Redistribution of corrosion products on steel bar/concrete interfaces in repaired concrete under influenced of aggressive ions

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Abstract. The important cases contribute to deterioration of reinforced concrete structure were due to corrosion attack to the reinforcing steel bar. Instead of penetration of aggressive ions for example chlorides, sulphates, acids and others; the selection of materials used for repair should be concern as well. Due to this factor, the understanding on the electrochemical behavior of reinforcing steel bar using different materials for repairing for deteriorated concrete structures will be considered. To understand this phenomenon, the ready-cast specimens mixed with chloride as prepared earlier will be demolished at 301 days of concrete age. Surprisingly, potential measurement of reinforcing steel bars was reoriented to a lower corrosion risk at 301 days of concrete age. The chemical and microstructural factors related to corrosion products were quantitatively identified and correlated it using electrochemical measurements results. For corroding reinforcing steel bar by fully and partially influenced of chloride ions, the corrosion products were mainly contained wuestite, magnetite and lepidocrocite confirmed by XRD patterns. Depending on morphology and multi-elemental content, it shows that chloride ion is approaching the reinforcing steel bar that lead to greater corrosion rate in Reference specimen compared to repaired ones. However, the existence of Ca(OH) in the vicinity between concrete/reinforcing steel bar helps to prevent further corrosion attacks.

Introduction

Normally, the problem of chloride attack arises when chloride ions ingress from the external side either from airborne or de-icing salts [1]–[3]. The chloride ingress could be transported through water with chlorides, and ion diffusion or absorption. As time increases, it results in greater concentration of chloride at the surface of reinforcing steel, and subsequently leads to spalling, cracking and/or delamination of concrete structure. To overcome this problem, the deteriorated part of the concrete structure can be repaired and rehabilitated by applying patch-repair method. This method is bearable to restore both appearance and integrity of a concrete structure [4], [5].

According to [4], [6], a variety of repair materials have been produced as an alternative to customary ordinary Portland cement (OPC) since the patch repair works using OPC is claimed to be
less convincing to retard corrosion attack [6], [7]. In this case, polymer modifier for instance styrene butadiene, acrylic and some vinyl copolymers; pure polymer which is epoxy resins, polyesters and some polyurethane based systems, and non-Portland cement that contains high alumina cements and magnesium phosphate based [3], [4], [6] are viable to consider as other candidate for repairing materials. Between these materials, polymer modifier mortar (PMM) has been largely accepted owing to greater resistance in corrosion and also becomes an advantageous material in the concrete experimentation [8], [9].

The present work is focused on capability of different repairing materials to slower or retard the chloride ingress at the patch repair part by referring the corrosion distribution at steel/concrete interfaces and provide a quantitative description of the corrosion products on the steel bar surface. For this goal, a deteriorated reinforced steel bar under influenced of chloride ions and repaired using two different repairing materials aged 28 to 301 days were studied in terms of electrical, chemical and microstructural analysis.

2. Experimental method

2.1. Raw materials and casting procedures

Details concrete mix design and casting procedure can be referred to [10-13]. In this study, ordinary Portland Cement (OPC) admixed with coarse aggregate and fine aggregates in size smaller than 15.0 and 5.0 mm, respectively were used as concrete material ingredients. Forty-five test specimens were cast into two conditions in divergent water to cement (w/c) ratio and types of repair materials under the influence of admixed Sodium Chloride (NaCl). Hence, concrete substrate with 0.6 of w/c ratio containing 9 kg/m³ of NaCl recognized as Reference meanwhile chloride-free repair concrete materials with w/c 0.4 designated as R-OPC and Polymer Modifier Mortar as R-PMM, separately.

2.2. Experimental procedures

2.2.1. Electrical measurements. In reinforced concrete structures, concrete represent as an electrolyte and the reinforced steel bar will develop a potential depending on the concrete environment that might differ from one place to another. Therefore, procedure in American Standard Testing Materials (ASTM) C876 [14] for performing Half-cell potential (HCP) of reinforcing steel bar was implemented for routine inspection of reinforced concrete specimens. The value was expressed in relation to silver/silver chloride (Ag/AgCl) reference electrode and Table 1 was used to interpret the HCP result. This measurement was conducted for the whole concrete specimens from concrete depth ratio between 0.2 and 1.0.

| Corrosion risks (possibility) | Potential, $E_{corr}$ (versus Ag/AgCl) | Potential, $E_{corr}$ (versus Cu/CuSO₄) |
|-------------------------------|----------------------------------------|----------------------------------------|
| Severe                        | $E_{corr} < -404$ mV                   | $E_{corr} < -500$ mV                   |
| High (90 %)                   | -404 mV $\leq E_{corr} \leq -254$ mV  | -500 mV $\leq E_{corr} \leq -350$ mV  |
| Medium (50 %)                 | -254 mV $\leq E_{corr} \leq -104$ mV  | -350 mV $\leq E_{corr} \leq -200$ mV  |
| Low (10 %)                    | $> -104$ mV                           | $> -200$ mV                           |

2.2.2. Microstructural analysis. As presented in Figure 1, the test specimen was divided into five sections according to 1:76 mm ratio. The interesting area discovered at third section was selected and cut into a size of about 20x20 mm. Then, the specimens required metallurgical sample preparation consist of sectioning, mounting in epoxy materials, grinding and followed by polishing. To avoid misinterpretation of the features of interest, the test specimens were polished until they emerged a mirror-like surface. The SEM analysis using backscattered electron (BSE) detector was distinguished at 130X magnification correlating to a 0.185 μm per pixel resolution with aid of energy dispersive
spectrometer (EDS) and elemental mapping to discover the elemental exploration of the test specimens.

![Diagram of specimen cutting section and sample preparation](image)

**Figure 1.** Schematic diagram for sample preparation for SEM observation.

To analyse the corrosion products appears on the reinforcing steel bar, the X-ray Diffraction (XRD) were employed for quantitative characterization of corrosion products. Firstly, all the rust appeared on the reinforcement were collected and followed by pulverization into fine particles before compacted and placed on a glass holder. Rigaku X-ray Diffractor was used with a Copper X-ray target under condition of 40 kV and 100 mA. The data of the experiment was collected over a 2-theta between 5 and 90° with a wavelength 1.5406 of K-alpha with a speed of 1°/min. The results obtained were analyses using Rigaku software.

3. Results and discussion

3.1. *Estimation time of corrosion initiation*

After completed 301 days chloride induced in the test specimen, visual inspection for the external appearance of the concrete specimens was investigated. Based on the observation, test specimens show the condition of breakdown in protective layer of the reinforcing steel bar that lead to the initiation of corrosion attack. The cracks obviously visible with differ crack length ranging 0.10 to 0.35 mm on top face of the Reference specimen. Nonetheless, only corrosion marks were appeared for both repaired specimens at the substrate part. To identify further the causes that influenced the physical changes of test specimens, reinforced concrete specimens were carefully destroyed with aid of compression machine. The concrete residual attached on the reinforcing steel bar were cleaned using brush without destroyed the corrosion constituent on its surface. As presented in Table 2, the condition of reinforcing steel bars before and after cleaning process for all test specimens were severely corroded with pitting corrosion at the substrate part as forecasted since it contained NaCl that purposely admixed into concrete composition to expedite the corrosion activity. Surprisingly, the reinforcing steel bar at the repair part for both repaired test specimens were virtually insignificant of corrosion attack. Nevertheless, a notable whitish color product identified as ferrite and calcium hydroxide was distinguishable on reinforcing steel bar surface of R-PMM test specimen.

In chloride environments, the passive layer breakdown during corrosion initiation is caused by considerable chloride amount in the region of reinforcement surface. Therefore, the determination of
corrosion initiation against time can be determined by considering the half-cell potential readings for reinforcing steel bar embedded in concrete materials. Consequently, the determination of chloride thresholds by applying potential mappings is preferable. In some extent, the potential readings can be significantly affected by the environmental conditions, bulk materials resistivity besides degree of pore network saturation, the qualitative information for the electrochemical behaviour of the reinforcing steel bar in that system. Hence, corrosion potential readings were used in the existing study as supportive information.

Table 2. Crack pattern, corrosion stains and samples of corroded steel bar after demolished. The ‘S’ and ‘R’ denoted as substrate and repaired concrete.

| Test specimen | Reference | R-0.4OPC | R-PMM |
|---------------|-----------|----------|-------|
| Before cleaning | ![Image](reference_before_cleaning.png) | ![Image](0.4OPC_before_cleaning.png) | ![Image](PMM_before_cleaning.png) |
| After cleaning | ![Image](reference_after_cleaning.png) | ![Image](0.4OPC_after_cleaning.png) | ![Image](PMM_after_cleaning.png) |
| Corrosion weight loss (%) | 3.91 | 3.46 | 3.42 |

In different concrete age starting at 28 to 301 days with continuous exposure of NaCl to the reinforced concrete specimens, the presence of corrosion activity in each reinforcing steel bar was weekly monitored using non-destructive technique known as Half-cell potential (HCP). The trend of corrosion activity development at the steel bar reinforcement in the test specimen denoted as $E_{corr}$ taken around the perimeter of test specimen can be viewed in Figures 2(a)-(c). As depicted in the figures, the HCP of reinforcing steel bars were tended to become less negative potential corresponding with their level of corrosion risk possibility with time. However, during 301-day of inspection, the reinforcing steel bars exhibited a drastic changed in potential readings. It was noticed, the HCP values for reinforcement in Reference specimen was designated ranging -0.4 to -0.1 V vs. Ag/AgCl that reassessed the corrosion possibility risk from 90 to 50%. For R-0.4OPC specimen, the potential readings for R-0.4OPC specimen was recorded as low as 0.0 V vs. Ag/AgCl meanwhile R-PMM specimen was obtained between -0.37 and -0.05 V vs. Ag/AgCl. Contradict to repaired specimens, their corrosion activity was reduced from 90 to 10 %.
Figure 2. The behavior of potential-time for reinforcement at different concrete depth with respect to concrete age for (a) Reference, (b) R-0.4OPC and (c) R-PMM specimens.
Figure 3. The EDS multi-elemental map and BSE image of the cross-section reinforced concrete at 130X magnification
The most striking result to emerge from the reorientation of HCP results is the formation of green rust [11] identified as iron hydroxide into a stable compound reveals as wuestite (FeO), magnetite (Fe₃O₄) and lepidocrocite (γ-FeOOH) relevant to XRD analysis. Furthermore, strong evidence on the existence of stable compound was visualized when conducting a microstructural analysis around the perimeter of a corroded steel bar. As depicted in Figure 3, three boundaries of steel bar corrosion were clearly seen for specimens made of OPC instead of PMM namely millscale, corrosion layer and steel bar. As clarified by [12], the millscale itself was firstly developed on the steel bar before being used in the concrete specimens and it consists of primarily of Fe₃O₄ meanwhile the corrosion layer was the compound of wuestite. As presented in Table 3, it provides the average thickness for millscale and corrosion layer on the steel bar for each specimen studied. In general, corrosion layer contains greater amount compared to millscale. Nonetheless, no data was detected on corrosion layer for R-PMM specimen.

Figures 3(a)-(c) provide a typical BSE image cross-section of the test specimens analysed at 130X magnification using SEM. By combining EDS analysis, the 2D elemental mapping provided chemical composition and their related elements namely Sodium (Na), Chloride (Cl), Iron (Fe), Calcium (Ca) and Silicon (Si) in the vicinity of reinforced concrete that lead to corrosion activity in the reinforcement test specimens. In addition, the brightness of the image represents concentration of multi-elements involved. In the figures, Reference specimen distinguished greater concentration NaCl disclose the arrival of chloride ions at the reinforcement compared to repaired ones. Meanwhile, the appearance of calcium hydroxide, Ca(OH)₂ according to Ca mapping shows that the test specimens still intact to inhibit the reinforcing steel bar from further corrosion attacks.

4. Conclusion
Within a limited scope of investigations, the following summaries can be drawn:
- Corrosion activity of the reinforcing steel bar for all test specimens were changed from severe to low corrosion risk possibility during 301-day of concrete age with existence of FeO and Fe₃O₄ as a stable compound.
- The performance of test specimens can be correlated with evidence of chloride and Ca ions concentrations using BSE image and EDS elemental mapping.
- Good quality of OPC with lower W/C ratio and new introduced materials (PMM) as repairing materials implies successful delayed of corrosion attack.

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