

# Three Colorimetric Methods for Evaluating Chloride Penetration of Cracked and Coated Concrete

Panthawit Watanasrisin, Khomkrit Supatnantakul, and Thatchavee Leelawat

**Abstract**—The purpose of this study was to evaluate the chloride penetration depth of cracked and coated concrete by using three colorimetric methods; including silver nitrate, combination of silver nitrate and potassium chromate, and combination of silver nitrate and fluorescein. Three groups of specimens were classified; including non-cracked, 0.2 mm-cracked, and 0.5 mm-cracked specimens. Each group was applied with three different types of surface protection; namely hydrophobic, sealing, and coating materials. The chloride penetration was accelerated into the specimens by applying the direct current of 60 voltage for 6 hours. Thereafter, the specimens were split into halves across their diameter along the crack plane. The split specimens were then sprayed with the colorimetric solutions. The results found that hydrophobic materials exhibited the lowest chloride penetration depth of non-cracked specimens. Moreover, the coating materials exhibited good resistance to chloride penetration for cracked and non-cracked specimens. The silver nitrate and potassium chromate method was found to observe color change at the chloride-contaminated zone of the specimens clearly, comparing to the other methods. Moreover, the depths of chloride penetration measured by spraying with both the silver nitrate and potassium chromate solution were no significantly different from those applying with only silver nitrate solution. Spraying with both silver nitrate and fluorescein solution was found to be the most sensitive method for the determination of chloride content at a low concentration.

**Keywords**— Colorimetric methods, Surface protection, Cracked concrete, Chloride penetration depth

## I. INTRODUCTION

THE acid-soluble chloride content of drilled samples is commonly used for the determination of chloride content in the concrete. However, the preparation for testing of the method is time-consuming, and the method requires to use expensive equipments and consumable substances. Alternatively, some researchers [1-6] recommended to use the

easier and quicker method for determination of the chloride penetration depth by using colorimetric method.

Otsuki et al. [3] investigated the different types and quantities of colorimetric solutions, which included silver nitrate, lead nitrate, and thallium nitrate solutions. Spraying with the silver nitrate ( $\text{AgNO}_3$ ) solution was observed to distinguish the clearest color change between chloride-contaminated zone and free-chloride zone. Otsuki et al [3] and Myung-Yu et al [4] recommended to dilute silver nitrate in water with the concentration of 0.1 mol/liter for clearest color change. Ve'ronique et al [5, 6] found that spraying with both silver nitrate and potassium chromate ( $\text{AgNO}_3 + \text{K}_2\text{CrO}_4$ ) solutions on the broken surface of concrete was found to distinguish the color change between chloride-contaminated zone and free chloride zone easier than spraying with silver nitrate only. He et al [2] reported that measurement of chloride penetration depth using spraying both silver nitrate and fluorescein ( $\text{AgNO}_3 + \text{fluorescein}$ ) solutions was found to be deeper than the others.

The surface treatment is commonly used to improve the performance and the service life of repaired concrete [7-9]. However, very limited researches were found to study the determination of chloride penetration depth for cracked and coated concrete using colorimetric methods. Therefore, the main aim of the study was to investigate the color change of chloride-contaminated zone for cracked concrete being coated with various material using the colorimetric methods.

## II. METHODOLOGY

### A. Materials

Ordinary Portland cement conforming to ASTM C150 [10] was used in this study. The coarse aggregate was crushed limestone with the maximum nominal size of 19 mm, and the fine aggregate was river sand with the maximum nominal size of 4.75 mm.

Six different surface protection materials, which were classified into three groups; including hydrophobic, sealing, and coating materials, were applied in this study. The hydrophobic materials; including silane (SL) and siloxane (SX), were used. The sealing material was silicate-based material (SB). The coating materials; including three different brands of acrylic coating materials (AA, AB, AC), were used.

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The colorimetric solutions used in the study were prepared from the analytical grades of chemical substance. The silver nitrate ( $\text{AgNO}_3$ ) solution was prepared by diluting the silver nitrate powder with the de-ionized water to obtain aqueous solution with the concentration of 0.1 M. Whereas the 5% by weight of potassium chromate ( $\text{K}_2\text{CrO}_4$ ) solution was prepared by diluting potassium chromate in 1 liter of the de-ionized water. Additionally, 1 g/liter of fluorescein ( $\text{C}_{20}\text{H}_{12}\text{O}_6$ ) solution was prepared by diluting fluorescein in 1 liter of 70% ethyl alcohol.

### B. Concrete Proportioning and Specimen Preparation

Concrete mixture was designed for 28-day compressive strength of 35 MPa. The details of mix proportion are given in Table I. The concrete mixture was cast in thirty-five  $\phi 100 \times 200$  mm cylindrical moulds. The mixture was poured in three layers and each layer was consolidated on a vibrating table for 15 seconds. After casting, the specimens were covered with plastic sheet for  $20 \pm 4$  hours, demoulded, and then cured in moist-cured room for 7 days. Thereafter, seventy  $\phi 100 \times 100$  mm cylindrical specimens were prepared by cutting at the middle of thirty-five  $\phi 100 \times 200$  mm cylindrical specimens. All of the cut specimens were then returned to the moist-cured room. At the age of 14 days, the cut specimens were removed from the moist-cured room and pre-cracked using a controlled splitting test. Similar technique used for developing cracks along the surface of specimens was recommended by Yi et al [11]. Thereafter, seven points along the crack plane of cut specimens were measured by a digital microscope and then averaged. The cracked specimens were separated into two ranges of crack widths; including 0.1-0.3 mm and 0.4-0.6 mm.

TABLE I  
MIX PROPORTIONS

| Mix Proportion ( $\text{kg}/\text{m}^3$ ) |       |                  |                | w/c  |
|---|-------|------------------|----------------|------|
| Cement                                    | Water | Coarse aggregate | Fine aggregate |      |
| 342                                       | 205   | 897              | 870            | 0.60 |

The specimens were then separated into 4 groups based on the types of surface protection; including uncoated specimens (non), specimens applied with hydrophobic materials (SL and SX), specimens applied with sealing material (SB), and specimens applied with acrylic coating materials (AA, AB, and AC). Preparation for applying each surface protection used on the surfaces of specimens was performed according to the manufacturers' recommendation.

The uncoated specimens, which were the first group, were kept in the moist-cured room until the testing age of 28 days.

The cut specimens in the second group were removed from the moist-cured room at the age of 21 days, cleaned, and dried in the laboratory condition for 2 days. Thereafter, two layers of silane (SL) or siloxane (SX) were applied on the surface of cut specimens. The specimens were then kept in the laboratory condition until the testing age at 28 days.

The cut specimens in the third group were removed from the moist-cured room at the age of 14 days. The surfaces of specimens were roughed using sandpaper and then cleaned.

The silicate-based material (SB) proportioning with the ratio of 3 parts of powder to 1 part of water was applied on the surfaces of specimens which were controlled to have the thickness of coating about 2 mm. The applied specimens were then allowed to dry in the laboratory condition for 24 hours and transferred to the moist-cured room until the testing ages of 28 days.

The cut specimens in the fourth group were removed from the moist-cured room at the age of 21 days, cleaned, and dried in the laboratory condition for 2 days. Thereafter, one layer of the acrylic coating material (AA) or the acrylic coating material (AB) was applied on the surface of cut specimens. Whereas two layers of the acrylic coating material (AC) were applied on the surface of the other specimens. The first layer was proportioned with the ratio of 1 part of AC material and 1 part of water, and then applied on the surface of cut specimens. The second layer containing only AC material was applied consecutively on the first layer of cut specimens. The specimens were then kept in the laboratory condition until the testing age at 28 days.

At the age of 28 days, chloride ingress was accelerated into all of the cut specimens by using the electrical potential method. Preparation of the method was described in ASTM C1202 [12]. After applied with the 60 Vdc for 6 hours, the specimens were split across their diameters along the crack plane and then sprayed with colorimetric solution.

### C. Testing Method

Three types of colorimetric solutions; namely  $\text{AgNO}_3$ ,  $\text{AgNO}_3 + \text{K}_2\text{CrO}_4$ , and  $\text{AgNO}_3 + \text{fluorescein}$ , were used to evaluate the depth of chloride penetration for coated and cracked specimens.

The  $\text{AgNO}_3$  solution was sprayed immediately on freshly broken surfaces of sixty-three specimens; including non-cracked and uncoated, cracked and uncoated, non-cracked and coated, and cracked and coated specimens, and left for 45 minutes. The color changes appearing on the sprayed surfaces were monitored and the depth of color change for each specimen was measured from the coated surfaces.

For  $\text{AgNO}_3 + \text{K}_2\text{CrO}_4$  method, the  $\text{AgNO}_3$  solution was also sprayed on the freshly broken surfaces of sixty-three specimens. Next, the broken surfaces were left for 45 minutes and then sprayed with the  $\text{K}_2\text{CrO}_4$  solution, as recommended by Ve'ronique et al [5]. The sprayed surfaces were left for further 10 minutes. The color changes at the sprayed surfaces were also monitored and their depths of color changes were measured.

For  $\text{AgNO}_3 + \text{fluorescein}$  method, the fluorescein solution was sprayed on the freshly broken surfaces of the other sixty-three specimens and left for 3 minutes. Thereafter, the  $\text{AgNO}_3$  solution was sprayed on the surfaces of specimens being sprayed with the fluorescein solution, as recommended by He et al [2]. The specimens were left for further 3 minutes.

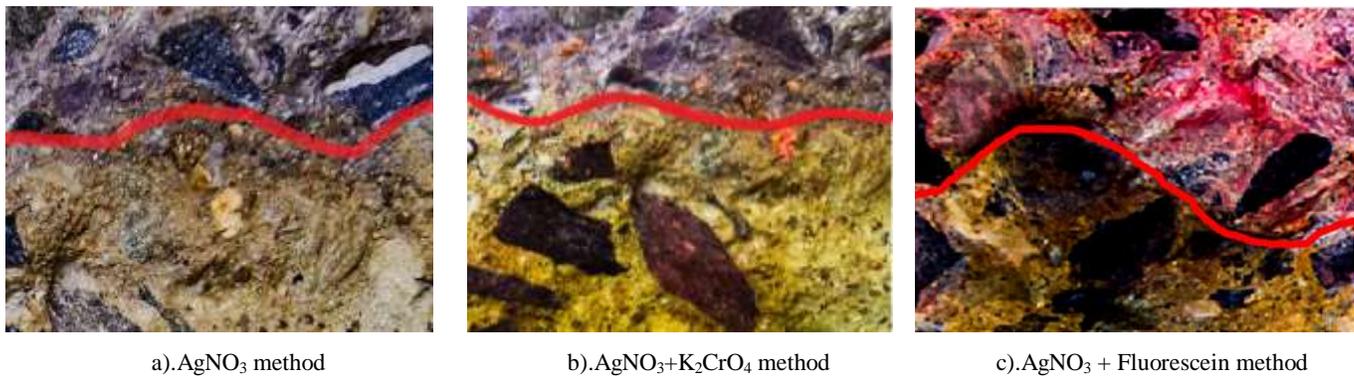


Fig. 1 Color changes obtained from colorimetric methods used

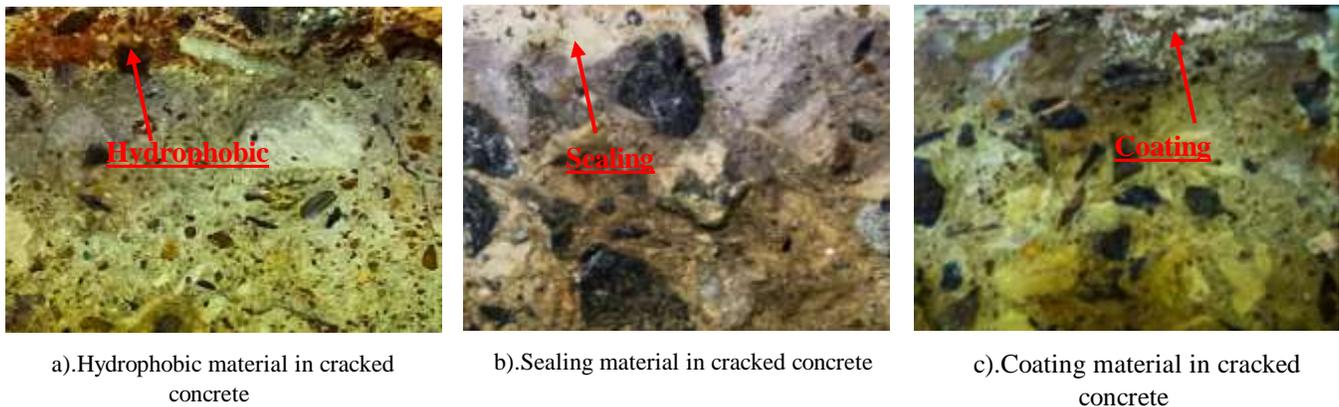


Fig. 2 Color changes of coated specimens having the range of crack width between 0.1 and 0.3 mm

The sprayed surfaces of specimens were photographed. The contrast of color changes at the sprayed surfaces was then increased by a graphic program. Thereafter, the depths of color changes for the sprayed specimens were measured.

### III. RESULTS AND DISCUSSION

#### A. Visual Appearance of Three Colorimetric Methods

Fig. 1 shows the appearance of color change at the split surfaces obtained from three colorimetric methods.

For the  $\text{AgNO}_3$  method, the color of chloride-contaminated zone was change to white or light grey color and the color of free-chloride zone changed to light brown color as shown in Fig. 1 (a). The color change was in line with Otsuki et al and Myung-Yu et al [3, 4], which also found that duration of changing color depended on reaction between chloride and  $\text{AgNO}_3$  on the sprayed surface. In our study, the changing color of some specimens could be seen in the first 10 to 15 minutes. Noted that, if the specimen was carbonated, the carbonated area had been changed to white color within 10 minutes after being sprayed.

The color change of the  $\text{AgNO}_3+\text{K}_2\text{CrO}_4$  method is shown in Fig. 1 (b). After being sprayed with the  $\text{K}_2\text{CrO}_4$  solution, the chloride-contaminated zone changed from light grey to dark grey color and the free-chloride zone changed to dark brown color. The color changes obtained from the  $\text{AgNO}_3+\text{K}_2\text{CrO}_4$  method were clearer than those obtained

from the  $\text{AgNO}_3$  method. It was also found that the carbonation zone changed from white to red brick color. The color changes of chloride-contaminated and free-chloride zones were similar with those reported by He et al.[2] and Ve´ronique et al [5, 6] and the color change of carbonation zone was in line with Ve´ronique et al. [5].

For the  $\text{AgNO}_3 + \text{fluorescein}$  method, the color of chloride-contaminated zone changed to faded pink and color in free-chloride zone turned to yellow brown as shown in Fig. 1 (c). The  $\text{AgNO}_3 + \text{fluorescein}$  method was found to be the most complicated method because color change was difficult to observe clearly. Therefore, image editor software was used to increase the contrast of color change before measuring the chloride penetration depth. In this method, no carbonation zone could be observed.

Fig. 2 shows the color changes of cracked concrete applied with different types of surface protection. It was found that hydrophobic materials exhibited red brick frontline inside the concrete as shown in Fig. 2 (a). It may indicate the chloride ion penetrating up to this frontline. In addition, small hydrophobic bubbles could be observed between the coated surface and the frontline after the colorimetric solution was sprayed on the broken surface of concrete. This indicated that hydrophobic materials only adsorbed on the crack walls without filling all of the crack areas. Therefore, the chloride ion could be observed to penetrate deeply inside the concrete.

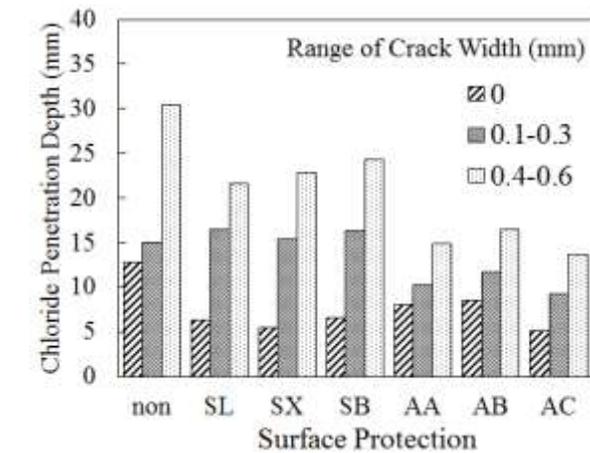
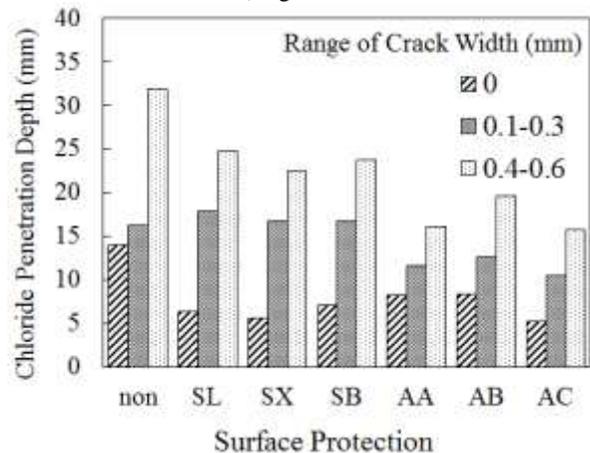
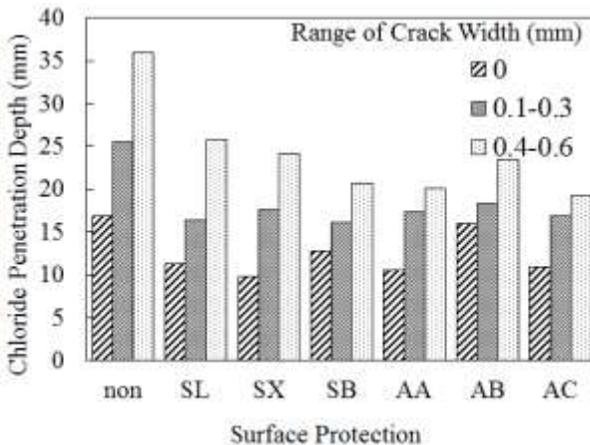
a).AgNO<sub>3</sub> methodb).AgNO<sub>3</sub>+K<sub>2</sub>CrO<sub>4</sub> methodc).AgNO<sub>3</sub> + fluorescein method

Fig. 3 Comparison of chloride penetration depth among surface protection materials used

For sealing material, crystallization appearing as white areas could be observed to fill in the crack areas as shown in Fig. 2 (b).

Fig. 2 (c) shows that only AC acrylic coating could penetrate into the cracks, fill in the crack areas, and cover the upper surface of concrete. The penetration of AC material assisted in improving the crack-bridging areas. The

penetration depth of AC material was about 20-25 mm from the applied surface of concrete, depending on the crack widths and their patterns. However, the other acrylic materials; namely AA and AB, were found to cover only the coated surface of concrete without penetrating into the cracks.

In the case of non-cracked specimens, the hydrophobic and sealing materials were found to penetrate slightly into the concrete. No penetration depth of coated material was observed, irrespectively to the brands of coated materials.

### B. Chloride Penetration Depth

The chloride penetration depths of three colorimetric methods are shown in Fig. 3. Non-cracked specimens applied with surface protection obtained from silane (SL), siloxane (SX), or acrylic (AC) exhibited the lowest chloride penetration depth. Since silane (SL) and siloxane (SX) had very small particle size which could easily penetrate into the pore of concrete, thereby decreasing the chloride ingress into the concrete.

In the case of cracked specimens, the acrylic coating materials exhibited chloride penetration depth, measured by AgNO<sub>3</sub> and AgNO<sub>3</sub>+K<sub>2</sub>CrO<sub>4</sub> methods, lower than the other protective materials used. Moreover, acrylic coating (AC) was found to exhibit the lowest chloride penetration depth, irrespectively to the measured colorimetric methods. This is due to the filling cracks, which could be observed only from acrylic coating (AC) as shown in Fig. 2(c). However, all of the protective materials used in the study had no significant difference in chloride penetration depth of concrete containing with the range of crack width between 0.1 and 0.3 mm, when their depths were measured by AgNO<sub>3</sub> + fluorescein method. Since the AgNO<sub>3</sub> + fluorescein method was sensitive to low chloride concentration as mentioned in He et al [2]. It could be noted that applying with silane (SL) or siloxane (SX) on the surface of concrete containing large sizes of cracks was not an effective method to minimize the chloride ingress. Since the silane (SL) or siloxane (SX) only adsorbed on the surface of crack walls without filling the whole crack areas. Moreover, the chloride penetration depth of concrete coated with silicate-based material (SB) was similar to that of the corresponding concrete applying with silane (SL) or siloxane (SX). Since the silicate-based material could also penetrate into the pore structures and cracks inside the concrete (Fig. 2 (b)) and then develop the crystallization of silicate products in the concrete.

### C. Comparison of Three Colorimetric Methods

Fig. 4 shows trend lines obtained from average chloride penetration depths of three colorimetric methods for all surface protection materials for each range of crack width using SPSS program. The chloride penetration depths increased with increasing the crack width, irrespectively to colorimetric methods.

Spraying with both AgNO<sub>3</sub>+K<sub>2</sub>CrO<sub>4</sub> solutions exhibited the chloride penetration depth slightly higher than spraying with only AgNO<sub>3</sub> solution. The result was in line with Veronique [5, 6]. Moreover, spraying with AgNO<sub>3</sub> + fluorescein

solution exhibited the chloride penetration depths approximately 1.5 times higher than spraying with  $\text{AgNO}_3$  and spraying with both  $\text{AgNO}_3 + \text{K}_2\text{CrO}_4$  solutions. The finding was in line with He et al. [2]. The  $\text{AgNO}_3 + \text{fluorescein}$  method was the most sensitive method to determine the low chloride content. However, no significant difference in the chloride penetration depth obtained from  $\text{AgNO}_3$  and  $\text{AgNO}_3 + \text{K}_2\text{CrO}_4$  methods could be observed as shown in Fig. 5, with a two-side p-value higher than 0.05.

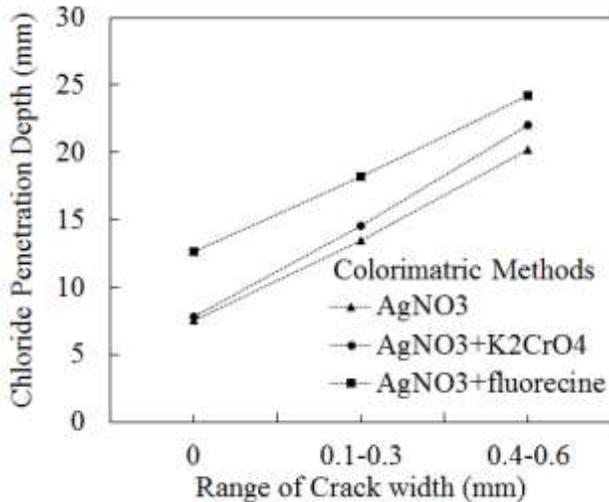


Fig. 4 Chloride penetration depth of three colorimetric method

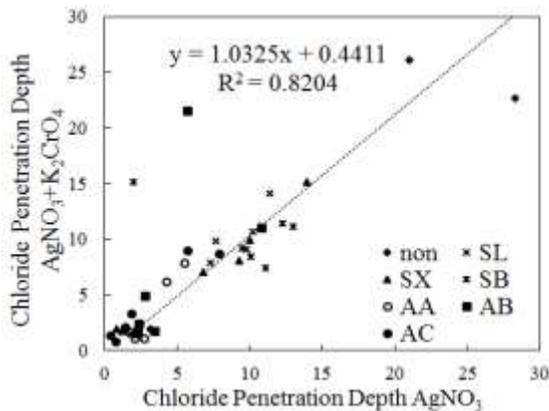


Fig. 5 Chloride penetration depth between  $\text{AgNO}_3$  and  $\text{AgNO}_3 + \text{K}_2\text{CrO}_4$  method

#### IV. CONCLUSIONS

- The hydrophobic and coating materials provided the better performance against the chloride ingress for non-cracked concrete.
- Only coating materials showed the better chloride penetration than the other protection materials used. Coating material AC can penetrate into the crack and increase the crack bridging ability.
- The chloride penetration depths obtained from of  $\text{AgNO}_3$  solution was no significantly different, when compared to those obtained from  $\text{AgNO}_3 + \text{K}_2\text{CrO}_4$  method. The

$\text{AgNO}_3 + \text{fluorescein}$  has shown the of chloride penetration deeper than the other methods.

- The  $\text{AgNO}_3 + \text{K}_2\text{CrO}_4$  method provided the clearest color change among three colorimetric methods.  $\text{AgNO}_3 + \text{fluorescein}$  method exhibited the most unclear color change. Therefore, the graphic program should be used to increase the contrast of color change prior to determination of chloride penetration depth.

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