

BASIC STUDY ON CORROSION PROGRESSION IN HIGH NICKEL WEATHERING STEEL BY SIMULATED LIQUID TEST

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ABSTRACT

Currently, no study is published discussing the behavior of high Nickel weathering steel in concrete. The present research, therefore, will provide a baseline data about durability performance of high-Ni steel embedded in concrete. A series of steel specimens were subjected to laboratory immersion test, simulating the effect of alkalinity, oxygen, and chloride ions. The time-exponent of the famous power-function was used to compare its effectiveness with conventional steels. Results showed that the material does not produce any rust that has corrosion protective effect when used in concrete.

Keywords: Weathering steel, high Nickel steel, reinforced concrete, corrosion

1. INTRODUCTION

Weathering steel (WS) is a collective term used for an array of low-alloy steels that exhibit resistance against atmospheric corrosion by formation of highly stable oxide layer (“patina”) that develops over several years of exposure [1]. The passive layer is responsible for the attractive rusty appearance of WS structures, eliminating the need of paint maintenance, thereby reducing its life cycle cost. It is for this reason that the use of WS as structural material for many infrastructures, particularly bridges, has been gaining popularity in recent decades [2]. Conventional WS was first standardized in 1968 under JIS G 3114 SMA in Japan. It was a counterpart to the original WS commercialized by United States Steel Co. in the 1930s [3]. In 2015, WS bridges accounted for 25% of the newly constructed bridges in Japan [4]. However, under high airborne salt (more than 0.05 mg/dm²/day) that is primarily found in coastal and marine regions, conventional JIS-SMA does not form stable rust and, therefore, can no longer be used [5].

A new type of WS was introduced to Japanese market in 1997 by Nippon Steel Co., which was developed on the basis of increasing the weight percentage of Nickel (Ni) and elimination of Chromium (Cr) [4]. It is now well understood that addition of Cr contributes to denser rust layer due to its doping effects [6]. However, Cr was considered to interact with corrosive ions relatively easier than Ni [7], and accelerates the corrosion process beyond the effective limit in high airborne salt environment [8]. In the case of high Ni steel, on the other hand, Kimura et al. [9] were able to uncover the protective nature of rust due to its double-layered structure, in addition to its fine and dense grains. The inner layer is believed to possess negative surface charge due to nucleation of Fe₂NiO₄ phase at

early stage of corrosion reaction, preventing the corrosive chloride ions to come in contact with steel surface [10]. In a series of reports [5,11], the newly developed enhanced WS has been documented to provide much greater resistance under relatively high airborne salt than conventional JIS-SMA WS.

While high Ni WS has been extensively studied and used in relation to atmospheric and alternating wet and dry cycle, in the knowledge of authors, no published literature is currently available that explicitly described its implications when used in concrete environment. A well-cured concrete has very low permeability, and a very high pH due to alkaline ions from hydration products, mainly Ca(OH)₂. In this respect, the authors hypothesized that by using a highly durable reinforcement, such as Ni-type steel, the concrete pore environment may provide an ideal condition for a much more passive state. An answer to this research point is a first step in understanding the mechanism of concrete deterioration using the newly developed material. Therefore, this research aims to provide baseline data with regards to the corrosion progression of 1-wt% Ni-containing steel by conducting weight loss analysis on steel bars exposed to liquid phase that simulates concrete pore and cracked condition.

2. EXPERIMENTAL

2.1 Materials

(1) Steel bars

The chemical composition of steels used for the test is listed in Table 1. PC is the control specimen, which is an ordinary carbon steel specified in JIS G 3505. CT has relatively high Cr but low Ni content, whereas NT has high Ni with almost no Cr. Steel samples were shipped in coil shape, and stretched in a factory to form

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Table 1 Chemical composition of studied steels.

Steel type	Alloying element (% in mass)							
	C	Si	Mn	P	S	Cu	Ni	Cr
PC	0.08	0.01	0.33	0.026	0.01	-	-	-
CT	0.11	0.65	0.45	0.10	0.00	0.40	0.47	1.06
NT	0.10	0.21	0.88	0.01	0.01	0.74	1.15	0.02

Variable parameters

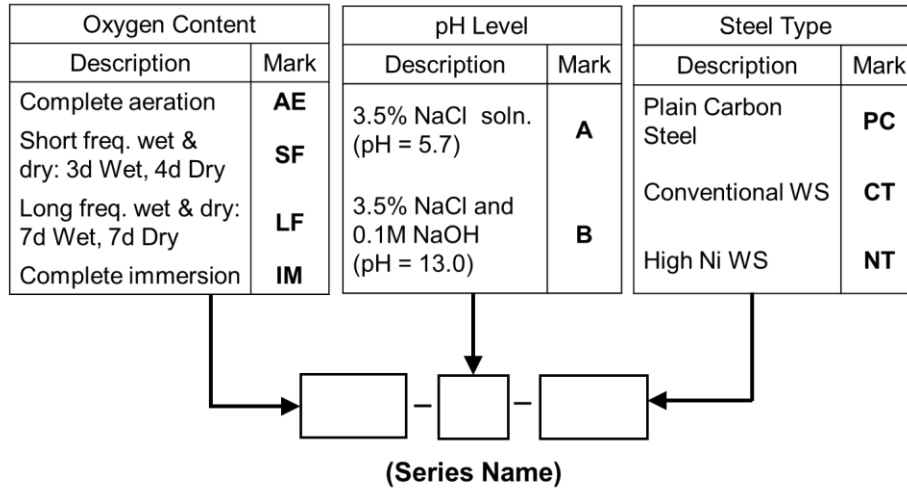


Fig.1 Parameters and corresponding symbols used in Immersion Test.

rod shape with 5 mm diameter. Samples were then cut to lengths of 50 mm and polished at ends by SiC paper No. 120 to remove the sharp edges.

(2) Simulated Solution for Immersion Test

Fig. 1 provides the experimental variables used in the study. To promote corrosion on steel samples, 3.5 wt% NaCl solution (average salinity of seawater) was initially prepared (case A). Furthermore, to investigate the effect of alkalinity of concrete in suppressing the corrosion of high-Ni WS, a solution with high pH was also prepared. This was done by dissolving NaOH in the previous saline water, enough to produce pH around 13 (case B). Both test solutions were placed in 500mL polypropylene bottles, and were replaced every 2 weeks to account for changes in alkalinity and salinity as rusting progresses. Specimens were also arranged so as not to create contact with each other during immersion. Before every replacement, pH of aqueous solutions was measured and the average value was found to be 5.72 ± 0.02 for the NaCl solution, and 13.06 ± 0.03 for the NaCl and NaOH solution.

The absence of oxygen will not induce significant corrosion, even if there is abundant water and very high Cl⁻ ions present in environment [12]. To clarify this effect in weathering steel, four levels of exposure were set based on the amount of air that will interact with steel surface, namely: continuous liquid immersion (IM), short-frequency wet and dry cycle (SF), long-frequency wet and dry (LF), and continuous aeration (AE). Aeration (AE) was facilitated by simple electronic aerator with air flow rate of about 1 L/s. For cyclic wet-dry, short-frequency (SF) consisting of 4 days wetting and 3 days drying was employed; while 7 days wetting, and 7 days drying was used for long-frequency (LF). The

exposure was carried out in a closed chamber with temperature kept at 20 °C. Fig. 1 also gives the case symbols used in the study.

2.2 Corrosion Performance

(1) Corrosion depth measurement

The specimens were retrieved for analysis after about 14, 21, 30, 60, 90, 120, 150 days. In each of these time intervals, the samples were cleaned manually, according to the procedure similar to ASTM G1 [13]. The derusting procedure involved light sanding of corrosion products in water using SiC paper No. 400. Rusts that are strongly adhering were further sanded by SiC paper No. 120. The second stage of cleaning involved immersing the samples in hot ferric ammonium citrate solution (70 to 90°C) for 20 minutes. Finally, samples were lightly scraped to remove the remaining rust layer, rinsed in acetone, and weighed. Weight loss is converted to corrosion depth using Eq. (1) [10]:

$$d = \frac{\Delta m}{\rho A_s} \tag{1}$$

where,

- d : corrosion depth (μm)
- Δm : weight loss after exposure (g)
- ρ : metal density (g/cm³)
- A_s : exposed area of the specimen (mm²)

While it is necessary to evaluate localized corrosion, this study is a basic investigation on the influence of an environment on weathering steel, and Eq. (1) was simply utilized as a corrosion index. The uneven depths, in case of localized pitting, could be alternatively resolved to an average value over the exposed area of steels. Thus, the basic equation was still used for the

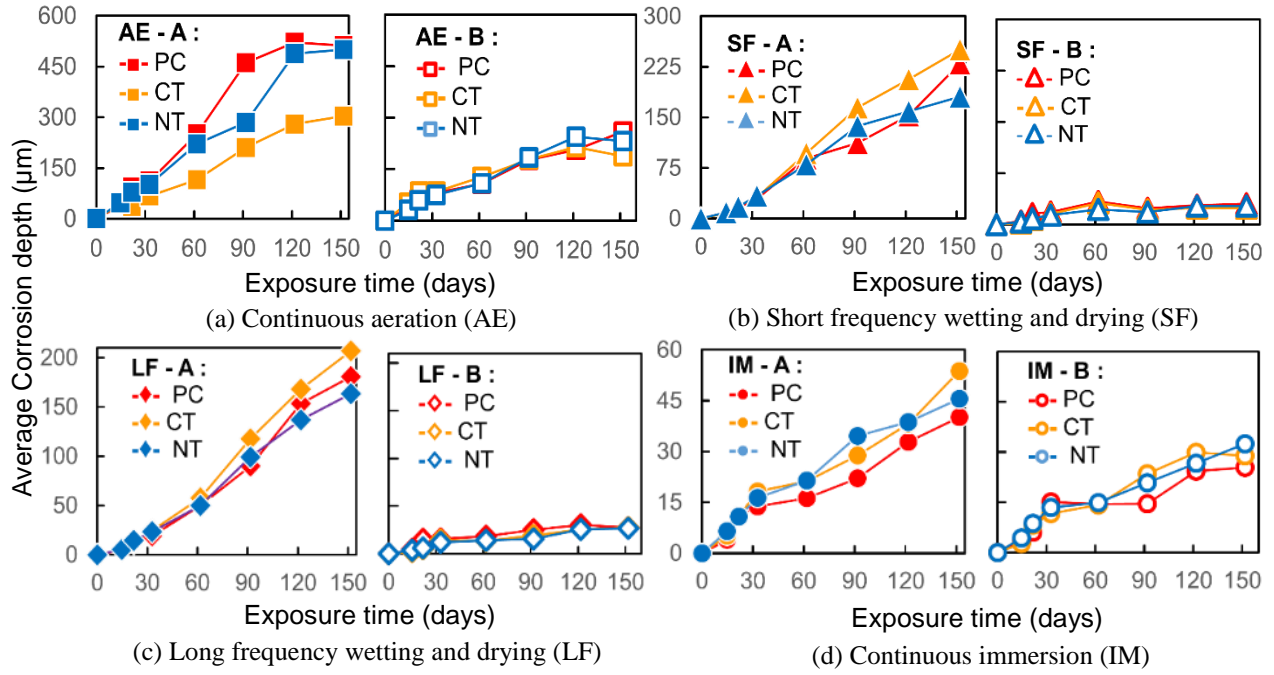


Fig.2 Variation of corrosion depth with time under highly corrosive environment of immersion test.

evaluation. In response, the density of each steel was estimated by measuring the length and mass of specimens using Vernier caliper (0.05mm precision) and analytical balance (0.001g precision), respectively. Consequently, the densities obtained were 7.68 g/cm³, 7.69 g/cm³, and 7.73 g/cm³ for PC, CT, and NT steel, respectively.

(2) Statistical Comparison

In order to establish comparison, the penetration depths were resolved to a single, time-independent parameter by making use of the power function. It is well established from laboratory and field measurements [10,14,15] that the behavior of corrosion depth in carbon and weathering steels fits with the following relationship,

$$d = At^n \quad (2)$$

where,

- d : corrosion depth (μm)
- t : time of exposure (days)
- A : initial-reactivity constant
- n : corrosion rate constant

Here, n serves as an index of diffusive property of rust layer [14], and reflects whether the corrosion products remains stable on the metal surface to act as a barrier [10,15]. Thus, a lower n under certain condition means that the corrosion layer is protective. Knowing the initial reactivity (A) of a material to a given exposure, each pair of corrosion data (t_i, d_i) yields a value n_i , unique to a particular metal and local condition [1], which should cluster around a central value given by Eq. (3):

$$n_i = (\log d_i - \log A) / \log t_i \quad (3)$$

where,

- n_i : time-exponent at i th observation
- d_i : corrosion depth at i th observation (μm)

- t_i : time at i th observation (day)
- A : fitted constant from the whole data
- i : observation number, where $i = 1, 2, \dots, 7$

Statistical comparison was carried out using Mann-Whitney U -test. This test is a non-parametric method generally used for detecting the shift in distribution of a variable (n in this case) between two unrelated populations with small sample size (< 30) and when there is no certainty that the data meets the assumption of normality [16]. The test commences by declaring a null hypothesis that there is no difference in n of NT and other types. Because we only wish to detect whether NT would reduce the corrosion parameter n (i.e. distribution of NT shifted to the left of PC and CT, or not), one-tailed test was employed. The Mann-Whitney U -statistic is obtained by ranking all n observations (1 being the lowest value) from two groups that are being compared, and applying Eq. (4) [17]:

$$U = N_1N_2 + 0.5N_1(N_1 + 1) - W \quad (4)$$

where,

- U : test statistic
- N_1 : number of observations in NT
- N_2 : number of observations in other steel types
- W : sum of ranks of observations in NT

We will reject the null hypothesis and resort to an alternative that NT significantly reduces n if Eq. (5) is true [17]:

$$U \geq N_1N_2 - U_o \quad (5)$$

where,

- U : observed test statistic
- U_o : computed statistic corresponding to the number of observations made, N_1 and N_2 , and a pre-set level of significance.

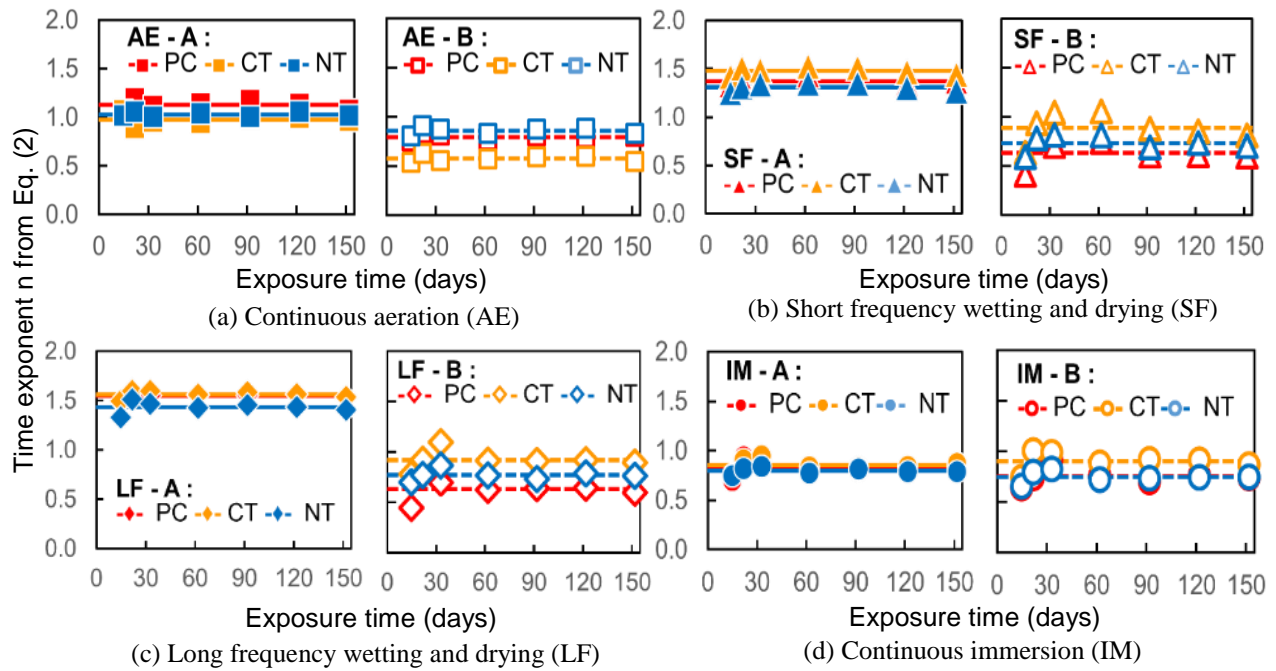


Fig.3 Plot of corrosion parameter n showing time independence.

3. TEST RESULTS

3.1 Effect of exposure

Fig. 2 shows the result of mass loss investigation on each steel type under different oxygen level and alkalinity. From these figures, it is evident that with same oxygen supply, corrosion depth is suppressed when pH of the solution is high regardless of steel type (PC, CT, or NT). The damage incurred in alkaline electrolyte was reduced, as expected, most likely due to formation of some passive and stable products made of Fe_2O_3 or Fe_3O_4 during the anodic dissolution of iron at very high pH [18]; however, the rate of growth of these oxides, and the interaction of Cl^- ions with iron near the rebar surface do not appear to be influenced by the amount of Ni or Cr in WS. Moreover, irrespective of steel type, an increase of oxygen supply increases the corrosion depth by fueling the cathodic side of electrochemical process, consistent with what is generally recognized in metallic corrosion.

3.2 Effect of steel type

(1) CT specimen

The time-exponent n computed for each treatment series is plotted with time as shown in Fig. 3. Comparing the steel types, it can be seen that while CT corroded the most at low oxygen level, its positive influence under continuously oxygenated medium (AE) is remarkable. This would seem to agree with previous studies [6], stating that Cr^{3+} in rust layer of Cr-steel combines with multiple O^{2-} to form complex CrO_x^{3-2x} anions. These ions are believed to partially substitute some positions of Fe^{3+} in fine Cr-goethite rust, making the rust crystals difficult to grow up [19]. Thus, CT was able to suppress penetration depth due to abundant availability of oxygen.

(2) NT specimen

As a result of immersion period up to 150 days, NT did not seem to change the corrosion behavior in low

oxygen and highly alkaline environment, which are typical conditions of concrete pore. The Mann-Whitney U -test is used to objectively realize this ineffectiveness. By consulting statistical tables [17] corresponding to $N_1 = 7$ and $N_2 = 7$, and significance level of 0.01, it is found that $U_o = 7$. Thus, the right-hand side of Eq. (5) is equal to 42. There is enough evidence to accept the alternative hypothesis that NT suppressed the corrosion depth (at 99% confidence level) if the U -statistic is equal or greater than this value. The result of analysis and resulting decisions made are summarized in Table 2.

It is clear based from the result that NT was able to reduce the corrosion parameter n only under two conditions, namely: acidic electrolyte, and presence of drying regimes, i.e. LF-A and SF-A series. Both conditions are in fact found in atmospheric environment. The presence of SO_2 in atmosphere normally causes the

Table 2 Summary of Mann-Whitney U-test.

Treatment	Control	U -stat	Decision
IM-A-NT	IM-A-CT	41	
	IM-A-PC	35	
IM-B-NT	IM-B-CT	46	○
	IM-B-PC	24	
LF-A-NT	LF-A-CT	48	○
	LF-A-PC	48	○
LF-B-NT	LF-B-CT	47	○
	LF-B-PC	5	
SF-A-NT	SF-A-CT	49	○
	SF-A-PC	44	○
SF-B-NT	SF-B-CT	42	○
	SF-B-PC	14	
AE-A-NT	AE-A-CT	7	
	AE-A-PC	47	○
AE-B-NT	AE-B-CT	0	
	AE-B-PC	4	

○: Significant at 99% confidence level

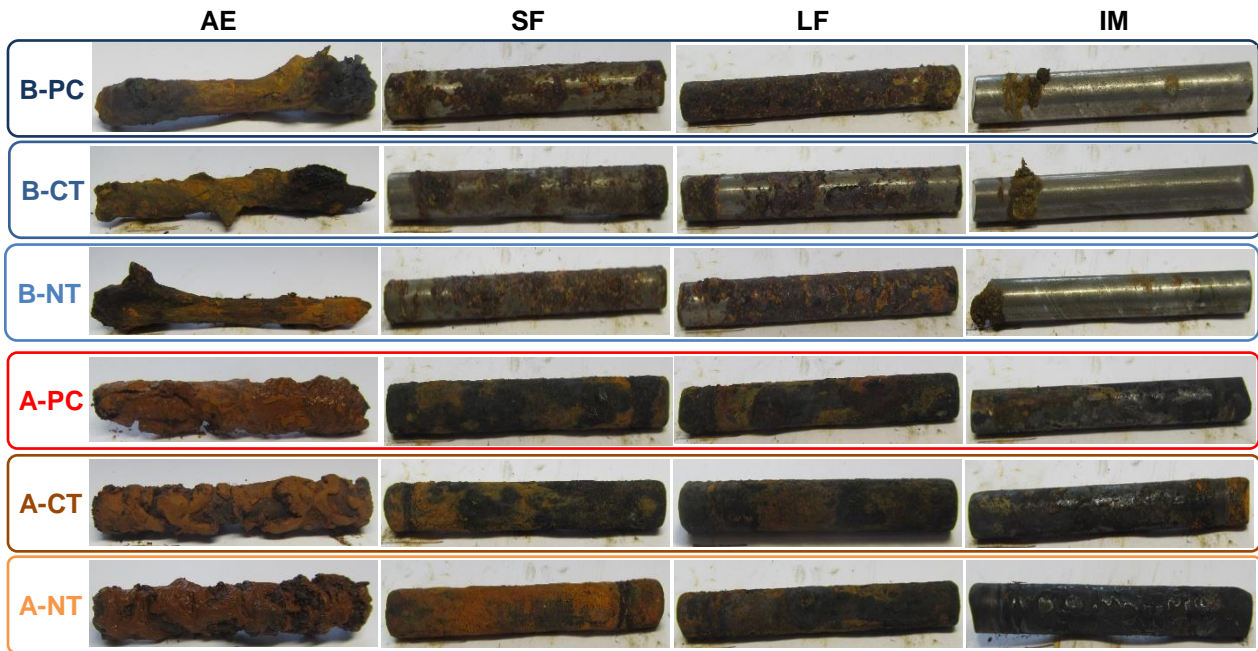


Fig.4 Macro-morphology of corroded samples after 120 days of immersion test.

ambient air to be acidic [20]. Wen et al. [10] employed cyclic immersion of Ni-alloyed steel in chlorinated and acidic solution, and observed lowering of n relative to carbon steel because the rust the developed was uniform and tightly adhering, in line with the observable rust coating captured in Fig. 4. Previous researchers were also able to establish the role of periodic drying as a prerequisite for developing the protective patina in Ni-containing WS [4,5,9,11]. The results, thus, conform to the strongly established claim about successful use of Ni-containing steel for weathering applications.

On the other hand, the statistical analysis supported that NT did not provide any beneficial reduction of n compared to other types in alkaline environment, regardless whether oxygen is depleted or not. According to Ahmad [21], the electromotive force (emf) that drives the corrosion current between microcells in reinforcing steel is given by Eq. (6),

$$e = 2.109 + 0.0148 \log [O_2] - 0.0591(\text{pH}) - 0.0296 \log [Fe^{2+}] \quad (6)$$

where,

- e : emf of reinforcement corrosion cell (V)
- $[O_2]$: molar concentration of oxygen (mol/l)
- pH : pH of concrete electrolyte
- $[Fe^{2+}]$: mass concentration of $Fe(OH)_2$ per unit volume of concrete (mol/l)

At pH range (12.5 to 13.5) and low oxygen level normal to hardened concrete, (IM-B, LF-B, and SF-B series), the amount of electromotive force would be significantly impeded. This reduction might have prevented iron atoms and alloying elements (Cr or Ni) to oxidize and mature into compact and adhering rust phases, i.e. α - $FeOOH$ [8], or Fe_3O_4 and Fe_2NiO_4 [9], normally found in protective patina. Morphology of samples after 120 days of exposure, presented in Fig. 4, shows incomplete and non-uniform corrosion products,

suggesting that this is the case. Rust layer that formed in this manner cannot be considered actual patina because they are not uniform [20]. In case of abundant oxygen (AE-B series), although the emf is high, the continuous wetting and high amount of OH^- in an alkaline solution facilitate the growth of expansive and loose rust, mainly, $Fe(OH)_2$ [12,21], instead of the desirable protective type. The presence of thick rust observed in the AE-B sample (see Fig. 4) confirms this premise, explaining why NT did not reduce the corrosion parameter n even with abundant oxygen. Further examination of Fig. 4 reveals that rusts formed in all steel types under alkaline environment (case B) are similar in terms of color and uniformity, all the more suggesting that incorporation of alloying elements barely has any effect on rust development under high pH and low oxygen.

Morcillo et al. [1] emphasized that indoor exposure does not favor the formation of adhering rust in WS due to low corrosivity of the environment. Basically, a key consideration for protective patina to form is when rust is facilitated by periodic draining of accumulated moisture on steel. In indoor exposure, the stable layer may evolve very slowly, or not at all, in which case, the difference in corrosion rate between WS and mild or carbon steel will be practically undetectable [1]. In similar manner, reinforcing steel in service is virtually concealed from outside environment by virtue of the concrete cover. Because of this, in addition to suppressing effect of alkalinity, the rate of rust promotion in actual concrete will be limited, unlike in highly corrosive media used in the study. What is more, even as the wet front of permeating moisture comes in contact with steel, the concrete cover will prevent the moisture to dry out easily, reducing the chances of forming a protective patina. The interplay of these factors would suggest that the observations made in dipping test may not change much in actual concrete. However, it should be noted that real RC structures

actually sustain fine and well distributed tensile cracks during their service life, allowing the embedded steel to undergo a slow process of wetting and drying. Moreover, while the rust that formed in liquid phase easily separate from base metal due to continuous presence of moisture, the rust in embedded steel may stabilize and remain intact on the surface of base metal due to relatively low moisture and confining effect of concrete cover. This was not accounted in the immersion test, and is, therefore, a subject of future research.

4. CONCLUSIONS

The performance of high-Ni WS in concrete environment was studied by subjecting a series of steel samples to immersion in simulated liquid phase. The corrosion depth was monitored and plotted according to the commonly used power relation. Statistical analysis of the time exponent (n) from the model revealed the following:

- (1) The weathering application of high-Ni steel was confirmed by the lowering of the corrosion rate constant (n) under acidic and cyclic wet-dry exposure.
- (2) High-Ni WS did not reduce the time-exponent under oxygen-depleted and highly alkaline environment. It was also observed that corrosion products that formed are expansive and easily separates from the steel substrate, instead of the desirable adhering rust found in atmospheric condition. These results imply that concrete environment does not have clear effect on the protective nature of the material, in contrast to what was initially thought. Previous studies complementing this work pointed that repetitive wetting and drying in the presence of oxygen is an essential prerequisite to form the protective rust.

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