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THE EFFECT OF CRYSTALLINE COATINGS DEFECTS OF STEEL-CORROSION IN REINFORCED CONCRETE

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ABSTRACT:

This study focus on corrosion behavior of reinforced concrete with crystalline coating materials. The efficiency of crystalline coating was considered comparing with different water to cement ratios. Determination of steel corrosion protection provides a comparison between the uncoated and coated concrete. This study was evaluated by using half-cell potential measurements in accordance with ASTM G109. The specimens were exposed to chloride environment, 5% NaCl solution by weight in wet-dry cycles. The coated concrete specimens were partly coated with crystalline material on top surface of the concrete. The coated area was considered defective to the different degrees 0, 1, 2 and 3%. A total of 90 specimens were cast with dimension 280 x 150 x 115 mm. The concrete was designed to have different water to cement ratios at 0.45, 0.50 and 0.60. The specimens had been exposed to humidity room environment for 365 days before coated. Half-cell potential of steel was measured at 0, 14, 21, 28, 42, 49 and 56 days. The results indicated that concrete with crystalline coating material performed better than uncoated concrete. The potential measured in all specimens were resemble regardless all of the defects on coated areas. The results of half-cell potential measurements indicate that there was reasonably no corrosion in coated concrete specimens. However, it revealed that the uncoated specimens with w/c ratios of 0.6 were attacked by corrosion. For the others mix of uncoated concrete, the corrosion activity gradually proceeded within duration of 56 days. By using difference water to cement ratios. It showed that the higher the water to cement ratios, the greater the probability of corrosion. In term of corrosion current density, the condition of the coated concrete rebar was found to be in passive condition but for the uncoated concrete, the result showed that the condition of the rebar was low to moderate corrosion. Crystalline coating materials delay the onset of corrosion in reinforced concrete under severe environment.

KEYWORDS: Crystalline Coating, Steel-Corrosion, Reinforced Concrete, Chloride

1. Introduction

At present, structural engineer usually design the reinforced concrete structures by considering the durability including the corrosion. Due to the increasing demand for the long service life of reinforced concrete structure and the high cost of construction and maintenance. Corrosion is one of the principal causes of concrete deterioration. The damage is especially in the structures exposed to marine environment. The main reasons of steel-corrosion in reinforced concrete structure is chloride ion. Chlorides act as a catalyst to corrosion and destruction of the passive layer of oxide on the steel. Corrosion leads to several coupled effects: longitudinal cracking of concrete cover due to expansive corrosion products, steel cross-section reduction, the degradation of steel–concrete bond [1]-[3] thus the service life and the load-bearing capacity of reinforced concrete elements are considerably reduced.

Many researchers have demonstrated in steel-corrosion behaviors under chloride attack. The concrete types have been focused in steel-corrosion processes [4]-[7]. However, there is the new technique of the most obvious method to prevent harmful substances from penetrating into the concrete. The main idea is used to protect the concrete surface. Concrete surface treatments may take several forms. The simplest treatment is a coating that creates a continuous protective layer on the concrete surface [1], [8]. In the past, the most commonly used methods were directly coatings concrete surface with protective materials such as acrylic, polymer emulsion, epoxy resin, polyurethane, and chlorinated rubber. These coatings provide resistance to chloride and other chemical ingress into concrete [9]-[11]. It does not make the concrete denser. If there is a discontinuity on coated area, fluid can also penetrate the concrete.

The method to obtain denser concrete and prevent harmful substances is to apply crystalline materials. This material, when applied to the concrete, makes the concrete denser by forming acicular-structured crystals which is filling capillary pore of concrete. The coating penetrates under the concrete surface [12]. There were researchers [12]-[14] having conducted a chloride permeability test in concrete. The results showed that coating with crystalline material resulted in lower chloride ion penetrability compared to the uncoated concrete.

The role of crystalline materials influencing the durability properties of concrete was investigated [15]. The results showed that crystalline materials increased chloride resistance in concrete, either used as coatings or admixture.

The effect on chloride penetration in coated concrete with surface-applied protection materials was studied [16]. Coated concrete with crystalline materials reduced chloride content better than coating concrete with silane materials and uncoated concrete.

Moreover, the influence of crystalline additives and the curing environment on the mechanical properties of concrete was investigated [17]. Crystalline admixtures mixing 3, 5, and 7% of the cement content were added to fresh concrete. The results showed that the addition of 3% crystalline admixture increased the compressive strength and splitting tensile strength of concrete as the most effective amount under moist curing.

Under repair technique, [18] studied the chloride penetration of concrete after repairing with fly ash concrete and crystalline material. The results showed that concrete coating with crystalline material on the surface of original concrete before being repaired with the repair concrete can reduce chloride penetration in the original concrete. Concrete repairing with fly ash concrete has lower chloride penetration after repairing.

The possible to reduce the capillary porosity in concrete was evaluated and demonstrated [19]. They concluded that the use of crystalline coating reduces the water absorption and voids. The concrete with crystalline admixture increased compressive strength. These results agree with [20] that studied the influence on the water transport in concrete with crystalline by the electrical resistivity method. The results showed that the concrete with crystalline coating decreased moisture content percentage in comparison with untreated specimens

In addition, [21] showed that the comparisons of the mass of water absorption of between the crystalline coating and polymer coating. The crystalline coating applied to smooth and rough substrates is lower substrate water absorption (in percentage) than polymer coating.

The results of study conducted by [22] indicated that crystalline admixtures added in an amount 2% of cement weight reduce the water vapor permeability of concrete by 16-20 %. The concrete structure with a crystalline admixture could be ready for water loading already on the 12th day after casting the concrete specimens under the water pressure test.

Influence of curing environment on concrete with crystalline materials was conducted, [23] and [24] investigated the effect that a combination of crystalline protection material and wax based curing agent. The concrete specimen was designed strength of 40 MPa. The results showed that both coated concrete and concrete with 2% crystalline admixture increased compressive strength of concrete under normal and adverse curing.

This research aims to study the possibility of corrosion of reinforcing steel in concrete structure. The concrete was designed to have different water to cement ratios. The study used half-cell potential measurements in accordance with ASTM G109-99a standard [25] and made a comparison between the uncoated and coated concrete. The coated area was considered defective to the different degrees 0, 1, 2 and 3%. These specimens were exposed to severe environment with wet-dry 5% NaCl solution.

2. Experimental program

2.1 Materials and mixture proportions

The concrete in this study comprised of ordinary Portland cement type I conforming to ASTM C150. Fine aggregate with a specific gravity of 2.476 in saturated surface dry (SSD). Coarse aggregate with specific gravity of 2.598 in saturated surface dry and a maximum size of 19 mm. The experiments were conducted to evaluate half-cell potential and corrosion current density. The mix proportion is shown in Table 1.

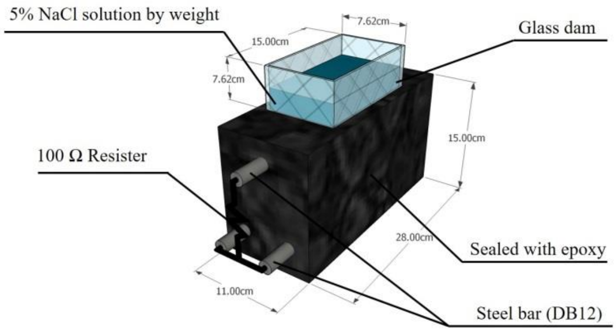
Table 1 Mix Proportion of concretes

Mix Proportion	*water to cement ratios*		
	0.45	*0.5*	*0.6*
Cement (kg/m^3)	456	410	342
Water (kg/m^3)	205	205	205
Sand (kg/m^3)	641	678	730
Gravel (kg/m^3)	964	964	964

The crystalline coating material is grey powder consisting of Portland cement, silica sand, calcium dihydroxide and chemical compounds. They are mixed with water to form a slurry and applied to the inner or outer side of the concrete structure with a brush. For brush application, the ratio between crystalline coating material and water ratio was 5:2 by bulk volume.

2.2 Specimens preparation

Cylindrical concrete specimens 150 mm in diameter and 300 mm high were cast to evaluate the compressive strength in accordance with standard ASTM C39 [26]. Concrete prism was cast with dimension 280 x 150 x 115 mm in accordance with ASTM G109-99a as shown in Figure 1. and was used for the determination of the relative corrosion protection by using macrocell corrosion measurements, in order to make a comparison between the uncoated and coated concrete. In addition the coated areas are deliberately defective of the coating. A total of concrete specimens as shown in Table 2.



(a) Schematic illustration of concrete specimen

(b) Type of concrete specimen

Figure 1 The concrete beam specimens was exposed to chloride environment

Table 2 No. of uncoated and coated concrete specimens in this study

Specimens	*Uncoated concrete*	*Coated concrete with Crystalline material*			
		Perfect coated	*Defect Coated*		
			1%	*2%*	*3%*
Concrete (w/c = 0.45)	6	6	6	6	6
Concrete (w/c = 0.50)	6	6	6	6	6
Concrete (w/c = 0.60)	6	6	6	6	6

2.3 Surface treatments

The concrete specimens are required to be in saturated surface dry condition, the surface being coated need cleaning before the application of the coating, allowing the chemistry to better diffuse into concrete. Concrete specimens were coated on the exposed surface. Apply crystalline coating with brush. The coating must be uniformly applied and should be approximately 1 mm thickness as shown in Figure 2. The coverage rate for each crystalline coating is 0.65-1.0 kg/m^2. Coated concrete specimens need to be cured for 3 days and allowed to set for18 day before exposed to severe environment as per the manufacturer's specifications.

(a) Perfect Coated

(b) Defect 1%

(c) Defect 2%

(d) Defect 3%

Figure 2 The specimens was coated on the area expose chloride environment with crystalline coating material.

2.4 Exposure chloride environment

In marine environment, the service life of reinforced concrete structures depends mainly on deterioration due to reinforcement corrosion. This study investigated the possibility of corrosion of reinforcing steel in concrete structure, which had been exposed to humidity room environment for 365 days before coated. Over the period of testing, the concrete specimens was exposed to wet-dry cycles chloride environment (5% NaCl solution by weight), wet for 2 weeks and dry for 2 week repeatedly.

3. Test Procedure

3.1 Compressive strength

Concrete cylinders with diameter of 150 mm and 300 mm in length were cast and demolded after 24 hrs. The specimens were cured for 28 days. The universal testing machine was used to test specimens at the age of 28 days. The results of concrete aged 28 days were average from 3 specimens. This test conforms to ASTM C39. After the specimens was exposed to chloride environment for 56 days. Coated and uncoated concrete underwent compressive strength test.

3.2 Half-cell potential measurements

The half-cell potential measured during the experiment refer to a standard copper/copper-sulphate (CSE) as per ASTM C876-91 [27] in Table 3. The specimens were measured on surface concrete at expose chloride environment. The results were averaged from 3 point at left, middle and right on surface that average should not exceed 10%. Concrete specimens were measured at 0, 14, 21, 28, 42, 49 and 56 days.

Table 3 Probability of corrosion according to corrosion potential as per ASTM C876

Corrosion potential (CSE)	*Corrosion activity*
> -200 mV	90% probability of no corrosion
-350 to -200 mV	Uncertain
< -350 mV	90% probability of corrosion

3.3 Current measurements

Corrosion current density, icorr ($\mu A/cm^2$) was calculated as per Equation (1) from corrosion current (μA) per exposed surface area of the reinforcing steel in 18 cm of length (cm^2), the current was evaluated by measuring voltage (mA) and resistor (Ω). Calculate the current (I_j) is calculated based on Ohm's law as per Equation (2), R from the measured voltage across the resistor and V_j from measured in volts (drop across the resister). [28] The following criteria for corrosion have been developed from field and laboratory investigations [29], [30] as shown in Table 4. The specimens were measured simultaneously with Half-cell potential was measured.

$$i_{corr} = I / A \qquad (1)$$

$$I_j = V_j / R \qquad (2)$$

Table 4 Corrosion current

Corrosion current (I_{corr})	*Condition of the rebar* [29]	*Corrosion level* [30]
I_{corr} < 0.1 $\mu A/cm^2$	Passive condition	Negligible
I_{corr} 0.1 - 0.5 $\mu A/cm^2$	Low to moderate corrosion	Low
I_{corr} 0.5 - 1.0 $\mu A/cm^2$	Moderate to high corrosion	Moderate
I_{corr} > 1.0 $\mu A/cm^2$	High corrosion rate	High

4. Results and discussions

4.1 Compressive strength

The compressive strength of concrete at the age 28 days for control concrete with w/c ratios 0.45, 0.50 and 0.60 were 414.0, 381.6 and 312.8 ksc respectively. The results show that higher w/c ratios lead to lower compressive strength.

After the experiment finished, compressive strength of uncoated and coated were tested again. The value in the uncoated concrete specimens with w/c ratios 0.45, 0.50 and 0.60 were 583.7, 562.2 and 442.2 ksc respectively. In the coated concrete with w/c ratios 0.45, 0.50 and 0.60 were 595.8, 567.7 and 444.5 ksc respectively. The results show that coated concrete with crystalline material increased compressive strength. The main hydration products of crystalline materials are C-S-H gel and $CaCO_3$. It reduces porosity and appears more effective in sealing pores or cracks. [15], [19], [24]. There is no significant disparity in both types of specimens as shown in Figure 3.

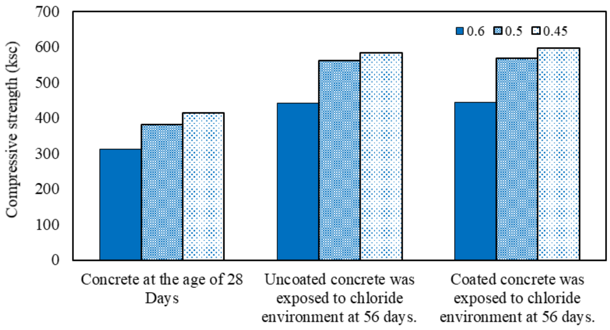


Figure 3 Compressive strength of concrete at the age of 28 days and coated and uncoated concrete after was exposed to humidity room environment for a year before investigate the possibility of steel corrosion.

4.2 Half-cell potential

The half-cell potential can serve as the most stable indicator for rebar corrosion initiation in chloride contaminated concrete [31]. The half-cell potential measures increase with increasing w/c ratios, The compressive strength resulting from w/c ratios is one of the most important and useful properties of concrete, lower strength concrete shows the greater steel corrosion than higher strength concrete as shown in Figure 4, 5 and 6. The cementitious capillary crystalline waterproofing coatings significantly delayed the onset of corrosion compared to the uncoated control samples [32]. Coated concrete with crystalline material show lesser voltage difference than uncoated concrete, meaning that crystalline material reduces probability of corrosion activity. Crystalline coating makes concrete denser because of the acicular-structured crystals which is the hydration products of crystalline filling capillary pores in the concrete [12], [13], [32]. Crystalline coating will reduce porosity and chloride permeability [12]-[16], [19]. Concerning the coated concrete, the reduction of chemical and moisture absorption can suppress the corrosion of reinforcing steel in concrete, giving rise to better long-term durability [33].

The potential measured in all specimens were resemble regardless all of the defects on coated areas because the discontinuities are too small, in contrast to coating defects on metal only a small defect significantly affect the corrosion activity [34]. The results of half-cell potential measurements indicate that there was greater than 90% probability of no corrosion in coated concrete whereas it showed greater than 90% probability of corrosion in 0.6 water to cement ratios – uncoated. However for the others mix of uncoated concrete, the corrosion activity was uncertain. Probability of corrosion as shown in table 3.

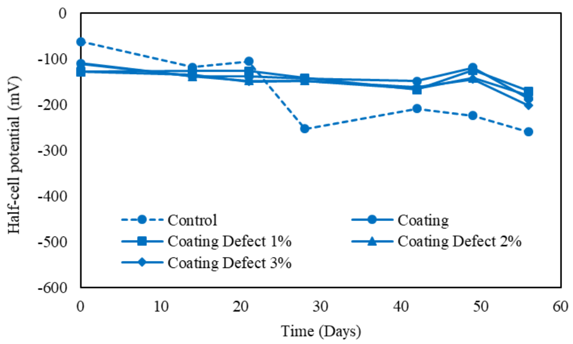


Figure 4 Half-cell potentials of reinforcing steel in uncoated and coated concrete (w/c=0.45)

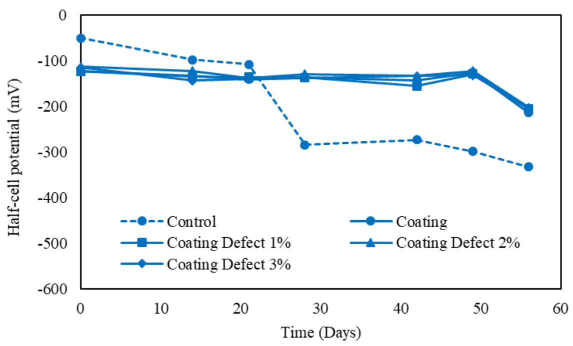


Figure 5 Half-cell potentials of reinforcing steel in uncoated and coated concrete (w/c=0.5)

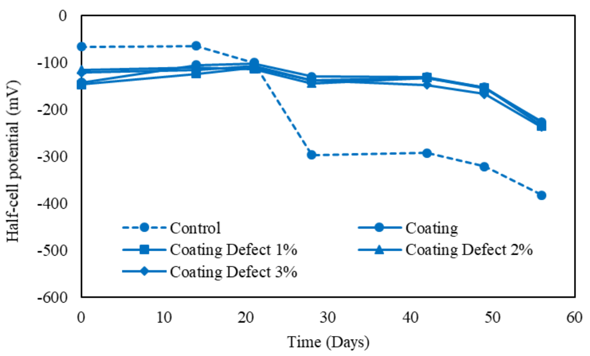


Figure 6 Half-cell potentials of reinforcing steel in uncoated and coated concrete (w/c=0.6)

4.3 Corrosion current density

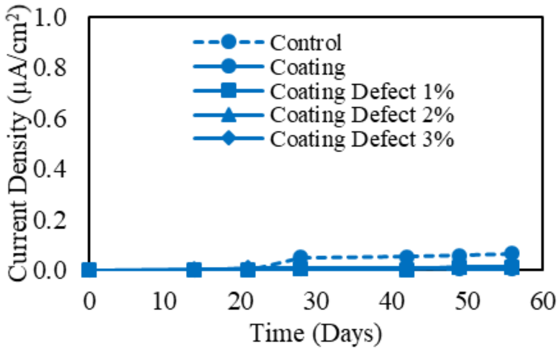
Corrosion current depends on the resistivity of concrete and chloride ions ingress into concrete. The higher the resistivity, the smaller the corrosion current. Chloride penetration in concrete structure is highly dependent on concrete quality and exposure surface condition, coated and uncoated concrete. The amount of chloride ions play an important role in corrosion rate. It's obvious that higher corrosion the activity results in higher current density. From the experiment, the results showed that concrete with water to cement ratio 0.6 showed the greater corrosion steel than water to cement ratios 0.45 and 0.50 as shown in Figure 7. Concerning the relationship between the free and total chloride diffusivity in concrete, lower water to cement ratios lead to lower chloride concentration in concrete [35]. It's known that the possibility of corrosion of reinforcing steel in concrete depends on the chloride concentration at steel surface. Coated concrete show that condition of the rebar is still in passive condition in all water to cement ratios while uncoated concrete is low to moderate corrosion in water to cement ratios 0.50 and 0.60 following in Table 4.

The corrosion current density of the reinforcing steel in coated concrete is lower than corrosion current density of those in uncoated concrete. The higher chloride content cause an increase in corrosion current density [36]. The coatings are beneficial to seal the surface against penetration of harmful oxygen, CO_2, chloride ions, sulfate ions, and water into concrete [11].

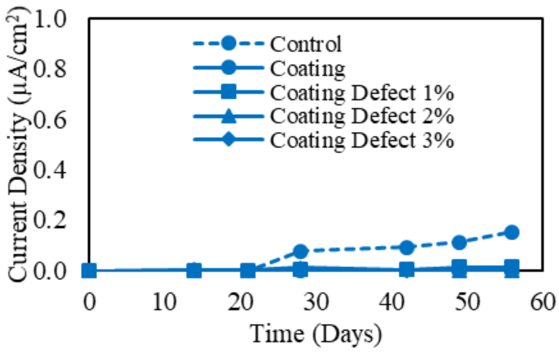
In this studied the coated concrete with crystalline material showed no corrosion in reinforced concrete under chloride environment. Because crystalline coating can reduced chloride ion concentration in concrete [15], [16], [18]. Thus crystalline coating significantly delayed the onset of corrosion and improve the service life of concrete structures under chloride environment. Because Chloride ions destroy the passive film on the steel when their concentration exceeds a critical value [37].

In the presence of aggressive environments, the use of coating must be associated with a good quality concrete [38]. Coated concrete with crystalline materials enhance the durability of concrete in terms of compressive strength, water sorptivity, water permeability, carbonation resistance, acid resistance, and chloride resistance [15]. From the experiment, Crystalline coating can reduced water permeability into concrete [12], [13], [19]. Because crystalline materials make concrete denser. From observing the specimen by scanning electron microscopy (SEM) indicates that the C-S-H gel (acicular crystals) penetrates and seals pores in concrete in the presence of moisture [12], [13], [17], [21], [23], [24], [32]. Calcium silicate hydrate (C-S-H) gel is the main hydration products of crystalline materials, found experiments Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) [12], [13].

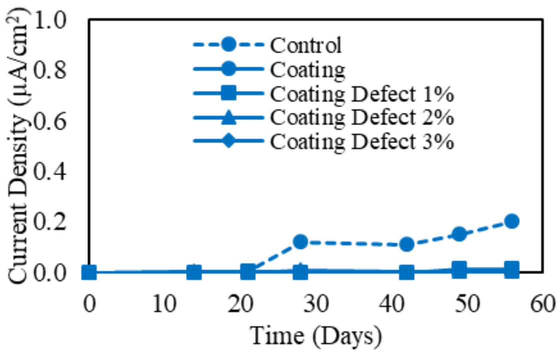
Oxygen is one of the steel corrosion process [39]. In concrete, oxygen is usually able to penetrate through the pores and micro-cracks into the steel surface [40]. The relationship between total porosity and air permeability showed that air permeability increases with increasing in total porosity of concrete [41]. Teng et al. [12] and Chen et al. [13] used the mercury intrusion porosimetry (MIP) technique to determine the volume distribution of pores in coated concrete with crystalline materials and uncoated concrete. The results showed that the values of porosity are smaller for the crystalline coating nearly 20% than uncoated concrete and crystalline coating has more effective in ability to clog capillary pores in concrete. In conclusion, Repair coating systems create a physical barrier to seal-off the surface, inhibiting ingress of CO_2, moisture and oxygen into reinforced concrete, in turn restricting the corrosion process [42].



(a) w/c=0.45



(b) w/c=0.50



(c) w/c=0.60

Figure 7 Corrosion current density of reinforcing steel in uncoated and coated concrete

5. Conclusion

From the study to investigate the possibility of corrosion of reinforcing steel in concrete structure with crystalline coating materials in different water to cement ratios, the following conclusions can be drawn.

1.Concerning about the compressive strength of concrete, lower water to cement ratios lead to higher compressive strength. Value of compressive strength in coated concrete is similar to uncoated concrete.

2.Influences of water to cement ratios, higher water to cement ratios showed the greater steel corrosion than lower water to cement.

3.Coating concrete with crystalline material resulted in retarding the corrosion process.

4.Considering the effect of defect on coated surface. The results of half-cell potential and Corrosion current density of coated concrete having a defect on coated area were resemble regardless the degree of defects on coated areas.

6. Acknowledgments

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