

Committee Report : JCI- TC134A

## **Technical committee on systematization of electrochemical measurement based on physicochemical theory**

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### **Abstract**

The technical committee on systematization of electrochemical measurement based on physicochemical theory aims to 1) systematically organize the physicochemical theories to be considered while applying electrochemical measurement methods of various kinds on a concrete structure, and 2) summarize references useful for actual application such as knowhow for executing highly reliable measurement and methods of interpreting the acquired data. This report summarizes the basics of electrochemistry in concrete engineering, overviews electrochemical methods used for evaluating performances and physical properties and their mechanisms, and summarizes the physical properties of concrete based on electrochemical property values, electrochemical diagnosis of corrosion of steel in concrete, measurements in actual structures and specimens, and electrochemical methods for preventing corrosion.

Keywords: Electrochemistry, corrosion of steel, concrete cover, protection performance, measurement technology, systematization

### **1. Introduction**

In Japan, social infrastructures have been actively maintained and operated even before the ceiling collapse of Sasago Tunnel in December 2012, but the accident certainly triggered off further activation of maintenance activities. Recent actions of the Ministry of Land, Infrastructure, Transport and Tourism are summarized in **Table-1**, including the registration system of private sector qualifications, which aims for sound execution of maintenance works. Concrete structures play an important role in construction of social infrastructures; and thus Japan Concrete Institute also started the qualification system for “Authorized concrete diagnosis & maintenance engineer” in 2001. A concrete structure may undergo diverse kinds of damage and deformation; and an inspection method appropriate to the purpose needs to be used for diagnosing a concrete structure. Various kinds of inspection methods have been proposed and

**Table-1 Recent trend of maintenance and operation activities**

2012.7	Subcommittee on maintenance of social infrastructures established
2012.12	Ceiling collapse of Sasago Tunnel
2013.1	Conference on social infrastructure aging prevention established
2013.3	“Currently necessary measures for maintaining and renovating social infrastructures” published
2013.10	Inter-ministerial liaison conference on promotion of measures for aging infrastructures established
2013.11	“Basic plan for elongating the life of infrastructures” published
2013.12	Report on “How social infrastructures should be maintained and renovated”
2014.5	“(Action) plan for elongating the life of infrastructure” published
2014.8	“Urgent proposal toward establishment of the system for maintaining social infrastructures: Creation of the registration system of private sector qualifications” published
2015.1	A total of 50 private sector qualifications applied by 10 organizations were registered on January 26.
2015.2	“Toward establishment of the sustainable system for maintaining social infrastructures at municipal governments” and “Three missions related to maintenance information of social infrastructures and measures for promoting them” published

actually implemented, including studying documents, visual inspection, inspection using nondestructive measurement methods, and examination of core samples. The majority of nondestructive measurement methods and chemical analysis of core samples are application of methods that were developed in other fields in concrete engineering and thus require expertise knowledge for interpreting the measurement data. One of measurement methods that require advanced knowledge is electrochemical measurement, which is mainly used to detect corrosion of steel in concrete. As the name implies, electrochemical measurement is a technique that uses knowledge of electrochemistry, which is a field of physical chemistry. The most widely used method of electrochemical measurement in concrete engineering is the half-cell potential method. There are cases in recent studies and reports that the authors do not sufficiently understand the theoretical background of the method. This is likely because electrochemistry is a field that is difficult to understand; and measurement via concrete cover, which is common, makes interpretation of measured data further difficult.

The committee worked over a period of two years from FY2013 aiming to systematically organize the physicochemical theories to be considered while applying electrochemical measurement methods of various kinds on a concrete structure and to summarize useful references for the practices of application such as knowhow for executing highly reliable

measurement and methods of interpreting the acquired data. This report summarizes the basics of electrochemistry in concrete engineering, overviews electrochemical methods used for evaluating performances and physical properties and their mechanisms, and summarizes the physical properties of concrete based on electrochemical property values, electrochemical diagnosis of corrosion of steel in concrete, measurements in actual structures and specimens, and electrochemical methods for preventing corrosion. This is an overview report. For details, please refer to the full report (hereinafter referred to as the “Report”)

JCI-TC134A: Technical committee on systematization of electrochemical measurement based on physicochemical theory

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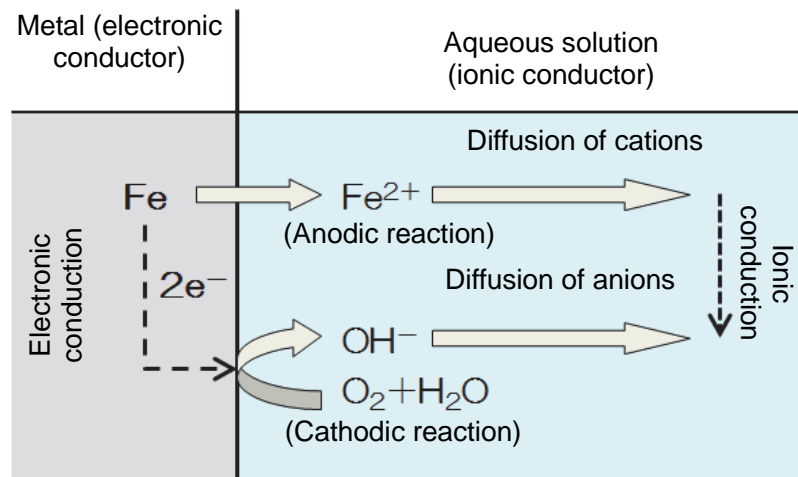
## 2. Basics of electrochemistry in concrete engineering

### 2.1 Mechanism of corrosion

Corrosion is a process in which a metal is corroded by chemical reaction with its environment. For a metal to corrode, the metal needs to be at least exposed to either water in the form of solution or to a high temperature. At high temperatures, corrosion progresses by direct chemical

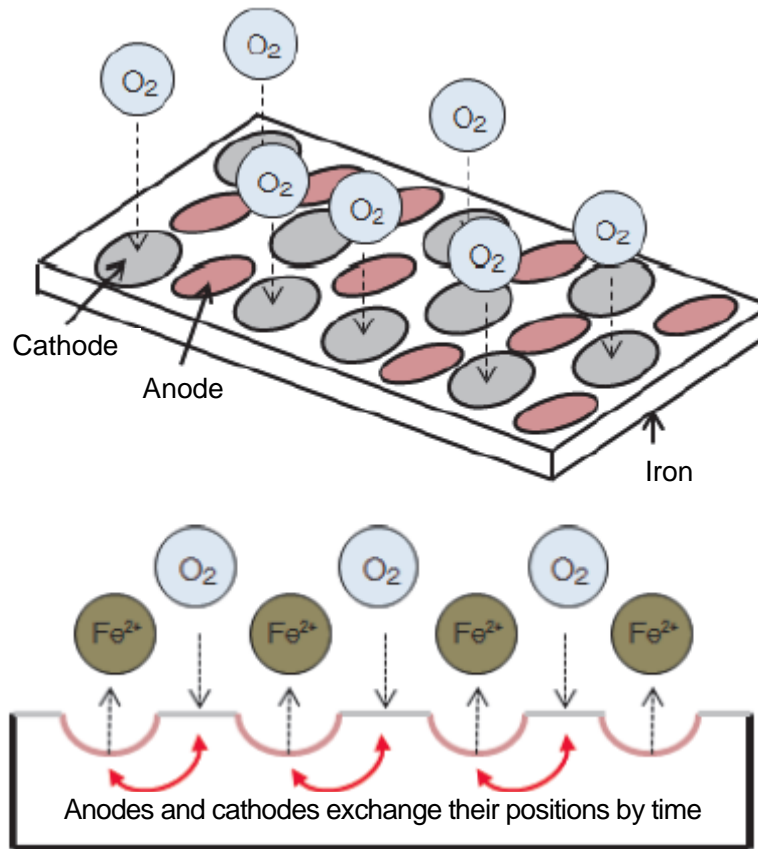
reaction between the metal and its environment. At normal temperatures, corrosion occurs by electrochemical reaction between the metal and ambient water. The former is called “dry corrosion”, and the latter is “wet corrosion”. Corrosion of steel in concrete falls under the category of “wet corrosion” because concrete can be deemed as a porous media with continuous capillary pores and the steel corrodes by reacting with aqueous solution (alkaline due to the presence of calcium hydroxide generated by hydration reaction of cement) existing in the pores <sup>1)</sup>.

The mechanism of corrosion is described below by exemplifying corrosion of steel in a neutral environment. For actual structures, steels (Fe-C alloy) produced by adding 0.2 to 0.6wt% of carbon to iron are commonly used. In this report, corrosion is explained by focusing on iron (pure iron), which is the most basic corrosion. A schematic illustration of electro-chemical reactions at the surface of iron is shown in **Fig.-1**.

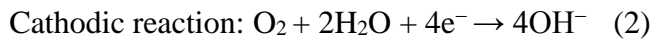
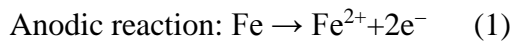


**Fig.-1 Schematic illustration of electrochemical reactions at iron surface**

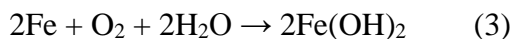
On an iron surface that is immersed in water, an infinite number of cells (corrosion cells or local cells) are formed, and anodes and cathodes are generated. Corrosion reaction starts by iron atoms dissociating from the crystal lattice and moving into water where they are converted into iron ions ( $\text{Fe}^{2+}$ ). During the process, two electrons are released per iron atom. This is called anodic reaction (oxidation reaction). However, this reaction does not occur independently but requires a coupled reaction because of electroneutral requirement. In other words, dissolved oxygen molecules in water receive the electrons at the iron surface, are reduced, and produce hydroxide ions ( $\text{OH}^-$ ). This process is called cathodic reaction (reductive reaction). When anodes and cathodes mutually exchange their positions, uniform corrosion (microcell corrosion) occurs. When the anodes and cathodes are fixed, local corrosion (macrocell corrosion), including pitting corrosion, takes place (**Fig.-2**).



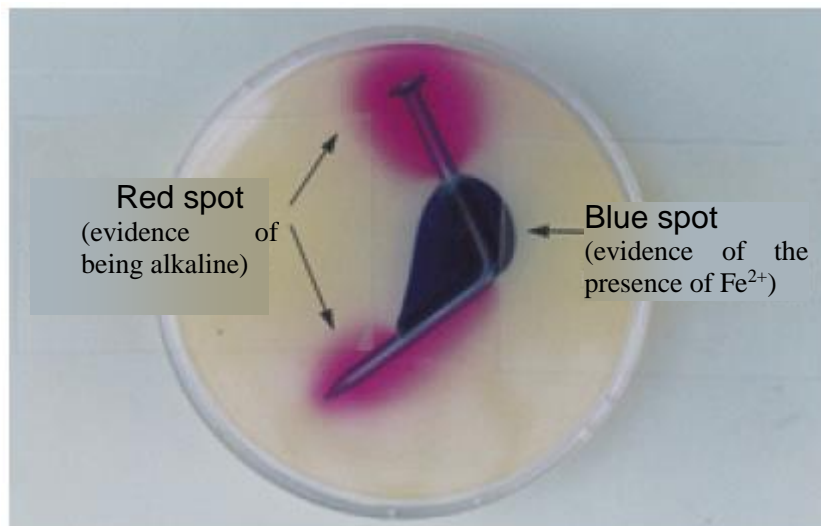
**Fig.-2 Local cell model <sup>2)</sup>**



The entire reaction of iron corrosion in water is expressed as:



An experiment that supports the coupling of anodic and cathodic reactions is exemplified below. A bent iron nail was immersed in an agar gel containing a 3% saline solution. A blue and red spots appeared (**Fig.-3**) when phenolphthalein and potassium ferricyanide were added to the saline solution. The blue spot proves the presence of  $\text{Fe}^{2+}$ , and the red spot shows that the zone was alkaline. Therefore, the corrosion reaction was shown to have involved electrochemical reactions <sup>3)</sup>.



**Fig.-3 Presence of anodes and cathodes**

The pH of sound concrete has been reported to be about 12.5. Under such an alkaline condition, a passive film (passivation) is formed on the surface of the steel, and thus corrosion scarcely occurs. However, when the pH of the solution in the pore lowers below 11 by CO<sub>2</sub> in the ambience, the passive film is destroyed, causing corrosion of the steel by the water and oxygen (corrosion caused by carbonization of concrete). Penetrating chloride ions, such as those from the sea and thawing agent used in winter, are suspected for breaking the passive film and thus causing corrosion of the steel (corrosion caused by salt damage). Salt damage accompanies generation of FeCl<sub>2</sub>, which releases H<sup>+</sup> ions by hydrolysis reaction, lowers the pH of the corroded section and thus further accelerates corrosion. Therefore, corrosion occurs faster by salt damage than by carbonization.

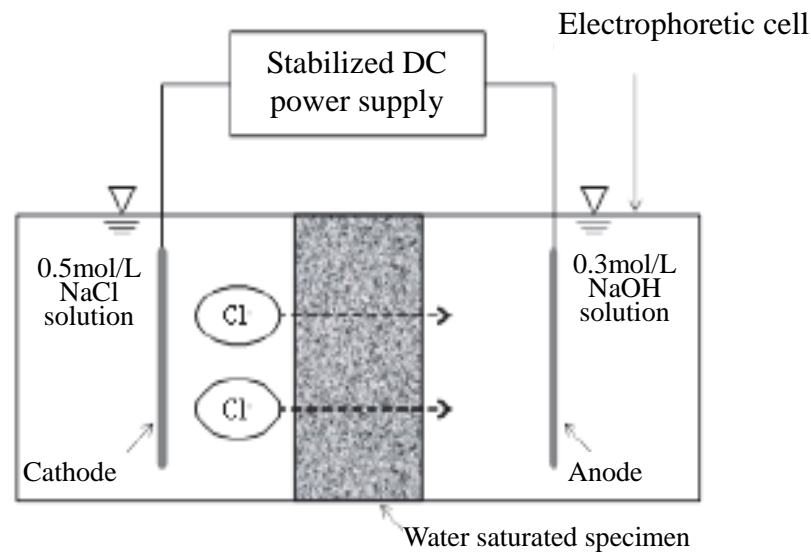
## 2.2 Movements of substances and electric charges in concrete

For steel within concrete to corrode or suffer deteriorated corrosion, there must be substances that induce corrosion such as CO<sub>2</sub> and Cl<sup>-</sup> or other substances that are involved in corrosive reaction such as H<sub>2</sub>O and O<sub>2</sub> penetrating into the concrete from the outside environment. Therefore, the material transfer within concrete and evaluation methods constitutes an unavoidable issue.

In the three phases that constitute hardened cement, i.e. the gaseous, liquid and solid phases, various phenomena interact with each other in an interactive manner, including diffusion of vapor and advection of water in the pores by changes in moisture content, movements of the dissolved chemicals of various kinds in the advecting water in the pores, and generation and dissolution of hydrates that solidify the dissolved chemical substances. In

order to predict the movements of the substances that are involved in corrosion of steel by considering the various kinds of phenomenon that take place in hardened cement, models of moisture transport and multi-species substance transport should be combined with an phase equilibrium model and be dynamically linked.

In a model of multi-species substance transport, Nernst-Planck equation is used to describe the speed of dissolved chemical species (ions) in pore solution. Nernst-Planck equation assumes that dissolved chemical species move powered by concentration gradient and potential gradient and describes the speed of movement by using diffusion coefficient and mobility. Of the two, mobility is defined by the moving speed of an ion in a unit potential gradient and can be interpreted as an index that shows the easiness of the ion to move in an electric field. The Nernst-Einstein relation is known as a relational expression between diffusion coefficient and mobility. Based on the knowledge, a method of calculating diffusion coefficient (defined as effective diffusion coefficient) from mobility has been standardized also in the field of concrete engineering <sup>for example 4) and 5).</sup>



**Fig.-4 Example of electrophoresis (steady-state electrophoresis) <sup>4)</sup>**

Electrophoresis is known as a method for measuring mobility. For example as shown in **Fig.-4**, a specimen that has a disk shape and is water saturated is placed in an electrophoretic cell, constant DC voltage is applied by using a stabilized DC power supply, and the pH of the solution in the electrophoretic cell and the concentrations of various ion species are measured.

In concrete, almost no electric conduction occurs in aggregates, which are an insulator, or hydration products, which are solid. Electric conduction occurs in the solution that exists within capillary pores of the concrete. The movements of ions in the solution within the capillary pores are expressed by Nernst-Planck described above. A relational expression

between diffusion coefficient and electrical resistivity (or electric conductivity, which is its reciprocal) can be derived by further considering the current density at an arbitrary cross section and ion concentration. Based on the knowledge, it is intelligible that electric conduction in concrete is governed by the pore structure (pore ratio, tortuosity, and constrictivity) and concentrations of various ion species in the concrete as well as the amount of water in the pores under a dry environment.

Another electric property of a substance besides mobility and electrical resistivity is dielectric constant. Dielectric constant is an index that shows the easiness of dielectric polarization when an electric field is given to the medium from outside. In actual concrete engineering practices, relative dielectric constant, which is the ratio to the dielectric constant of vacuum, is more widely used than dielectric constant.

### **3. Measurement methods of electrochemical property values**

#### **3.1 Evaluation of the properties of concrete related to steel corrosion**

The performance of concrete cover to reinforcement in protecting reinforcing steel directly links with the mass transfer resistance and moisture content of the concrete. Electrochemical measurements of concrete cover, i.e. the protective layer, are performed to evaluate the mass transfer resistance and moisture content of the concrete. In practice, electrical resistivity (electric conductivity), mobility and dielectric constant are measured as electrochemical property values and are used to directly or indirectly evaluate the physical property values that are theoretically or empirically relevant.

Measurement methods include tests that use specimens and nondestructive tests.

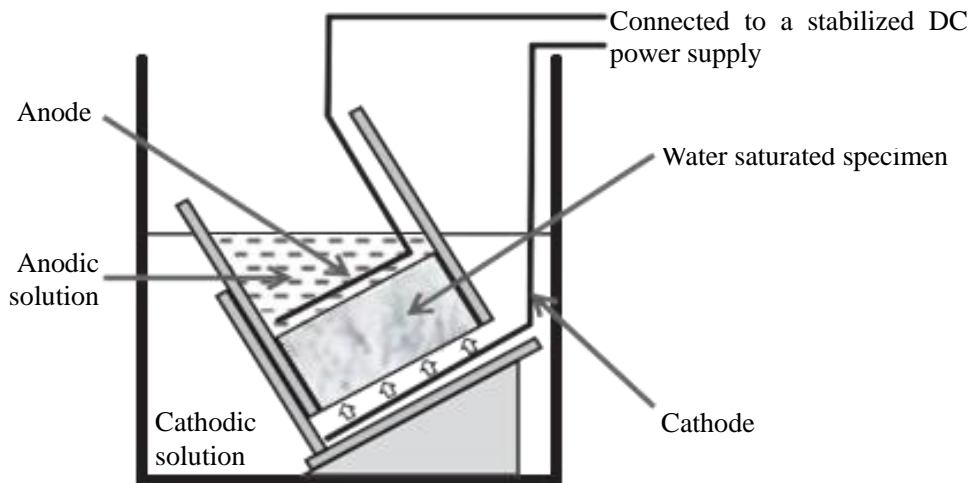
For example, methods for measuring electrical resistivity are classified by the shape and arrangement of electrodes into the two electrodes method, four electrodes method, four probes method (Wenner method), counter electrode method (one electrode method) and embedded electrode method. All methods involve setting electrodes to the specimen, measuring the electric current that flows between the electrodes and the voltage, and calculating the electric resistance. Electrical resistivity is calculated by dividing the resistance by the cell constant in which the shapes and dimensions of the specimen and electrodes are considered.

Cell constant is expressed in the order of the reciprocal of the length and can be theoretically derived by solving the partial differential equation of electrostatic potential in a certain case of measuring system. When the specimen or/and the electrodes has a complicated shape, it may be necessary to experimentally determine the cell constant by measuring the electric resistance of a solution of a known electrical resistivity or to numerically calculate the



cell constant by using the three-dimensional finite element method.

Mobility can be measured by electrophoresis that is based on nonsteady-state process shown in **Fig.-5** as well as steady-state electrophoresis shown in Fig.-4. Both tests commonly move the target ion(s) by electrophoresis but use different formulas for calculating the effective diffusion coefficient, which mutually differ in preconditions; and thus care is required upon using them.



**Fig.-5 Electrophoresis (nonsteady-state process)**

Dielectric constant of concrete can be measured by using electromagnetic waves or impedance. In Japan, electromagnetic radar for probing reinforcing steel is commonly used. The frequency of the electromagnetic waves emitted by major electromagnetic radar probes used in Japan varies by model but is around 2.0GHz. For using an electromagnetic radar probe for detecting rebars on the market to measure relative dielectric constant, the characteristics of the probe and the frequency of waves used for measurement need to be considered because dielectric constant depends on frequency.

Factors that affect electrochemical properties of concrete include the measurement conditions of the device such as the shape and dimensions of electrodes and the frequency of current applied as well as the conditions of the measuring object such as arrangement of reinforcing steel, concrete mix proportion, the states of concrete (moisture content, amount of electrolytes such as chloride ions, cracks, etc.), and environmental conditions (temperature, humidity, etc.). The details are summarized in the Report for each electrochemical property.

### 3.2 Methods for diagnosing corrosion

#### (1) Half-cell potential

ASTM established evaluation standards (ASTM C876) for measuring the half-cell potential of reinforcing steel. The method enables easy testing; and thus a number of organizations have issued standards and norms according to the ASTM standards. Also in Japan, Japan Society of Civil Engineers has established its standards (JSCE-E 601-2007). It involves wetting the concrete surface by spraying water, pressing a reference electrode (saturated silver chloride electrode, copper sulfate electrode, etc.) on the measuring surface, and measuring the potential difference to reinforcing steel with a high resistant potentiometer. Another method involves embedding a reference electrode (such as manganese dioxide electrode and lead electrode) within the concrete and monitoring the potential. There are various kinds of reference electrode as shown in **Table-2**.

**Table-2 Representative reference electrodes used for potential measurement**

Reference electrode	Electrolytic solution	Potential (V vs. SHE 25°C)
Saturated copper sulfate electrode (CSE)	Saturated copper sulfate solution	+0.316
Lead electrode (PRE)	Ca(OH) <sub>2</sub> +CaSO <sub>4</sub> (solid)	-0.483
Manganese dioxide electrode (MNO)	Saturated Ca(OH) <sub>2</sub> solution	+0.120
Saturated silver chloride electrode (SSE)	Saturated KCl solution	+0.196
Silver chloride electrode in seawater (SSE <sub>[sw]</sub> )	Seawater	+0.250
Saturated calomel electrode (SCE)	Saturated KCl solution	+0.242

Criteria that are widely used for half-cell potential measurement are exemplified in **Tables-3** and **4**. They show a common concept of the lower the potential suggesting the higher the susceptibility for corrosion, but the boundary values are not clear. It is a common recognition in half-cell potential assessment that the boundary values for judging corrosion of steel cannot be clearly defined.

Here, ASTM C876 states the potential standards in values of copper sulfate electrode (CSE). When another reference electrode is used for measurement, the measurement should be converted into CSE value for judgment. For example, when a saturated silver chloride electrode (SSE) is used at an ambient temperature of 25°C, the protective potential of steel is -725mV. This can be converted into CSE value just by adding the potential difference between SSE and CSE:  $-725\text{mV} + (-125\text{mV}) = -850\text{mV}$ .

**Table-3 Standard for judging corrosion by the half-cell potential method**  
 – ASTM C 876 –

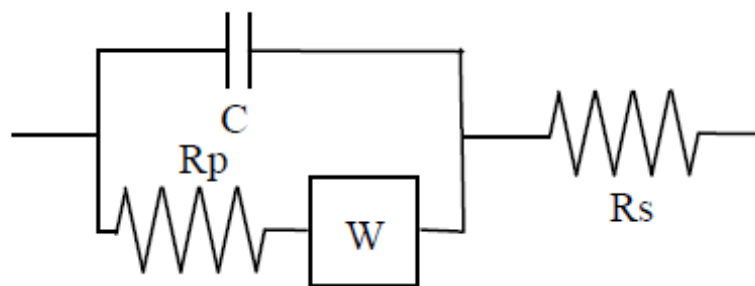
Half-cell potential E (mV vs. CSE)	Probability of corrosion
$E > -200$	No corrosion with a probability of at least 90%
$-200 \geq E > -350$	Uncertain
$E \leq -350$	Corrosion with a probability of at least 90%

**Table-4 Standard for judging corrosion by the half-cell potential method**  
 – Soundness diagnosis manual –

Half-cell potential E (mV vs. CSE)	Susceptibility to corrosion
$E > -150$	None
$-150 \geq E > -250$	Slight
$-250 \geq E > -350$	Rather high
$E \leq -350$	High

**(2) Polarization resistance**

The half-cell potential method is a qualitative method for estimating the possibility of corrosion of steel in concrete. On the other hand, the polarization resistance method is a quantitative testing that estimates the corrosion rate of steel. The method is widely known in the field of electrochemistry for testing the corrosive characteristics of a metal in a solution. No unified methods or technologies have been established for measuring the polarization resistance of steel in concrete.



**Fig.-6 Example of equivalent circuit model**

At the interface between a metal and a solution, a region (0.01 ~ 0.1μm) called an “electric double layer” is formed by adhesion of water molecules or the like where one side is continuously charged positively and the other is negatively charged. The area possesses electrostatic capacity, is charged to a certain degree, and thus has properties of a condenser C in an electric circuit. The current applied from the counter electrode is given via a solution. Here, to measure the polarization of steel in a concrete structure, the concrete cover from the

set counter electrode to reinforcement corresponds to solution. Therefore, solution resistance (concrete resistance)  $R_s$  is included in the total resistance measured by the system. Because it takes a certain time for iron atoms to exchange charges to become  $Fe^{2+}$  and for oxygen to move to the surface of steel, the easiness and difficulty of the movements (Warburg impedance,  $W$ ) show charge transfer resistivity. Simplified models such as the one shown in Fig.-6 have been proposed as an equivalent circuit that shows an electrically equivalent response to such complicated electric properties.

Polarization resistance  $R_p$  shown in the model cannot be determined directly but by giving electrochemical disturbance (polarization) to the steel in a state of half-cell potential and calculating the responses. In other words, a small amount of current ( $\Delta I$ ) is applied from the counter electrode to the steel and causes slight changes ( $\Delta E$ ) in potential from the half-cell potential of the steel. The potential changes and applied current are measured with an electrometer and ammeter, respectively; and the resistance  $R$  shown in the following equation is calculated. The applied current should be controlled so that the potential change  $\Delta E$  does not exceed  $\pm 10\text{mV}$  because application of excessive current would cause deviation from the range of linear polarization.

$$R = \frac{\Delta E}{\Delta I} \quad (4)$$

As an example, the standard of CEB for judging corrosion is shown in **Table-5**.

**Table-5 Standard for judging corrosion by the polarization resistance method**

Corrosion rate measurement $I_{\text{corr}}$ ( $\text{iA}/\text{cm}^2$ )	Judgment of corrosion rate	Polarization resistance $R_p$ ( $\text{k}\Omega \cdot \text{cm}^2$ )
Less than 0.1 - 0.2	Passive state	Larger than 130 - 260
0.2 - 0.5	Corrosion rate of low to intermediate degree	52 - 130
0.5 - 1.0	Corrosion rate of intermediate to high degree	26 - 52
Larger than 1.0	Severe and high corrosion rate	Less than 26

#### 4. Evaluation of the performance and quality of concrete based on electrochemical property values

There are diverse electrochemical methods for evaluating concrete, such as for testing the physical properties during hardening, evaluating the moisture content and permeability of hardened concrete, and estimating the risk of steel corrosion based on the electric physical

property values of concrete. The methods vary greatly also in development level ranging from being under development to completed standardization and/or normalization. In this section, the characteristics of the method are described for each target of evaluation.

#### **4.1 Evaluation of physical properties during the hardening process**

Setting or the degree of hardening of concrete can be perceived by 1) inserting an electrode into fresh concrete, measuring the electric conductivity, and estimating the setting from the correlation between the time-dependent changes in conductivity and proctor intrusion resistance value, or 2) indirectly determining the amount of water consumed while in framework and estimating the compressive strength.

#### **4.2 Evaluation of the moisture content in hardened concrete**

In general, the electrical resistivity (electric conductivity) of concrete increases (decreases) as the concrete dries. When organized by the degree of saturation (moisture content at each relative humidity / percentage of saturated water content), the same electrical resistivity value is shown at the same degree of saturation for any kind of concrete. By using this relationship, the moisture content of concrete can be determined by measuring either the electrical resistivity or electric conductivity. Similarly, the moisture content of concrete can be determined from relative dielectric constant, which is affected by the continuity of water in voids.

#### **4.3 Evaluation of resistance to chloride ion penetration**

A most highly developed electrochemical measurement of concrete is rapid methods for evaluating the resistance to chloride ion penetration, such as rapid chloride penetration test, as well as durability design methods, which use the rapid chloride penetration test.

ASTM C1202 (AASHTO T-277), which measures the quantity of charge during electrophoretic cell test, has long been known as a method for evaluating the resistance of the chloride ions penetration into concrete. In these years, steady-state electrophoresis and nonsteady-state electrophoresis have been standardized in and outside Japan. NT BUILD is an acknowledged nonsteady-state method; and JSCE-G 571 and NT BUILD 355 are known as steady-state processes. There is also AASHTO TP-95, which determines the electrical resistivity of a water-saturated cylindrical specimen by using the four probes method (Wenner method) and calculates the resistance to chloride ion penetration based on the results and the criteria shown in **Table-6**. The electrical resistivity values shown in Table-6 are for cylindrical specimens having

dimensions of  $\phi 100 \times 200$  mm and  $\phi 150 \times 300$  mm measured with an electrode spacing of 1.5 inches. The reference values need to be appropriately modified when testing a specimen of a different shape or different dimensions or using different electrode spacing.

In the Report, examples of durability assessment that used these tests in North America, Scandinavia, Singapore, India and China are explained, providing further information.

#### 4.4 Relationship with water permeability and air permeability

The relationship between electrical resistivity and unsaturated hydraulic conductivity has been intensively investigated in the field of geotechnical engineering. There have been Archie's law and the relational expression by Worthington between the electrical resistivity of the ground and coefficient of permeability developed and their application limits being identified. Further evolutionary studies of the relationships have also been performed. Also in the field of concrete engineering, experimental studies have been performed on the relationship between electrical resistivity and the diffusion coefficient of water although the number of studies is not large. It has been reported that the diffusion coefficient of water tended to decrease as electrical resistivity increased regardless of the kind of binder but the degree of reduction varied greatly by the binder<sup>7)</sup>.

The air permeability of concrete has been used to evaluate the quality of the concrete. In that case, it is necessary to consider the influence of the water content ratio in concrete on the air permeability. Therefore, some study proposed to evaluate the quality of concrete based on a nomogram which consists of air permeability and water content ratio estimated by electrochemical property.

**Table-6 Criteria for judging resistance to chloride ion penetration in AASHTO  
Designation: TP 95-11<sup>6)</sup>**

Chloride Ion Penetration	Surface Resistivity Test	
	100-mm $\times$ 200-mm (4-in. $\times$ 8-in.) Cylinder (kilohm-cm) $a = 1.5$	150-mm $\times$ 300-mm (6-in. $\times$ 12-in.) Cylinder (kilohm-cm) $a = 1.5$
Hgih	< 12	< 9.5
Moderate	12-21	9.5-16.5
Low	21-37	16.5-29
Very Low	37-254	29-199
Negligible	> 254	> 199

$a =$  Wenner probe tip spacing

**Table-7 Example of proposed criterion for evaluating the risk of corrosion from electrical resistivity <sup>8)</sup>**

Concrete resistivity			Risk of corrosion
$\Omega$ m	k $\Omega$ cm	$\Omega$ cm	
> 1000	> 100	> 100 000	Negligible
500 – 1000	50 – 100	50 000 – 100 000	Low
100 – 500	10 – 50	10 000 – 50 000	Moderate
< 100	< 10	< 10 000	High

#### 4.5 Evaluation of the risk of steel corrosion

Several semi-quantitative grading methods have been proposed for evaluating the risk of steel corrosion in concrete, which use electrical resistivity. As an example, the method mentioned in the summary of RILEM TC 154-EMC report is shown in **Table-7**. In the Report, proposed methods other than that shown in Table-7 are summarized; so please use them as reference. All methods grade that the risk of steel corrosion is larger at lower electrical resistivity in accordance with the assumption based on the following phenomena and observations.

- (1) In concrete that contains much chloride ions and/or water, which are corrosion factors, the electrical resistivity tends to be low.
- (2) Resistance of concrete is considered a portion of corrosion cell, and the decrease of the electric resistivity of concrete increases the corrosion current on a steel bar.
- (3) Chloride ions, water and oxygen, which are corrosion factors, penetrates easily into concrete that have a porous pore structure. Concrete susceptible to steel corrosion has large moisture content in general. Under such conditions, electrical resistivity can be used as an index for evaluating mass transfer resistance.

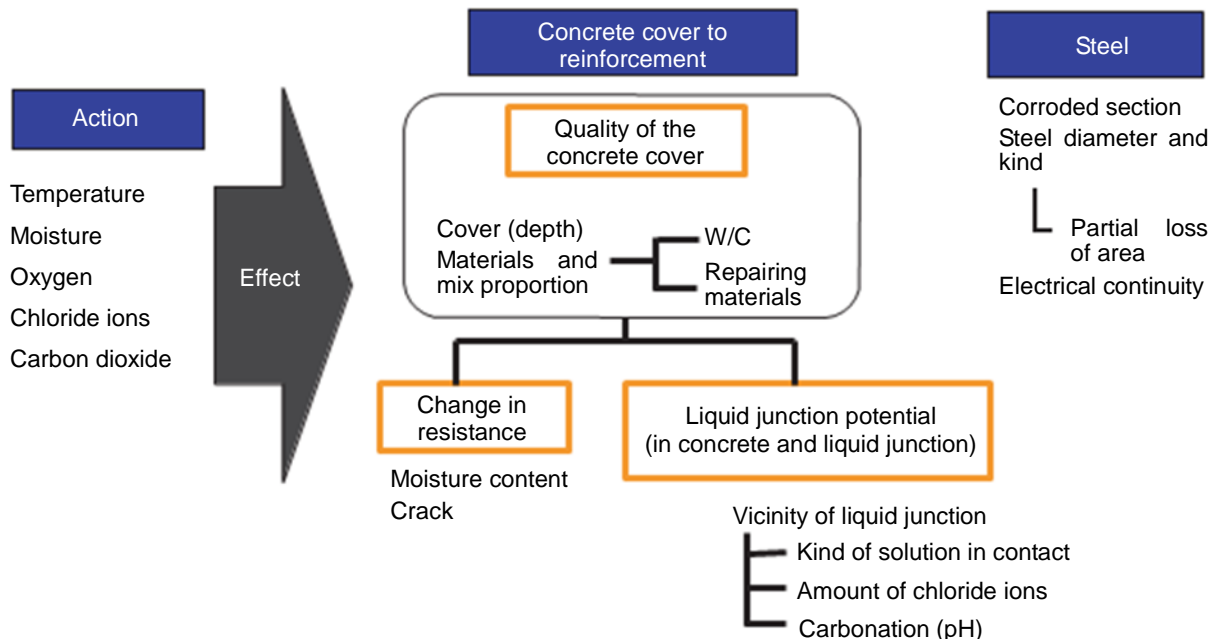
#### 5. Electrochemical methods for evaluating the corrosion of steel in concrete

Measuring the half-cell potential or polarization resistance of steel is a commonly used electrochemical method for grasping the corrosive state of steel in concrete. In such a measurement, the concrete cover to reinforcement is likely to affect the measured values. Therefore, the technical committee organized the effects by the kind of cement and admixture, conditions of concrete cover to reinforcement, and kind of reinforcement on measurement.

For example, Takagi et al. investigated the relationship between half-cell potential and the

degree of steel corrosion and reported that corrosion of steel that was induced by carbonation had the induction boundary (between Score 1 (no corrosion) and Score 2 (slight corrosion on the steel surface)) at - 50mV vs. SSE, which is a potential higher than existing standards for corrosion induced by salt damage. They estimated that this was because carbonation caused large reductions in the potential of the concrete cover to reinforcement<sup>9)</sup>.

Such literature researches suggest that it is important to quantitatively understand the effects by the properties of concrete cover to reinforcement and concrete and the kind of reinforcement on measurement in order to correctly monitor the corrosive state of steel in concrete by an electrochemical approach. The relationships among various factors in electrochemical diagnosis and measurements on steel in concrete, which have been summarized in the activities of this study committee, are shown in **Fig.-7**. The effects of various kinds of factor on electrochemical measurement are shown in **Table-8**. Points to note for conducting electrochemical measurement of an actual structure are summarized in **Table-9**.



**Fig.-7 Effects of various kinds of condition on measurement**



**Table-8 Effects of various kinds of factor on electrochemical measurement**

			Specific resistance (large)	pH (low)	Amount of chloride ions (large)	Electrical continuity between steels	Deaeration environment (in water)	Pitch (narrow)	Polarization resistance of steel (high)	Steel diameter (large)
Half-cell potential method	Half-cell potential	High	○	○						
		Low			○	○	○			
Polarization resistance method	Liquid junction resistance	High	○	○						
		Low			○		○			
	Polarization resistance	High								○
		Low	○			○		○	○	

How to read the table: When the specific resistance of concrete cover to reinforcement is large, it may result in a large measurement for half-cell potential and low value for polarization resistance.

**Table-9 Points to note for evaluating corrosion of steel in actual structure by electrochemical approaches**

Method	Points to note
Common to both methods	Measurement values fluctuate by conditions during the measurement, such as air temperature and moisture content of concrete, fluctuation factors should be appropriately understood, and the results of the measurement should be evaluated by considering the ambient conditions of the structure.
	It is desirable to diagnose corrosion of steel by conducting a chipping test and/or measuring chloride ion concentration and/or carbonation depth at the same time to supplement the results of electrochemical measurement.
	Steel must be in direct contact with concrete. The methods are thus not applicable to sections where steel is not adhered to concrete (where electrical continuity has been lost) such as by severe cracks accompanying corrosion. Therefore, points of measurement should be examined in advance by hammering, etc.: and points that are free of float, exfoliation and cracks should be selected.
	The methods are in principle inapplicable to steel reinforcement that is coated with epoxy resin or galvanized. There have been a number of application examples in research level for stainless steel reinforcement.
	The methods are inapplicable to sections that are constantly covered by water (immersed in water). Measurement should be conducted by removing the excess sprayed water (bleeding) from the concrete surface.
	The methods are inapplicable to sections where stray current or strong magnetic field exists.
	Electric continuity should be secured by removing corrosion product, etc. from points where working electrode is to be connected.
Half-cell potential method	The evaluation by the criterion may not agree with the actual corrosion of the steel. It is thus important to check the distribution of half-cell potential in the entire structure such as by preparing a contour map of electric potential.
Polarization resistance method	The method is inapplicable to concrete where the surface is so dry that is almost electrically insulated or is coated with an insulating material like the coat. According to the 2004 Report of RILEM <sup>10)</sup> , measurement is difficult when the electric resistivity of concrete is larger than 1000Ωm. Therefore, full attention is required for applying at a section covered by section repair material, for example, which has high electric resistivity. Even coated, the concrete can be measured by removing the coat from the concrete surface and keeping the surface layer moist.
	Measurement should be conducted at a point where the concrete surface is smooth. When the surface is not smooth, a measure should be implemented to prevent the contact resistance from increasing between the concrete surface and the counter electrode of the probe, such as by grinding the surface and applying water-soluble gel.

## 7. Concluding remarks

The technical committee on systematization of electrochemical measurement methods based on physicochemical theory prepared a report that helps correct understanding of electrochemical measurements for concrete engineers and researchers who study electrochemistry for the first time in the concrete engineering field and engineers and researchers who are using electrochemical approaches in practice but do not have full understanding of their theoretical backgrounds. The Report also describes the theories of electrochemistry, which are deemed to be difficult by many people. Therefore, unlike guidebooks that are entitled “Easy ...” and “How to ...”, which are easy to read and understand but do not necessarily contain substantial discussions, the Report needs to be read with perseverance, but careful reading of the Report would help readers to acquire substantial understanding the theories, latest technologies and points to note at measuring actual structures, etc.

Finally, we thank all persons involved for their cooperation in summarizing this Report.

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