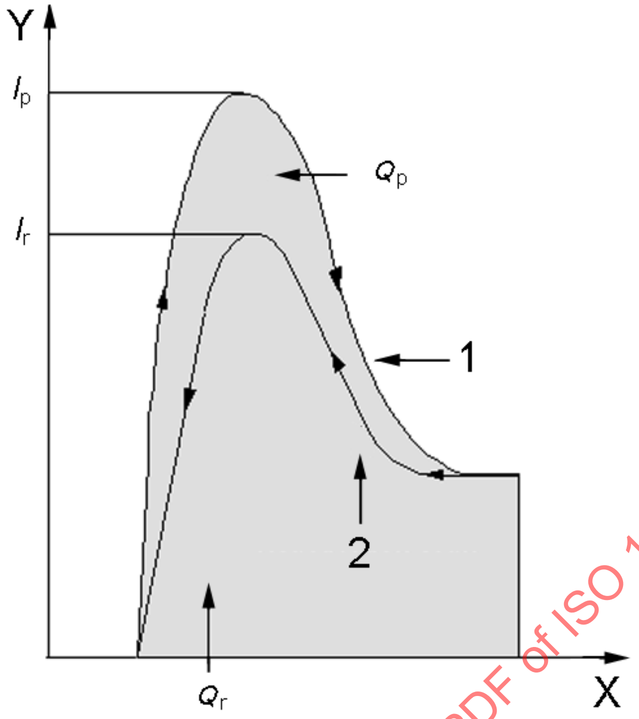
4 Principle

Heat treatment (including welding) of corrosion-resistant alloys can lead to formation of particles, such as chromium carbide in the case of 304 SS or σ-phase (FeCrMo) in duplex stainless steels. This will lead to local depletion of alloying elements, unless replenished by matrix diffusion, the extent of which will be temperature dependent. This process is commonly referred to as sensitization, because depleted zones have an intrinsic lower resistance to localized corrosion and, where appropriate, to stress corrosion cracking. The extent to which these damage mechanisms develop and propagate will depend on the extent of depletion and the density of depleted zones. There was a need for a simple laboratory test to rapidly identify potentially deleterious thermal effects on stainless steels and nickel-based alloys. The EPR test was developed for that purpose. Although two methods have been used in laboratory testing, the single loop and the double loop, the former, which involves polarization scanning from the passive to the active state, has the disadvantage that the method can be sensitive to surface finish. The EPR test may also be applied to in-field testing, provided some adaptation be made to the cell and assembly**.**

The double loop version of this method is preferred. Here, the specimen is immersed in an acid solution such that it is in the active state under freely corroding conditions, but then anodically polarized into the passive domain. As surface features are dissolved during initial immersion under active corrosion conditions, the likelihood of surface preparation having an impact diminishes. From the passive state, the specimen is polarized at a controlled scan rate in the cathodic direction. A schematic illustration is shown in Figure 1. In the absence of active depleted zones, the passive film can become unstable as the potential becomes less positive and can start to dissolve (e.g. by reductive dissolution). However, the rate of dissolution is small and, with the sweep rate employed, the anodic current is not able to rise substantially, so that only a modest anodic peak current is measured. The process of anodic dissolution during the cathodic scan is referred to as reactivation. Occasionally, the current may go transiently cathodic on lowering the potential, as the passive current density may be less than the cathodic current at the potentials of relevance.

When a depleted zone is present, the passive film is locally less protective and is more easily reduced. Hence, active dissolution of the depleted zones will occur more readily whilst adjacent material still retains some passive film, albeit a gradually thinning passive film. Thus significant active dissolution occurs. The reason for the gradual rise in current is probably a reflection of the spread in activity associated with a spread of the extent of depletion and corresponding variations in the passive film properties (some sections reduced at higher potentials and some at lower potentials). Gradually, as the activity of all the sites build up, this begins to be counteracted by the decrease in potential reducing the current of the active regions because of Tafel behaviour; thus a reactivation peak is observed. The peak in the current density, and the charge passed associated with that peak, depend on the extent of alloy depletion.

The ratio of the reactivation peak to the activation peak, or the reactivation charge to the activation charge, when compared with the values for the solution-annealed specimen, gives an index of sensitization. However, for sensitized grain boundaries, these values have to be normalized to the grain size. At the end of the test, the specimen is examined to confirm the nature of the localized corrosion process.



Key

X potential

Y log of current

1 anodic scan

2 reactivation scan

Figure 1 — Schematic polarization curves of the double loop EPR test method

5 Apparatus

The apparatus necessary for obtaining EPR data consists of electronic instruments and a test cell. The electronic instruments may be integrated into one instrument package or may be individual components. Either form of instrumentation can provide acceptable data.

5.1 Scanning potentiostat

The potentiostat should be capable of controlling the potential to within ± 1 mV accuracy, over the range of potential and current encountered in the EPR measurements. The potentiostat should have a potential range of –2 000 to +2 000 mV and a current range of 1 µA to 1 A.

5.2 Electrode potential-measuring instrument

The electrode potential-measuring circuit should have a high input impedance of the order of 10^{11} Ω to 10^{14} Ω, to minimize current drawn from the system during measurements. Such circuits are provided with most potentiostats. Instruments should have sufficient sensitivity and accuracy to detect a change of 1,0 mV over a potential range between –2 000 and +2 000 mV.

5.3 Current-measuring instruments

The current in the circuit is evaluated from the potential drop measured across a known resistor. In many potentiostats, this measurement is made internally but measurements can also be made externally by locating a resistor in the current line from the counter electrode to the auxiliary connection on the potentiostat. The current intensities encountered in an EPR test are usually in the range of 1 μA·cm^{-2} to 100 mA·cm^{-2}. An instrument that is capable of measuring a current accuracy to within 1 % of the absolute value over a current density range between 1,0 μA·cm^{-2} and 105 μA·cm^{-2}, for a specimen with a surface area of approximately 1,0 cm^2 to 5,0 cm^2, is recommended.

5.4 EPR test cell

The test cell should contain the working electrode (the metal to be polarized), a reference electrode for measuring the electrode potential and counter electrode(s). The test cell shall be constructed of materials that will not corrode, deteriorate, or otherwise contaminate the test solution. Borosilicate glass and poly-tetrafluoroethylene (PTFE) have been successfully used.

The counter electrode/s should be positioned so that the current distribution about the specimen is symmetrical.

The reference electrode may be inserted directly into the main cell. To avoid mutual contamination, a double-junction reference electrode may be used or the reference electrode may be located in a separate chamber and linked to the main cell by a salt bridge. To minimize the potential drop between the reference electrode and the working electrode, a Luggin capillary should be used. The tip of the capillary probe shall be positioned so that it is at a minimum distance from the working electrode of 2 times the diameter of the tip.

The volume of solution in the test cell shall be such as to reduce to insignificance any change in the solution chemistry, as a consequence of the reaction processes. Typically 250 ml is sufficient, with a minimum requirement of 100 ml·cm^{-2} of working electrode.

5.4.1 Electrode holder. The working electrodes shall be mounted in such a way that the holder and mounting material have no influence on the measurement. An example of an electrode-mounting assembly is shown in Figure A.2. For steels with a protective oxide film, the seal of the test specimen to the holder can sometimes lead to undesired crevice attack of the steel at the interface. A method of preventing such crevice attack for certain applications, using a flushed port cell or using a flushed specimen holder, is outlined in Annex A.

5.4.2 Working-electrode material. The working electrode is prepared from the test material of interest, usually in the form of a rod or sheet. See Clause 7 for surface finish and cleaning of the working electrode.

5.4.3 Reference electrode. The type of reference electrode used will depend on the application, e.g. temperature and environment. Commonly used electrodes include the saturated calomel electrode and silver/silver chloride electrode. The potential of these electrodes at 25 °C, relative to the standard hydrogen electrode at 25 °C, is given in Annex B.

5.4.4 Counter-electrode preparation. The counter electrode shall be free of any product that would contaminate the solution. The counter electrode is commonly prepared from high-purity platinum. For platinum electrodes, dipping in concentrated HCl and thoroughly rinsing in distilled water is usually sufficient. Other materials may be used, provided they are inert. The area of the counter electrode should be at least the area of the working electrode.

NOTE Graphite may be used as a counter electrode but care must be taken to avoid contamination; desorption of species retained in the graphite may be necessary prior to usage. This contamination can be avoided by routinely replacing the graphite electrode.

6 Test solutions

The test solution most often consists of a mixture of sulfuric acid (H_2SO_4) and potassium thiocyanate (KSCN), prepared from analytical reagent-grade chemicals and distilled water (the solution can be made up in bulk in a large quantity and stored for 1 month at room temperature). The composition of the test solution is chosen depending on the tested material and varies between 0,5 M to 2,5 M H_2SO_4 and 0,001 M to 0,05 M KSCN.

NOTE KSCN is deliquescent. For super-duplex stainless steel, 3,0 M HCl without KSCN has been shown to be an effective test solution.

Fresh solution should be used for each test.

7 Test specimen preparation

Specimens to be given a thermal sensitizing treatment prior to DL-EPR testing should be treated according to the procedure given in Annex C.

The shape of the specimens should not allow crevice corrosion and be without sharp edges. Care should be taken to avoid overheating of specimens when machining or grinding.

Although corrosion in the active state should limit the influence of the surface state, it is advisable to prepare specimens to a well-defined surface finish, for example to Ra less than 0,25 µm. The specimen shall then be cleaned. Ultrasonic cleaning in distilled water, washing with alcohol and rinsing with acetone is usually adequate. The time between grinding and exposing the specimen may have some effect on the rate of subsequent dissolution in the active state. This delay should be limited to 1 h. After grinding, specimens shall be stored in a dessicator cabinet when possible.

Specimens should be pre-treated according to the procedure given in Annex C.

The use of control specimens with a known degree of sensitization is recommended. These can be used to confirm the performance of new cells for field applications, and the quality of the apparatus and reagents used.

8 Procedure

Place the specimen, counter electrode, salt bridge probe, and other components in the test cell. Add the solution, ensuring that the Luggin capillary is filled with the test solution and contains no air bubbles, particularly in the restricted space within the tip region.

Record the open circuit (rest or corrosion) potential of the test specimen after 1 min to 2 min. If the rest potential does not register normal for the class of alloys being evaluated (–350 mV to –450 mV vs. SCE for Cr18 Ni9 type steel), cathodically polarize the specimen so as to remove any existing oxide layer, for instance to –700 mV vs. SCE for 0,1 min to 1 min, and recheck the rest potential.

Expose the specimen for about 5 min. at the free corrosion potential, then polarize anodically into the passive region at a controlled scan rate. Typically, the potential will be about 200 mV to 600 mV (SCE). As soon as this potential is reached, the scanning direction is reversed and the potential is decreased at the same rate to the initial free corrosion value E_{corr}. The scan rate chosen is designed to give a clear distinction between the activation and reactivation process and will be alloy sensitive. Initial tests should be undertaken to establish the optimum rate. Values in the range 2 000 $mV \cdot hr^{-1}$ to 15 000 $mV \cdot hr^{-1}$ are typical. The sequence of the polarization steps should be performed at least three times.

For types 304, 321, and 347, the following test conditions shall be used:

- test solution composition: 0,5 M H2SO4 +0,01 M KSCN;
- scan rate: 6 V/h;
- polarization range from E_{corr} (about –400) up to +300 mV/SCE;
- temperature: 25 °C (however, acceptable temperature range for field applications requires experimental justification).

9 Metallographic inspection

At the end of the test, the specimen surface shall be examined to ensure that there are no other factors, such as pitting, that might have influenced the results.

A grain size measurement is required when normalizing the data obtained to the grain size. This should be done using ISO grids on micrographs of the sample for determination of the grain size number, and dividing the data by the grain-boundary area per unit of specimen area, or by the length of grain boundary per unit of specimen area.

10 Evaluation of results

Measure the peak current for the reactivation scan (I_{r}) and for the activation scan (I_{p}), and take their ratio. Do likewise for the charge (Q_{r} and Q_{p} respectively) by integrating the current under the peak over the time. The ratio, when compared with results from tests of a solution-annealed specimen, will give an index of the extent of depletion. When depletion is homogeneous, this index provides a sufficient criteria for ranking the impact of different heat treatments.

For sensitized grain boundaries, divide the activation peak current by the area of the specimen and divide the reactivation peak by the area of the grain boundary, in order to account for specimens with different grain sizes. This assumes that the reactivation peak is associated with the grain-boundary sensitization only, and not depleted zones or other active corrosion regions in the matrix. The exercize is repeated for the charge. The relevant relationships are:

$$(I_{\mathrm{r}}/I_{\mathrm{p}})_{\mathrm{GBA}} = \frac{I_{\mathrm{r}}}{S_{\mathrm{GBA}}}\Bigg/\frac{I_{\mathrm{p}}}{A_{\mathrm{s}}} = \frac{I_{\mathrm{r}}}{S_{\mathrm{A}}\,A_{\mathrm{s}}}\Bigg/\frac{I_{\mathrm{p}}}{A_{\mathrm{s}}} = \frac{I_{\mathrm{r}}}{S_{\mathrm{A}}\,I_{\mathrm{p}}} = \frac{I_{\mathrm{r}}}{I_{\mathrm{p}}\,10^{-3}\sqrt{2^{G+5}}} \qquad (1)$$

$$(Q_{\mathrm{r}}/Q_{\mathrm{p}})_{\mathrm{GBA}} = \frac{Q_{\mathrm{r}}}{S_{\mathrm{GBA}}}\Bigg/\frac{Q_{\mathrm{p}}}{A_{\mathrm{s}}} = \frac{Q_{\mathrm{r}}}{S_{\mathrm{A}}\,A_{\mathrm{s}}}\Bigg/\frac{Q_{\mathrm{p}}}{A_{\mathrm{s}}} = \frac{Q_{\mathrm{r}}}{S_{\mathrm{A}}\,Q_{\mathrm{p}}} = \frac{Q_{\mathrm{r}}}{Q_{\mathrm{p}}\,10^{-3}\sqrt{2^{G+5}}} \qquad (2)$$

where

Q_{r} is the charge for the reactivation loop (in coulombs);

Q_{p} is the charge for the anodic loop (in coulombs);

I_{r} is the maximum current for the reactivation loop (μA·cm^{-2});

I_{p} is the maximum current for the anodic loop (μA·cm^{-2});

S_{A} is the grain-boundary area per unit of specimen area;

$$S_A = 4 \times 10^{-3}\sqrt{2^{G+1}};$$

A_s is the specimen area (cm^2);

S_{GBA} is the grain-boundary area (cm^2);

$$S_{GBA} = S_A \times A_s;$$

G is the grain-size number (see ISO 643).

For convenience purposes, $(I_r/I_p)_{GBA}$ and $(Q_r/Q_p)_{GBA}$ ratios can be multiplicated by 100 to be expressed as percentage values.

An alternative approach is to normalize the reactivation currents or charge to the grain-boundary length, to provide a dimensional ratio defined by:

$$(I_r/I_p)_{GBL} = \frac{I_r}{L_{GBL}}\bigg/\frac{I_p}{A_s} = \frac{I_r}{10 L_A\ A_s}\bigg/\frac{I_p}{A_s} = \frac{I_r}{10 L_A\ I_p} = \frac{I_r}{I_p\,10\sqrt{2^{G+5}}}\ \text{(cm)} \tag{3}$$

$$(Q_r/Q_p)_{GBL} = \frac{Q_r}{L_{GBL}}\bigg/\frac{Q_p}{A_s} = \frac{Q_r}{10 L_A\ A_s}\bigg/\frac{Q_p}{A_s} = \frac{Q_r}{10 L_A\ Q_p} = \frac{Q_r}{Q_p\,10\sqrt{2^{G+5}}}\ \text{(cm)} \tag{4}$$

where

L_A is the length of grain boundary per unit of specimen area (mm^{-1});

$$L_A = \sqrt{2^{G+5}};$$

A_s is the specimen area (cm^2);

L_{GBL} is the grain-boundary length (cm);

$$L_{GBL} = 10 \times L_A \times A_s$$

The ratios can be used as a relative index for comparing the relative effect of different heat treatments on sensitization. The degree of sensitization can only be confirmed by separate complementary measurements but Annex D provides preliminary guidelines.

11 Test report

The test report shall include the following information:

a) a full description of the test material from which the specimens were taken, including UNS number, composition, heat treatment, type of product;

b) method of manufacture of the specimens and details of the surface preparation;

c) number of test repeats and whether the sample surface is reprepared after each test;

d) the solution composition, pH, volume and temperature and any variations with time;

e) area of the specimen exposed to the test solution;

f) description of cell and electrodes used;

g) time of immersion prior to polarization;

h) open circuit potential prior to scanning, and whether this was steady;

i) the potential shall be quoted with respect to the standard hydrogen electrode;

j) full details of potential scanning, including scan rate, upper potential value and final potential value;

k) typical example of polarization scan;

l) individual values of reactivation peak current and activation peak current and their ratio for both the test specimen and for the solution-annealed specimen, together with details of grain size and normalization parameters used for characterizing sensitized grain boundaries;

m) individual values of reactivation charge and activation charge and their ratio for both the test specimen and for the solution-annealed specimen, and the normalized values for sensitized grain boundaries.

n) result of the metallographic inspections.

Annex A
(informative)

Flushed port cell and flushed electrode holder

A.1 Flushed port cell

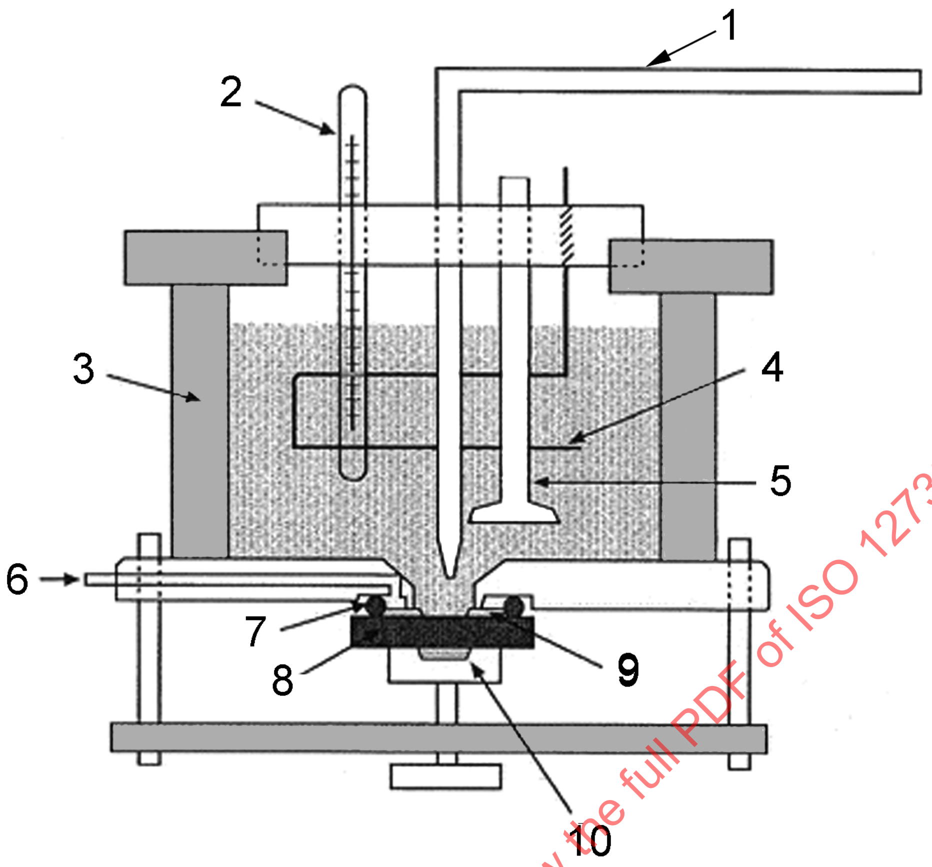
The flushed port cell (Figure A.1) consists of a circular double-walled glass chamber to facilitate heating by an external recirculating heating bath and various inlets, connections for temperature measurement, electrodes and gas purging.

The bottom of the cell incorporates the specimen holder. The specimen is mounted outside the cell. Elimination of crevice corrosion at the contact point of the specimen and the cell port is achieved by continuously pumping a small volume of distilled water into the contact area of the cell port.

The specimen is separated from the cell port by one or more filter-paper rings, creating a diffusion barrier between the purified water, the specimen and the test solution. The distilled water pumped into this region displaces any electrolyte that would otherwise be in the crevice-like region. The water flow is typically in the range of 4 $\text{ml}\cdot\text{h}^{-1}$ to 5 $\text{ml}\cdot\text{h}^{-1}$ for a 1 cm^2 port opening. The cell shall be large enough to ensure sufficient test solution volume to minimize the dilution effect from the purified water within the timeframe of the test. Where necessary, the dilution of the test solution should be balanced by addition of appropriately concentrated test solution at the same rate.

The test area exposed to the electrolyte is not isolated from the test solution by the distilled water because the difference in density between the distilled water and the test solution makes the distilled water flow upwards just on the port sides. Furthermore, stirring of the solution will cause effective mixing.

Because the specimen is mounted outside the cell, there can be a difference in temperature between the electrolyte and the specimen when testing at elevated temperatures. This can be minimized by stirring, and by a combination of insulation and by minimization of the volume of the metal to reduce its effectiveness as a heat sink.



Key

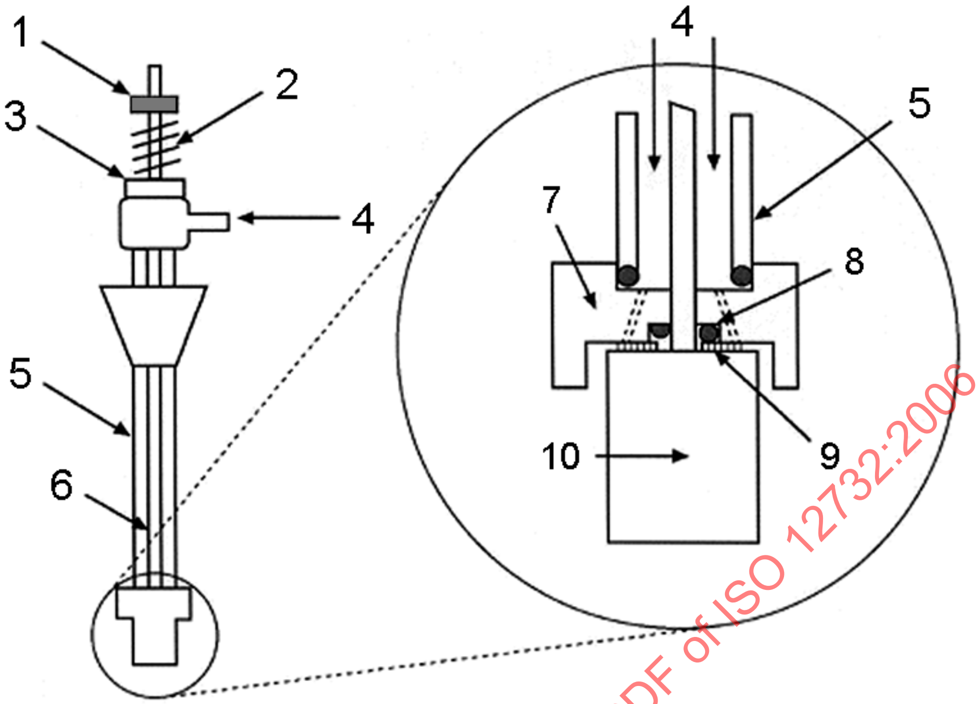
1	luggin capillary (to reference electrode)
2	thermometer
3	double-walled glass chamber
4	counter electrode
5	gas dispenser
6	distilled water
7	O-ring
8	specimen
9	filter peper
10	mounting screw for specimen

The double wall facility allows the temperature to be well controlled.

Figure A.1 — Example of general-purpose flushed port cell

A.2 Flushed electrode holder (Figure A.2)

Distilled water is fed through a glass tube sealed with O-rings to the PTFE mount at the bottom. The water is distributed through the filter paper on top of the specimen. The stainless steel connecting rod, on which the specimen is mounted, is painted to avoid electrical contact with the distilled water. A typical flow rate is about 1,5 mL·h^{-1} for a 10 mm diameter cylindrical specimen.



Key

1	screw
2	spring
3	PTFE disc and O-ring
4	distilled water
5	glass tubes
6	painted connecting rod
7	PTFE mount
8	O-ring
9	filter paper
10	cylindrical specimen

Figure A.2 — Example of flushed electrode holder

Annex B
(informative)

Potential of selected reference electrodes at 25 °C with respect to the standard hydrogen electrode (SHE)

Reference electrode	**Potential with respect to SHE** V
Saturated calomel electrode	0,241
Silver/silver chloride electrode in 1 molar KCl	0,222
Silver/silver chloride electrode in 0,1 molar KCl	0,281