Application Note

An Introduction to the Parameters Measured by the ECI-1 and Their Use in Determining Concrete Corrosivity

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The ECI-1 measures four parameters that can assist in the determination of the corrosivity of concrete structures. Several questions are often raised

- **Why measure four parameters and why these parameters: polarization resistance (R_p), concrete resistivity, temperature, and open circuit potential (OCP)?**
- **How is each parameter measured and what are the interpretation issues for each parameter if it is the only parameter measured?**
- **How can I use the combination to help assess the corrosivity of the concrete towards reinforcing steel?**

Why measure four parameters and why these parameters?

The more relevant information one has about a corrosion system, the better position one is in to make an accurate assessment of the corrosion activity and what remedial actions might be necessary. The goal of the sensor is to provide an early warning of what could be expected to occur on the steel used in the structure.

Each of the parameters measured by the ECI-1 is linked to the corrosivity of the concrete. If concrete was a simple physical and chemical system, measuring only one parameter would be sufficient. However, concrete is a dynamic, highly variable system that interacts with the external atmosphere in myriad ways. As such, measurements of any *single* parameter can become uncorrelated with corrosivity as discussed in detail below, leading to incorrect interpretations. By using multiple inputs, the robustness of the decision system is increased, as the likelihood that ALL four parameters will become uncorrelated to corrosivity under the same conditions.

In recent publications [1-5], the parameters used by the ECI-1 have been deemed important in gaining insight to better understand the corrosion conditions present on the reinforcing steel. The R_p value can be directly related to the instantaneous corrosion rate of the steel sensor, *when correctly normalized for the active area and if the relevant electrochemical parameters are known*. The concrete resistivity influences the ability of anodic and cathodic regions on the steel to interact, with higher resistivities hampering that interaction, and *generally* leading to lower corrosion rates. The electrochemical reactions involved in corrosion as well as the movements of ions through solution are thermally activated processes, and increased temperature *generally* leads to increased corrosion rates. The OCP value has been correlated to the likelihood of active corrosion on steel in concrete, *albeit with some caveats.*

The italics in the previous paragraph are the reason that a multi-probe approach is used by the ECI-1. By integrating the results of the four parameters that are individually important, but are measured independently, the confidence in the final assessment is enhanced.

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How is each parameter measured and what are the interpretation issues for each parameter if it is the only parameter measured?

For each parameter, the literature data supporting its importance are reviewed, the means by which the ECI-1 parameter is measured, and the interpretation issues are discussed.

Open Circuit Potential (OCP) or Corrosion potential (E_{corr})

Why measure OCP?

OCP/E_{corr} measurements[1] are often used as an indication of the corrosion risk of the steel. Reinforcing steel in concrete once in pseudo steady state can show different OCP/E_{corr} values according to the humidity and chloride content in concrete. These measurements are linked by empirical comparisons to the probability of corrosion.

ASTM C-876 standard [7] has been available for more than 20 years; this standard indicates the potential ranges in relation to the probability of corrosion. These ranges are based on wide experience of corrosion in chloride contaminated concrete bridge decks, but when carbonation is the cause of corrosion or cathodic processes are modified, the range of the corrosion potential may be different.

NOTE: Recall that ECI-1 uses an MnO2 reference electrode, which is part of the instrument and is exposed to the concrete adjacent to the steel sensor.

Table 1. According to ASTM C-876[7]

Probability of corrosion	E_{corr} (vs Cu/CuSO4)	E_{corr} (vs SCE)	E_{corr} MnO_2
> 95 %	< -0.35	< -0.276	< -.43
< 5 %	> -0.2	> -0.126 V	> -0.28
approx. 50%	-0.2 to –0.35 V	-0.126 to –0.276 V	-0.28 to –0.43

Assuming that MnO_2 vs SCE is +154 mV

Table 2. Typical Ecorr values of the different corrosion states of steel in concrete, according to Arup [8]

Corrosion state	Range of possible Ecorr /$mV_{(SCE)}$	Converted to $mV_{(MnO2)}$
Passive state	+200 to -200	40 to –360
Pitting corrosion	-200 to -500	-360 to -510
General corrosion	-450 to -600	-610 to –760
Corrosion with limited oxygen access	Around -1000	-1160

↑ Higher

E_{corr}

↓ Lower

Assuming that MnO2 vs SCE is +160 mV

It is important to note that **NO** quantitative (corrosion rate) conclusion can be drawn from E_{corr} values.

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[1] OCP is also referred to as the corrosion potential (E_{corr}).

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The reinforcing steel when passive usually has a noble potential (> 0.2 V_{SCE}, as indicated in Table 2). Experimental values as low as –0.1 V_{SCE} usually indicate that the reinforcing steel is still passive. When the corrosion of the reinforcing steel is due to chlorides, it usually initiates as localized corrosion (pitting corrosion – see [9-11] for further explanation). Once this type of corrosion starts the E_{corr} of the reinforcing steel falls/drops between –0.2 V_{SCE} and –0.5 V_{SCE}.

How are OCP measurements made?

OCP values are measured by connecting a reference half-cell, such as copper/copper sulphate, to the embedded steel via the concrete. A complete electrical cell is thus created and an electrical potential can be measured between the rebar within the concrete and the reference electrode. In the case of ECI-1 an MnO_2 reference electrode is part of the instrument and is exposed to the concrete adjacent to the steel sensor. A recent technical report [6] from NACE gives more detailed background on reference electrodes used in concrete.

E_{corr} depends on the following factors:
- type of metal (including surface condition, oxide film, etc)
- composition of the environment (moisture content, pH, salt content, impurities)
- oxygen content
- contact to other metals
- stray currents
- temperature

What are the interpretation issues with OCP?

Effect of temperature on the corrosion potential

According to the Nernst-equation for the electrochemical potential, the corrosion potential should change linearly with the temperature. For a simple redox-couple, the slope $\Delta E/\Delta T$ will be dependent on the number of electrons involved in the redox reaction and on the concentrations of the oxidized and reduced species. If the logarithmic expression in the Nernst equation is >1 then $\Delta E/\Delta T$ will be positive, otherwise the temperature dependence will be negative. [12]

A falling tendency of the corrosion potential with temperature was found by Benjamin, et al. [13]. For samples with 1% NaCl per weight of ordinary portland cement (OPC) added and collected during 300 days at different temperatures, Benjamin, et al., found that the corrosion potential falls between 6 and 7 mV per ºC.

Effect of moisture content

When the concrete is completely submerged the concrete could become so devoid of oxygen that cathodic polarization would result in a reduction in E_{corr} to values of around –1.0 V_{SCE}. (A similar effect could be observed if the concrete were completely water saturated for a extended period of time.) In aerial structures it is unlikely that oxygen access could be limited (except during the curing stages or if subject to several continuous days of rain). When the supply of oxygen is severely limited, corrosion at a slow rate can occur. The corrosion products under these conditions (saturated concrete) are less voluminous than under normal circumstances. The corrosion products may travel into voids in the concrete without a progressive development of cracking or spalling.

Polarization Resistance (R_p)

Why measure R_p?

There is extensive experimental evidence the R_p is inversely proportional to the dissolution rate for a material undergoing uniform dissolution. For steel in concrete, the transition from the passive state to an actively corroding state is accompanied by a substantial change in the polarization resistance as shown in Table 3. Thus, an accurate measurement of the R_p of a structure would allow a direct calculation of the thinning rate of the steel, if the active area were known.

Table 3. Typical Rp values (After Elsener [1])

	Specific polarization resistance (Rp) kΩ cm^2
Passive steel state (Laboratory)	> 500
Passive steel field (current not well containied)	~50 or larger
Corroding	< 10 (if <2 heavily corroding)

How is R_p measured?

The polarization resistance (R_p) technique is often used for determining the reinforcing steel corrosion rates by using electrolytic test cells (ASTM G59 [14]). Briefly, the technique involves measuring the change in the OCP of the connected electrolytic cell when an external current is applied to the cell. For a small perturbation about the OCP, generally there is a linear relationship between the change in voltage ΔE and the change in applied current per unit area of electrode Δi. The ratio $\Delta E/\Delta i$ is called the polarization resistance R_p. Because the current is expressed per unit area of an electrode that is polarized, the units of R_p are ohms times area. It important to note that R_p is not a true resistance in the usual sense of the word, but the term is broadly used.

Stern and Geary[15] established the underlying relationship between the corrosion rate of the anode and the polarization resistance. However, describing the implementation of these relationships is out of the scope of this present document (the reader should consult a textbook and/or specialized literature of Rp of steel in concrete). In a recent publication Elsener [1] presented parametric curves, in which the B factor varied between 16 and 29 mV. A value of 26 mV is often used when the reinforcing steel is corroding as reported by Andrade [16] and recommended [5].

As long as the polarization resistance remains high and the open circuit potential is noble (usually > -0.2 Vcse), the reinforcement steel is passive and corroding at a very small rate. As the steel begins to depassivate due to an increase in [Cl-] or other corrosive environmental conditions, the OCP will become more negative accompanied by a decrease in the polarization resistance.

What are the interpretation issues with R_p?

One of the major issues regarding Rp is that is not easy to determine the area of structure being probed, hence precautions should be taken if Rp values needs to be converted to corrosion rates. This in part depends if the reinforcing steel is passive or not [1,16].

The Rp is also influenced as result of a change in temperature, directly due to changes in the rate constant k [17] due to a different temperature. Moreover, any temperature and humidity changes also effect E_{corr} and the concrete electrical resistivity. It is important to emphasize that Rp measurements give an instantaneous value, influenced by daily as well as seasonal climatic changes. A comparison between average Rp values can be performed after integrating Rp data[1] over time. The effect of climatic and environmental issues are presented.

Relate R_p to corrosion rate assuming B values

The values reported by ECI-1 are in kΩ-cm^2. These values can be converted to corrosion current densities if the constant B is known. However, the value of B is not constant and usually goes from 52 mV when the system is not corroding to 26 mV or even 13 mV when corrosion has started. Additionally, localized corrosion is usually the main form of corrosion, therefore the area under attack is not well known and it is different from the area of the sample. Additionally, as indicated above, the probed area is not always known.

Millard [30,31] observed that diurnal cycles affect the Rp measured. Millard reported considerable scatter for the Rp values: the Rp values varied depending on when during a given day the measurement was made.

THIS IS WHY CHANGES IN Rp are to be used as indicators, and should not be directly converted to corrosion rates.

Temperature

The influence of the temperature on the corrosion process of steel in concrete, especially on the corrosion potential and on the corrosion rate (Rp values) has been described above. The temperature effect on the concrete electrical resistivity and transport processes in concrete is briefly discussed in this paragraph. Transport processes as well as the electrolytic concrete resistivity strongly depend on the physicochemical properties of the pore water solution. The most important parameter is supposed to be the viscosity of water. The temperature dependence of the viscosity of water is mainly important for how it effects the concrete resistivity and diffusion processes. [12,17]

Concrete Resistivity. [18-22]

Concrete resistivity is a geometry-independent material property that describes the resistance to the flow of charge. It is defined as the ratio between an applied voltage and resulting current in a cell of defined geometry.

The dimension of resistivity is resistance multiplied by length, with units of Ω m or kΩ -cm. The resistivity of concrete may vary over a wide range, from 10^1 to 10^6 Ω m, influenced by the moisture content of the concrete (environment) and the concrete composition. In concrete, the current is carried by ions dissolved in the pore liquid. More pore water (wet concrete) as well as more and wider pores [high water to cement ratio (w/c)] cause a lower resistivity. For a constant moisture content, the resistivity is increased by a lower w/c, longer curing hydration and by the addition of reactive minerals such as blast furnace slag, fly ash and silica fume. The resistivity increases when the concrete dries out and when it carbonates in particular in Portland cement concrete. The effect of the penetration of chloride ions is relatively small. However, within a particular structure, more permeable spots will have a comparatively low resistivity and stronger chloride penetration.

Why measure concrete resistivity?

Resistivity is usually a good indication of the transport rate of the corrosion front through the concrete. Several researchers have suggested that one can relate the concrete resistivity and likeliness of corrosion. Three sets of data are shown below.

Table 4. Empirical conductivity thresholds for depassified steel reinforcement (After McCarter[23])

Resistivity kΩ–cm (Conductivity, S/m)	Probable Corrosion Rate
(< 5 kΩ–cm) (> $2x10^{-2}$)	Very High
(5 to 10 kΩ–cm) (1 to $2 x 10^{-2}$)	High
(10 to20 kΩ–cm) (1x10-2 to $5x10^{-3}$)	Moderate/low
(>20 kΩ–cm) (< $5 x 10^{-3}$)	Low

Table 5. After Langford [24]. Langford did numerous measurements on depassivated steel using Wenner four point probe

Resistivity	Probable corrosion rate
>20 kΩ cm	Low corrosion rate
10- 20 kΩ cm	Low to moderate corrosion rate
5 to 10 kΩ cm	High corrosion rate
< 5 kΩ cm	Very high corrosion rate

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Table 6. Researchers working with a field linear polarization device to detect corrosion on lab and field samples found the following correlation between corrosion rate and resistivity [2.b,25]

Resistivity	Probable corrosion rate
> 100-200 kΩ cm	Cannot distinguish between active and passive steel – negligible corrosion, concrete too dry
50 – 100 kΩ cm	low corrosion rate
10 – 50 kΩ cm	moderate to high corrosion where the steel is active
< 10 kΩ cm	Resistivity is not the controlling parameter

The relationship shown in the above tables were derived after analyzing measurements of corrosion rate and resistivity, with Tables 4 and 5 showing the same ranges. Table 6 shows resistivity values that are larger for corresponding conditions shown in tables 4 and 5, which could be explained by different concrete mixtures of more recent concrete structures. **Resistivity measurements are not to be used as a stand alone technique.**

How is concrete resistivity measured?

In the case of the ECI-1 the concrete resistivity is measured by using four stainless steel electrodes. A galvanostat circuit drives a stepped current through the outer pair of these electrodes, and measures the potential between the inner pair at each step. Electronics within the ECI then perform a linear regression to calculate the resistance between the inner pair of electrodes. The ECI multiplies this figure by the cell constant of its resistivity sensor to derive the resistivity of the concrete in units of ohms-cm.

The concrete resistivity is often measured by a four point (Wenner probe) resistivity meter which is used for soil resistivity measurements. The instrument has been modified for concrete application and is used by pushing (wood) pins directly onto the concrete surface with moisture on the pin tips to enhance the electrical contact. There is more than one versions of this equipment.

What are the interpretation issues with concrete resistivity?

Factors affecting the concrete electrical resistivity are:

Paste Volume. It has been observed that for concretes with constant water to cement ratio, increasing the paste volume decreases the resistivity at a rate of approximately 1% per 1 % paste increase. The increased paste content creates more channels for electrolytic liquid.

Water Cement. Increasing the water/cement ratio results in a coarser pore structure and more continuous pore structure. Therefore, an increase in w/c ratio will cause a decrease in the electrical resistivity

Temperature. The concrete electrical properties are also affected by temperature. This phenomenon is also complicated by the change in the pore water chemistry that occurs along with change in temperature. At higher temperature, more ions will dissolve into the pore water, and then precipitate as the water cools.

As indicated above, there are other factors that effect the electrical resistivity of the concrete e.g. curing temperature, the presence of Silica Fume or Fly Ash, etc.

Climatic and environmental considerations

One of the most challenging aspects of on-site measurements is the fact that the measured corrosion Rp is weather dependent and, therefore, its actual value will depend on the particular climatic conditions surrounding the structure.

The pore system in hardened cement paste is a major factor influencing corrosion. In electrical terms, it is the resistance of the “connection” through the concrete that controls the flow of current. The electrical resistivity of the concrete is greatly influenced by its moisture content, by the ionic composition of the pore water, and the continuity of the pore system in the hardened cement paste. Thus a concrete with high electrical resistivity will be less susceptible to corrosion. However, under certain circumstances it is still possible to have a concrete with high concrete resistivity (but with high moisture content) and low Rp, but where this low Rp value is a reduction from earlier high Rp.

Moisture content is a major factor effecting the electrical resistivity of concrete, as the pore water acts as an electrolyte with lower resistivity than that of the matrix. Saturated concrete has a resistivity between 1 to 20 kΩ-cm, depending on mix parameters, while dry concrete reaches 100 – 1000 kΩ-cm, showing the importance of pore water on resistance.

Relative Humidity

Water must be present at the cathode for the cathodic reaction to occur. Moisture is also needed to provide a transport pathway for the ions from the anode to the cathode to balance the electronic pathway through the steel. Tuutti [29] showed that corrosion rate increases with relative humidity (below 60% RH corrosion is not likely), peaks and then decline to close to zero as the concrete becomes totally saturated, presumably stifling oxygen access.

In a recent publication [21] the internal and external Temperature and RH were monitored over more than a year. The following observation were made when the internal temperature increases:

1) “A reduction in the oxygen content of the pore solution;
2) A decrease of the pore solution resistivity;
3) This likely increases the Cl/OH ratio; and

4) Some evaporation might take place (that increases the RH in the pores but also increases the concrete resistivity due to less full pores).”[21]

Relate resistivity (T corrected) to literature on concrete quality and wetness.

The resistivity once corrected to a normalized temperature, is still dependant on the moisture content and the concrete quality. In a new structure the resistivity evolves from relative low values (due to high moisture content and the concrete being fresh) at early times toward higher resistivity values as the concrete hydrates and partially dries (due to external temperature and RH). In the case of the ECI-1 the sensor is usually located several inches from the surface, this location might remain at a high RH and moisture content for a longer time than the concrete closer to the surface. Seasonal weathering effects the concrete resistivity, depending on how many hours of rain the location is subject to and the concrete quality: the expected average concrete electrical resistivity could be determined. In a recent publication Andrade [22,26] suggested a set of resistivity values for known weathering and concrete properties.

After the structure is in service for a few years, seasonal cyclic trends will be observed. When analyzing the results, it is important to distinguish if the resistivity is high or low with respect to the average resistivity value of the season, as this might also help in determining how wet the concrete was when the measurement was made. Under certain circumstances additional visual inspection might be needed to determine how moist the concrete area of interest is.

How can I use the combination to help assess the corrosivity of the concrete towards reinforcing steel?

A generally applicable table for assessment is shown in Table 7.

R_p	OCP	Resistivity	Temperature**	Likelihood of Corrosion
Low	Low			Highly Likely
High	Low	Low		Unlikely if concrete is immersed
Low/Medium	Low	High		Likely, but a a modest rate
High	High	High		Unlikely

** In general the resistivity should be corrected for temperature, and the current temperature also affects the OCP and Rp. If the temperature is at 0 °C or below corrosion can not take place because the solution is frozen.

Nonetheless, several examples will discuss the interpretation in more detail.

<u>Examples of Interpretation Using Multiple Parameters</u>

Rp in new structures.
The measured Rp and resistivity at early times might be low, due to high moisture content. The low resistivity might be due to the concrete being fresh cured and the pores filled with high moisture content. The low Rp could be due in part to a high saturation state of the pore solution and/or that the passive layer on the working electrode is just being formed or not having reach a pseudo steady state with the pore solution.
If low Rp and resistivity values are accompanied by E_{corr}/OCP values < -700 mVsce, then the oxygen limitation is likely taking place and the corrosion rate is limited. However, as the passive film thickens (assuming that no chlorides are present) in the high pH of the concrete pore solution the measured value of Rp will increase. Lynchburgh data from ECI instruments perform by VTI during the first year are an example of this behavior. In summary, early in the life of the structure the Rp values measured are expected to fluctuate.

Rp in older structures (usually after 1 or 2 years).
With a history of high Rp values that then shifts from high Rp to low Rp, with E_{corr} <-200 mVsce, and with resistivities not significantly different from previous values (either low, medium or high) could indicate that the rebar sensor has activated. The temperature and the season at the time of the measurement might give further insight. Once Rp reduction

is observed it's a good idea to monitor the suspect sensor more closely. This additional monitoring could be done by additional tests e.g. after one or two weeks or during the following scheduled measurements.

If E_{corr} starts showing a value that suggest corrosion (95%), but Rp and the resistivity values are high. The likehood of corrosion has started is low. Again, it might be a good idea to monitor the trend of the three measurements during the following readings. This is important to determine if activation has occurred.

If E_{corr} is low and the resistivity is small, but Rp is high. It is likely that corrosion has not started. Additional monitoring in addition to the scheduled test might be necessary. If later measurements are accompanied with lower Rp this might indicate activation.

For conditions going from high Rp and high resistivity with noble E_{corr} to low Rp, E_{corr} within 95%, but no change in resistivity, corrosion might have initiated. However, the corrosion rate will be from low to moderate due to high resistivity.

If the concrete is immersed or very wet (i.e. no saturation is present), and the Rp shifts towards low Rp values and nobler E_{corr}, no change in resistivity, corrosion might have just started, but this needs to be confirmed with drop in E_{corr} (within 95%) and continuous low Rp in subsequent measurements.

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