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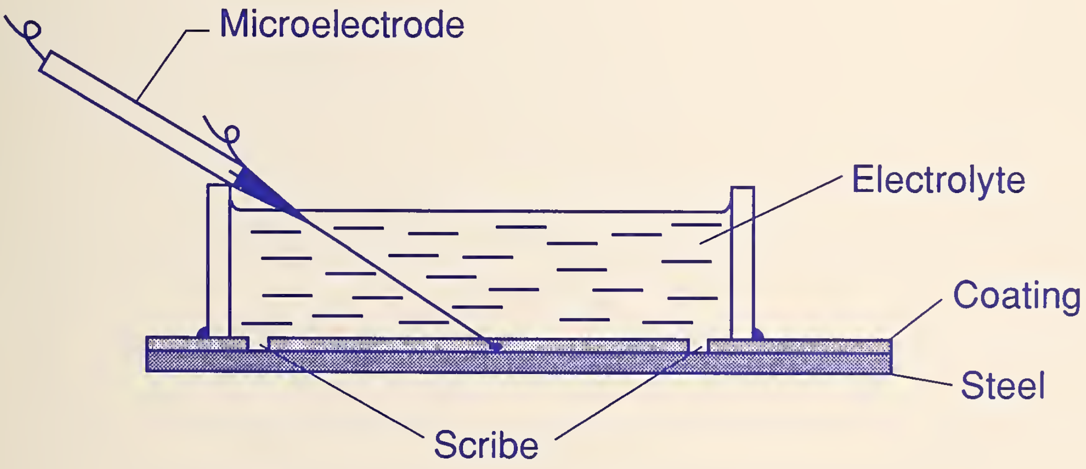
NIST Technical Note 1266

Development of a Method to Measure In Situ Chloride at the Coating/Metal Interface

Tinh Nguyen and Changjian Lin



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July 1989

NOTE: As of 23 August 1988, the National Bureau of Standards (NBS) became the National Institute of Standards and Technology (NIST) when President Reagan signed into law the Omnibus Trade and Competitiveness Act.

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Contents

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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/steel interface. We have developed a procedure based on microelectrodes for studying in situ the behaviors of potential and chloride ions in blister and at a coating/metal interface. The procedure requires an attachment of a double-barreled Cl^- selective microelectrode at the coating/metal interface, thus allowing direct measurements of Cl^- concentration and corrosion potential changes at localized areas under a coating. Although it is intricate to prepare these microelectrodes, 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 on metal. The procedure should also be very useful for studying the roles of Cl^- in localized corrosion. The utility of an inverted electrode microsampling method for studies of Cl^- in very small volumes such as blisters was also demonstrated.

Key words: blister; chloride; coating; coating/metal interface; corrosion; in-situ; microelectrode; microsampling; potential.

1. 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. A close examination of 50 questions raised by leading coating 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 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 bare steel, organic-coated steel, and steel in reinforced concrete. 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. A method needs to be developed to monitor, in situ, the appearance of the chloride ion at the coating/metal interface and the way its concentration changes with time.

This paper describes a procedure to measure in situ a) the presence, as well as the change in concentration, of the chloride ion at the coating/steel interface, and b) the concentration of Cl^- ion in a blister formed at the coating/steel interface during environmental exposure. In addition, the application of a microelectrode method using μL sample size to measure Cl^- ion concentration in blister solutions will be demonstrated. The latter method will be useful for determining the concentration of Cl^- ion in an area in which the liquid volume is small.

2. Experimental Procedures

2.1 Materials and Preparation of Coated Panels

Unless otherwise stated, 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 substrates. The 100 × 150 mm substrates had a surface roughness of 0.9 to 1.3 μm and had been vapor-degreased at the factory. These substrates were cleaned further by rinsing repeatedly and alternately with acetone and methanol (reagent grades) to remove any dirt deposits and contaminants just prior to coating application. Except for one case where the coating was applied by a brush, all coatings were applied on the substrate using a draw down blade. The coated panels were then cured at ambient conditions for at least five days before use. The coating thicknesses of the panels were in the 50–100 μm range. 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 exposure environments, 0.5 M NaCl in deionized water was used.

2.2 Preparation of Chloride-Containing Specimens

Two types of specimen configuration were used in obtaining in situ measurements of Cl^- ion at the coating/steel interface; these configurations are shown in figures 1a and 1b. The first type (type I), shown in figure 1a, is labeled the "cathodic blistering configuration" because the blisters at the coating/steel interface are generally known to result from cathodic reactions induced by the anodic reactions at the exposed metal surface [2]. A cylinder, 25 mm in diameter, 15 mm in height, and 2 mm in thickness, was mounted on the coated panel using a silicone adhesive. A continuous scribe was made on the panel section around the inside of the cylinder. A second cylinder 10 mm in height and twice the diameter of the first one 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 section around the outside of the NaCl-containing cylinder.

The second specimen configuration (type II) prepared for Cl^- ion in situ measurements was an "artificially delaminated defect configuration." A schematic example of this configuration is shown in figure 1b. A small area of about 5 mm in diameter on a coated panel was soaked with distilled water (using a rubber gasket) for a few hours to soften the coating. The thickness of the coating was about 95 μm. A chisel was used to scribe three sides of a square area adjacent to the soft spot and then a 5 × 5 mm section of the coating was lifted as depicted in figure 1b. After the cylinder was mounted on the coated panel, the microelectrode was inserted into the artificially delaminated defect and the loose coating was pressed down and sealed with a silicone adhesive. The cylinder was filled with 0.5 M NaCl prior to making in situ measurements.

In addition to the in situ measurements of Cl^- ion at the coating/steel interface, measurements (in situ) of the corrosion potential at the coating/metal interface were also made. For this purpose, a microelectrode-imbedded specimen, as depicted in figure 1c (type III specimen), was employed. The tip of the microelectrode was coated first with a water soluble adhesive to prevent direct contact between the Cl^- ion sensing element and the coating. The microelectrode was placed on a cleaned, bare steel panel at 30° angle from the horizontal plane in such a way that the tip just touched the substrate. The latter was accomplished by the use of a stereo microscope and a micromanipulator similar to that shown in figure 5. The coating then was applied by brush and cured for 5 days before exposure to 0.5 M NaCl solution. The adhesive was dissolved by the electrolyte present during measurement enabling the electrode to be in direct contact with the liquid layer between the electrode and the coating. It was determined that this test configuration would provide more stable readings than would be obtained if the coating was placed in direct contact with the electrode. In addition, blisters that normally occur as a result of exposure for extended periods in NaCl solution were prepared to demonstrate the use of the inverted electrode microsampling method, to be described later.

2.3 Preparation of Microelectrodes

Two types of microelectrodes were prepared for use in this study. The first was the single-barreled reference electrode to be used in the inverted electrode microsampling method for Cl^- ion measurements and for making measurements of corrosion potentials at the coating/metal interface. The second was the double-barreled Cl^- ion selective microelectrode, used for Cl^- ion in situ measurements.

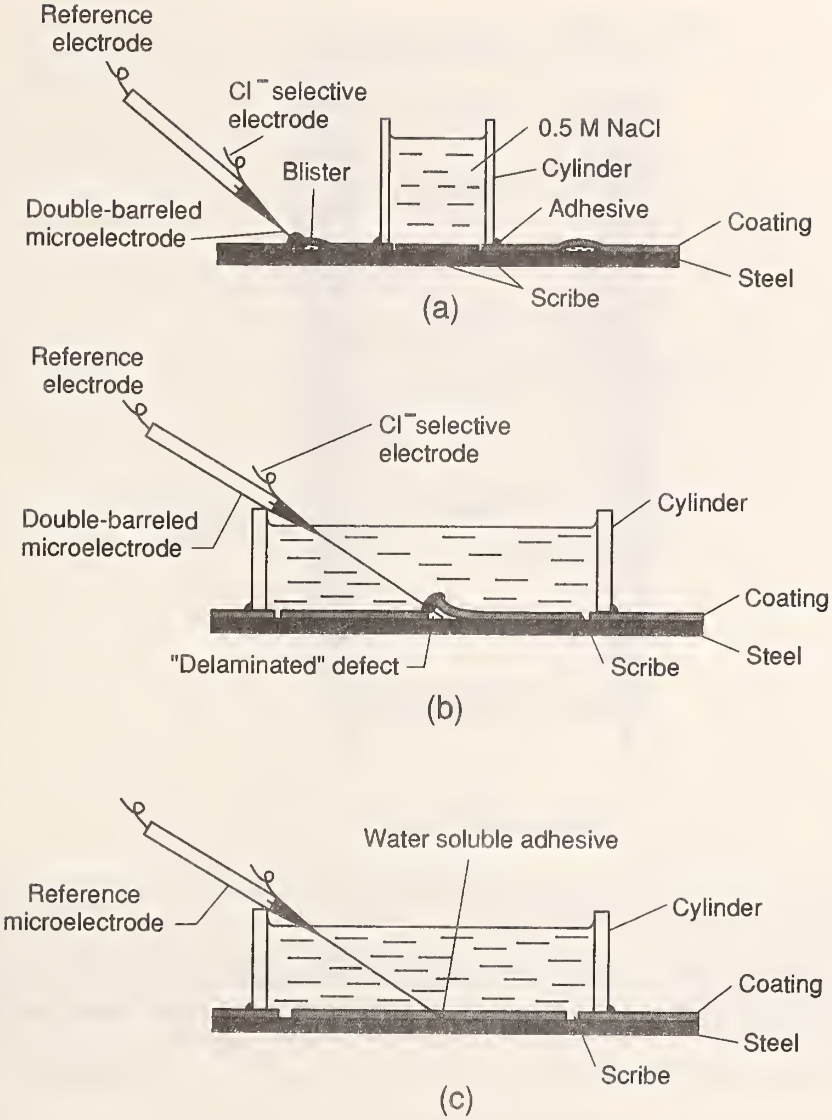

Figure 1. Three types of specimen configurations for in situ measurements of chloride ion and corrosion potential at the coating/metal interface: a) and b) type I and type II for Cl^- ion measurement; c) type III for potential measurement.

2.3.1 Reference Microelectrodes

Reference microelectrodes, shown in figure 2, were made following several careful steps. The first step was the pulling (using a puller under heat) of the heavy-wall (1.0 mm o.d. by 0.58 mm i.d.), single-barreled, borosilicate glass capillary into a micropipette having the shape shown in figure 2. The tip of the micropipette was about 10 μm in diameter. The micropipettes were filled with a KCl-saturated gel. The gel was prepared by mixing 3 g of agar in 100 mL of boiling 0.5 M KCl solution. After the agar was completely dissolved, the micropipettes were totally immersed in the boiling solution for 5 minutes. After withdrawing the micropipettes from the solution and allowing them to cool, each tip of the micropipettes was checked visually under a microscope to verify the completeness of the filling and to insure the absence of air bubbles in the filled micropipettes. 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. A section (opposite the tip) of the agar gel-filled micropipette was then cut off to obtain a micropipette of about 40 mm in length.

Each micropipette was inserted into a pyrex glass tube (i.d. 3 mm) and sealed with molten wax at the joint (fig. 2). The glass tube was then filled with the reference electrolyte (0.5 M KCl). Care was taken to insure that there were no air bubbles in the glass tube. Finally, a silver/silver chloride electrode (Ag wire coated with AgCl) of 250 μm in diameter was placed in the glass tube and sealed with wax to prevent the

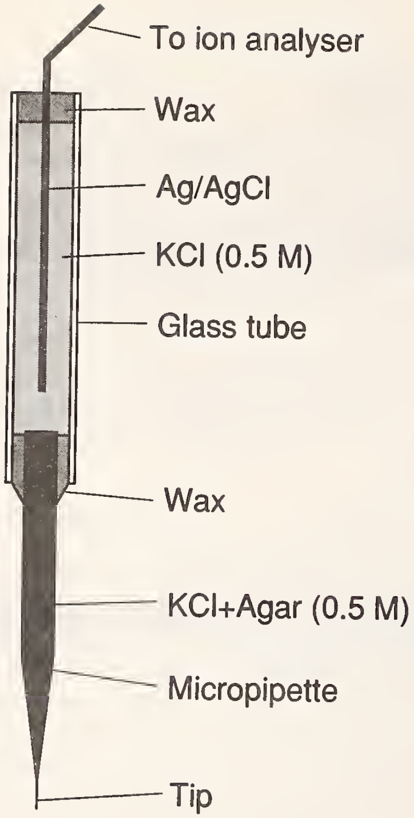

Figure 2. Single-barreled reference micro-electrode.

evaporation of the KCl filling solution. A voltmeter or reference input of an ion analyzer was connected to the end of the Ag/AgCl wire. The Ag/AgCl wire was made by electrodeposition of AgCl on Ag wire. Because Ag/AgCl electrodes are sensitive to light, care was taken to minimize exposing the electrodes to light during the preparation and measurements.

2.3.2 Double-Barreled Chloride Ion Selective Microelectrodes

While the construction of the double-barreled Cl^- ion selective microelectrodes is difficult, the double-barreled microelectrodes offer many advantages for use in the coating/metal interfacial studies over that of 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.

Double-barreled Cl^- ion selective microelectrodes were constructed from double-barreled capillaries. These microelectrodes, which are illustrated in figure 3, contain two compartments: one serves as the reference electrode; the other serves as the Cl^- ion selective electrode. As for the reference electrode, many steps are involved in their construction. A double-barreled, 1.5/0.8 mm (o.d./i.d.) borosilicate glass capillary was first pulled into a pointed shape and one of the two barrels was truncated at the tip (fig. 3). 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 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. 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 Ag/AgCl wire (made by the same electrodeposition method as described earlier), 100 μm 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

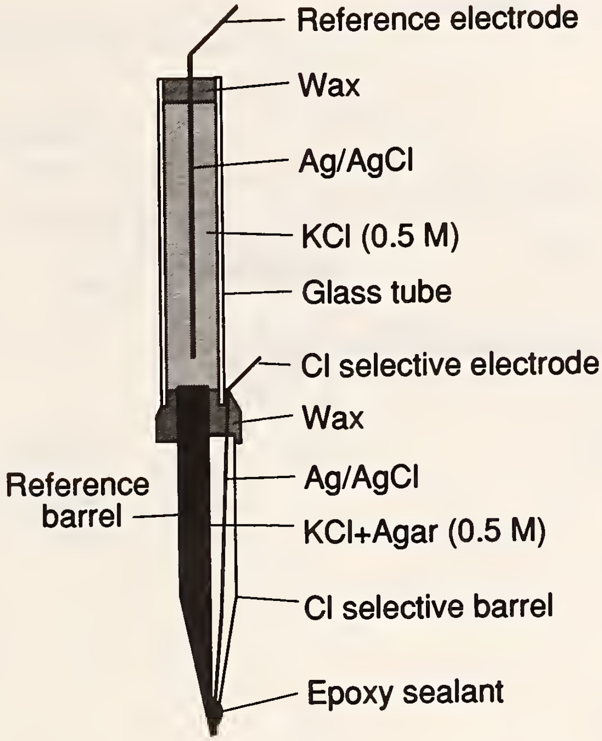

Figure 3. Double-barreled chloride ion selective microelectrode.

possible contamination of the Ag/AgCl wire by the sample environment. Precaution was taken to insure that the Ag/AgCl wire did not touch the tip and wall of the longer barrel (the reference electrode compartment). The gel-filled, reference electrode compartment was inserted into a glass tube and sealed, and the same procedures were followed as those described for the preparation of the single-barreled, reference microelectrodes. Wax was also used to seal the top of the Cl^- ion selective electrode compartment.

2.4 Chloride Ion Measurements

2.4.1 Inverted Electrode Microsampling Method

The method used in this experiment follows a microanalytical procedure reported for measuring nanoliter volumes of F^- and Cl^- ions containing solutions [3]. The method utilizes a reference microelectrode brought in contact with a microdrop of the measured solution deposited on the surface of an inverted selective macroelectrode. This method is referred to in this paper as the inverted electrode microsampling method. Figure 4 presents the Cl^- ion measurement set-up using the inverted electrode microsampling method. An Orion[1], half-cell, flat surfaced, Cl^- ion selective macroelectrode was adapted for use in the inverted position (as opposed to the upright position conventionally used). The electrode surface, which was clamped in the inverted position, was first rinsed with triply-distilled water and then dried by wiping to remove any dirt or contamination deposits on the electrode surface that could interfere with the sensitivity of the electrode. A cylinder (about 2 mm in height) above the electrode surface was made by placing pressure sensitive tape around the top of the electrode to hold the samples (fig. 4). Mineral oil was first poured into the cylinder, and then a sample of about 1–2 μL was deposited on the surface of the Cl^- ion sensing element of the electrode using a 5-μL chromatographic syringe. Mineral oil prevented the evaporation of a sample during the measurement.

The reference microelectrode and the inverted Cl^- ion selective macroelectrode were connected to the reference and Cl^- ion sensing inputs, respectively, of a high impedance (10^{14} ohm) Orion EA 940[1] ion analyzer. The tip of the reference microelectrode was brought into the center of a sample with the help of a

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[1] Certain commercial equipment is identified in this paper in order to adequately specify 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.

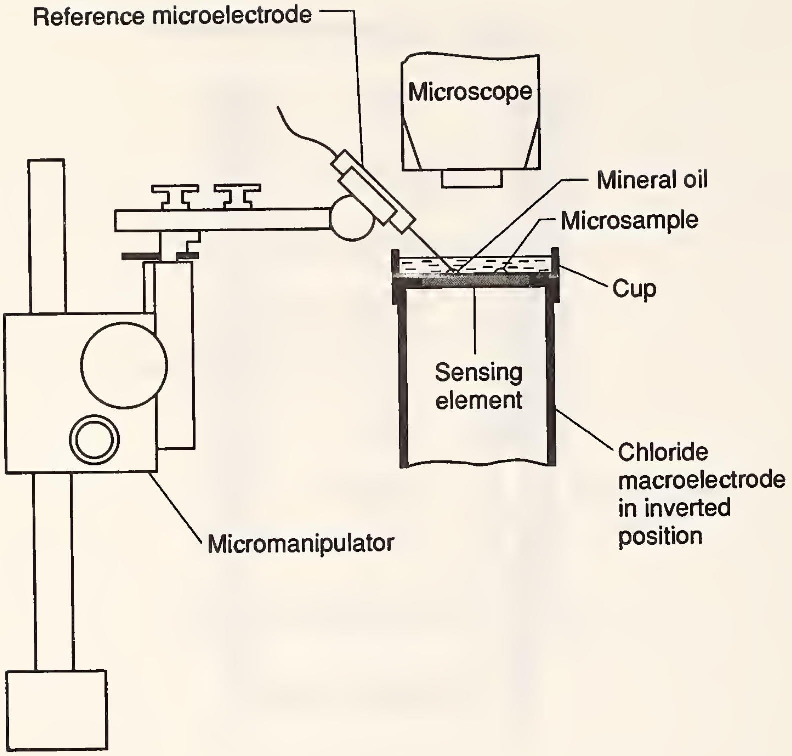

Figure 4. Experimental set-up for chloride ion measurement using inverted electrode microsampling method.

stereo microscope, a micromanipulator attached to the reference microelectrode, and a manipulator attached to the Cl^- ion selective macroelectrode. The concentration was read directly from the analyzer. (Multiple samples can be present on the electrode surface at the same time.) To insure the reliability of the data, microdrops of the Cl^- ion standard solutions were also deposited on the electrode surface, and their concentrations measured just prior to sample measurements. If space on the electrode surface were available, additional samples were added and measurements made; otherwise, samples and mineral oil were removed by suctioning or wiping. 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. However, because the measurement system was calibrated in terms of concentration, we report our results in terms of concentration.

2.4.2 In Situ Chloride Ion Concentration

In situ measurements of Cl^- ion concentration in type I and type II specimens were carried out using double-barreled Cl^- ion selective microelectrodes following the arrangement shown in figure 5. For a type I specimen (fig. 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 formation and growth of the blisters were quite 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. After a blister of measurable size had formed, the water in the area 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 was then inserted into the blister at the punched hole. Care was taken so that the electrode tip just touched the substrate surface without damaging it. A fast-curing silicon adhesive was used to seal around the hole (see fig. 1a). The reference and Cl^- ion selective electrodes of the double-barreled microelectrode were connected to the 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 (fig. 1b), the measurements started as soon as 0.5 M NaCl solution was placed into the cylinder. The analyzer was programmed to print Cl^- ion concentration at desired time intervals; that is, 10 minutes at the beginning of exposure and one hour at later exposures.

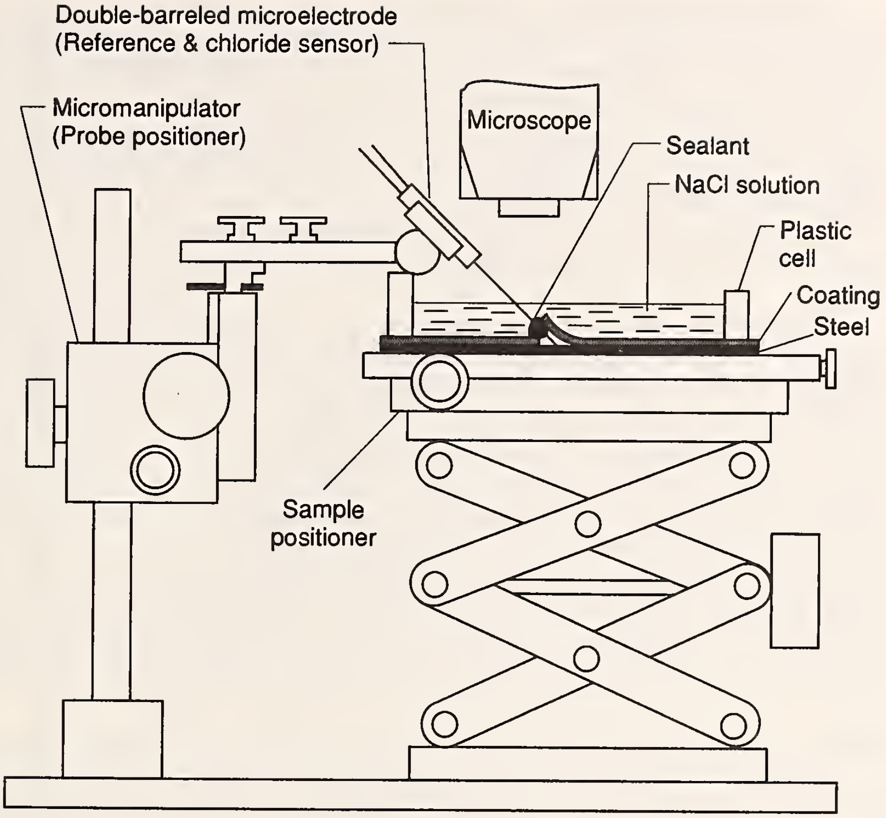

Figure 5. Experimental set-up for in situ chloride ion and potential measurements at the coating/metal interface.

2.5 Corrosion Potential Measurements

Measurements of corrosion potential at the coating/steel interface were carried out using a reference microelectrode and the type III specimen configuration (fig. 1c). After the coating was cured, a cylinder was mounted on the coated panel in such a way that the electrode leaned on the cylinder (fig. 1c). An area of the coating outside the cylinder was removed to expose the metal. The bare metal served as the working electrode. The reference microelectrode and the exposed metal of the coated panel were connected to a voltmeter, and corrosion potentials as a function of exposure time were measured as soon as 0.5 M NaCl solution was placed into the cylinder.

3. Results and Discussion

3.1 Calibration

Microelectrode methods are widely used today in biological systems. However, appropriate microelectrodes are not commercially available at present, and their use is not standardized, nor routine. Researchers must fabricate the microelectrodes themselves to suit their own needs following many careful steps. The first steps in any measurement using the microelectrode method are to insure that the electrodes, both reference and ion selective types, are working and to calibrate them. This is done by using standard solutions in the concentration range of interest to establish a potential-concentration calibration curve.

Figure 6 presents four calibration curves for the three chloride electrode systems under study in NaCl solutions having concentrations ranging from 1 to 0.00015 M; the concentration is expressed in the logarithmic form. Curve 1 was obtained using a commercial combination Cl^- ion selective macroelectrode (Cl^- ion selective and reference electrodes are built in one body) in 10-mL standard solutions following the normal procedures (upright position). Curve 2 was from Cl^- ion measurements by the inverted electrode microsampling method using 2 μL of the same standard solutions. Curves 3 and 4 were obtained by using two different

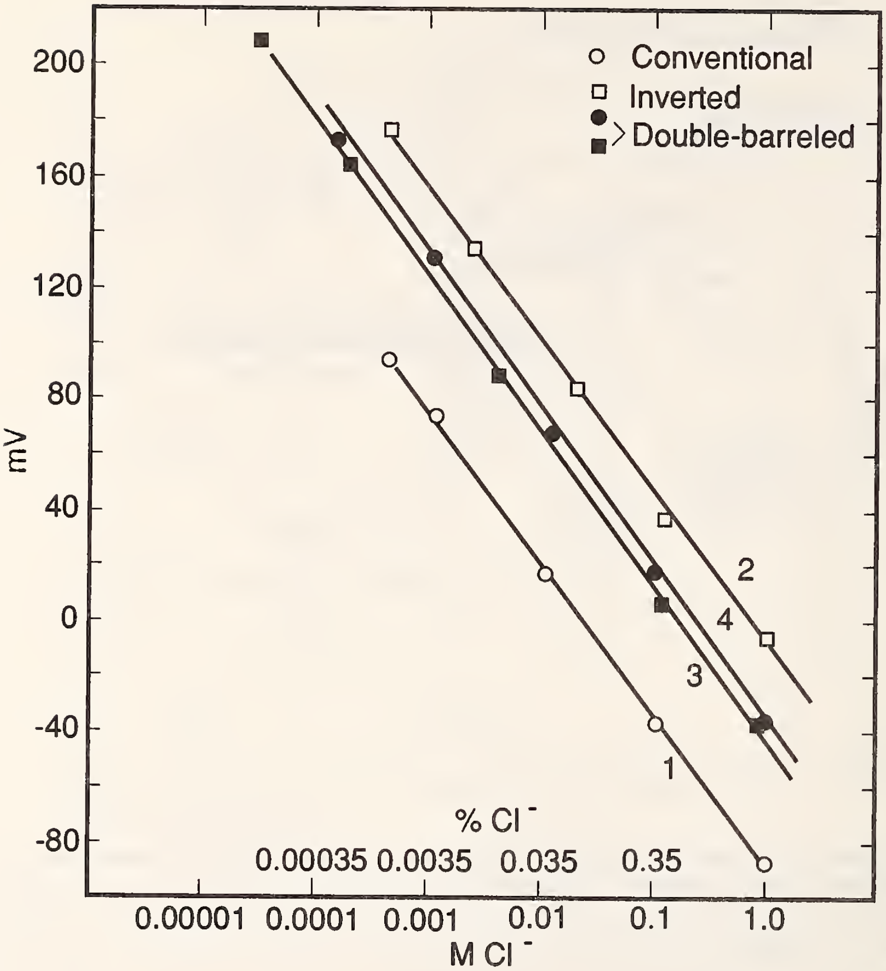

Figure 6. Calibration curves of the three chloride ion measurement methods. Curve 1: conventional; curve 2: inverted electrode microsampling; and curves 3 and 4: double-barreled microelectrode.

double-barreled Cl^- ion selective microelectrodes constructed at two different times and 10-mL volumes of sample solution, an indication of the excellent reproducibility of the construction of these electrodes. The parallelism of the four curves in figure 6 indicates that the three measurement methods are equivalent in providing Cl^- ion concentration. All four curves show no evidence of a deviation from the Nernstian law (potential is inversely linear with logarithm of concentration) in the concentration range studied. Previous works [4] also showed a straight line relationship between the potential and the logarithm of concentration of an Ag/AgCl electrode in KCl solutions between 5 and 0.001 M concentration.

3.2 Measurements of Chloride Ion at the Coating/Steel Interface

3.2.1 Inverted Electrode Microsampling Method

As indicated earlier, the inverted electrode microsampling method is useful for measuring Cl^- ion concentrations in small volumes of electrolyte, such as that in blisters formed between coatings, in blisters formed between a coating and a metal surface, and in other areas where the liquid sample size is small, such as in the corrosion of crevices and pits. Since the tip of a reference microelectrode can be made very small (as small as 0.045 µm has been reported [5]), the limiting factor of this method is the ability to obtain and transfer very small samples to the macroelectrode surface. For coated metal, this factor restricts the use of the inverted electrode microsampling method for measuring Cl^- ion concentrations to blisters that are visible and perforable so that the liquid can be withdrawn. This means that the Cl^- ions found in the blister may not be present at the early stage of the blister formation. The following example demonstrates the usefulness of the inverted electrode microsampling method for studies of corrosion of coated metals.

A TiO_2-pigmented alkyd coated panel (top coat only) of about 100 μm thick was allowed to stand (without constant stirring but with distilled water added occasionally to maintain the solution level in the cylinder) under a 0.5 M NaCl solution. Two large blisters formed after six months of exposure; one was formed prior to the other. Chloride ion concentrations of the two blisters and of the bulk solution were measured using the inverted electrode microsampling method. It was interesting to find that the Cl^- ion concentration of the larger of the two blisters was 5.2 M and that of the smaller blister was 1.2 M. These were more than 10 and 2 times higher, respectively, than that of the bulk solution, which changed very little after 6 months exposure. Early workers [6], 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 that in the bulk.

Apparently, the migration of Cl^- ions was more favorable to one blister than the other. When the coating was peeled off the substrate, it was observed that the substrate under the blister having the higher Cl^- ion concentration was heavily corroded over the entire blister area, while the area under the other blister appears to be free of corrosion products. Thus, it appears that the metal area under the blister having the higher Cl^- ion concentration was in an anodic state, while the other was in a cathodic state. The latter was probably formed as the result of the extended anodic region of the former. This phenomenon seems to be similar to the cathodic blistering observed for a scribed coated panel subjected to an electrolyte [2,7]: corrosion occurs at the scribe which serves as the anodic site; and cathodic blisters, resulting from the cathodic reactions, were formed around and away from the scribe. The higher level of Cl^- ion concentration in the cathodic blister (the lower Cl^- ion concentration blister) as compared with the bulk solution suggests that some Cl^- ions from the blister having the higher Cl^- ion concentration migrated to the blister having lower Cl^- ion concentration, probably through a water-thickened layer at the coating/steel interface or a breakthrough between the two blisters.

Heavy chloride deposits on the corrosion products at the scribe of a scribed coated panel immersed in a NaCl solution analyzed by an electron microanalysis technique was also reported [8]. The preferentially higher concentration of Cl^- ions at the anodic sites (i.e., the higher Cl^- ion concentration blister and the scribe) was similar to that observed in crevice and pitting corrosion [9]. For example, the fluid within crevices exposed to neutral NaCl was reported to be 3 to 10 times greater in Cl^- ion concentration than that of the bulk solution. The acidic environment created by the anodic reactions at the corroded sites in the blister having the higher Cl^- ion concentration was probably responsible for the higher concentration of Cl^- ion of this 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, which probably migrate from the bulk solution to the blister through the defects or expanded pores of the coatings, are needed to counterbalance the positive charge of the H^+ ions.

3.2.2 In Situ Chloride Ion Measurements

Figure 7 presents the Cl^- ion concentration as a function of exposure time for a type I specimen configuration (as shown in fig. 1a). The coated panel was immersed in a 0.5 M NaCl solution and a double-barreled Cl^- ion selective microelectrode was used. As mentioned earlier, the insertion of an electrode into this type of specimen was only possible after the specimen had been immersed 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 7.

The Cl^- ion concentration in the blister increased rapidly after inserting the electrode. A value four times that of the bulk solution was reached after 3 days of insertion. After that the Cl^- ion concentration remained almost constant for the next 4 days. It is noted here that the blister, in which the measurements were made, formed on the coated panel section immersed in water external to the NaCl-containing cylinder. 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 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 [2,10]. The loss of adhesion as the result of water buildup at the coating/metal interface before blistering begin facilitates lateral movement of ion

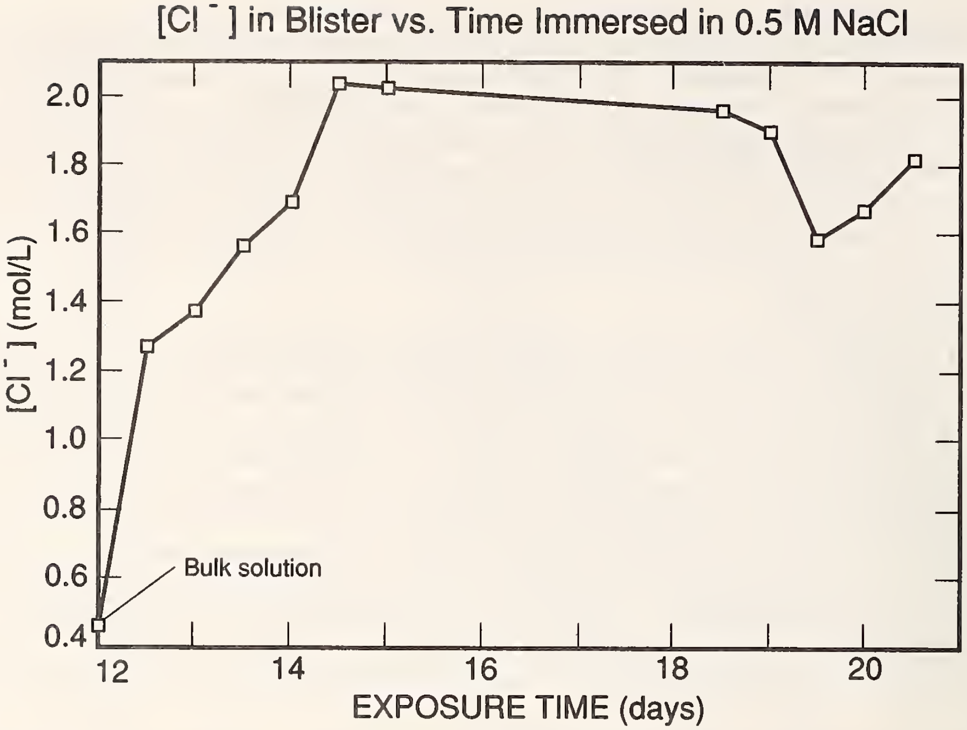

Figure 7. Chloride ion concentration as a function of time obtained by using double-barreled chloride ion microelectrode for type I specimen immersed in 0.5 M NaCl solution.

between the anodic and cathodic areas [7]. 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 [6].

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 attributed to the decrease of corrosion of iron immersed in these solutions [11]. 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 are associated or bound, the ions will not be measured by the ion selective electrode method.

Figure 8 is the curve representing Cl^- ion concentration change as a function of exposure time in a blister immersed in 0.5 NaCl solution for a type II specimen configuration. 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 3 hours after immersion and the Cl^- ion concentration rose almost steadily up to 65 hours. 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 two times 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 8, it was estimated that 1.8×10^{-4} g of Cl^- ions had entered the 5×5 mm artificially delaminated defect 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, we obtained a diffusion coefficient of 4.0×10^{-10} cm^2s^{-1}. This is somewhat higher than the "migration" coefficient values of 0.6×10^{-10} and 0.83×10^{-11} cm^2s^{-1} reported [12] for scribed and unscribed, respectively, alkyd top coat panels immersed in 0.5 M NaCl solution without an applied potential. It is not known how the silicone adhesive and the sealed areas around the defect affected the calculated value reported here.

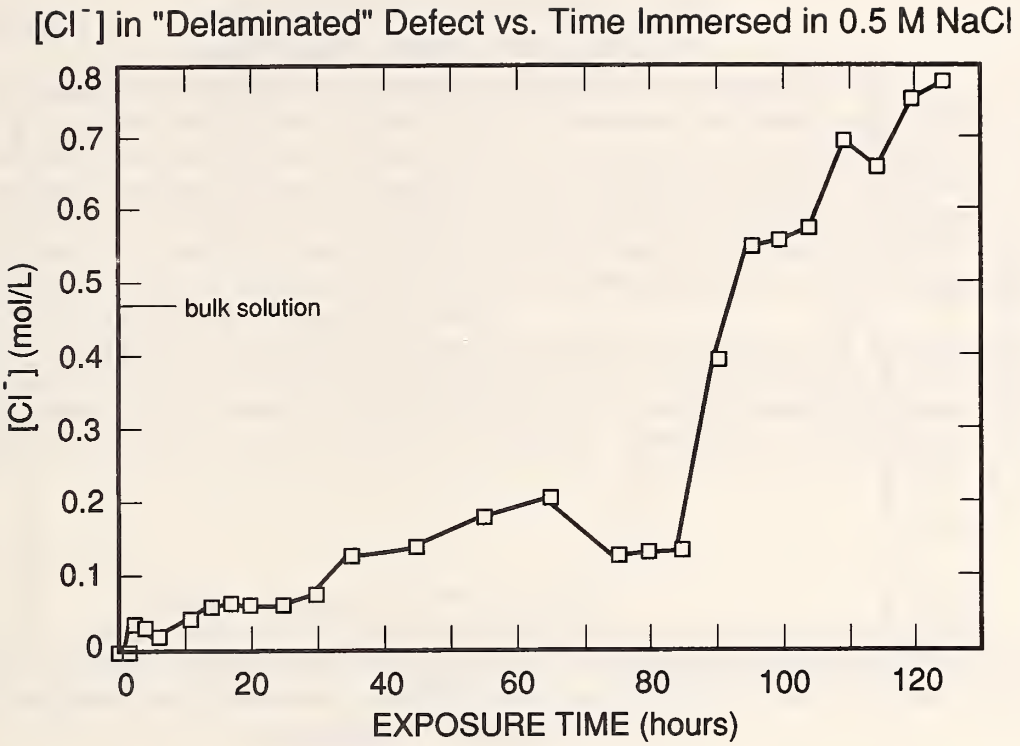

Figure 8. Chloride ion concentration as a function of time obtained by using double-barreled chloride ion microelectrode for type II specimen immersed in a 0.5 M NaCl solution.

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 [12]. 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 corrosion. Chloride ions can accelerate the corrosion of metals 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 [13].

3.3 Corrosion Potential Measurements

The value of the corrosion potential of a metal substrate (acquired when a corroding metal is in contact with an electrolyte) by itself is of little value, but its change as a function of immersion time may provide valuable information about the mechanism of the corrosion reactions and the rate controlling factors [14]. In general, a rising potential indicates passivity and a falling potential denotes activity. In the case of coated metals it is a function of the permeability of the coating to water and ions and the integrity of the coating.

Figure 9 depicts the results of measurements of the corrosion potential at a coating/steel interface using the microelectrode method and a type III specimen. The corrosion potential moved in the active direction at first, then moved to the noble direction and finally moved in the active direction, reaching a corrosion potential of 0.675 V vs Ag/AgCl at the end of the test. The potential decreased sharply after 100 hours of exposure indicating that the coated panel had severely corroded with a great increase in the anodic/cathodic surface area ratio. Although the time span is quite different, the trends shown in figure 9 are similar to the general potential-time curve obtained by the conventional method [14], in which the potential is measured by immersing a reference macroelectrode in the electrolyte solution, not at the coating/metal interface. The time required for the onset of corrosion (the beginning of the decline after the peak) to occur took only a few days in this experiment compared to weeks using the conventional method.

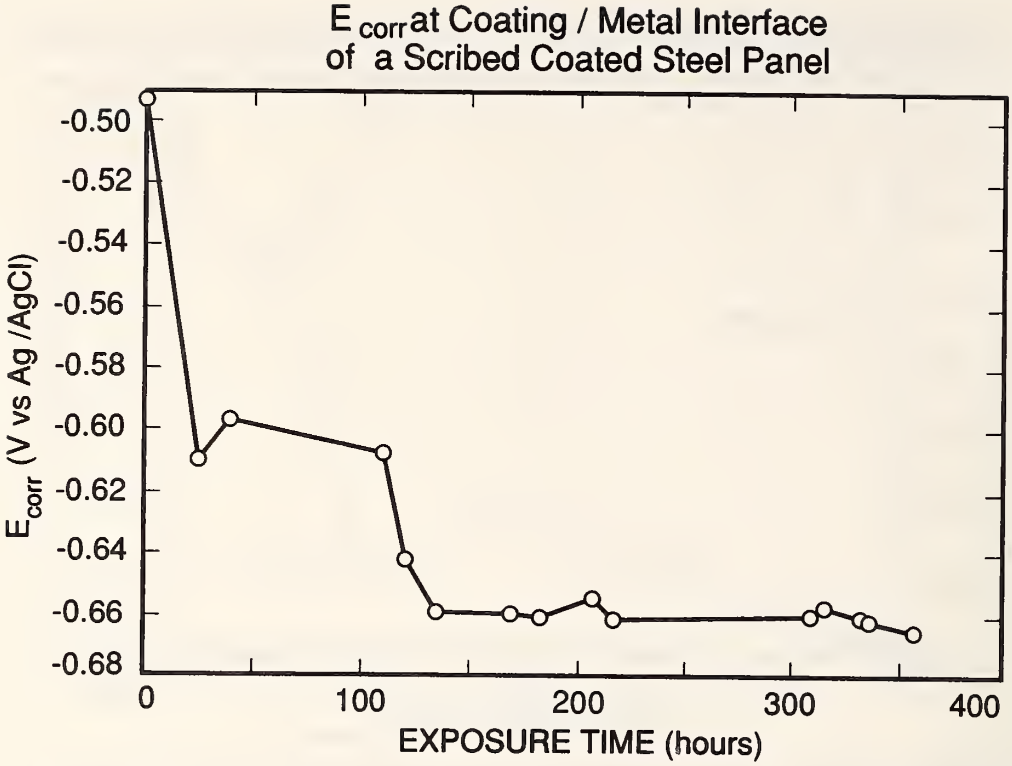

Figure 9. Corrosion potential at the coating/metal interface as a function of time obtained by using reference microelectrodes for type III specimen immersed in a 0.5 M NaCl solution.

The main advantage of measuring corrosion potential using the microelectrode at the coating/metal interface is the ability to obtain the corrosion potential at microareas, such as in blisters, cracks, and pits; this cannot be measured by a conventional reference electrode. Another advantage is the ability to obtain the potential as soon as the electrode is in contact with electrolyte at the coating/metal interface rather than waiting until a continuous conductive pathway through the coating is established. Not many coated metals provide a continuous pathway from the moment of immersion. For example, it has been reported that a corrosion potential could not be measured on a 25-µm vinyl coated aluminum sample in 5 percent (0.86 M) NaCl solution until the 41st day [15]. An electrolyte at the interface may be formed, as a result of corrosion reactions, the presence of surface contaminations, or migration of ions from the coatings, before the arrival of electrolyte from the bulk solution.

One of the biggest concerns in measuring Cl^- ions and corrosion potentials 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; this test is still on going and data on long term stability will be reported when further results become available.

Another concern is the relatively large tip, ~200 µm, 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 µm using a liquid ion exchanger in place of the Ag/AgCl wire at the tip. However, their stability was poor (about 3 days) and not suitable for the in situ measurements. The current limitation of the tip size of a solid state, double-barreled microelectrode is the size of the Ag/AgCl electrode. Thus, we see no reason why a smaller tip double-barreled microelectrode using a solid state electrode could not be made if smaller size Ag wire were available.

4. 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 based on using a microelectrode for studying in situ the behaviors of chloride ions and corrosion potentials 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. In addition, we have also demonstrated a useful microsampling electrode method for measuring Cl^- ion concentrations in small volumes, such as in blisters.

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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11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

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/steel interface. We have developed a procedure based on microelectrodes for studying in situ the behaviors of potential and chloride ions in blister and at a coating/metal interface. The procedure requires an attachment of a double-barreled Cl^- selective microelectrode at the coating/metal interface, thus allowing direct measurements of Cl^- concentration and corrosion potential changes at localized areas under a coating. Although it is intricate to prepare these microelectrodes, 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 on metal. The procedure should also be very useful for studying the roles of Cl^- in localized corrosion. The utility of an inverted electrode microsampling method for studies of Cl^- in very small volumes such as blisters was also demonstrated.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)
blister; chloride; coating; coating/metal interface; corrosion; in-situ; microelectrode; microsampling; potential

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