



Simulation of water absorption and desorption behavior for anti-corrosion coatings in existing and new accelerated corrosion tests



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ABSTRACT

A cyclic corrosion test (CCT) that ensures compatibility with acceleration of corrosion and approximation of actual outdoor corrosion is in high demand, and many kinds of CCTs have been developed. We have proposed a new CCT for evaluating corrosion resistance of anti-corrosion coatings. In this work, we measured the water diffusion coefficients of three kinds of anti-corrosion urethane/epoxy coatings at 20–60 °C and calculated their activation energies. In addition, the water absorption/desorption behaviors of the coatings in several CCTs, including our new CCT, were simulated.

It was found that the desorption diffusion coefficients of the coatings are much higher than their absorption diffusion coefficients. It was considered that water molecules might need to push out the mesh of the molecular network to penetrate the coatings during water absorption, but that they might not need to do so during water desorption. Therefore, the dry step in the new CCT might be sufficient even though the time is shorter than in existing CCTs. In addition, the temperature in the dry step in the new CCT is also higher than in the salt fog step and humidity step. Therefore, drying is much faster than wetting. In the new CCT, by minimizing the time in the dry step, the corrosion rate of steel and zinc is accelerated more than in existing CCTs without sacrificing the approximation of the water absorption and desorption behaviors of the coatings.

It was also found that the desorption activation energies, 45 ~ 55 kJ/mol, are lower than the absorption activation energies, 74 ~ 96 kJ/mol. It was considered that water molecules widen the mesh of the polymer network more easily at higher temperatures in water absorption; however, in water desorption, water molecules need not expand the mesh. In addition, the results of the simulation of water absorption and desorption behaviors show that water absorption in three kinds of CCTs is insufficient or excessive and that two kinds of CCTs, including our new one, can reproduce the same level of water absorption and desorption as in the summer outdoor environment.

1. Introduction

The salt water spray test (SST) and cyclic corrosion test (CCT) are widely used as accelerated corrosion tests for evaluating the corrosion resistance of anti-corrosion coatings. Though SST is the most basic accelerated corrosion test, its corrosion behavior does not approximate that in the actual environment. Therefore, the anti-corrosion coatings with good corrosion resistance in the SST do not always express good corrosion resistance in the actual environment in Japan [1–6]. For this reason, in place of the SST, the CCT, in which some steps are repeated (ex. salt fog step, dry step, and humidity step), has been popularized.

The CCTs for coatings are mainly ISO 11997-1, ISO 11997-2, and ISO 20340. ISO 11997-2 and ISO 20340 have a UV irradiation step, while ISO 11997-1 does not. Four types of CCTs are defined in ISO 11997-1, and cycles A and D in ISO 11997-1 are widely used in Japan as

JIS K 5600-7-9 cycle A (CCT-A) and cycle D (CCT-D). These CCTs simulate the corrosion behavior in the actual environment of Japan relatively well, and it has been reported that the superiority/inferiority of the sample in these tests and the real environment are in good agreement. [4–6]. CCT-A is specified in Japanese Automobile Standards JASO M 609-91 and JASO M 610-92. CCT-D is used for anti-corrosion coatings for general use. Other types of CCTs have been proposed in recent years, most of which aim for high approximation of actual environment corrosion.

However, the corrosion acceleration rates in such CCTs are generally low. Anti-corrosion coatings for outdoor infrastructure are tested for over 1000 h by CCT-A/D, but such high-approximation CCTs require a prolonged period of testing time to corrode samples equally to CCT-A/D.

With the upgraded performance of recent anti-corrosion coatings, a

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longer testing time than ever before is required in order to judge the relative merits of their corrosion resistance. Therefore, there is an increasing need for a test method that can be performed in a short time.

Therefore, we are developing a new CCT with the aim of realizing both high approximation of actual environment corrosion and a high corrosion acceleration rate using existing CCT instruments [7,8]. We set the following targets: the approximation of actual environment corrosion should be equal to or better than that of CCT-A/D, and the corrosion acceleration rate should be better than that of SST and CCT-A/D. If the new CCT can achieve these targets, SST users would benefit because high approximation of actual environment corrosion could be obtained without extending testing time, and the CCT-A/D user could shorten testing time without sacrificing test reliability.

In our past study, we proposed three kinds of new CCTs that we developed on the basis of CCT-A [7]. In two of them, the periods of the salt fog step and dry step were shortened and that of the humidity step, which is high-temperature and high-humidity step, were extended relatively to CCT-A. Consequently, they achieved the target in terms of the corrosion behavior of steel and zinc [7].

In the literature, it has been considered that a low wet ratio in CCT, defined as the sum of the times for the salt fog and humidity steps divided by total testing time, is important for the approximation of actual environment corrosion. Thus, CCTs in which the wet time ratio is 50% or less have been recommended up to the present [1–5]. However, the authors consider that continuous wetting time, not the wet ratio, is of major importance for achieving corrosion approximation. This is because absorbed water in the coatings takes some time to reach the coating/substrate interface. Consequently, the water quantities at the interface are much different between dry and wet steps, which are repeated at short intervals and long intervals even if the wet ratios of the CCTs are the same value. According to the research in the CCT literature, the authors consider that four hours or less is appropriate as the continuous wetting time in CCT [7].

From these considerations, we decided to maximize the wet ratio and set the continuous wetting time was four hours or less. As expected, the new CCTs achieved a higher corrosion rate than CCT-A by minimizing the drying time after corrosion had stopped.

On the other hand, it has been reported that continuous wetting time of 20–50 h is dominant in the total wet time in the actual outdoor environment in Japan [9]. Then, the appropriate continuous wetting time in the CCT (four h or less) is much different from the continuous wetting time in the actual environment. Furthermore, the existing CCTs were developed empirically based on experiments. A complete consistency in water absorption/desorption behaviors between CCTs and outdoor environments has not been satisfactorily studied.

In another paper [8], we focused on the fact that the temperature in CCT is higher than that in the actual environment. It is known that the diffusion of water in polymer materials has temperature dependence [10,11]. The activation energies of water diffusion in the coatings has also been reported [12,13]. The temperature dependence of water absorption behavior could explain the difference in the continuous wetting times between CCT and the actual environment. Then, we measured the diffusion coefficient of three kinds of coatings in water absorption and calculated their activation energies [8]. The results clarified that water absorption in four hours or less at the CCT temperature (35–50 °C) is equivalent to water absorption in several hours or tens of hours at 25 °C, which is the average temperature in wet situations in summer [8]. We showed that one of the new CCTs could approximate water absorption behavior of anti-corrosion coatings in the actual outdoor environment. However, water desorption behavior was not considered in the paper. Therefore, we need to establish whether such a short dry step is sufficient to dry coating samples, because the new CCT is characterized by a shorter dry step than that in existing major CCTs.

Electrochemical impedance methods have been used by many researchers to estimate water absorption in organic coating films

[14–26]. These methods are capable of determining the water content of the coating film without peeling the coating film from the substrate, but it is not possible to ascertain the water content distribution in the depth direction in the coating film. We consider that the supply of water and oxygen to the coating/substrate interface is of great importance in underfilm corrosion. Oxygen is abundant but moisture is poor in the dry coating film. Therefore, it is necessary to clarify the variation of the moisture content distribution in the depth direction in the coating film and to ascertain the moisture content at the coating/substrate interface. In this study, we obtained the water diffusion coefficient and activation energy of the coating film in CCT using the gravimetric method, and we determine the water absorption/drying behavior at the coating/substrate interface using the difference method.

In this study, we focused not only on water absorption but also on water desorption of coatings. The absorption and desorption behavior approximation of the coatings between the actual outdoor environment and CCTs is crucially important for confirming the validity of our new CCT for the evaluation of anti-corrosion coatings. We measured the water diffusion coefficients of three kinds of anti-corrosion urethane/epoxy coatings at 20–60 °C and calculated their activation energies. In addition, the water absorption and desorption behaviors of the coatings in several CCTs, including our new CCT, were simulated.

2. Theory

2.1. Water absorption

Percent water content $Mt(\%)$ at a given time t can be determined by

$$M_t(\%) = 100 \times (m_t - m_0)/m_0 \quad (1)$$

where m_0 and m_t are the initial dry weight and the weight of the sample at time t , respectively. Saturated water content M_∞ can be found by measuring Mt as t approaches infinity. As t approaches infinity the mass of the sample will asymptotically approach a stable value, M_∞ .

If the absorption behavior is expressed by the Fickian equation of diffusion, the water uptake and diffusion process is described by the following equation at the early absorption stage [27]:

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{l^2} \right)^{1/2} \quad (2)$$

where D is the diffusion coefficient and l is the thickness of the sample. A plot of Mt/M_∞ as a function of $t^{1/2}/l$ can be created, and the initial slope of the graph calculated. By rearranging Eq. (2), the initial slope of the plot, I , can be related to D as follows:

$$D = I^2 (\pi/16) \quad (3)$$

A weighted least squares fit was used to determine the value of I , with the weighting factor equal to $1/\sigma^2$, where σ^2 is the variance of the measured values for each point.

As Eq. (2) is only valid during the early stages of absorption, the criterion $Mt/M_\infty < 0.6$ was chosen to expressly define the “early stages”. Some authors have chosen different values in their analyses of various materials [27–31]. However, as there is no commonly accepted value, it is necessary to determine one that fits the particular experiment. The chosen criterion falls within the range of values used by other authors, and it describes the measured behavior well since the absorption curve of Mt/M_∞ vs. $t^{1/2}/l$ is reasonably linear within the $Mt/M_\infty < 0.6$ range for all measured samples.

2.2. Activation energies of water Absorption/Desorption

The temperature dependence of the diffusion coefficient is indicated by the following Arrhenius equation:

$$D = D_0 \exp\left(-\frac{A_D}{RT}\right) \quad (4)$$

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