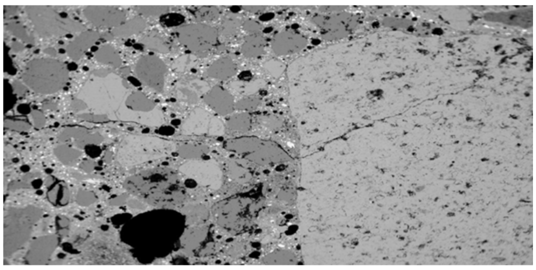
Electrical and electrochemical techniques

Electrical and Electrochemical techniques

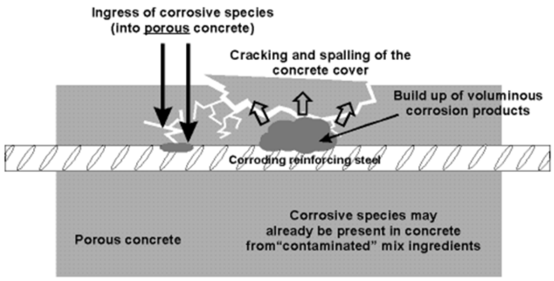
Concrete resistivity
Half-cell potential
Corrosion rate

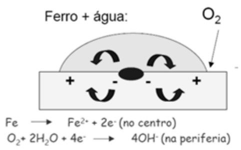
Electrical and electrochemical techniques

The concrete is a semi-conductor material and the electrical proprieties are essentially related with the electrolytic nature of concrete interstitial solution.



Electrochemical process





CORROSION RISK

- Cover depth
- Concrete proprieties: air permeability, water absorption, chloride diffusion, carbonation

- Electrical and electrochemical testing techniques are non destructive or semi-destructive techniques and allow to evaluate the corrosion state of reinforcements in concrete.
  - ✓concrete resistivity
  - ✓half cell potential – Risk of corrosion activity: identification of active zones - Most commonly used
  - ✓corrosion rate

Electrical resistivity

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Electrical and electrochemical techniques

Application field

- Identify concrete zones with HIGH corrosion risk (low electrical resistance)
- Evaluate coatings performance

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Electrical and electrochemical techniques

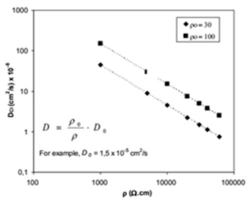
Resistivity – Applications

•Quality control of concrete (durability indicator)
HAVE TO BE DETERMINATED UNDER WELL KNOWN CONDITIONS OF HUMIDITY (SATURATED CONDITIONS)

• **Concrete service life model**

Initiation period:
A relationship between chloride diffusion coefficient and resistivity can be established

$$D_e = \frac{k_{Cl,CO2}}{\rho_{ef}} = k_{Cl,CO2}\,\sigma$$



Propagation period :
Relationship with the corrosion rate for a same concrete

$$I_{corr} = \frac{k_{corr}}{\rho_{ef}}$$

Kcorr=3x10^4 μA/cm^{2}kΩcm

Electrical and electrochemical techniques

Resistivity in concrete

•Aggregate particles are essentially isolating bodies

•The resistivity of concrete depends:
- ✓ of the volume of paste
- ✓ pore volume and pore-size distribution of the cement paste
- ✓ the pore-water composition
- ✓ moisture content of the concrete.

Electrical and electrochemical techniques

Factors affecting resistivity

- The resistivity increases with the binder hydration
- The resistivity increases when the concrete is drying out
- The resistivity increases when the concrete carbonates: Carbonation seals the pores near the surface
- The resistivity is higher in concrete with low w/c ratio and with blended cements
- For non-carbonated concrete, the effect of the penetration of chloride ions on the resistivity is relatively small.
- Zones with low resistivity are more susceptible to chloride penetration and higher corrosion rate
- The resistivity decreases with temperature increase

Depending on the environmental conditions and concrete quality, resistivity may vary from 100 to 100 000Ω m

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Electrical and electrochemical techniques

Resistivity - Measurement

For on site measurements three kinds of methods can be used:

- ✓a disc, being the other electrode the reinforcing bar
- ✓two electrodes
- ✓four electrodes

The most usual is four electrodes method- Wenner Method

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Resistivity - Measurement

Setup for **two point measurement** of concrete resistivity

The two electrodes are place on the concrete surface or inside holes drilled at a depth of 8 mm and filled with conductive gel.

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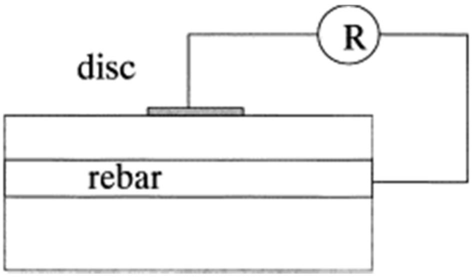
Electrical and electrochemical techniques

Resistivity - Measurement

Setup for **disc measurement** of concrete resistivity,

The disc is placed on the concrete surface and the other electrode is the rebar



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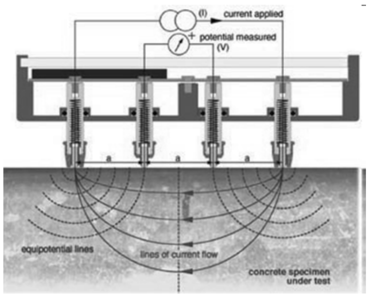
Resistivity - Measurement

Wenner method
Four-electrode measurement of concrete resistivity,
Four equally spaced point electrodes that are pressed onto the concrete surface.
The two outer point electrodes induce the measuring current (usually AC with a frequency between 50 and 1000 Hz, normally sinusoidal) and the two inner electrodes measure the resulting potential drop in the electric field.



The resistance, R, measured is converted to resistivity, ρ, using a cell constant based on theoretical considerations by:
$\rho = 2 \pi a R$ where a the electrode spacing

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Electrical and electrochemical techniques

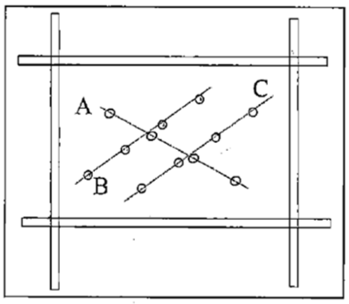
Resistivity - Measurement

Rebars conduct current much better and disturb the measurements.

Is important previous to localize the rebars.

Measure the resistivity as far from the rebar as possible.

With a four electrode device measure diagonally inside the rebar mesh



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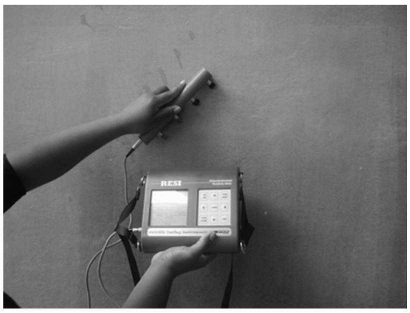
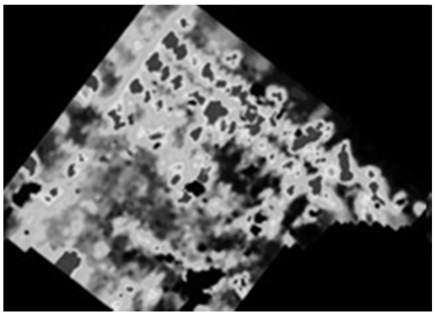
Resistivity – Results

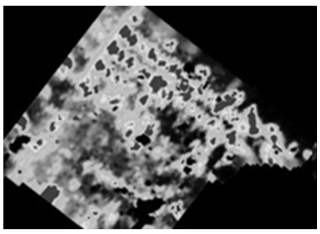
Drawing a grid on concrete surface to guide the resistivity measurements the resistivity map can be performed





Resistivity – Interpretation of results

Resistivity mapping show zones with different resistivities



Exemple of a resistivity map.
Red spots correspond to lower resistivity values

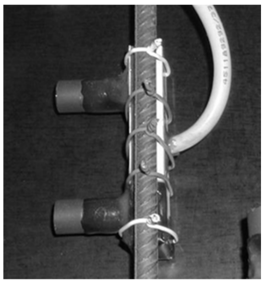
Low resistivity areas identify zones where:
CORROSION COULD BE FIRST INITIATED (depending on cover depth, water and oxygen access)

AND

AFTER CORROSION INITIATES, CORROSION RATE WILL BE ALSO HIGHER IN THIS AREAS

Electrical and electrochemical techniques

Resistivity – Embedded sensors



Two electrodes arrangement sensor to embed in concrete for electrical resistance measurements.

- When new structures are designed and build or when structures are repaired, resistivity sensors may be embedded
- In addition to monitoring chloride content, steel potential or corrosion rate, the resistivity is measured periodically during the lifetime and together they may indicate the risk of corrosion of the embedded steel or the effectiveness of protection systems such as *coatings*.
- The sensor should be calibrated and the electrical resistance measured

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Electrical and electrochemical techniques

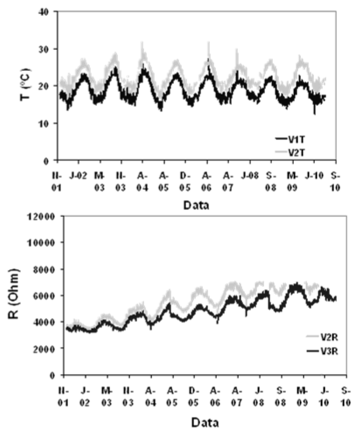
Resistivity – Influence of environment factors

Resistivity depends on environmental factors: moisture and temperature

- Saturated concrete have his lower resistivity
- If temperature increases resistivity decrease

This is caused by changes in the ion mobility in the pore solution.

Temperature correction of resistivity data is very complex. For simplicity, it may be assumed that in the range of 0ºC to 40 ºC, doubling of resistivity takes place for a 20ºC decrease, or that a change of 3% to 5% per degree occurs.



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Resistivity – Interpretation of results

Limits to evaluate the risk of corrosion of reinforcement associated with concrete resistivity (20 C and OPC concrete) [RILEM].

Concrete resistivity (Ω m)	Likely corrosion rate
<100	High
100-500	Moderate
500-1000	Low
>1000	Negligible

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Resistivity – Interpretation of results

RILEM recommendation. Resistivity dependence on type of concrete and environment conditions

Environment	Concrete resistivity $\rho_{concrete}$ (Ω·m)	
	Ordinary Portland Cement Concrete (CEM I)	Blast furnace (> 65 % slag, CEM III/B) or fly ash (>25 %) cement or silica fume (>5 %) concrete
Very wet, submerged, splash zone, [fog room]	50-200	300-1000
Outside, exposed	100-400	500-2000
Outside, sheltered, coated	200-500	1000-4000
Hydrophobised [20 ºC/ 80 % RH], not carbonated	1000 and higher	2000-6000 and higher
Ditto, carbonated, Indoor climate (carbonated) [20 ºC/ 50 % RH]	3000 and higher	4000-10000 and higher

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Resistivity – Key aspects

- ✓ The concrete surface layer may be carbonated or strong dried out, resulting in a higher resistivity than the concrete bulk
- ✓ After rain a surface layer may have a lower resistance than the bulk.
- ✓ Rebars conduct current much better than concrete, they will disturb homogeneous current flow. In extreme cases (four probes on top of one rebar), an artificial low resistivity is measured. To minimise this effect, none of the measuring electrodes should be placed above or near rebars.
- ✓ Before measurements are undertaken, the concrete surface may be wetted slightly to improve the contact. Strong wetting will influence the resistivity, which shall be avoid if the resistivity under the prevailing conditions must be obtained.

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Electrical and electrochemical techniques

Corrosion Potential

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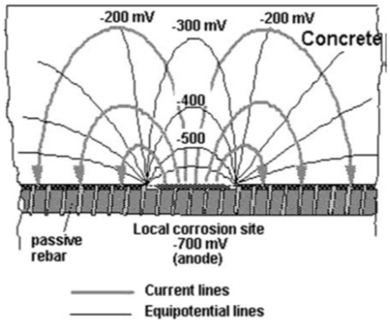
Electrical and electrochemical techniques

Corrosion Potential



Corroding and passive rebars in concrete show a difference in electrical potential

A macrocell is generated and current flows between these areas.

This electric field can be measured experimentally with a suitable reference electrode (half-cell) placed on the concrete surface

The most negative values corresponds to corroding zones

Electrical and electrochemical techniques

Corrosion Potential

- ✓ Half-cell potentials measure the corrosion potential, E_{corr} which is related to the corrosion state of steel in concrete.
- ✓ Half-cell potential mapping provides a non-destructive mean to locate areas of corrosion before it become visible at the concrete surface.
- ✓ E_{corr} is the electrode potential spontaneously acquired by a material which corrodes in a particular environment
- ✓ Does not provide information on the corrosion rate
- ✓ Half cell potential measurements can be performed on structures with carbon, stainless steel or galvanized rebars.
- ✓ Based on potential mapping, other destructive and laboratory analysis (e. g. cores to determine chloride content), concrete resistivity and corrosion rate measurements can be performed more rationally.
- ✓ In addition, the amount of concrete removal in repair works can be minimized because the corrosion sites can be located precisely.

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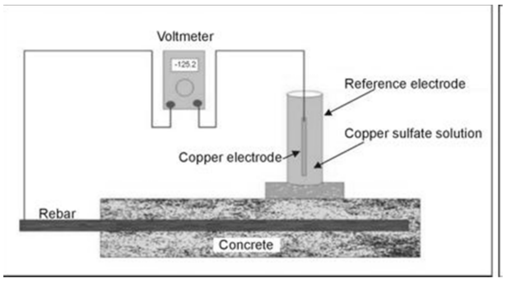
Corrosion Potential - Measurement

- Seleccion of measuring area
- Rebar Localization
- Connection to the rebar
- Position of reference electrode over site to measure



An electrical connection is made to the reinforcement, an external reference electrode is placed in a wet sponge on the concrete surface and potential readings are taking with a high impedance voltmeter (>10 MOhm) along a regular grid on the free concrete surface.

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Electrical and electrochemical techniques

Corrosion Potential – Reference Electrodes

Typical reference electrodes are silver/silver chloride (SSE) and copper/copper sulphate (CSE) and these should be taken into account for the interpretation of the results

Table 2 – Potentials vs. SHE for some reference electrodes (20°C)

Electrode		Potential (V vs. SHE)
Copper/copper sulphate sat	CSE	+0,318
Calomel	SCE	+0,241
Silver chloride	SSE	+ 0,199

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Electrical and electrochemical techniques

Corrosion Potential - Measurement

Different equipments are commercially available, from the simplest solution with only a reference electrode, until multiple electrode arrays devices that simultaneously record potential readings and position on site

Wheel electrode device for E_{corr} measurements in RC structures

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Electrical and electrochemical techniques

Corrosion Potential – Limitations on Measurement

- ✓ The method is suitable mainly on reinforced concrete structures exposed to atmosphere, special electrodes should be used for water immersion.
- ✓ Half-cell potential measurements should be taken only on a free concrete surface (the presence of isolating layers (asphalt, organic coatings or paints, etc. may turn the measurements erroneous or impossible)
- ✓ Corrosion of prestressing steel in concrete can be assessed in the same way. Prestressing steel in the ducts of post-tensioned cables can not be assessed: metallic ducts shield the strands from the concrete surface, plastic ducts isolate the strands.
- ✓ Epoxy coated bars usually are electrically isolated from the each other and cannot be measured.
- ✓ Galvanized steel can be measured in the same way but different criteria applied.
- ✓ The degree of saturation of the concrete influence the results
- ✓ Concrete delamination enables the measurements

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Electrical and electrochemical techniques

Corrosion Potential – Results Interpretation

- ✓ The half-cell potential read at the concrete surface depends on:
  - The actual corrosion potential of the steel
  - The concrete cover depth
  - The concrete resistivity
  - The oxygen availability.
- ✓ Depending on the moisture and chloride content, temperature, carbonation of the concrete and cover thickness, potential ranges indicative of corrosion of the rebars could change in a same structure and from a structure to another.
- ✓ For reinforced concrete structures exposed to the atmosphere, the American Standard ASTM C876:91 provides an indicative criteria for the interpretation of half-cell readings.

Electrical and electrochemical techniques

Corrosion Potential – Results Interpretation

Table 3 – Interpretation of potential measurements according to ASTM C 876:91

Potential (E_{corr} vs. CSE)	Probability of corrosion
E_{corr} >0,2	< 10%
-0,2> E_{corr} >-0,35	Unknown
E_{corr} <-0,35	> 90 %

It is important to point out that this criteria was derived empirically from chloride-induced corrosion of bridge decks in the USA.

In immersion conditions in the ground or in seawater, or water saturated (or in any other condition of lack of oxygen) very negative potentials are reached (lower than -0,7 V vs. CSE) without meaning corrosion initiation

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Corrosion Potential – Results Interpretation

The corrosion potential of passive steel in concrete further depends on the oxygen availability and can vary over a wide range of potentials. Typical ranges of potentials of normal steel in concrete are given in RILEM TC 154-EMC recommendation

RILEM TC 154-EMC recommendation

Table 4 – Typical ranges of potentials of normal steel in concrete (Volts CSE)

Water saturated concrete without oxygen	-0,9 to -1,0 V
Wet, chloride contaminated concrete	-0,4 to -0,6 V
Humid, chloride free concrete	+0,1 to -0,2 V
Humid, carbonated concrete	-+0,1 to -0,4 V
Dry, carbonated concrete	+0,2 to 0 V
Dry concrete	+0,2 to 0 V

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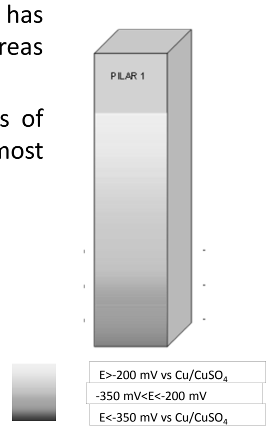
Corrosion Potential – Results Interpretation

Due to the difficulty to interpret absolute values of half-cell potential measurements, potential mapping has been recognized as a more valuable tool to locate areas of corroding rebars.

Corroding areas are often identified by the analysis of half-cell potential gradients corresponding to the most negative zones in the potential field



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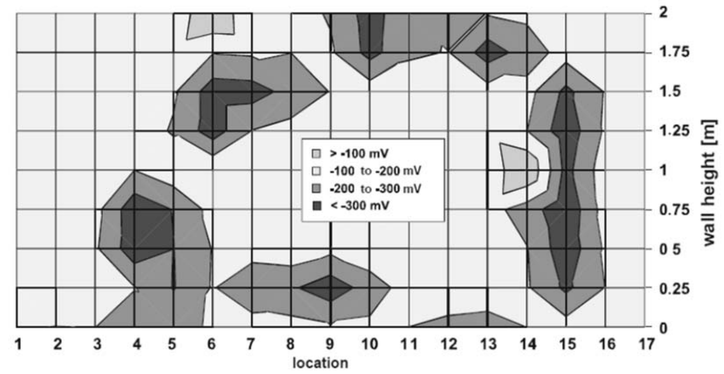
Corrosion Potential – Results Interpretation



Potential map showing clear potential gradients.

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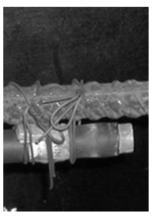
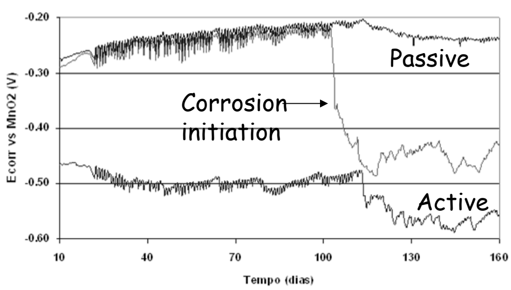
Electrical and electrochemical techniques

Corrosion Potential – Embedded sensors

Other approach uses special reference electrodes (e.g. MnO_2), to embed in concrete at critical areas of the structure and the rebars. E_{corr} is monitored permanently over a large period of time



Reference electrode to embed in RC structures



Electrical and electrochemical techniques

Corrosion Potential – Key aspects

- ✓ Half-cell potentials cannot be correlated directly with the corrosion rate of the rebars.
- ✓ Good electric and electrolytic contact is essential to get stable readings.
- ✓ The potential changes with cover depth *.The increase of Cover depth reduce the delta V between the anodic and cathodic areas and it is more difficult to distinguish anodic from cathodic areas*.
- ✓ The location of a small corroding spot becomes more difficult with high cover depth..
- ✓ In low resistive concrete, the location of very small corroding spots is much easier. in cases of chloride induced corrosion than in carbonated concrete.
- ✓ In low resistive concrete even very small corrosion spots can be identified with a comparatively large grid size (0,15 m). In high resistive concrete only a very small area of passive rebars is polarized and for the detection of small corroding spots a smaller grid size should be used.

Electrical and electrochemical techniques

Corrosion Rate

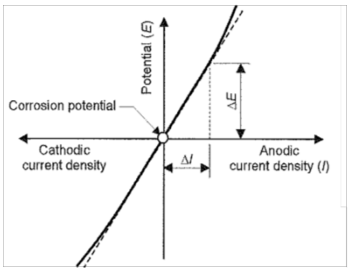
Electrical and electrochemical techniques

Corrosion Rate – Application field

- Evaluate the active corrosion of rebars in concrete.
- Gives quantitative information on the loss of steel section in concrete
- Is importance for the assessment of corroding structures and service-life prediction, as well as for the evaluation of repair methods in laboratory and on site.

Electrical and electrochemical techniques

Corrosion Rate – Principle



$$Rp = \frac{\Delta E}{\Delta I}$$

ΔE from 10 to 50 mV (from Ecorr)

$$i_{corr} = \frac{B}{Rp}$$

$B = 26mV$ or $B = 52mV$

For on site measurements the recommended value is 26mV

Cause of error factor 2

$$V_{corr}(mm/s) = \frac{i_{corr}(A/cm^2) \times 27.92 \times 10}{7.85 \times 96500}$$

Eq. weight Fe = 27.92

d(Fe) = 7.85

Coulomb Const = 96500

Determination of Polarization Resistance
Convert it to icorr (using Tafel coefficients)
Convert to Corrosion Rate (using Fraday's law)

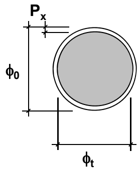
We need to know the mass loss or the loss of section in the rebar with time.

Electrical and electrochemical techniques

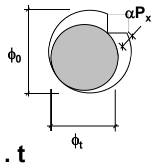
Corrosion Rate Modelling

Andrade et al. reinforcement corrosion propagation model [1]

Uniform Corrosion



Pitting



$$\phi(t) = \phi 0 - 0{,}0116 \cdot \alpha \cdot i_{corr} \cdot t$$

$\phi_{(t)}$ = rebar diameter at t (mm)
ϕ_0 = initial rebar diameter (mm)
i_{corr} = corrosion current density (mA cm^{-2})
t = time (years)
α= pitting factor (uniform α=2; pitting α=10)

[1] – C. Andrade et al., *IABSE Symposium, "Durability of Structures*", Lisboa, 1989, pp. 359-364.

Electrical and electrochemical techniques

Corrosion Rate Measurements

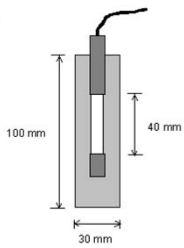
R_p measurements are usually made with a three-electrode arrangement, using the reinforcing steel as working electrode (WE), a counter electrode (CE) and a reference electrode (REF).

TYPICAL ARRANJEMENT IN LABORATORY TESTS WITH SMALL SAMPLES

The CE should be at least of equal size of the rebar and of non-corroding material well dispersing the polarizing current.

The REF serves to apply an electrical signal, inducing a shift of about 20 mV from E_{corr} potential, either in the anodic or in the cathodic direction

In laboratory tests the polarised area is well known.



Electrical and electrochemical techniques

Corrosion Rate Measurements

- ✓ The polarized area has to be known
- ✓ The electrolytic contact between the counter electrode and concrete is often assured by a wetted sponge.
- ✓ The supply unit (potentiostat) is connected to the reinforcement (WE), to the CE and to the REF.
- ✓ After having select the measuring position (often based on half-cell potential mapping), E_{corr} is measured and then a predetermined variation of potential (ΔE), in general 10 mV, is applied and the current ΔI that the system requires to achieved this variation is recorded.
- ✓ Commercial equipment automatically calculates R_p and i_{corr} from the recorded measurements. Often E_{corr} and concrete resistance are also given.

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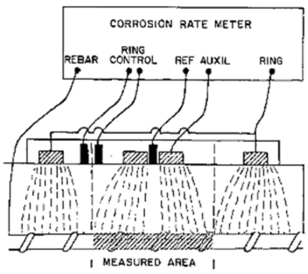
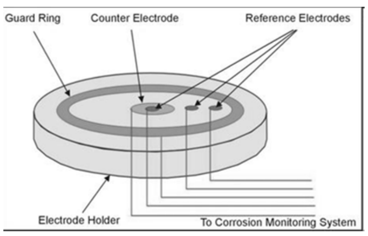
Electrical and electrochemical techniques

Corrosion Rate In situ Measurements

Devices for measuring R_p on site usually use a counter-electrode disk and a central reference electrode placed on the surface of the structure.

Special counter-electrodes were developed and are commercially available with "guard rings" to avoid the current spread-out from the counter electrode and know the polarized rebar surface in order to relate it with the measured polarization resistance.





Electrochemical cell for in situ i_{corr} measurements

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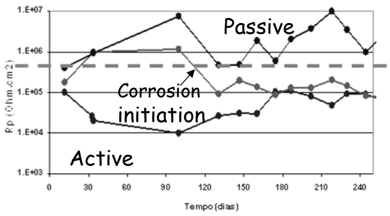
Corrosion Rate – embeded sensors

Other approach uses sensors embedded in concrete at critical areas of the structure and the steel reinforcement corrosion rate is monitored permanently over a large period of time

i_{corr} sensor to embed in RC structures



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Corrosion Rate Results Interpretation

RILEM Recommendation

i_{corr} (μA cm^{-2})	V_{corr} (mm year^{-1})	Corrosion level
$\leq$ 0,1	< 0,001	Negligible
0,1 – 0,5	0,001-0,005	Low
0,5 – 1	0,005-0,010	Moderate
>1	> 0,010	High

- Values of i_{corr} below 0,1 μA cm^{-2} indicate negligible corrosion from a practical point of view and, therefore, the steel reinforcement can be classified as "passive".
- The range between 0,1-0,2 μA cm^{-2} can be considered the transition region between passive and active corrosion.
- Values of i_{corr} above 1 μA cm^{-2} are seldomly measured in real structures
- Values higher than 10 μA cm^{-2} have almost never been recorded. In consequence **the most common values for actively corroding rebars range from 0,1 to 1 μAcm^{-2}**

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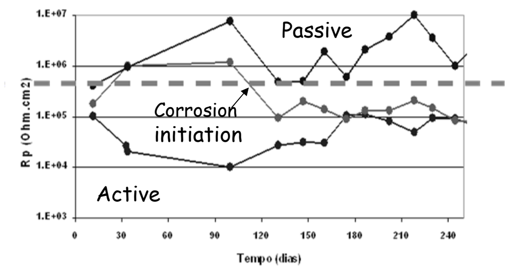
Corrosion Rate Results Interpretation

- ✓ Icorr is very sensitive to variable environmental conditions, the steel presents periods with low and high corrosion rates (moisture condition) and Temperature
- ✓ A unique measurement of the instantaneous corrosion rate obtained by an electrochemical method could not give a realistic estimative of the average corrosion rate. In practice i_{corr} values should be measured at representative periods during the life of a structure.



Electrical and electrochemical techniques

Corrosion Rate Key aspects

- ✓ Local corrosion attack could be underestimated by icorr measurements due to the difficulty to correctly estimate the area of the real polarized surface.
- ✓ To provide a low electrical resistance path between the sensor and the concrete surface, a wet sponge or any other conductive substance or cloth has to be used. The concrete prewetting should be intensive enough to establish a good electrolytic contact.
- ✓ Several precautions have to be taken in order to get reliable values, namely, compensation of the high electrical resistance of the concrete cover (ohmic drop), linearity of the $\Delta E/\Delta I$ slope and achievement of a quasi steady state. Also the polarized surface has to be known

Thank you