Technical report

Space-Averaged Non-Local Analysis of Electric Potential for Polarization Reactions of Reinforcing Bars in Electrolytes

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Abstract
For assembly of reinforcing bars embedded in electrolyte like concrete, space-averaged non-local analysis for electric potential is proposed and the anodic and cathodic polarization reactions are formulated in association with the exchange of electric charge between steel reinforcing bars and the electrolyte as matrix. In order to verify the proposed scheme like smeared crack modeling of cracked concrete mechanics, transparent sodium poly-acrylate superabsorbent polymer with calcium hydrate solution was made so that we may identify the location of anodic and cathodic reactions of reinforcement at regular time intervals. The analytically predicted locations of corrosion were compared with the experiments, and its functionality of non-local formulation was verified and its applicability was experimentally examined.

1. Introduction
Corrosion of reinforcing bars in structural concrete is a critical deterioration associated with electro-chemical reaction, which is generally classified as micro-cell circuit where anodic and cathodic polarization proceeds locally at one place, and the macro-cell one where oxidation and reduction separately progress in space with great rapidity (Suzuki et al. 2016; Angst 2018). For the former case, global electric field is not necessarily solved for estimating rate of corrosion.

For the latter case, however, the global electric potential over the analysis domain is to be solved for assessment of corrosion rates and locations. For example, local improvement of corrosive environments sometimes brings about macro-cell circuit along reinforcing bars and neighboring concrete leading to rapid corrosion (Kranck and Sagüés 1997, 2001; Roberge 2008; Nanayakkara and Kato 2009; Cao 2014; Cao and Cheung 2014). As for gigantic macro-cell circuits, stray electric currents leaked from railway systems have been reported to cause rapid corrosion of underground facilities. Therefore, it is necessary to take into account the corrosive environment by an external charge. In these cases, the electric potential field, electric current, anodic cathodic polarization and ion kinetics in electrolytes interact mutually, and global analysis of the potential field is required to assess the rate of corrosion in concrete.

A number of researches have been reported on the corrosion of reinforcement experimentally and analytically (Hsu et al. 2000; Isgor and Razaqpur 2006; Ghods et al. 2007; Kim and Kim 2008; Kim and Ann 2010a, 2010b; Otieno et al. 2011, 2012; Özbolt et al. 2011; Zhao et al. 2012a, 2012b, 2014; Cao 2014; Cao and Cheung 2014; Michel et al. 2016). It has been discussed by coupling the electric potential governed by Laplace equation and the polarization reaction rate that can be estimated by Butler-Volmer’s theorem (Bard et al. 1980; Kranck and Sagüés 1997; Soleimani et al. 2010). As these thermodynamic laws are simply robust, the affinity with the prediction of corrosion rate at the member level has been recognized to some extent, and the mainstream of analysis has formed up to today.

Here, let us consider the analysis of the whole structural reinforced concrete (RC). The anodic and cathodic reactions develop on the surface of reinforcing bars and the rate of reactions is governed by the electric potential gap of concrete and steel. Furthermore, on the surface of each reinforcing bar, local transfer of electron from concrete to steel proceeds for anodic reaction accompanying the ionization of ferrite (corrosion). The opposite transfer develops for the cathodic reaction tied with produced hydroxyl ion and/or hydrogen gas in relation to pH, oxygen concentration and others.

When we apply finite element discretization to solve the potential field, interface elements have to be placed on all surfaces of reinforcing bars. As thousands of bars are generally placed in RC structures, space discretization of high complexity is a problem in practice. We have the same issue for nonlinear structural analysis, and so called smeared crack model has been applied for simulation of RC nonlinear mechanics (Maekawa et al. 2003). Here, steel bars are converted to be a reinforcement assembly having the common degree of freedom. It mechanically implies a space-averaged fictitious medium in concrete.

This report aims to propose the formulae to analyze the rate of polarization reaction of large numbers of reinforcing bars as a space-averaged smeared media that
are overlaid on electrolytes such as concrete with micro-pores. The authors expect that space-averaging of electric potential on steel reinforcement will be consistently integrated with the structural analysis in consideration of the impact of corrosion.

2. Volumetric non-Local formulation

Figure 1 shows the concept of space-discretization of the electric potential. As stated in Section 1, we have a direct way to reproduce the polarization reactions on the interface accompanying the exchange of electrons by means of joint interface elements to represent the potential of both concrete and steel. Here, let us consider the finite volume including the interface and its overlapped volume of neighboring concrete and steel as shown in Fig. 1. This element logically has to include the nodal degrees of freedom (NDOF) of both concrete and reinforcing bars. As reinforcing bars are electrically conductive, the overlapped element may include the whole volume and surface of the reinforcement.

Provided that reinforcing bars are uniformly distributed and common potential is shared inside the overlapped element, the electric potential may represent the whole reinforcement as smeared RC element as shown in Fig. 1. This process follows the formulation of mechanistic smeared crack modeling, where the local bond stress developing on the interface between steel bars and concrete is converted to the equivalent tension as a space-averaged local bond after cracking.

As the polarization reaction can be identified by using NDOFs of both concrete and steel, we may compute without identification of the exact location of the interface on which the local thermodynamic events occur. Thus, this space-averaging procedure is brunt and non-local. When we define an infinitely small volume to include a single rebar’s surface, the non-local formulation may converge to the exact local one where the location of steel and concrete exactly coincides with each other. Although the non-local formulation with regard to space is coupled with sink term of the charge balance as discussed in the following section, there is no violation of physics, which does not allow simultaneous communication without any delay of time.

Here, let Gauss’s law be integrated with the non-local potential. We have Maxwell’s equation applied to continuum of both concrete and steel as,

\[ \nabla \cdot D = \rho \]  \hspace{1cm} (1)

where \( \rho \) is the charge density (C/m\(^3\)) and \( D \) the electric flux density (C/m\(^2\)). The electric flux density and its field strength are known to have a linear relation as,

\[ D = \varepsilon E \]  \hspace{1cm} (2)

where \( \varepsilon \) is the dielectric constant (C\(^2\)/Nm\(^2\)), and \( E \) is the electric field (N/C). The electric current between two points is simply expressed by the Ohm’s law as,

\[ J = \sigma E \]  \hspace{1cm} (3)

where \( J \) is the current flux density (A/m\(^2\)) and \( \sigma \) means conductivity (S/m, S = 1/\( \Omega \)) of the field. The electric field is expressed by the potential gradient as,

\[ E = -\text{grad}(\phi) \]  \hspace{1cm} (4)

where \( \phi \) is the electric potential (V).

The conductivity of concrete is closely linked with the multi-ion concentration, micro-pore structures of CSH solid, the degree of saturation and the several solvents of salts. When we integrate the transient kinetics of solved ions in electrolytes, the Nernst-Plank equation shall be applied for multi-chemo thermodynamics (Bard et al. 1980; Elakneswaran and Ishida 2014). The conductivity of electrolytes is assumed to be simply constant here, since the primary aim of this study is to verify the scheme of the simulation qualitatively. The complete overlay of multi-ion and the electric potential will be discussed after verification of these non-local formulae in the future.

The total amount of electric charge in a closed system does not depend on the passage of time and is always invariant. Then, we have the conservation of electric charge for a single media of concrete and steel as,

\[ \text{div}(J) + \frac{d\rho}{dt} = 0 \]  \hspace{1cm} (5)

As described in Fig. 1, conservation of electric charge of steel and concrete as an electrolytic solid in an RC element is specified with the mutual interaction term denoted by \( Q \) as,

Concrete in RC \( \text{div}(JJ_r) + Q(\phi_r - \phi_s) = 0 \) \hspace{1cm} (6)

Steel in RC \( \text{div}(JJ_r) - Q(\phi_s - \phi_r) = 0 \) \hspace{1cm} (7)
\[ Q = Q_{\text{anod}}(\phi_c - \phi_s) + Q_{\text{cathod}}(\phi_s - \phi_i) \]  

where \( J_{c} \) and \( J_{s} \) are the flux (current) of electric charge through concrete electrolyte and steel’s volume in the RC element, \( Q \) is the exchange of the electron through the joint interface driven by anodic and cathodic polarization reactions of \( Q_{\text{anod}} \) as oxidation to produce ferrite ion (corrosion) and \( Q_{\text{cathod}} \) of reduction to consume dissolved oxygen in pore solution.

The polarization reaction is governed by the potential gap of concrete and reinforcing bars as \( \phi_c - \phi_s \) where \( \phi_c \) is the electric potential of the concrete electrolyte element (V) and \( \phi_s \) is that of the reinforcement (V). Equations (6) to (8) are the highlights of the space-averaged non-local formulation proposed in this study. By using the inter-linked terms of \( Q \), the local reactions on the surface of reinforcing bars are converted to the equivalent volumetric governing equations, which can be simply discretized based on the continuum theorem.

We have the conservation of electric charge of the RC element by simple summation of Eqs. (6) and (7). It is evident that the total number of electrons and protons (minus and plus charge) are exactly equal, although their distribution over the analysis domain is not necessarily uniform as in the case of macro-cell corrosion.

The electron is charged into the volume of steel in RC element as denoted by \( Q_{\text{anod}} \) of anodic polarization and the one in the volume of steel is lost by \( Q_{\text{cathod}} \) of cathodic reduction. When both anodic and cathodic rates of electric charge are the same, the internal flux of concrete and steel becomes zero as we have Eqs. (6) and (7). Then, the macroscopic currents of steel and concrete become zero together. Thus, the micro-cell corrosion is concurrently covered as the solution of the proposed non-local formulation,

\[ J_{c} = -\sigma_c \text{grad}(\phi_c) \]  
\[ J_{s} = -\sigma_s \text{grad}(\phi_s) \]

where \( \sigma_c \) is the conductivity of concrete element (S/m) and \( \sigma_s \) that of the rebar element (S/m). The dielectric constant can be ignored if we play with the time scale of day or year, because its capacity term is extremely small unlike the cases of thermal analyses of concrete. The conductivity of concrete expresses the averaged electron transfer by multi-ions in pore solution. Then, when we couple the non-local electric governing formulae with ion-transfer modeling by Nernst-Plank theorem, \( \sigma \) can be obtained not as the material constant but as the computed variable. This is the next step development in future work.

### 3. Polarization reaction model

This section outlines anodic and cathodic polarization reaction models that are used for verifying the space-averaged non-local framework. The authors apply generally proven electro-chemical models of simplicity. Since it is obvious that the computed mass of corrosion depends on the accuracy of the polarization models quantitatively, in this report the authors focus not on the amount of corrosion but on the polarization location, which has much to do with the frame of analysis accompanying macro-cell corrosion under the external charge.

#### 3.1 Anodic and cathodic polarization curves

Anodic and cathodic reactions with respect to corrosion in concrete are expressed by,

\[ Fe \rightarrow Fe^{2+} + 2e^- \]  
\[ \frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- \]

These oxidation and reduction are a kind of electrode accompanied by charge transfer at the interface between metal and solution. The reaction rate is explained with Evans diagram as shown in Fig. 2 and formulated as (Stern and Geary 1957; Hsu et al. 2000),

\[ E_a = E_{a0} + \beta_a \log_{10} \left( \frac{i_a}{i_{a0}} \right) \]  
\[ E_c = E_{c0} + \beta_c \log_{10} \left( \frac{i_c}{i_{c0}} \right) \]

where \( E_a \) is the electrode potential in anode polarization curve \( (V: = \phi_c - \phi_s) \), \( E_{a0} \) the spontaneous electric potential of iron in equilibrium \( (V) \), \( \beta_a \) the Tafel slope in anodic polarization curve, \( i_a \) the anode current density \( (A/m^2) \) and \( i_{a0} \) the exchange current density of iron at equilibrium \( (A/m^2) \). \( E_c \) is the electrode potential in the cathode polarization curve \( (V: = \phi_s - \phi_i) \), \( E_{c0} \) the spontaneous potential of oxygen in equilibrium \( (V) \), \( \beta_c \) the Tafel slope of cathode polarization curve, \( i_c \) the

![Evans diagram of electrode potential-current density relation.](image-url)
cathode current density \((A/m^2)\) and \(i_0\) is the exchange current density of oxygen at equilibrium \((A/m^2)\).

The relation of the potential gap and the current density is given by the Butler-Volmer equation and built in Eqs. (6) and (7). Here, the Tafel slope, which gives the gradient of the anodic and the cathodic polarization curves, and the natural potentials of iron and oxygen are formulated with reference to the previous studies (Ishida and Maekawa 1999; Maekawa et al. 2008) as,

\[
E_{an} = E_{Fe}^{\infty} + \frac{RT}{z_{Fe}F} \ln h_{Fe}^{2} \tag{15}
\]

\[
E_{cu} = E_{Fe}^{\infty} + \frac{RT}{z_{Fe}F} \ln \left( \frac{P_o}{P^0} \right) - 0.06\,pH \tag{16}
\]

\[
\beta_a = \frac{2.303RT}{az_{Fe}F} \tag{17}
\]

\[
\beta_c = \frac{2.303RT}{(1-\alpha)z_{Fe}F} \tag{18}
\]

where \(E_{Fe}^{\infty}\) is the standard electrode potential of iron at 25°C (= -0.44 V, SHE), \(E_{Fe}^{\infty}\) the standard electrode potential of oxygen at 25°C (= 1.229 V, SHE), \(R\) the gas constant, \(T\) the absolute temperature (K), \(z_{Fe}\) the number of charges of iron (= 2), \(z_{O}\) the number of charges of oxygen (= 2), \(h_{Fe}\) the ion concentration (mol/L), \(P^0\) the atmospheric pressure (Pa), \(P_o\) the oxygen partial pressure (Pa), \(F\) the Faraday constant (= 96 485 C/mol) and \(\alpha\) is the symmetry factor (= 0.5) used here.

### 3.2 Anodic polarization curve with passive film

In metals in the active state, the anodic current density increases with the increase of the electrode potential gap, but the cathodic current density decreases sharply at a certain electrode potential. Here, we have to consider the passivation that forms a dense oxide film on the metal surface and slows down the anodic reaction (Roberge 2008). Reinforcing bars in concrete with high alkalinity (pH = 12 to 13) are also known to form a passive film from the thermodynamic point of view and may be rate-limiting for steel corrosion.

Here, referring to the previous research, the authors use the simple anodic polarization curve of steel concrete with a passive film (shown in Fig. 3) for the verification of the non-local formulation. In fact, corrosion rate greatly relies on the polarization curves quantitatively. In this study, however, we use non-concrete transparent matrix whose exact characteristics are not well known although it is expected to be similar to concrete. Thus, the computed solution is mainly focused on in view of the verification qualitatively.

According to Nagataki et al. (1997), the general shape of the anodic polarization curve of metal can be roughly divided into three types: active, passive and active-passive behaviors as,

**Active Zone** : \(E_a < E_{pass} : E_a = E_0 + \beta_a \log_{10} \left( \frac{i_a}{i_0} \right) \)

**Passive Zone** : \(E_{pass} < E_a < E_{piti} : i_a = i_{piti} \)

**Trans-passive Zone** : \(E_{piti} < E_a : \)

\[
E_a = E_{piti} + \beta_a \log_{10} \left( \frac{i_a}{i_{piti}} \right) \tag{19}
\]

where \(E_{pass}\) is the passive potential (= -0.45V, SHE), \(E_{piti}\) the passive breakdown potential (= 0.5V, SHE), and \(i_{piti}\) is the passive current density (= \(10^{-6}\) A/m²). Here, by defining the electrode potential for passivation of metal and the electrode potential for reactivation, it is possible to correspond to the polarization curve of any pattern.

### 3.3 Micro-cell corrosion current density

When anode and cathode parts are in close proximity and uniformly distributed on the surface of bars and these parts fluctuate constantly over time, uniform corrosion on the surface of bars occurs as micro-cell corrosion. At that time, the electric charge generated by the anodic reaction of bars is consumed by the cathodic reaction of the dissolved oxygen so that the local charge conservation law is satisfied, and the electrical neutrality of each place is maintained. In this model, the current density and electrode potential during micro-cell corrosion are assumed to satisfy \((i_{micro}, E_{micro})\), which is indicated at the intersection in Fig. 2. Thus, it is assumed that Eqs. (20) and (21) are satisfied in Eqs. (13) and (14) as,

\[
E_a = E_c = E_{micro} \tag{20}
\]
Then, we have the corrosion current density at the time of micro-cell corrosion by substituting Eqs. (20) and (21) into Eqs. (14) and (15) as,

$$\log_{10}(i_{\text{corr}}) = \frac{(E_{\text{corr}} - \beta_e \log_{10} i_{\text{corr}}) - (E_{\text{corr}} - \beta_a \log_{10} i_{\text{corr}})}{\beta_e - \beta_a}$$  \hspace{1cm} (22)

where $i_{\text{corr}}$ is the corrosion current density (A/m$^2$).

### 3.4 Macro-cell corrosion

Macro-cell corrosion is the mode where anode and cathode parts are formed more or less apart accompanying the electric circuit of finite size though the electrolytes and steel. The electrons generated in the anode move along bars and consumed at the cathode area. The total amount of electric charge is conserved as a whole of the target domain. Similar to micro-cell corrosion, the polarization reaction proceeds with the electrode potential on the steel surface as the driving force for macro-cell corrosion (Jones 1996). The reaction rate and the determination of the anode and cathode parts are explained on Evans Diagram as shown in Fig. 4.

It is assumed that anodic and cathodic reactions are respectively determined for the electrode potential at each location. As shown in Fig. 4 as $E_{\text{red},\text{an}}$, the anodic reaction is predominant where the electrode potential is relatively high, and as shown in the same figure as $E_{\text{red},\text{cat}}$, the cathodic reaction is predominant where the electrode potential is relatively low. In this section, therefore, both anode and cathode current densities in each element were defined with respect to the electrode potential, and the current flowing from above the electrode was defined as the total current density.

The schematic explanation of micro and macro-cells is actualized in the scheme of non-local formulation. Let us consider non-zero exchange of charge in Eqs. (6) to (8). It means that anodic and cathodic reaction rates are not equal ($Q \neq 0$) at some place. Here, the flux of concrete and steel is equally provoked as Eqs. (6) and (7) be satisfied. Then, the RC element can be a part of driving force to create current in steel and concrete (macro-cell circuit). As the electric charge is hardly stored in volume, closed circuit is reproduced concurrently by solving the simultaneous equations.

#### 3.5 Calculation of polarization current density

As mentioned in previous section, micro-cell corrosion proceeds with the current density at the intersection of the anodic and cathodic polarization curves in order to satisfy local charge conservation. On the other hand, in case of the macro-cell corrosion, in order to conserve the total amount of electric charge in the whole system, the anode reaction proceeds approximately independently by the electrode potential at each location. Therefore, the anode current density in the active, passive and the trans-passive areas can be obtained by reforming Eq. (19) as,

**Active Zone**

$$\log_{10}(i_a) = \frac{E_{\text{red}} - E_{\text{an}}}{\beta_a} + \log_{10}(i_{\text{an}})$$

**Passive Zone**

$$\log_{10}(i_a) =\frac{(E_{\text{red}} - E_{\text{pass}})}{\beta_a} + \log_{10}(i_{\text{pass}})$$

**Trans-passive Zone**

$$\log_{10}(i_a) =\frac{(E_{\text{red}} - E_{\text{trans-pass}})}{\beta_a} + \log_{10}(i_{\text{trans-pass}})$$

where $E_{\text{red}}$ is the electrode potential (V).

Similar to the calculation of the anode current density, the cathode current density is also modified from Eq. (14) as,

$$\log_{10}(i_c) = \frac{E_{\text{red}} - E_{\text{cor}}}{\beta_c} + \log_{10}(i_{\text{cor}})$$

In the charge transfer process in Eq. (8), the total current density at each position is defined as the sum of the anode and the cathode current density by,

$$Q = S \cdot i_{\text{cor}} = i_a + i_c$$

where $S$ is the specific surface area of reinforcing bars per unit volume of electrolyte's matrix. When it takes a positive value, the cathode reaction is dominant at that position, whereas the value is negative when corrosion is dominant.

In the charge transfer process, the ratio of the anodic reaction rate is defined as $i_a/(i_a + i_c)$. As this anodic reaction ratio approaches unity, the anodic reaction predominates, and as the anodic reaction ratio approaches nil, the cathodic reaction predominates.

The corrosion rate in the element is calculated from Faraday's law shown in Eq. (26) by using the corrosion...
current density as,

\[ \Delta R_{\text{corr}} = \frac{\text{corr} \cdot \Delta t \cdot M_{Fe}}{z_{Fe} \cdot F} \]  

(26)

where \( \Delta R_{\text{corr}} \) is the corrosion rate (g/cm²), \( \Delta t \) the time increment and \( M_{Fe} \) is the atomic weight of iron (55.85 g/mol).

4. Verification of the non-local formulation

This section is to verify the proposed non-local formulation. The key factor is to reproduce the non-uniform electric field, which is mutually linked with non-local polarization reactions. Then, the external power supply and corresponding macro-cell corrosion are selected for the computational system’s verification.

Here, identification of anodic and cathodic reactions is critical for model verification. Then, sodium poly-acrylate superabsorbent polymer is used as the electrolyte that is equivalent to the pore solution of concrete composites (Elkey and Sellevold 1995; Duffò and Farina 2016). Ca(OH)₂ solution is mixed with the superabsorbent polymer in order to make the transparent material electrolyte with pH = 12 to 13 (Kilic et al. 2016).

As this polymer is transparent in nature, we can identify the anode location at regular time intervals, where the created brownish ferrite hydro-oxide can be seen. As oxygen is limited in the matrix, hydrogen gas is produced. Then, the cathodic reaction’s location is identical owing to the hydrogen bubbles that remain inside the viscous polymer. In case of the micro-corrosion, we can see both bubbles and corrosive substances as shown in Fig. 5. In fact, when the electrode potential is about -0.7 to -0.75 (V, SHE) under highly alkaline solution, the cathodic reaction generates a hydrogen gas as reported later. This does not quantitatively correspond to the environment of concrete, but suits the verification of the proposed model.

4.1 Series of experimental verification

A fictitious mock-up, which is equivalent to a RC slab, was made of 980 × 980 × 90 mm with cast-in round bars as shown in Fig. 6. The rebar spacing is 410 mm for Case-1 and 205 mm for Case-2 and Case-3. In Case-1 and Case-2, upper and lower reinforcing bars are in contact. In Case-3, the upper and lower bars are completely separated by about 4.5 cm (see Fig. 7).

In Case-1 and Case-2, the bars were fixed by using a plastic binding, and the contact area was lapped with epoxy resin. Table 1 shows the composition of the solution used. As stated in previous section, the solution of
the polymer electrolyte is a calcium hydroxide dissolved in tap water at a ratio of 0.16/100 (g/g), and a sodium poly-acrylate superabsorbent polymer was added at an external ratio of 1/100 (g/g) to the calcium hydroxide solution.

After arranging steel bars in a mold, calcium hydroxide solution was poured and the superabsorbent polymer was charged evenly. After swelling and hardening by crosslinking of the superabsorbent polymer and the top surface of the specimen was sealed with a transparent vinyl sheet to prevent drying.

DC power of 25 volts was charged to the diagonal ends as shown in Fig. 8. The cathode electrode is a carbon rod, and the anode one is a platinum-plated titanium, which was replaced every 120 hours. The electrodes of each pole were inserted from the top of the specimen and fixed with no connection with steel bars as shown in Fig. 8.

Full three dimensional analyses were conducted with finite discretization as shown in Fig. 9. The positions of RC elements that include steel bars are indicated in gray. A thin layer in Z direction (thickness) is placed when we have electric insulation between top and bottom layers of steel bars. The constants used in the analyses are lined up in Table 2 (Elkey and Sellevold 1995). In Eq. (17), the standard electrode potential used for cathodic polarization accompanying hydrogen gas was 0.0 (V, SHE) in accordance with the test conditions.

| Water (kg/m³) | Polymer (kg/m³) | Ca(OH)₂ (kg/m³) |
|--------------|----------------|-----------------|
| 1000         | 10.0           | 1.6             |

Table 1 Composition of superabsorbent polymer.
4.2 Estimated anodic reaction

Figure 10 shows the computed ratio of the anodic reaction rate (Section 3.5) at the maximum rate at 24 hours after charge. The blank cells mean the cathodic reaction dominant area where the ratio of the anodic reaction rate is less than 0.5 (= the anodic and cathodic reactions are in balance like micro-cell corrosion).

The plus charge was applied at the extreme left-upper of the diagonal as shown in Fig. 8. The distribution of the anodic reaction is not uniform in each case. In general, the anodic reaction is predominant near the cathode (minus) electrode (right-lower of the diagonal) and the cathodic one as opposite. These distributions are forcibly formed by the applied external charge. In Case-3, the anodic reaction is predominant on the cathode electrode side.

Figure 11 shows the distribution of corrosion rate of logarithmic scale. It should be noted that the color scheme of the bar graph is set up for easy drawing, and the shade of color is used for identifying 3D location. Thus, it does not represent the corrosion rate.

In Case-1 and Case-2, the right-lower edge of the diagonal in the cathodic electrode side corrodes rapidly, and the corrosion area is gradually extended from the cathode electrode side to the anode. The analysis captures the trend of corrosion rate’s profile in comparison with experiments.

In Case-3, severe corrosion is locally generated at the upper right and lower left as well as the right-lower edge. Here, the bars serve as a shortcut of the electric current, resulting in predominant corrosion near the intersection. When electric current passes through a polymer with higher resistance, the intersection of the rebar becomes a current brake, and corrosion gets predominant at both ends where the crossings are the least.

4.3 Corrosion by electrolytic experiment

We can see the steel corrosion (brownish color) of each specimen though the transparent electrolytes as shown in Figs. 12 to 15. The external charge was applied by using three types of electrodes (carbon, titanium, platinum-plated titanium) since the electrodes were eroded as well as the reinforcing bars in each specimen.

After the external charge applied for Case-1, corrosion computationally starts from the cathode electrode side (right-lower edge of the diagonal), develops symmetrically and grows in the direction of cathodic pole (see Fig. 12). In the experiment, the transparent matrix turned black at the top left of the anode electrode position because of the elution of the carbon electrode, but no corrosion of steel was observed as the analysis predicts. The bar placed at the extreme edge of the specimen was first corroded.

After the replacement of the electrode to the titanium one, further growth of rebar corrosion was observed along the intermediate bars as well. This is consistent

| Item                                | Constant |
|-------------------------------------|----------|
| Electrical resistivity of polymer [\(\Omega m\)] ※ | 5.5E-04  |
| Electrical resistivity of rebar [\(\Omega m\)]  | 1.0E-05  |
| External voltage (V)                | -12.5, 12.5 |
| Voltage application position (anode) | (0, 1000, 90) |
| Voltage application position (cathode)| (1000, 0, 90) |

※ measured by the four electrode method

Fig. 10 Typical analysis result of anodic reaction rate.
with the analysis. After 48 hours later, other corrosion locations were visually found at the lower left and the upper right symmetrically. At the same time, a red rust is generated from the rebar placed vertically in the center of the panel, and it seems that the corrosion rate is faster than that in the lower left and the upper right. In addition, the cathodic reaction was confirmed on the anode electrode side of the rebar located horizontally at the bottom and the rebar placed vertically at the right end. After that, there was no new generation of corrosion, and each corrosion was directed to the polarization direction and developed in the same range.

In Case-2, corrosion was identified visually from the cathode electrode position at 24 hours after the charge, and was similar to the analysis, developing from the lower right to the upper left. This fact is consistent with the analysis as shown in Fig. 11. It was observed at 48 hours that corrosion developed symmetrically from the cathode (lower-right) to the anode electrode (upper-left), and it further expanded near the edge. At 70 hours, corrosion reached the lower left and upper right.

Corrosion was not identified along bars located in the upper left of the specimen, and bubbles of hydrogen gas due to the cathodic reaction were observed as well. This is consistent with the analysis. At 96 hours, new corrosion was visually found close to the anode electrode at the leftmost vertical rebar of the specimen.

In Case-3, corrosion is accelerated from the upper rebar on the right side of the specimen as shown in Fig. 14. Corrosion is severe at the end close to the cathode electrode and around the spacer. After a couple of days, corrosion was visually identified at the end of the upper bar on the side of the cathode electrode and also occurred at the end of the three lower reinforcing bars on the cathode electrode side. As with Case-1 and Case-2, corrosion took place at the lower left end of the upper rebar and at the right upper end of lower ones for 72 to 120 hours. Moreover, in the upper rebar farthest from the cathode electrode, corrosion accelerated in the vicinity of the spacer. Finally, no new corrosion was seen, and the corrosion and reduction areas were fixed.
corrosion develops over the 3D extent.

An enlarged view of the corrosion near the spacer and a side view of the corrosion at the upper right end are shown in Fig. 14. Near the plastic spacer, corrosion developed severely on the cathode electrode side from the spacer. It is inferred that local electric circuit is sharply formed in between the upper and the lower layers of reinforcement. In the upper right of the specimen, three points of corrosion were formed discontinuously in the lower rebar.

In any corrosion on the upper right end, corrosion occurred on the cathode electrode side against the upper rebar. Even when the upper and lower bars were separated by 4.5 cm, an electrical path was formed, resulting in the occurrence of local corrosion, too. As a result, the pattern of corrosion varies unlike those of Case-1 and Case-2. It can be said that non-local analysis may capture the corrosion pattern of 3D extent. Figure 15 shows the visually identified corrosion area in red frame and the reduction one in blue. In Case 1, corrosion occurs from the cathode electrode side (lower-right) and grows toward the upper left. Through the region where neither anodic nor cathodic reaction can be identified visually, bubble generation due to cathodic reaction occurs on the anodic side and the end of each bar.

In Case-2 as with Case-1, corrosion develops over time from the side of cathode electrode to the anode. The region where no corrosion takes place but gaseous bubbles are formed as an indication of the cathode reaction can be seen on the anode side. In both Case-1 and Case-2, the forefront of the corrosion area is regarded as
5. Conclusions

(1) The anodic and cathodic reactions that develop on the surface of metals are non-locally formulated over the volume that includes a group of reinforcing bars.

(2) Non-locally formulated polarization is discretized volumetrically by the scheme of finite element method and solved with the conservation of electric charge to predict the rate of corrosion of reinforcement.

(3) The profile of corrosion over the non-uniform electric potential was experimentally obtained by using the transparent sodium poly-acrylate superabsorbent polymer as electrolyte similar to the pore solution of concrete.

(4) The experimental verification was conducted by comparing the analytical results with the corrosion profiles for three kinds of rebar arrangements under external electric power supply.

(5) The solution of non-local modeling of polarization may capture the overall profile of corrosion of reinforcement of 3D geometrical extent.

(6) Not only the global profile of corrosion but also the localized corrosion along the surfaces of the reinforcing bars was sparsely observed nearby the contact points of reinforcing bars. It is thought that this is attributable to the local stray current through the electrolyte caused by the contact resistance of bars.

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