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# NUCLEAR ENERGY AGENCY COMMITTEE ON THE SAFETY OF NUCLEAR INSTALLATIONS

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# ELECTROCHEMICAL TECHNIQUES TO DETECT CORROSION IN CONCRETE STRUCTURES IN NUCLEAR INSTALLATIONS

**TECHNICAL NOTE** 

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The mission of the NEA is:

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- to provide authoritative assessments and to forge common understandings on key issues, as input to government decisions on nuclear energy policy and to broader OECD policy analyses in areas such as energy and sustainable development.

Specific areas of competence of the NEA include safety and regulation of nuclear activities, radioactive waste management, radiological protection, nuclear science, economic and technical analyses of the nuclear fuel cycle, nuclear law and liability, and public information. The NEA Data Bank provides nuclear data and computer program services for participating countries.

In these and related tasks, the NEA works in close collaboration with the International Atomic Energy Agency in Vienna, with which it has a Co-operation Agreement, as well as with other international organisations in the nuclear field.

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CSNI constitutes a forum for the exchange of technical information and for collaboration between organisations which can contribute, from their respective backgrounds in research, development, engineering or regulation, to these activities and to the definition of its programme of work. It also reviews the state of knowledge on selected topics of nuclear safety technology and safety assessment, including operating experience. It initiates and conducts programmes identified by these reviews and assessments in order to overcome discrepancies, develop improvements and reach international consensus in different projects and International Standard Problems, and assists in the feedback of the results to participating organisations. Full use is also made of traditional methods of cooperation, such as information exchanges, establishment of working groups and organisation of conferences and specialist meeting.

The greater part of CSNI's current programme of work is concerned with safety technology of water reactors. The principal areas covered are operating experience and the human factor, reactor coolant system behaviour, various aspects of reactor component integrity, the phenomenology of radioactive releases in reactor accidents and their confinement, containment performance, risk assessment and severe accidents. The Committee also studies the safety of the fuel cycle, conducts periodic surveys of reactor safety research programmes and operates an international mechanism for exchanging reports on nuclear power plant incidents.

In implementing its programme, CSNI establishes co-operative mechanisms with NEA's Committee on Nuclear Regulatory Activities (CNRA), responsible for the activities of the Agency concerning the regulation, licensing and inspection of nuclear installations with regard to safety. It also co-operates with NEA's Committee on Radiation Protection and Public Health and NEA's Radioactive Waste Management Committee on matters of common interest.

#### Foreword

The CSNI/Integrity and Ageing Working Group (WG) publishes this report as a CSNI technical note. In CSNI classification, a technical note is a document addressing a particular issue serving as an input to the relevant WG/SEG activity. The audience is members of the relevant WG and the report was reviewed and approved by them.

The objective of this technical note is to describe the electrochemical non-destructive techniques that can be used in real size reinforced concrete structures to assess the corrosion condition of their reinforcement. These techniques can be used indistinctly in conventional civil engineering structures or in those of nuclear installations.

The complete list of CSNI reports, and the text of reports from 1993 on, is available on http://www.nea.fr/html/nsd/docs/

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## **CSNI Technical Note on:**

# ELECTROCHEMICAL TECHNIQUES TO DETECT CORROSION IN CONCRETE STRUCTURES IN NUCLEAR INSTALLATIONS

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## 1. SCOPE OF THE REPORT

The objective of this report is to describe the electrochemical NDT that can be used in real size reinforced concrete structures to assess the corrosion condition of their reinforcement. These techniques can be used indistinctly in conventional civil engineering structures or in those of nuclear installations.

Electrochemical techniques are used to detect electrochemical corrosion activity of metallic reinforcements. They cannot quantify stress corrosion cracking or hydrogen embrittlement although may give some qualitative information about them. The aims of their applications may be one of the following circumstances:

- 1. Quality control of new constructions
- 2. Condition evaluation of existing structures for:
  - Identification of steel despassivation
  - Detecting corroding areas for rehabilitation purposes
  - Calculation of residual load-bearing capacity of the structure
  - Prediction of the damage evolution
  - Determination of the optimum time for repair.
- 3. Control of efficiency of repair technologies

## 2. BACKGROUND

#### 2.1 Causes of steel corrosion

The mechanism of corrosion in aqueous media is of electrochemical nature. This means that the oxidation of the metal is counterbalanced by the reduction of another substance in another region of the metallic surface. Therefore, zones (anodes and cathodes) with different electrochemical potential, develop (1).

In the case of concrete the electrolyte is constituted by the pore solution, which is very alkaline. This pore solution is formed by mainly a mixture of KOH and NaOH presenting pH values ranging between 12.6-14. The solution is saturated in  $Ca(OH)_2$ . Steel embedded in concrete is naturally protected by this high alkalinity and by the barrier effect of the cover itself.

The two main causes of electrochemical corrosion are carbonation and the presence of chlorides (figure 2.1) (2). Carbonation usually induces a generalized corrosion while chloride will lead into pitting or localized attack. The corrosion can be easily recognized by the rust presence on the rebar and by the appearance of cracks running parallel to the rebars. In figure 2.1 is also identifies another particular type of corrosion, the stress corrosion cracking, SCC, that develops in prestressed wires subjected to special aggressive conditions.



*Figure 2.1* Types and morphology of the corrosion in concrete: generalized (carbonation), localized (chlorides) and stress corrosion cracking (in prestressing wires).

#### 2.1.1 Carbonation

Atmospheric carbon dioxide reacts with the calcium and alkaline hydroxides and cement phases, leading in a lowering of the pore solution pH value until values near neutrality. This process aims into the depassivation of the steel in contact with the carbonated zones.

Carbonation is a diffusion process and therefore, its depth progresses by an exponential attenuation along the time. The modelling of carbonation is generally made by means of the simplified expression:  $x=k_{co2}\sqrt{t}$ , where x is the carbonation depth, t is the time and  $k_{co2}$  is the carbonation factor of the particular concrete. It does not develop if the concrete is water saturated or in very dry conditions. However, as cycling wet-dry periods are the usual environmental out-door conditions, the carbonation front can advance relatively fast (2).

As the corrosion is generalized, cracks will appear running parallel to the rebars. Usually they appear not before 20 years life for a cover of 20-25 mm, what means that the corrosion rates are in general low. Spalling will be produced at later stages.

## 2.1.2 Chloride attack

The chloride ions may be present in the concrete if they are added in the mix (admixtures, water or aggregates). However, this is fortunately not common. The most frequent is that chlorides penetrate from outside, either due to the structure is placed in marine environments or because deicing salts are used.

Chlorides induce local disruption of steel passive layer dealing into pits or localized attack.

In submerged zones or in fully saturated concrete, chlorides penetrate by diffusion. However, in aerial zones or when submitted to cycles (deicing salts), capillary absorption may be a faster mechanism of penetration. In both cases, the penetration is as well dependent of the square root of time. Therefore,

its modelling may be made similarly to the carbonation, by means of the simplified expression  $x=k_{cl}^{-1}$ . The chloride ingress is usually modelled by means of the so called *error function equation* which is a particular solution of Fick's second law (2):

$$C_x = C_s(1 - \operatorname{erf}(\frac{x}{2\sqrt{Dt}}))$$
[2.1.]

where  $C_x$  is the chloride concentration at the depth x,  $C_s$  is the surface chloride concentration and D the chloride diffusion coefficient.

Depending on how extended or localized is the corrosion, cracks may appear or not. In submerged zones sometimes the rebar corrodes without any external sign of cover cracking.

Concerning the amount of chlorides needed to induce the onset of corrosion (threshold value), it depends on several factors not fully quantified. This multiple dependence makes difficult to fix a single value.

The factors influencing the chloride threshold are:

- Type of cement: finess, amount of  $C_3A$ , amount of gypsum, blending materials.
- Water/cement ratio (porosity).
- Curing and compaction (porosity).
- Moisture content and variation.
- Type of steel and surface roughness and condition (pre-rusted or not).
- Oxygen availability (corrosion potential when arriving the chlorides).

Each structure has its threshold which, in an already corroding structure can be verified by appropriate testing. To predict the threshold in a particular structure is difficult, but if the steel has depassivated in some areas, the testing of the concrete surrounding the rebar will enable a more precise knowledge. The threshold may be given as CI/OH of the pore solution of % of CI by weight.

In spite of this difficulty of fixing a reliable and general chloride threshold, all codes limit the chloride content in the mixing water. In absence of other value, this amount (in general 0.4% of cement weight) can be taken as reference.

## 2.1.3. Stress Corrosion Cracking

The SCC is a specialized type of corrosion which is produced when mechanical stresses act simultaneously to some specific aggressive agents. This type of corrosion may then develop in prestressed or postensioned wires.

The mechanism of this type of corrosion is not yet well understood and several theories exist in the literature (3). The phenomenon may occur accompanied by an embritlement of the steel due to the penetration in the steel of hydrogen gas produced by a corrosion reaction.

The three conditions necessary to develop the phenomenon are: 1) a type of steel susceptible to suffer this type of corrosion, 2) the steel has to be stressed beyond a minimum threshold below which the process is very slow, and 3) a specific aggressive media (producing or not hydrogen gas)

When the three conditions are found simultaneously the process develops in three steps: 1) one or several microcracks are generated at the surface of the steel, 2) these cracks grow until they reach a certain depth and then they propagate very quickly until 3) it aims into the brittle failure of the wire. This failure may be enhanced by hydrogen embritlement.

The phenomenon may then be slow during the generation of the crack and later it propagates very quickly leading to a sudden unexpected failure.

The corrosion during the first step cannot be noticed by means of measuring the corrosion rate, as the loss of metal is negligible and the corrosion potential measured at the concrete surface may not indicate the developing of the process. Therefore, this type of corrosion cannot be electrochemically measured during its occurrence. Only the risk of its appearance may be approached by the traditional electrochemical techniques.

The identification of the nature of the failure is not an easy task after being produced. It has to be detected by microscopical observation of the fractured surface when it is fresh, and not corroded or contaminated. In the case of having occurred SCC or  $H_2$  embritlement, the fractography enables the identification by the brittle aspect of the steel fractured surface.

This type of phenomenon has not to be mistaken with the failure induced by chlorides in prestressed wires. The ions inducing localized corrosion may also aim into a failure, but of simple reduction (localized attack) of the cross section produced by the electrochemical process. The SCC may not be of electrochemical nature and then its rates of propagation differ from those of normal localized corrosion.

Typical contaminants promoting SCC are sulphides sulphates or tiocyanides, while chlorides are less linked to this type of failure.

## 2.2. Consequences of steel corrosion.

In the case of reinforcement corrosion, the most simple and descriptive model for service life is due to Tuutti (2) and is shown in Figure 2.2.

This well known model considers:

- An initiation period which consists of the time from the erection of the structure until the aggressive agent (either chlorides or the carbonation front) reaches the rebar and depassivates the steel.
- A propagation period from the steel depassivation until a certain unacceptable level of deterioration is developed in the structure.



Figure 2.2 Service life model for reinforcement corrosion.

#### 2.2.1 Corrosion: structural effects

In the case of non prestressed reinforcements, the first direct effect of the reinforcement corrosion is its section decrease due to the corroding process, as shown in figure 2.3 (4), Iron oxides (rust) resulting from the corrosion process have a larger volume than the original steel, in the case of reinforced concrete structures, and this effect induces internal stresses in the concrete which may lead to cracking or even spalling of concrete cover.

Corrosion also may reduce the steel elongation at maximum load, affecting subsequently the structure ductility.

On the other hand, the composite action of concrete and steel in a reinforced concrete structure is based on the bond between them, and this is also affected by corrosion through several mechanisms: a) increasing of hoop stresses due to pressure of rust, producing concrete cracking, b) change of properties of the interface concrete-steel, and c) the corrosion of stirrups.



Figure 2.3 Consequences of the corrosion in the structural performance.

Accordingly, reduction of structural capacity of reinforced concrete elements affected by rebar corrosion is mainly due to the following three main phenomena, which are direct consequence of corrosion:

- reduction of rebar section due to corrosion
- reduction of bond strength
- loss of concrete integrity due to cover cracking and/or spalling

The rate of developing of these phenomena is function of different parameters as corrosion current  $(I_{corr})$ , type of aggressive, time since propagation period was initiated, and reinforcement or structural detailing.

In the case of SCC, the main difference lies in the fact that rust may not be generated and therefore the cracking of the cover is not produced. The main concrete characteristics affected are the ductility of the bars and their reduction in cross sectional area. When partial failure is produced, the reduction in structural ductility and the collapse of the main other parts, can be immediately achieved.

## 2.3. Environmental influence in the corrosion process

The reinforcement corrosion is the consequence of the ageing of the concrete in a particular environment. Then, the environmental actions are the aggressive which may shorten the concrete durability.

The main influencing parameter on the corrosion among the environmental conditions is the moisture content of the concrete, which is dependent on the external temperature and humidity. The concrete moisture controls the penetration of gases such as  $CO_2$  and  $O_2$ . Thus, when the material is water saturated the carbonation is delayed and the access of  $O_2$  is limited. On the opposite, chlorides penetrate quicker if the material is saturated. Regarding the corrosion process, the concrete moisture content will influence the electrical resistivity (porosity) (5).

All these effects are not uniform in the concrete mass, but a gradient of moisture is produced from the concrete surface towards the interior. It will depend on the rebar position (cover depth) how the climatic cycling will influence the corrosion process.

Temperature will influence as well the corrosion process. It produces also two opposite effects: acceleration or retardation of the reaction. When temperature rises, evaporation of pore water is induced and oxygen is removed from the pore solution. Therefore, although the corrosion process is stimulated by the rise in temperature, this may be counterbalanced by the increase in resistivity (evaporation) and the removal of oxygen (smaller solubility at higher temperatures). An opposite effect is induced by a lowering of temperature in semi-dry concretes as condensation is induced.

All this means that the effect of daily and seasonal variations of RH and T on the corrosion of rebars, cannot be directly deduced and quantified.

The experimental evidence shows that the humidity content of the concrete varies depending upon the external RH and the direct exposition to rain. Raining events dramatically affect the saturation degree of the concrete. The saturation degree is the most relevant parameter linked to the resistivity and the corrosion rate values.

The exposition of concrete to outdoor conditions will induce a saturation degree related to the particular climate. External moisture and temperature cycles will be followed by parallel changes in the concrete moisture content, which in consequence induce an evolution in the corrosion rate following dayly and seasonal cycles.

This experimental evidence accounts for the need to characterize a Representative value for the corrosion rate,  $I_{corr, Rep}$  which is an averaged value in the particular climatic conditions where of the concrete structure is placed.

#### 3. FUNDAMENTALS OF ELECTROCHEMICAL TECNIQUES

Traditionally, visual observation has been the common technique used to detect corrosion due to it induces rust, which in turn produces the cracking and spalling of cover. These damages are an indication of the corrosion activity developed underneath the cover.

However, due to the different degrees of aggressivity, of concrete quality and of structural geometry, the deductions taken from visual inspection, may be completely misleading.

Electrochemical techniques emerge as much more accurate means due to their potential non-destructive character. At this respect, it has to be again mentioned that the stress corrosion cracking may develop without the association of an electrochemical corrosion process and therefore, it might not be detected by means of electrochemical techniques. Up to now, no techniques are known to be able to detect SCC on-site in non-electrochemically corroding reinforcements.

Other techniques based in ultrasonic or electromagnetic excitation or in optic fibre observations, have been tried to measure electrochemical corrosion or SCC, but they have shown particular limitations, which suggest that they are not still mature or need much further development.

The main electrochemical techniques used to detect corrosion activity are:

The so-called Polarization Resistance,  $R_p$ , which enables the calculation of the instantaneous corrosion current,  $I_{corr}$ , and therefore, the quantification of the corrosion process.

The measurement of the corrosion (or half cell) potential,  $E_{corr}$ , which is of qualitative character and may be serve to locate corroding reinforcements and inform on the risk of corrosion.

The measurement of the electrical resistivity, which is an indication of the concrete degree of saturation and therefore, enables the identification of the risk of corrosion because in dry concrete the corrosion, does not progress.

## 3.1. Polarization Resistance, Rp, method

This electrochemical technique enables the measurement of the instantaneous corrosion rate. It quantifies the amount of metal per unit of area being corroding in a particular instant.

The method is based on the observation of the linearity of the polarization curves near the potential  $E_{corr}$ . The slope  $\Delta E/\Delta I$  ( $\Delta E$ = step of potential,  $\Delta I$ = change induced in the current) expresses the value of the polarization resistance ( $R_p$ ) if the increment tends to zero. Thus, (6):

$$R_{P} = \left(\frac{\Delta E}{\Delta I}\right)_{\Delta E \to 0}$$
[3.1]

This  $R_p$  value is related to the corrosion current  $I_{corr}$  by means of the expression:

$$I_{corr} = \frac{B}{R_{P} \cdot A}$$
[3.2]

Where A is the area of metal surface evenly polarized an B is a constant which depends on the Tafel slopes of the polarization curves,  $\beta_a$  and  $\beta_c$ :

$$B = \frac{\beta_a \cdot \beta_c}{2,303 \left(\beta_a + \beta c\right)}$$
[3.3]

B may vary from 13 to 52 mV for a wide range of metal/electrolyte systems. For the case of the steel embedded in concrete, the best fit with parallel gravimetric losses results from the use of a value of B= 26 mV, when the steel corrodes actively, and a value of B= 52 mV when it remains passive (6) the formula [3.2] has an intrinsic error of 2 if value of B= 26 mV is used as an average.

Although "corrosion current",  $I_{corr}$ , and "corrosion rate",  $V_{corr}$  are indiscriminately used, they are formally different. Corrosion current represents the instantaneous value when referred to the corroding area and its units are  $\mu$ A/cm<sup>2</sup>. It is converted into corrosion rate  $V_{corr}$  when measured periodically and refers to a particular period in order to characterize the development of the process. The  $V_{corr}$  units are mm/year.

The main precautions which have to be taken into consideration when measuring Rp in the case of the steel embedded in concrete are (6)(7):

The compensation of the ohmic drop due to the high electrical resistivity of the concrete. Modern potentiostats enable the elimination of this ohmic drop by means of positive feed-back devices or by means of the current interruption method. Too dry a reference electrode, located on it through a sponge or a conductive gel.

Achievement of a quasi steady-state response. This requires waiting times between 30 an 100 seconds in potentiostatic/galvanostatic measuremets or the use of scan rates between 2.5 and 10 mV/min, in the case of potentiodynamic operation. The shorter waiting times or faster scan rates are suitable for the case of active corrosion, while if the steel is passive, the quasi steady state is achieved at longer times or slower scans.

Linearity in the  $\Delta E/\Delta I$  slope, which is reached in general if the polarization remains below 20 to 30 mV, although in the case of active corrosion polarizations as high as 100 mV can fit into a linear response.

The method gives the total or general corrosion (when divided by the total area). Therefore if pitting is occurring, care has to be taken in analysing the meaning of the  $I_{corr}$  values. The error is greater, the larger the total area. If the corroding areas are known, the  $I_{corr}$  can be referred to it.

The method cannot be simply applied to real size structures, as the area really polarized is unknown, specific methodology is needed for measurements on-site, as will be described later.

#### 3.1.1. Particularities of measurement in real size structures.

The main characteristic of real size concrete structures regarding the corrosion measurements is the quasiinfinite length of their reinforcement. This circumstance calls for using techniques not affected by the metal size (8) (9). Direct estimations of true Rp values from  $\Delta E/\Delta I$  ratio are usually unfeasible in large structures, where the applied electric signal tends to decrease with increasing distance from the CE (figure 3.1.) rather than spread uniformly across the WE. Therefore, the action of the electric signal cannot be related to any specific WE (working electrode) zone. Hence, DE/DI measurements on large structures by use of a small CE provide an apparent polarization resistance (Rp<sup>app</sup>) that differs from the true Rp value depending on the experimental conditions.



Figure 3.1. Lateral attenuation of the electrical current when applied between a small counter placed at the concrete surface and the reinforcement. The critical length is the distance reached by the current.

If the metal is actively corroding and Rp is low, the current applied from a small CE located in the concrete surface is drained very efficiently by the rebars and it tends to confine itself on a small surface area as is shown in the top part of figure 3.2. Conversely, if the metal is passive and Rp is high, the current applied tends to spread far away (e.g., around 50 cm) from the application point. Therefore, almost any electrochemical method may provide reliable corrosion rates for actively corroding reinforcement, and all of them pose some difficulties in estimating the typically very low corrosion rates of passive reinforcement.



Figure 3.2. Arrangement of electrodes (4P) for measuring electrical resistivity

However, if an external circular counter electrode (guard ring) is used, as is shown in the bottom part of figure 3.2., then the current can be confined to a particular area.

Methods to determine Rp in large structures of reinforced concrete can be classified in three groups:

- A. Confinement of the applied electrical signal.
- B. Measurement or estimation of the lateral spreading of the electric signal.
- C. Minimization of the effect of the lateral spreading of the electric signal.

Examples of type A are methods using modulated guard ring (9). Among methods B, mention will be made to those resulting from application of transmission line models (8). Finally, the use of counter electrodes of very large size, or of increasing size to extrapolate the results to infinite size (10), belong to method C.

One of the most widely adopted solutions to limit the current lines from the CE to the WE is the modulated guard ring, figure 3.3 whereby the applied signal is confined by using a ring shaped CE, surrounding the main electrode. This way, the current field lines that originate from the central counter are confined within a known area of the reinforcement by means of two reference electrodes placed between central and guard in order to control the confinement by modulating the current applied from the external ring.



Figure 3.3. Principle of the modulated confinement of the current: the efficiency of the confinement is continuously monitored through two extra reference electrodes placed between central and external counter electrodes.

It is also possible to obtain rapid information on reinforcement corrosion rate by applying potentiostatic or galvanostatic short pulses (11). However, this information may be not very reliable with passive reinforcements, and these procedures call for further investigation to solve the field work problems posed by the uneven distribution of the current between the small CE placed at the concrete surface and reinforcements. Only qualitative information can be obtained from these pulses.

#### 3.1.1.1 Errors arising from unconfinement of the electrical signal

As has been mentioned  $Rp^{app}$  values measured under unconfined-signal conditions can differ considerably from Rp values obtained by using confined currents. Rp cannot be calculated directly by multiplying  $Rp^{app}$ by a given coefficient since such a coefficient would change with the experimental conditions (rebar activity, concrete electric resistivity, structure and reinforcements geometries, and concrete cover thickness). The lack of universality of the  $Rp/Rp^{app}$  ratio precludes the establishment of reliable correlations between data obtained with and without a guard ring (Fig. 3.4).



Figure 3.4. Variation of the ratio of the true polarization resistance (Rp measured with confined signal) and the apparent polarization resistance ( $Rp^{app}$  measured without signal confinement) with the corrosion current,  $I_{corr}$ , as calculated from true Rp. CE size 50cm<sup>2</sup>.

#### *3.1.1.2 Current distribution around the rebar circumference.*

Difficulties have been mentioned for Rp measurements which arise from a non-uniform distribution of the applied current lengthwise a long the rebars. However, in the case of current distribution around the rebar circumference, current uniformity is usually taken for granted, due to its relatively small size.

#### 3.1.1.3 Maximum depth of corrosion (pits).

The calculated values of  $I_{corr}$  are average values referred to the overall reinforcement surface polarized by the current. The integration of these values over the exposure time allows one to estimate an average penetration of corrosion (P), but it does not inform at all about the maximum penetration ( $P_{max}$ ) of the deepest pits when the attack is very uneven (see figure 3.2). For life predictions, when the mechanical weakening of the structure is affected by the bar section loss in those places where corrosion is intensified, the  $P_{max}$  value will be of more interest than the average value

 $P_{max}$  could be estimated from  $I_{corr}$  provided that a ratio between  $P_{max}$  and P could be established. Ratios ranging from about 5 to 10 in natural corrosion of reinforced concrete have been measured (12). This finding is of a great practical importance to predict residual life of chloride-contaminated concrete structures. It can be expected that pit growth proceeds 5-10 times or so more rapidly than the instantaneous  $I_{corr}$  (average rate) measured. Similarly, the maximum total depth of localized attack will exceeded by about 5-10 times the estimated average general penetration deduced from loss in weight after a given exposure time.

## 3.2. Electrical resitivity measurements

The electrical resistivity is defined as the ratio between the applied potential and the current circulating between two electrodes providing the arrangement enables the calculation of the geometrical characteristics. The electrical resistivity is an indirect measurement of the porosity and the connectivity of the pores (13).

It is used to detect wet areas in the concrete and therefore the measurement provides information about the risk of corrosion. Although it is inversely related to the corrosion rate, their results cannot be used to calculate it due to the big scatter detected in the measurements.

Two measurement methods can be used depending on whether direct contact to the reinforcements, is or not made.

#### 3.2.1. Four point method

It does not need a direct contact with the reinforcement. Concrete resistivity can be measured directly on the surface of the structure by means of Wenner technique. It was originally developed for geophysical prospecting, and widely used in soils. It has been applied to concrete more recently. This method uses four equally spaced point electrodes in contact with the concrete surface (as shown in figure 3.5).



Figure 3.5.

The resistivity is calculated as follows:

$$\rho_{\text{concrete}} = 2 \pi a R_{\text{measured}}$$
[3.4]

where  $\rho_{\text{concrete}}$  is the resistivity of the concrete (in  $\Omega$ m),  $R_{\text{measured}}$  the resistance from the four-electrode measurement (the voltage divided by the current, in  $\Omega$ ), and a is the distance between the measuring electrodes.

#### 3.2.2. Disk or one-point method

Other option for measuring concrete resistivity is based on the estimation of the ohmic drop from the resistance between a small disc placed al the surface of an electrolyte and the reinforcement. Whit this arrangement the resistivity is calculated from the expression:

$$\rho = 2R_e\phi \tag{3.5}$$

Where  $\emptyset$  is the diameter of the disk.



Fig. 3.6. Arrangement of connections in the 1P (disk) method to measure electrical resistivity. (See also figure 5.1).

#### 3.3. Half cell potential measurement

The corrosion or half cell potential, Ecorr, is defined as the voltage difference between the reinforcement and a reference electrode, RE, (figure 3.7). It characterizes the state of the metal in its environment (1).



Figure 3.7. Potential measurement of concrete reinforcement.

The  $E_{corr}$  cannot be measured locating the RE directly on the reinforcement surface, but through a layer or cover of concrete acting as electrolyte that has to exist in between. This means that the potential so measured may be affected by an error due to the relatively low conductivity of the concrete and the existance of macrocell currents.

The potential  $E_{corr}$  can only qualitatively inform on the risk of corrosion. It cannot account for it.

## 4. TYPES OF ELECTROCHEMICAL TECHNIQUES

#### 4.1. Techniques applied from the concrete surface (or non permanent techniques)

They encounter the use of portable equipment with sensors applied from the external surface of the concrete. The electrical access to the reinforcement is usually needed

As was mentioned three types of techniques are those used commonly:

The measurement of the instantaneous corrosion current,  $I_{\rm corr}$ . The mapping of the corrosion potential,  $E_{\rm corr}$ , and Of the electrical resistivity,  $\rho$ .

While  $I_{corr}$  represents the quantity of metal that goes into oxides by unit of reinforcement and time, the  $E_{corr}$  only expresses a difference of activity of the corrosion process and  $\rho$  indicates the degree of saturation of the concrete. All three complement each other for the sake of interpretation, although only the determination of the corrosion current,  $I_{corr}$ , is of interest for the long term assessment.

#### 4.2. Embedded electrochemical sensors

Their aim is a continuous monitoring, for which small electrodes are embedded in the concrete, usually in the cover at different cover depths. They may have wider purposes than the techniques applied from the exterior concrete surface.

Thus, apart from the measurement of  $I_{corr}$ ,  $E_{corr}$  and  $\rho$ , the embedded electrochemical sensors, EES, may monitor the following two other processes:

The advance of the carbonation or the chloride front. The availability of oxygen at the sensor level.

Sensors to be embedded in concrete have to be robust enough to support concrete fabrication and to resist concrete alkalinity at long term. They have to be also connected to devices able to operate in adverse conditions of humidity and temperature.

As sensors for monitoring corrosion potential, those of Mn/OMn have shown up to present to be the most durable. As well Titanium wires are suitable for the purpose of measuring the corrosion potential  $E_{corr}$ , although they have very high impedance which has to be taken into account by the equipment used for recording. Graphite electrodes have been also suggested.

Regarding the measurement of resistivity, arrangements of the disk type (a small disk of stainless steel having in its center a reference electrode) are suitable when using the reinforcement as the working electrode. However, two identical small bars or plates can be also used if proper calibration of the geometry is made. Examples of both are shown in figure 4.1.

For measuring the Rp ( $I_{corr}$ ), the same arrangement of the disk used for resistivity (figure 4.1.) results suitable, if laterally other reference electrodes are placed at determined distances in order to measure the attenuation of the signal. Embedding the guard ring arrangement results more difficult.



Figure 4.1. Relative error between Rp obtained confined and  $R_{p,app}$  measured unconfined. As smaller is  $I_{corr}$  higher is the error.

Concerning the measurement of the oxygen availability, the best results the arrangement of the two parallel small bars (figure 4.1) using one as working electrode and the other as counter, providing a third electrode is used as reference to fix the potential of oxygen reduction.

The measurement of the advance of the carbonation front or of that of chlorides can be made by placing small steel bars in parallel to the concrete surface. These steel bars will depassivate when reached by the aggressive front. The depassivation can be monitored by either recording their  $E_{corr}$  or their  $I_{corr}$ .

In summary, embedded sensors can be used for monitoring the evolution of several parameters related to the reinforcement durability.

#### 4.2.1. External application of embedded sensors

Although sensors for monitoring have been developed for being embedded during construction, they can be also placed in built structures.

This possibility enlarges the application of sensors to structures such as nuclear installations already operating.

These can be made in two ways:

- by making holes in particular sites filling the holes with mortar, or
- by placing the sensors attached to the surface and covering then also with an appropriate mortar.

The only precaution to be taken concerns the mortar used to attach the sensors: it has to be of similar nature of the concrete of the structure, in the sense that of using similar cements and w/c ratios. A siliceous sand can be appropriate as aggregate. In absence of this possibility, the recommendation is to use a mortar of cement/sand ratio 1:3 and a w/c  $\approx 0.4$ .

Prepacked mortars are not suitable for the purpose as they may of too high electrical resistivity.

## 5. PRACTICAL OPERATIONS

#### 5.1. Selection of measurement location

Before starting the survey it is necessary to select the number and location of points where corrosion rates will be measured. The number of points will depend upon : a) the amount of time available, access, and size of structure and, b) the aim of the inspection.

With regard to the duration of each measurement, each reading may take from less than 1 minute to about 5 minutes depending upon the actual corrosion conditions and the method of measurement. There may also be a set up time of 2-5 minutes due to the physical processing of placing the sensor. So the operator must allow 5 to 15 minutes per location.

The operator must also account for time taken to get access to each location, other measurements taken and other logistical factors associated with site work. This will control the total number of readings that can be taken. Obviously experience is important in being able to collect the most useful data for a reasonable expenditure of time and effort. The previous measurement of chloride concentration, rust staining, cover, carbonation depths, etc. can also be used as indications for selecting the measurement points.

In consequence with regard to the spatial frequency, the structure has to be divided in lots attending: a) the aggressivity of the ambient, b) the structural typology and c) the aim of the inspection. The groups of structural elements will be then statistically treated in order to obtain a representation value of each elements group or on the opposite, they will be mapped to obtain a pattern of the damage.

On the temporal frequency it will depend as well on upon the aim of the inspection. If this is only the identification of the corroding zones or to evaluate the efficiency of a repair work, a single visit may be enough. The lack of measurements along the time is recommended to be balanced by taking the larger possible number of readings in different locations of the structure, selected regarding several degrees of apparent damage or exposure aggressivity.

When the appraisal of the load-bearing capacity of the structure is searched, then, it is necessary to obtain an accurate enough representative value of the corrosion rate,  $I_{corr}^{REP}$ . This can be obtained by performing several measurements along a whole year following the seasonal changes.

## 5.1.1 Identification of rebar placement

Making use of a steel locator the definition of the bar layout is made. If needed, the bar pattern can be marked on the concrete surface, as well as the cover depth registered. The bar diameter and their distances are needed for the calculation of the steel area to be polarized during the measurements

#### 5.1.2 Coordinate system for measurements

When mapping of a zone or element is decided, measurements should be taken on a grid. It is recommended that readings are taken over a rebar so the grid size is partly dependent on the rebar spacing. A 0.25 m grid spacing is recommended, except on small structures or units with severe changes in condition.

## 5.2. Measurement of the corrosion rate, I<sub>corr</sub>

#### 5.2.1. General

The main aims of the measurement of corrosion current through the Rp technique are:

- a) The identification of corroding zones. Corrosion maps enable to identify the corrosion zones in the same manner than the potential mapping.
- b) The evaluation of the efficiency of repair techniques such as use of corrosion inhibitors, patching or realkalisation.
- c) The assessment of the structural condition or load-bearing capacity.

#### 5.2.2. Description and instrumentation

The measurement of the corrosion current is made by means of a reference electrode, which indicates the electrical potential, and an auxiliary electrode, which gives the current. In on-site measurements, a second auxiliary electrode (guard ring) is being used in order to confine the current into a limited reinforcement surface

The instrumentation needed for measuring linear polarization is now relatively simple, devices are commercially available (14)(15). With some small variants, the procedure for measuring the corrosion rate is as follows:

- Locate the reinforcing steel grid with a covermeter and mark it on the concrete surface.
- Selection of the measurement locations. Record the cover depth and bar diameters in these locations.
- Proper connection to the rebar and between the concrete surface and the measuring probe.
- Measure the corrosion potential.
- Application of the electrical current, and recording of the response in order to obtain the  $\Delta E/\Delta I$  ratio.
- Plot the potential versus the current per unit area of the bar, and determine the slope of the best-fit straight line. This is the polarization resistance. In the case where a sensorized guard ring is used, ΔE/ΔI ratio gives a true R<sub>p</sub> directly.
- Calculation of  $I_{corr}$  from the true  $R_{p}$ .



Figure 5.1. Aspect of a portable corrosion rate meter making use of a modulating guard ring.

The execution of the  $R_p$  measurement may take from few seconds to 5 minutes, depending upon the used method. Repetition of the measurement in the same location is recommended in order to check on the reproducibility and non-perturbative character of the method.

## 5.2.3. Interpretation of the results

With regard to the accuracy of these measurements, two main aspects have to be taken into account:

1. The morphology of the corrosion, that is to say, how much localised is the corroding area. If pits are produced, the maximum pit depth can be calculated by means of a factor ( $\alpha$ ) which takes a value between 3 and 10. Thus, the maximum penetration depend, P<sub>max</sub>, in a predetermined area is:

$$P_{\max} = I_{corr} \cdot \alpha$$
 [5.1]

2. In on-site measurements, the R<sub>p</sub> technique cannot be used in the same arrangement than in the laboratory, due to the auxiliary electrode is comparatively much smaller than the size of the structure. In consequence, the measurement has to be made by means of confining the current (use of a guard ring) or some mathematical calculations have to be applied. One of the two modes of operations have to be made, otherwise the error can be of several orders of magnitude.

Other influencing parameters related to the environment of the concrete itself are:

1) **Moisture content**. The moisture or liquid water in the concrete pores is the most relevant parameter influencing the corrosion current. It is responsible of the electrolyte continuity (pore connectivity) and of the oxygen availability at the steel surface.

Moisture fixes the electrical resistivity, which is the most comprehensive parameter determining the corrosion current. Oxygen content is more secondary unless below a certain

2) **Temperature**. It has an opposite effect on the corrosion rate. When the temperature increases, the moisture evaporates, which may counter-balance the trend to increase the corrosion rate. Only in water saturated structures, the temperature may present a direct relationship with the corrosion rate.

- 3) **Chloride content**. The chlorides not only act by depassivating the steel, but also enhance the corrosion rate. As higher is their amount, higher is the corrosion until a certain limit, beyond which the corrosion current may even decrease. This has been interpreted to be due to the saturation of the concrete pore solution and the removal of oxygen that a concentrated solution induces.
- 4) **Macrogalvanic effects.** The corrosion itself is based in a macrocell function, however macrogalvanic effects are called there have several centimetres or decimetres separating corroding form non corroding areas. This may lead into a misidentification of the corroding areas if not guard ring confinement is used.

Table 5.1 gives the range of values aiming into a preliminary interpretation of the corrosion currents when correctly measured.

Icorr values (µA/cm <sup>2</sup> )	Corrosion
< 0.1	Negligible
0.1 - 0.5	Low
0.5 - 1	Moderate
>1	High

Table 5.1.	Correlation	between	corrosion	rate and	level o	f corrosion
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#### 5.3. Resistivity Measurements

#### 5.3.1. Purposes

The main aim of electrical resistivity measurements is to identify the moisture content of the concrete, and in consequence to identify the more humid locations with higher risk of corrosion.

#### 5.3.2. Procedure and instrumentation

The measurement on-site of the resistivity is carried out directly on the surface of the structure. Two methods can be distinguished depending in whether direct contact to the reinforcement is or not made.

First it is necessary to moisten the electrode tips with a conducting liquid in order to provide a good contact with concrete. An alternating current with a frequency between 50 and 1000 Hz is passed between the outer electrodes and the potential difference is measured between the inner ones. Resistivity is obtained as a function of voltage, current and distance between tips (usually 50 mm).

A conductive material disk, a potentiostat and a reference electrode compose the device. After a good contact between electrode and concrete is obtained, a galvanostatic pulse is applied and then, the ohmic drop is recorded from the instant response. As with the 4-point Wenner method, the disk and the rebar must no be very close to obtain an accurate measure of bulk concrete resistance. Distance between disk and reinforcement has to be at least two times the disk diameter.

#### 5.3.3. Interpretation of the results

One of the most important problems arising for the measurement of concrete resistivity is its variability with changes in the environment. The factors which influence the resistivity are:

- a) <u>Humidity content</u>. The  $\rho$  decreases when concrete moisture increases and viceversa. The  $\rho$  is an indirect measure of saturation of the concrete.
- b) <u>Temperature</u>. The effect of temperature is controversial, as its effect on  $\rho$  depends on whether the concrete is shielded or not. That is, whether the water can evaporate or condensate. Thus, an increase of T will decrease the  $\rho$  unless it happens the opposite due to the drying induced by T increase. The opposite happens when T decreases, but only until a certain T (around 5°C), below which the  $\rho$  increases so much that the condensation cannot compensate this dramatic increase.
- b) <u>Chloride content</u>. The presence of chlorides or any other inorganic compound induces a certain decrease of the  $\rho$ .
- c) <u>Carbonation</u>. It aims into an increase in  $\rho$  due the densification that the formation of calcium carbonates usually induce.
- d) <u>Type of cement.</u> Blending agents (fly ashes, slags or silica fume) in general induce an increase of ρ when compared with ordinary Portland cement.
- e) <u>Porosity</u>. The porosity is a consequence of the w/c ratio and to the compaction and curing. An increase in w/c leads into a decrease of  $\rho$ .

<u>Type of aggregate</u>. The effect of the aggregate type cannot be generically predicted. It will depend on their nature and porosity, but for the same grading, the concrete resistivity is influenced by the aggregate nature.

Resistivity does not show, by itself, whether or not steel in concrete is in an active state of corrosion. It informs on the risk of corrosion due to the humidity content in the concrete. Table 5.2 shows the ranges of resistivity that can be related to the corrosion rate. This table is represented as well in figure 5.3.

Resistivity (kΩ·cm)	Corrosion risk
>100	Nil
- 100	Low
10 - 50	Moderate
< 10	High

Table 5.2. Resistivity ranges related to the risk of corrosion.



**Figure 5.3**.  $I_{our}$ - $\rho$  graph to help to detect anomalous measurements

## 5.4. Half cell potential measurements

#### 5.4.1. Purposes

The main objective of potential measurements on a structure is to locate areas in which reinforcement has become depassivated and hence, is able to corrode if appropriate oxygen and moisture conditions occur.

#### 5.4.2. Procedure and Instrumentation

The most common procedure involves the mapping of the structure. The standard test method is given in ASTM C 876-91 (16). As referred before, the objective of potential measurement is to determine those areas of corroding reinforcement. To achieve this goal, first it is completely necessary to define a work strategy that provides a fast and economical overview on the state of the structure. This strategy must involve the definition of a co-ordinate system to correlate readings and measuring points. A grid usually makes it with a cell size that varies from 15 square centimetres to 2 square metres, depending on the type of the structure, its characteristics and the scope of the work. The size of this co-ordinate system is determining the accuracy of the measurements.

To determine the optimum grid spacing, it is necessary to determine the maximum distance from a corroding rebar at which there is no evidence of potential change. Measurements made with a big grid cell size could not detect corrosion activity whereas minimum spacing generally should provide high differences between readings. The spacing must be adequate to the type of structure surveyed (cover and moisture content) and the expected use of measurements.

To measure the half-cell potentials on a structure, a good electrical connection to the reinforcement has to be made. It could be made by means of a compression-type ground clamp or by brazing or welding a protruding rod, but a direct contact should not be made if reinforcement steel is connected to an exposed steel member. The other input of the high impedance voltmeter must be a suitable external reference electrode, frequently copper sulphate copper electrode, placed on the concrete surface by a wet sponge in order to provide a good electrolytic contact between them. The sponge should be always wetted with a diluted solution of detergent.

It is completely necessary to assure the electrical continuity of the reinforcement steel. Measuring the resistance between separated areas checks it. If resistance values are less or equal than 0.3  $\Omega$ , electrical continuity is indicated.

Potential measurements can be performed with a single electrode or with one or several wheel electrodes. The unpolarizable reference electrodes (Calomel or  $Cu/CuSO_4$ ) are more accurate than other types (carbon, for instance). However their maintenance regime (contact membrane) is very crucial for their accuracy. Temperature influences less the potential, of the unpolarizable electrodes.

Copper/Copper sulphate electrode is the most used reference for in-situ potential measurement, whereas calomel and silver chloride electrodes are used more in lab works.

Once the data are obtained, the best way to their representation depends on their number and the type of the structure. So it varies from tables to a coloured grid map of the potential field, where every individual potential reading can be identified as a small cell and a contour line map can be obtained interpolating between point measurements with different algorithms.

In a grid map, a coloured cell to whom the potential value has been associated represents each measurement point. The colour gradation step should not be greater than 50 mV in order to provide a clearest way to result interpretation. A 3-D surface can also be represented both by measured and interpolated values.

Of course, potential measurement can be represented by all standard statistical ways as cumulative frequency distribution or histograms. The kind and depth of the study to be developed should impose the design requirements for these graphics.

Different devices are commercially available for single electrode or multiple (wheel) electrodes.

#### 5.4.3 Interpretation of the results

The interpretation of the potential readings has evolved during last years. According to ASTM C 876-91 standard, a threshold potential value of -350 mV CSE was established. Lower values of potential suggested corrosion with 95 % probability; if potentials are more positive than -200 mV CSE, there is a greater than 90 % probability that no reinforcement steel corrosion occurs, and for those potentials between -200 mV and - 350 mV corrosion activity is uncertain.

Later practical experiences have shown that different potential values indicate corrosion for different conditions so absolute values can not be taken into account to indicate corrosion hazard, that is, the relationship between concrete condition and potential values is not well-defined enough, with the exception of those potentials at extreme ends.

The statistical representation of the data by means of cumulative frequency plots as indicated in the ASTM standard gives a better indication of the boundary potential between active and passive zones and of their percentage in the tested area.

There are different aspects that must be considered in potential measurement.

A wide range of factors influences the corrosion potentials as:

- <u>Concrete moisture content.</u> Depending on moisture condition of concrete, its resistivity varies. Changes in moisture content may lead to a difference of potentials up to 200 mV. It is important to consider not only different moisture conditions in a determined point but changes along the whole structure. Potential values become more negative as concrete moisture increases.
- <u>Cover thickness</u>. As concrete cover increases, the difference between active and passive potential values diminishes, resulting on an uniform potential value at infinite. Thus, the location of small corrosion spots gets more difficult with increasing cover depth.
- <u>Concrete carbonation</u>. As carbonation process leads to an increase of concrete resistivity, potential measurements show more positive values on both passive and corroding rebars.
- <u>Polarisation effects</u>. The corroding zones polarize the passive rebars in their vicinity to more negative potentials. This shift is higher in lower resistivity concrete. This effect leads to the fact that wet concretes may difficult the detection of small corroding areas which however may be counterbalanced by the most active (negative) combine potential values.
- Oxygen content. Conditions of aeration, i.e. oxygen access, strongly determines rest potential values of passive steel in concrete. Low oxygen content leads to a pronounced decrease of the rest potential. In wet concrete due to very low oxygen diffusivity coefficient, conditions may arise in a shift of potential to comparably negative values so passive steel may show negative potentials similar to those of corroding steel. This leads to the risk that passive areas under low aeration conditions could be considered as corroding areas.
- <u>Chloride content</u>. Field experience on a large number of bridge decks has shown a certain correlation between concrete chloride content and the potential values. The most negative values coincide with the areas of higher chloride content.

Method	Purpose	Advantages	Limitations
Half-cell	Indication of	Lightweight, portable	Not applicable to epoxy-
potential	likelihood of	equipment if not multiple	coated bars.
	corrosion activity at	electrode system is used.	No indication of corrosion
	time of testing.		rate.
			Interpretation must be done
			by experienced personnel.
Resistivity	Information about the	Lightweight, portable	No indication of corrosion
	moisture content in	equipment.	rate.
	the concrete.	Execution of the	Interpretation must be done
		measurements very	by experienced personnel.
		quickly.	
Polarization	Indication of	Lightweight, portable	Testing and interpretation
resistance	corrosion rate of the	equipment.	must be done by experienced
	reinforcement at time		personnel.
	of testing.		

## 5.5. Summary of characteristics of the three techniques

## 6. APPLICABILITY IN NUCLEAR INSTALLATIONS

#### 6.1. Characteristics of concrete structures in nuclear plants

All nuclear plants have concrete structures which need a correct performance and aging for assuring the necessary protection to the public. The integrity of such structures also concerns during their dismantling and decommissioning.

The majority of concrete structures in nuclear plants are very similar to the conventional civil engineering ones: auxiliary and attached to the reactor buildings, are structurally traditional. It can be equally said about cooling towers, which are of similar shape than those of conventional power plants. However, the reactor cover is an unique structure which has many particularities.

In general, the main features which may difficult the application of non-destructive electrochemical techniques, NDET, to the inspection of nuclear concrete structures are:

- Section dimmensions: wall thickness exceeding 1 m are very common in safety related structures.
- High density of reinforcement: safety related structures are often heavily reinforced, which can lead to significant steelwork congestion.
- Liners and external cladding: In some structures the presence of liners prevent access to the surface of the concrete, in others cases they are embedded in concrete. Similar to liners, external cladding causes a physical barrier preventing direct access to the concrete surface.
- Accessibility: structural configuration or inadequate access; harsh ambient (high temperature and radioactivity levels), etc.

Nuclear concrete structures may suffer different aging processes depending on the particular environment where the plant is installed. It is out of the scope of present report to describe them. Regarding metallic corrosion, water is the main risk in developing or accelerating the degradation. In absence of liquid water, corrosion cannot progress.

Attention has to be also paid to cracks in the concrete, because they are a gap in the protection of the reinforcements. Cracks may develop either by the normal mechanical work of the structure or by the progression of other degradation mechanisms (freeze-thaw, alkali-aggregate reaction, etc). The cracks enable the environment to reach quickly a zone of the steel reinforcement not protected by the concrete. These zones are very localized and the loss in the bar section will be more risky than in zone of the uncracked cover.

Regarding postensioned and prestressing elements, it has to be repeated that NDET only will inform on the electrochemical corrosion developing, but cannot about phenomena of SCC or HE. Additionally, the possible corrosion developing in the wires inside the tendons cannot be detected from outside, as the metallic ducts shield the passage of the current through it. At this respect, pre-installed-inside-the-duct sensors could be a solution.

#### 6.2. Strategy of inspection and maintenance

Metallic corrosion is recognized as the most important degradation mechanism that may affect concrete structures. Its early detection will help the nuclear installations to be maintened in the necessary margin of safe operation. The monitoring of feasibility of occurrence of this process has, therefore, to be one of the

priorities in the overall plan of maintenance of nuclear plants and installations and an adequate periodicity should be established, linked to the particular environments and type of structure.

Regarding the necessary strategy of inspection and maintenance, particular non-accessible parts of concrete structures in new plants could be instrumented by sensors in order to help their assessment. Attached sensors can be also installed in existing plants, in operation or in decommissioning, when their aging is in a risky or critical situation. However, while simple periodical inspection using non-permanent NDET will be the correct operation in those cases of good aging performance of the metal embedded in concrete.

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