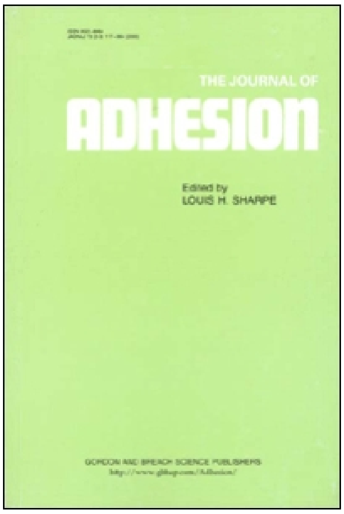

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Tihn Nguyen[a]; Changjian Lin[a]
[a] National Institute of Standards and Technology Gaithersburg, Maryland, U.S.A.

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# *In-Situ* Measurement of Chloride Ion at the Coating/Metal Interface†

TINH NGUYEN and CHANGJIAN LIN

*National Institute of Standards and Technology Gaithersburg, Maryland 20899, U.S.A.*

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One of the main reasons for the lack of a complete understanding of corrosion and adhesion failures of a coated metal is the lack of analytical instrumentation to probe the behaviors of corrosive agents at the coating/metal interface. We have developed a procedure based on microelectrodes for studying *in situ* the behavior of chloride ions at a coating/metal interface. The procedure requires an attachment of a double-barreled $Cl^-$ ion-selective microelectrode at the coating/metal interface, thus allowing direct measurements of $Cl^-$ concentration changes at localized areas under a coating. The procedure provided very useful information for mechanistic studies of corrosion under coatings, as well as for transport studies of $Cl^-$ ions through a coating. The procedure should also be useful for studying the roles of $Cl^-$ in localized corrosion.

KEY WORDS Mechanism of corrosion; ion selective microelectrodes; analytical instrumentation; blister formation; steel; surfaces.

## INTRODUCTION

Organic coatings are widely used to prolong the service life of a metal substrate. One important function of a protective coating is to act as a barrier between the environment and the substrate. Although the technology of protective coatings has progressed greatly in recent years, problems continue to exist in providing protection to metals from exposure to the environment. One of the key barriers to the effective selection, use, and maintenance of protective coatings for metals is the lack of measurement methods to characterize coatings and coating systems before and during service. Examination of the unsolved fifty questions raised by leading coatings researchers[1] reveals that more than half of the questions relate to measurement and characterization. For example, inadequate understanding of the role of such corrosive factors as oxygen, water, and ions in failures of a coated metal system is due, in part, to the inability to characterize the microstructure of the coating and to quantify these elements in the coating system and at the

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coating/metal interface. Without this information, reliable degradation and transport models cannot be developed.

Chloride is one of the most detrimental of the ions contributing to the corrosion of steel. Most of the present knowledge on the movement of the chloride ion in a coated metal system is derived from studies of the movement of this ion through a detached film. However, barrier properties of a detached film may not be the same as those of an attached film; thus, the controlling steps and the reaction processes may not be correctly interpreted. Surface analytical techniques can provide chemical information at the atomic level but the techniques must be used in a high vacuum environment. Therefore, they are not suitable for *in situ* measurements. Thus, there is a need to develop a method to monitor, *in situ*, the arrival of the chloride ion at the coating/metal interface and its concentration change with time. Such a method will aid greatly in understanding the roles of chloride ions in the corrosion of metals under coatings and the degradation of coated metals. Such information is lacking at present. This paper describes a method for measuring *in situ* chloride ion concentration and its behavior at the coating/steel interface during environmental exposure.

## EXPERIMENTAL PROCEDURES

### Materials and specimen preparation

All coated panels used in this experiment consist of a $TiO_2$-pigmented, alkyd top coat applied on SAE 1010, low-carbon, cold-rolled steel panels. The 100 × 150 mm substrates, which had a surface roughness of 0.9 to 1.3 $\mu$m and had been vapor-degreased at the factory, were cleaned further by rinsing repeatedly and alternately with acetone and methanol (reagent grades) to remove any dirt deposits and contaminants prior to coating application. The coatings were applied on the substrate using a draw down blade. The coated panels were cured at ambient conditions for at least five days before use. The coating thicknesses of the panels were in the 90–100 $\mu$m range (measured by an eddy current thickness gauge). Sodium chloride (reagent grade) standard solutions at various concentrations, as expressed in mole/liter (M), in triply-distilled water were prepared for calibration purposes. For immersion exposure, 0.5 M NaCl in deionized water was used.

Two types of specimen configuration, shown in Figures 1a and 1b, were used for *in situ* measurements of $Cl^-$ ion at the coating/steel interface. The first type (Type I), was made by mounting a 25 mm-diameter cylinder on the coated panel using a silicone adhesive. A continuous scribe mark (to the metal substrate), which serves as an artificial defect, was made on the panel section around the inside of the cylinder. A second cylinder, twice the diameter of the first, was mounted on the coated panel to enclose the first cylinder. A 0.5 M NaCl solution was added to fill the first cylinder and deionized water was placed in the space between the two cylinders. Blisters were observed to form on the coated panel

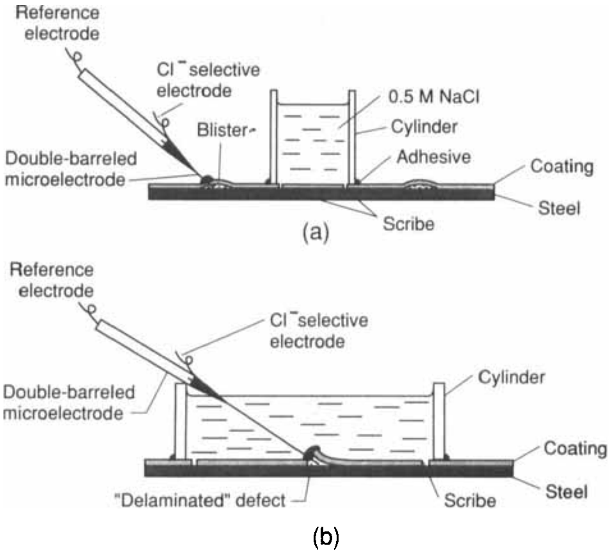

FIGURE 1 Two types of specimen configuration for *in situ* measurements of chloride ion at the coating/metal interface: a) Type I and b) Type II.

section around the outside of the NaCl-containing cylinder during immersion. The formation and growth of the blisters were difficult to observe because the coating was constrained by the two attached cylinders. However, with the help of a blunt toothpick, the location and the size of the blisters could be estimated. These blisters are commonly known as cathodic blisters and formed due to the presence of the highly-water soluble products produced by the cathodic reactions, which were induced by the anodic reactions at the scribe. They are reproducible and have been observed by other workers.[2,3] After a blister of measurable size had formed, the water in the space between the two cylinders was removed. The excess water was wiped up and the blister was punched with a sharp needle. The double-barreled microelectrode (described in the next section) was then inserted into the blister at the punched hole. Care was taken that the electrode tip just touched the substrate surface without damaging it. A fast-curing silicone adhesive was used to seal around the hole.

The second specimen configuration (Type II), shown in Figure 1b, was prepared by scribing and lifting up three sides of a 5 × 5 mm coating area. (The coated area was softened by immersing in water, using a rubber gasket, for a few hours before scribing.) After mounting the cylinder on the coated panel, the double-barreled microelectrode was inserted into the "artificially delaminated" defect, and the loose coating was pressed down and sealed with a silicone adhesive.

### Preparation of double-barreled chloride ion-selective microelectrodes

*In situ* measurements of $Cl^-$ ion concentration at the coating/metal interface were carried out using a double-barreled microelectrode. While the construction of the double-barreled $Cl^-$ ion-selective microelectrodes is difficult, they offer many advantages for use in the coating/metal interfacial studies over a single-barreled $Cl^-$ ion-selective microelectrode in conjunction with a reference microelectrode. The main advantage is the relative ease of inserting or attaching one, rather than two, electrodes to the specimen. Another advantage is that the double-barreled microelectrodes allow direct readings of $Cl^-$ ion concentration at almost the same point of the sample, thus reducing the effects of the environment between the two electrodes.

The double-barreled $Cl^-$ ion microelectrode consists of two separate compartments in one glass body. One of the compartments contains a chloride sensing element and the other has an internal standard solution. When the sensing element is in contact with a solution containing $Cl^-$ ions, an electrode potential develops across the sensing element. This potential, which depends on the level of free $Cl^-$ ion in the solution, is measured against a constant reference potential with a pH/mV or ion-selective meter. The measured potential corresponding to the level of $Cl^-$ ion in solution is described by the Nernst equation:[4]

$$E = E_0 + S \log a$$

where

$E$ = measured electrode potential

$E_0$ = reference potential

$S = RT/nF$, where $R$ is the gas constant, $T$ is the absolute temperature, $n$ is the number of equivalents per mole, and $F$ is the Faraday's constant.

$a$ = activity of free $Cl^-$ ion in solution. The $Cl^-$ ion activity is related to free $Cl^-$ ion concentration $C$ by the activity coefficient, $f$:

$$a = fC$$

Double-barreled $Cl^-$ ion-selective microelectrodes were constructed from double-barreled capillaries. These microelectrodes, which are illustrated in Figure 2, contain two compartments: one serves as the reference electrode; the other serves as the $Cl^-$ ion-selective electrode. The double-barreled $Cl^-$ ion-selective microelectrodes were made following many careful steps. The first step was the pulling (using a puller under heat) of a heavy-wall, double-barreled, 1.5/0.8 mm (o.d./i.d.) borosilicate glass capillary into a pointed-shape micropipette; one of the two barrels was truncated at the tip. In this way, the sensing parts at the tips of the two compartments could be electrically separated more easily. The longer of the two barrels, which had a 10 $\mu$m tip, was used as the reference electrode, and the shorter as the $Cl^-$ ion-selective electrode. The compartment that serves the reference microelectrode was filled with KCl-saturated agar gel, prepared by mixing 3 g of agar in 100 mL of boiling 0.01 M KCl solution. The agar gel prevented leakage of the KCl filling solution into the sample environment and also prevented possible contamination of the electrode from the sample solution.

The two barrels of the double-barreled micropipette were cut to the desired lengths, about 40 mm for the longer barrel and 32 mm for the shorter barrel. An

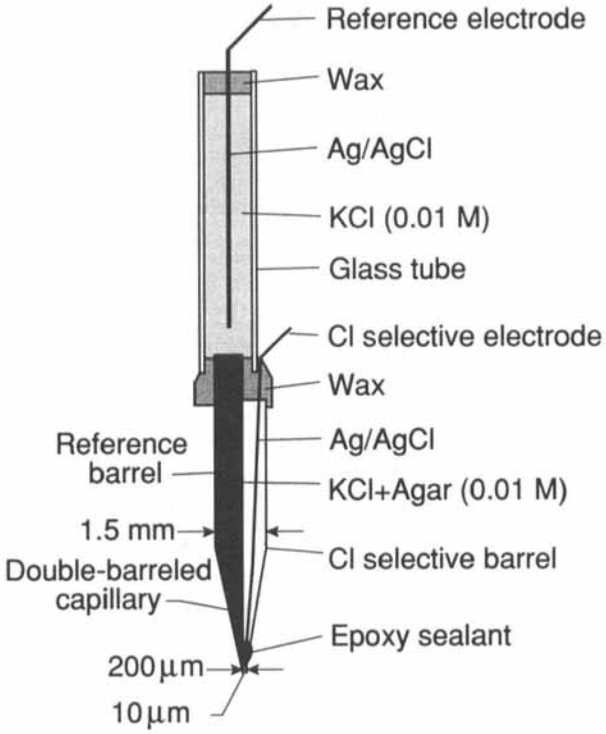

FIGURE 2 A schematic drawing of an Ag/AgCl double-barreled chloride ion-selective microelectrode (not drawn to scale).

Ag/AgCl wire (made by electrodeposition of AgCl on Ag wire), 100 $\mu$m in diameter, was inserted into the shorter barrel (the $Cl^-$ ion-selective electrode) and secured with an epoxy adhesive. In addition to securing the wire, the adhesive also serves as a seal to prevent possible contamination of the Ag/AgCl wire by the sample environment. Care was taken to ensure that the Ag/AgCl wire did not touch the tip and wall of the longer barrel (the reference electrode compartment). The tip of the double-barreled microelectrode was approximately 200 $\mu$m (Figure 2).

The gel-filled, reference electrode compartment was inserted into a Pyrex glass tube (i.d. 3 mm) and sealed with molten wax at the joint. The glass tube was then filled with 0.01 M KCl as an internal reference solution. KCl was used because of the similar mobilities of $K^+$ and $Cl^-$ ions, thus eliminating the possible interference of the diffusion potential, developed due to difference in the diffusion rates of two ions.[5] On the other hand, a low concentration of the internal reference solution was used to minimize its possible effect on the measured $Cl^-$ ion concentration of the samples. Care was taken to ensure that there were no air bubbles in the glass tube. Finally, an Ag/AgCl electrode of 250 $\mu$m diameter was placed in the glass tube and sealed with wax to prevent the evaporation of the KCl filling solution. Because Ag/AgCl electrodes are sensitive to light, care was taken to minimize exposing the electrodes to light during the preparation and measurements. Wax was also used to seal the top of the $Cl^-$ ion-selective electrode compartment.

### In situ measurement of chloride ion at the coating/metal interface

*In situ* measurements of $Cl^-$ ion concentration in Type I and Type II specimens were carried out following the arrangement shown in Figure 3. For a Type I specimen (Figure 1a), the insertion of the microelectrode and the actual measurements started only after the blisters had grown to a measurable size, about 1 mm in diameter. The reference and $Cl^-$ ion-selective electrodes of the double-barreled microelectrode were connected to the reference and $Cl^-$ ion-sensing inputs, respectively, of a high-impedance ($10^{14}$ ohm) Orion EA 940* ion analyzer and measurements were begun. It should be noted that water was not replaced in the volume between the cylinders during the measurement for this type of specimen. For a Type II specimen (Figure 1b), the measurements started as soon as 0.5 M NaCl solution was placed into the cylinder using the same

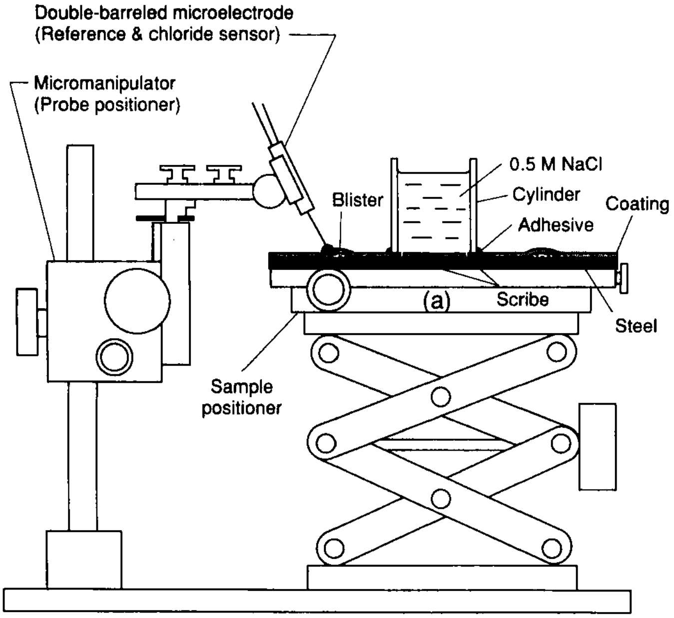

FIGURE 3 Experimental set-up for *in situ* measurements of chloride ion at the coating/metal interface.

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* Certain commercial equipment is identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily the best available for the purpose.

experimental set-up depicted in Figure 3. The analyzer was programmed to print $Cl^-$ ion concentrations at desired time intervals; that is, 10 minutes at the beginning of exposure and one hour at later exposures. It is to be noted here that the ion-selective electrode responds to activity, not to concentration. The activity is related to the concentration by the activity coefficient as indicated earlier. However, because the measurement system was calibrated in terms of concentration, we report our results in terms of concentration.

## RESULTS AND DISCUSSION

### Calibration

The double-barreled $Cl^-$ ion-selective microelectrodes were calibrated using standard solutions to ensure that they were in proper working condition before use. Figure 4 compares the potential-concentration calibration curves obtained by two double-barreled $Cl^-$ ion-selective microelectrodes fabricated at two different times (Curves 2 and 3) with that obtained by a conventional $Cl^-$ ion-selective macroelectrode (Curve 1), using 10 mL samples of 1 to 0.00015 M NaCl standard solutions; the concentration is expressed in the logarithmic form. The parallelism of Curves 2 and 3 indicates the good reproducibility of the construction of the double-barreled $Cl^-$ ion microelectrodes. On the other hand, the parallelism of Curves 1 and 2 indicates that the double-barreled $Cl^-$ ion-selective microelectrodes and the conventional $Cl^-$ ion selective macroelectrode are equivalent in

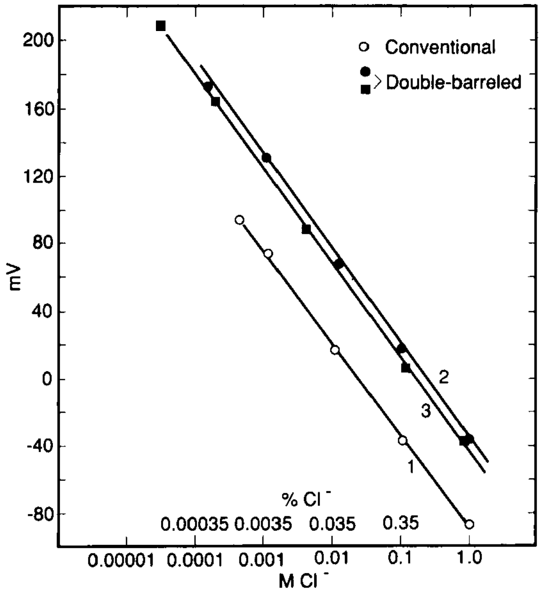

FIGURE 4 Calibration curves of the two chloride ion measurement methods. Curve 1: conventional; curves 2 and 3: double-barreled microelectrodes.

providing Cl$^-$ ion concentration (a 45 mV offset was applied to separate Curves 1 and 3). None of the curves show evidence of a deviation from the Nernstian law in the concentration range studied. Previous work[6] also showed a straight line relationship between the potential and the logarithm of concentration of a Ag/AgCl electrode in KCl solutions between 5 and 0.001 M concentration.

### In situ measurement of chloride ion at the coating/metal interface

Figure 5 presents the Cl$^-$ ion concentration as a function of exposure time for a Type I specimen configuration using a double-barreled Cl$^-$ ion-selective microelectrode. As mentioned earlier, the insertion of an electrode into this type of specimen was only possible after the specimen section between the two cylinders had been immersed in water for an extended period of time to cause formation of a sizable blister; the first measurement was made after 12 days of immersion as indicated in Figure 5. The Cl$^-$ ion concentration in the blister increased rapidly after inserting the electrode, reaching a value four times that of the bulk solution after three days of immersion and remained almost constant for the next four days. It is noted here that the blister in which the measurements were made was formed on the coated panel section immersed in water external to the NaCl-containing cylinder, and that there was no liquid medium in contact with the outside of the blister during the measurement. Thus, the Cl$^-$ ions measured were the result of their migration laterally along the coating/metal interface extending from the scribe inside the NaCl-containing cylinder to the blister area.

At the start of the measurement, the Cl$^-$ ion concentration in the blister was almost equal to that of the bulk solution. This indicates that the coating/metal

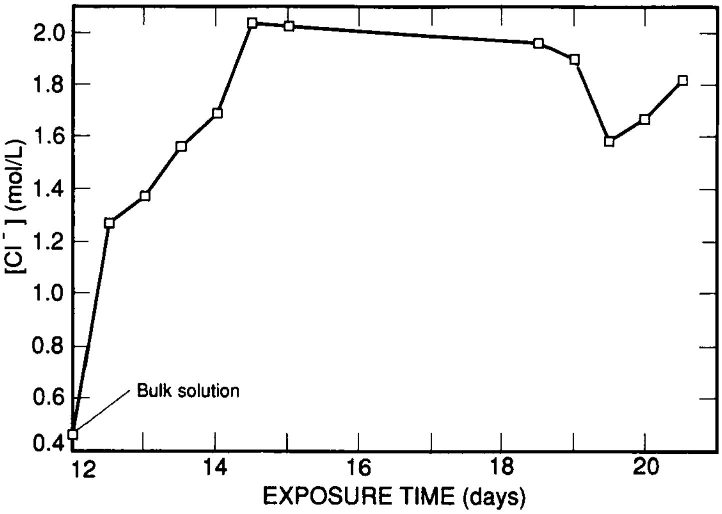

FIGURE 5 Chloride ion concentration as a function of time obtained by using double-barreled chloride ion-selective microelectrode for Type I specimen immersed in a 0.5 M NaCl solution.

interfacial region extending from the blister to the scribe has been delaminated and/or that the water layer in this region was sufficient to allow $Cl^-$ ions to pass through. This may be understandable in terms of the mechanisms of adhesion loss and the cathodic delamination processes of a defective coated panel exposed to an electrolyte.[2,7] The loss of adhesion as the result of water build-up at the coating/metal interface before blistering begins facilitates lateral movement of ion between the anodic and cathodic areas.[3] A breakthrough between the hollow cone of the anodic corrosion products near the scribe and cathodic blisters was also proposed as a mechanism to account for the higher $Cl^-$ ion concentration in the blisters than in the bulk.[8]

The rapid rise of $Cl^-$ ion concentration at the beginning of the measurement may be attributed to the increase of the corrosion activity resulting from the resupplying of oxygen into the blister during the insertion of the microelectrode. The reason for the leveling off is not certain at this time. One of the possibilities may be a cessation of corrosion reactions due to the depletion of $O_2$ in the blister. The low $O_2$ concentration in aqueous solutions containing greater than 3 percent (0.52 M) NaCl has been associated with the decrease of corrosion of iron immersed in these solutions.[9] A decrease between the 19th and 20th day of exposure may be a result of complexing or association of $Cl^-$ ions with corrosion products. The ion-selective electrodes respond only to free $Cl^-$ ion. If $Cl^-$ ions in an electrolyte are not free, that is, if they are somehow associated or bound, the ions will not be measured by the ion-selective electrode method.

It is interesting to observe that the $Cl^-$ ion concentration in the blister was five times higher than that in the bulk after 15 days exposure. Previous workers,[8] by drawing the liquid from a blister with a syringe and then analyzing it potentiometrically, also reported a three to four times higher $Cl^-$ ion concentration at the coating/steel interface than in the bulk. Similarly, $Cl^-$ ion concentration of the liquid inside a blister in which the steel substrate was severely corroded, was found to be 10 times higher than that in the bulk solution after six months of immersion in NaCl solution.[10] In contrast, the $Cl^-$ concentration inside a corrosion-free blister was only two times higher than that of the bulk solution after the same immersion period. Heavy deposits of $Cl^-$ on the corrosion products at the scribe mark of a scribed coated panel immersed in a NaCl solution were also observed.[11] The preferentially higher concentration of $Cl^-$ ions in the blisters in which corrosion occurs or at the scribe mark on the coated panels was similar to that observed in crevice and pitting corrosion. For example, the fluid within crevices exposed to neutral NaCl was reported to be 3 to 10 times greater in $Cl^-$ ion concentration than in the bulk solution.[12] The acidic environment created by the anodic reactions at the corroded sites in the blister was probably responsible for the high concentration of $Cl^-$ ion in the blister. At anodic sites, iron is dissolved and subsequently hydrolysed to form iron hydroxides and $H^+$ ions. The depletion of oxygen at the corroded areas, because of the barrier property of corrosion products, also enhances the positive properties of this region. Chloride ions are needed to counterbalance the positive charge of the $H^+$ ions.

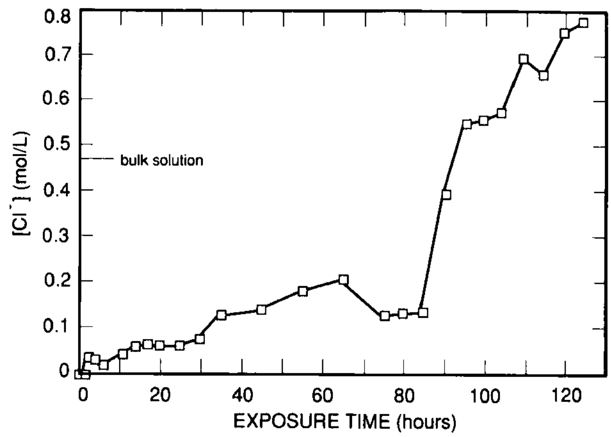

FIGURE 6 Chloride ion concentration as a function of time, obtained by using double-barreled chloride ion-selective microelectrode for Type II specimen immersed in a 0.5 M NaCl solution.

Figure 6 is the curve representing $Cl^-$ ion concentration change as a function of exposure time in the "artificially delaminated" defect of Type II specimen immersed in a 0.5 M NaCl solution. The measurement started immediately after the solution was added to the cylinder. It should be noted that there was a scribe through the coating to the steel substrate about 25 mm from the microelectrode. We started to detect the presence of $Cl^-$ ions at the artificially delaminated defect about three hours after immersion and the $Cl^-$ ion concentration rose almost steadily up to 65 hours. The possibility of an effect due to leakage of $Cl^-$ ion from the reference internal solution on the measured $Cl^-$ ion concentration was minimal because of the small tip of the reference electrode (10 $\mu$m) and the low concentration of the internal standard solution (0.01 M). Except for a possible decrease between 75 and 85 hours, the concentration of $Cl^-$ ions in the defect continued to rise. The concentration increased more sharply after 85 hours and reached almost twice the concentration of the bulk solution after 120 hours of exposure.

Assuming the delamination was 1 mm deep and using the $Cl^-$ ion concentration value given in Figure 6, it was estimated that $1.8 \times 10^{-4}$ g of $Cl^-$ ions had entered the 5 × 5 mm artificially delaminated area after 65 hours of exposure. Using Fick's first law of diffusion and assuming that the rate of diffusion of $Cl^-$ ions through the coating was constant and that no $Cl^-$ ion entered the defect through the scribe mark, we obtained a diffusion coefficient of $4.0 \times 10^{-10}\,cm^2\,s^{-1}$. This is somewhat higher than the "migration" coefficient values of $0.83 \times 10^{-11}$ and $0.4 \times 10^{-10}\,cm^2\,s^{-1}$ reported for unscribed and scribed, respectively, alkyd top coat panels immersed in 0.5 M NaCl solution without an applied potential.[13] It is not known how the silicone adhesive and the sealed areas around the defect affected the calculated value reported here.

One of the reasons for the rapid rise after 85 hours of exposure may be a breakthrough delamination between the scribe and the artificially delaminated defect allowing "flooding" of the delaminated area with NaCl from the bulk solution. A similar phenomenon has been reported to account for the difference in the migration coefficients of $Cl^-$ ions of unscribed and scribed coated panels immersed in $Cl^-$ ion containing solutions.[13] Another possible reason may be an increase in the corrosion activity in the delaminated area, which would cause an increase in $Cl^-$ ion concentration as discussed earlier. Judging from the rapid rise after the 85th hour and the continuation of the increase, it is suggested that both events probably occurred with flooding preceding the accelerated corrosion. The latter event was probably induced by the former because of the accelerating effect of $Cl^-$ ions on the corrosion of iron. Chloride ions can accelerate the corrosion of iron through one or a number of mechanisms: by adsorbing and penetrating the oxide layer, by complexing with the metal and by catalyzing the corrosion reactions.[14]

One of the main concerns in measuring $Cl^-$ ions using the microelectrode method is the stability of the electrode. For that reason, it is always recommended that the electrodes be reconditioned before use. Our experiences indicate that the microelectrodes produced and used in this study were very stable in the pure solutions. However, their long term stability in solutions containing complex corrosion products during the *in situ* measurements is not known. Our limited data indicate that these microelectrodes are still stable after one week of testing in a corrosion-products solution. Another concern is the relatively large tip, $\sim 200\,\mu m$, of the solid state, double-barreled microelectrode used in this study. This tip may reduce the optimal spatial proximity provided by the double-barreled method. We have made and tested the double-barreled microelectrodes having tips of about $10\,\mu m$ using a liquid ion exchanger in place of the Ag/AgCl wire at the tip. However, their stability was poor (about three days) and not suitable for *in situ* measurements. The current limitation of the tip size of the double-barreled microelectrode using the Ag/AgCl sensing element is the size of the Ag/AgCl electrode. Thus, we see no reason why a smaller tip double-barreled microelectrode using an Ag/AgCl electrode could not be made if smaller size Ag wire were available.

## CONCLUSIONS

Despite considerable research on the corrosion and failure of coated metals in the last decade, much is still unknown. One of the main reasons for that is the lack of analytical instrumentation to probe the behavior of corrosive agents at the coating/steel interface. We have developed a procedure using a microelectrode for studying *in situ* the behaviors of chloride ions at the coating/metal interface. This procedure will aid greatly in understanding the mechanisms of corrosion of steel under a coating, the blister formation of a coating system, and the corrosion of steel in reinforced concrete exposed to salt water. The major drawbacks of the method are the difficult procedures required for the preparation of the microelectrodes and microelectrode-imbedded specimens. The former is intricate and time-consuming while the latter is delicate. There should be as little disturbance as possible to the blisters and coating/metal interface while probing them. At the same time, the sensitivity and integrity of the microelectrode must be maintained.

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