Study of corrosion products induced under different environmental conditions

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Abstract. Corrosion in reinforced concrete structures is mainly governed by materials properties as well as environmental conditions. In this paper, the rust products produced under two different environmental conditions were investigated. In the first group of specimens, corrosion was induced by conducting wetting and drying cycles for about two years, whilst the other group was artificially corroded by impressed a voltage technique. Composition analysis of corrosion products assembled on steel reinforcement was carried out using X-ray diffraction (XRD), while the main elements existed in corrosion were identified via Energy-dispersive X-ray spectroscopy (EDX). The morphological characterization of tested corrosion was analysed by scanning electron microscopy (SEM). The results obtained from XRD and SEM at the same level of corrosion showed that lepidocrocite, goethite and magnetite were observed under both types of conditions, whilst akaganeite was only identified under exposure to natural conditions.

Key words: Corrosion Products; Impressed Voltage; Wetting and Drying; Mass Loss Method.

1. Introduction
Corrosion in reinforced concrete structures is a very slow process under natural conditions, which might last tens of years to reach the needed damage. Steel reinforcement embedded in concrete is generally protected from rust via a thin passive layer formed around reinforcement due to the high alkalinity of concrete [1]. Several investigations have been performed regarding the nature of this stable layer. For example, it is stated that Fe3O4 and Fe 2O3 are the major source of passivity of this layer [2], whilst in another study [3] gamma ferric oxyhydroxide was suggested as the main reason for the stability of such layer. The breakdown of such layer mostly occurs either by the reduction in concrete alkalinity or by the high concentration of chloride ions [4]. Reinforced concrete structures that frequently exposed to severe environmental conditions such as water contaminated by chloride, rain and snow are more prone to corrosion attack [5-9]. Some of such exposure occur periodically in natural conditions (e.g. wetting and drying cycles due to ocean waves). Wet and dry cycles can highly facilitate the progress of corrosion by...
helping the penetration of aggressive ions in concrete [10]. The penetration rate of chloride ions is highly dependent on the period of wetting and drying periods. During wetting stage, chloride ions penetrate concrete under the process of diffusion, whilst the evaporation of water during drying stage helps precipitating chloride ions inside concrete. Then, the next wet cycle might cause dissolving the precipitated chloride ions and ingress them into concrete up to reaching the surface of reinforcement. The process of corrosion initiates when the accumulated chloride ions at the surface of reinforcement exceeds a certain level (threshold value) [11].

Due to the limitation of time for conducting the experimental investigations, various methods have been applied to accelerate corrosion in a short time period since no standard procedures for accelerating corrosion in reinforced concrete are reported. A very common method used to accelerate corrosion is wet-dry cycle method due to its similarity with that occurs in nature. Artificially, impressed current/voltage is the most common method performed to induce corrosion during scientific investigations [12, 13], since the level of corrosion and the needed testing time for accelerating corrosion can be easily controlled by modifying either the applied current or voltage. Current density in natural corrosion typically ranges between 0.1 and 10 mA/cm², and it might reach 100 mA/cm², where cracked concretes submerged in seawater [14]. In the impressed current/voltage technique, great varying levels of current density have been stated in the literature, ranging between 45 and 10400 mA/cm², however, between current density between 200 and 3000 mA/cm² is typically used to speed up the laboratory test [15, 16]. The influence of such differences on the performance of RC members is still not fully understood. Chlorides are mostly used to speed up laboratory tests by providing electrical contact between the cathode and the anode with a level of concentration ranges between 3-5% to simulate the concentration of salt in seawater (almost 3.5%) [17].

The formation of rust products on reinforcing steel is dependent on different factors (e.g. exposure periods and environmental conditions). Several investigations explained the formation of rust products during oxo-hydroxide phases, namely Goethite (α-FeOOH), Maghemite hydrate (γ-Fe₂O₃ × H₂O), Lepidocrocite (γ-FeOOH), Hhematite (Fe₂O₃) and Magnetite (Fe₃O₄) and as shown in Figure 1 [18, 19]. Although studying these products seems are extremely complex, Epidocrocite and Goethite might be easily observed during the formation of corrosion products [20].

![Figure 1. Relative volumes of rust products [18].](image-url)
The aim of the current investigation is to study the corrosion products (rustiness) in reinforced concrete after exposure to two different environmental conditions. Whilst the first group of specimens was exposed to wetting-drying cycles for about two years, the other group was artificially corroded by impressed voltage technique. For comparative purposes, the rust products were only compared at a similar level of corrosion (approximately 5% mass loss). Composition analysis of corrosion products produced on reinforcement was carried out using X-ray powder diffraction method (XRD), while the main elements existed in corrosion products were determined by Energy-dispersive X-ray spectroscopy (EDX). The morphological characterization resulted from corrosion attack was determined using scanning electron microscopy method (SEM).

2. Experimental programme

2.1 Materials and mixture proportions
All tested specimens were prepared from the same concrete mixture (w/b=0.4) having Portland cement (CEM I/A-LL 52.5R). Natural stone having a maximum size of 20 mm and sand were utilized as coarse and fine aggregates, respectively. Both types of aggregate had a specific gravity about 2.60, whilst the water absorption was reported 2.6% and 1.6%, respectively. The concrete mixture proportions are demonstrated in Table 1. One deformed steel bar with a diameter of 12 mm was used in this investigation, conforming the requirements of BS 4449, 2005 [21]. After casting, samples were left 24h at room temperature before being de-moulded. Afterwards, all specimens were coated by plastic sheets for 28 days.

| w/c | Materials (Kg/m³) | Compressive strength (MPa) |
|-----|-------------------|---------------------------|
| 0.4 | NA 1180 FA 664 Cement 450 Water 180 | 47 |

2.2 Accelerated corrosion specimen
All specimens were made with the same concrete dimensions (200mm×200mm×200mm) containing one deformed steel bar (12mm), centrally embedded in the cubes as shown in Figure 2. The reinforcement was carefully placed in the center of each specimen to assure all directions can obtain the same cover. About 166 mm was selected to be exposed to corrosion, whilst the remaining length was wrapped by a PVC pipe in order to assure this part uncorroded. The higher part of reinforcing steel was 310mm from the top of concrete, whilst the lower part of steel was isolated in order to protect samples from being exposed directly to corrosion.
2.3 Methods of inducing steel corrosion in concrete
The periodic wet-dry cycle exposure was performed by immersing specimens in a solution containing 3.5% NaCl for two days and dried for five days for each cycle. The same scenario was repeated for two years. The impressed voltage corrosion set up is composed of a plastic tank filled up to about 90% of its volume by electrolytic solution (3.5% NaCl solution) to imitate the concentration of chloride available in seawater, a DC power supply and a stainless steel bar placed in the tank. The specimens were set inside the plastic tank filled by NaCl solution, and connected in parallel with a DC power supply to be as anode, while a bar of stainless steel was positioned inside the used tank, acting as cathode as exhibited in Figure 3.

![Figure 3. Accelerated corrosion technique.](image)

2.4 Measurement of corrosion rate
The rate of steel corrosion in the current work was determined by mass loss method. Measuring mass loss is the most used method in the literature, since the average mass loss would be easier to be calculated in practical applications, compared to other available methods. The mass loss can be simply described as the ratio between the mass loss occurred due to corrosion to the original mass of reinforcement (un-corroded) as shown in Eq.1

\[
\eta = \frac{(m_1 - m_2)}{g_0 \cdot l_d} \cdot 100
\]

where \( \eta \) is the rate of corrosion in reinforcing steel, \( m_1 \) and \( m_2 \) are the mass of reinforcement before and after the occurrence of corrosion, respectively, \( g_0 \) is the mass of reinforcement per the unit of length and \( l_d \) is the corroded length.

2.5 Analytical techniques
Composition analysis of corrosion products formed around steel reinforcement was performed via X-ray powder diffraction (XRD), using a scan rate of 8° /min, whilst the intensity of scan ranged between 10° and 80° with a step size of 0.03°. The main elements existed in corrosion rust were determined by means of Energy-dispersive X-ray spectroscopy (EDX). The morphological characterization of corrosion was analysed using scanning electron microscopy. It should be noted that in order to conductive the diagnosed specimens in SEM images, their surface were being coated using gold atoms [22].
3. Results and discussions

From the visual observations, it can be noted that at the same corrosion level, there is no clear difference between rust products formed due to wet-dry cycles and that artificially produced by impressed voltage as shown in Figure 4. Further, it can be seen that the rust with an orange colour (which mostly represents Lepidocrocite) seems more pronounced around the surface of samples subjected to wet-dry conditions, whereas blackish rust was slightly more distributed along the vicinity of steel embedment subjected to impressed voltage.

![Visual appearance of corroded specimens induced by: (a) Wet-dry cycle, (b) Impressed voltage.](image)

**Figure 4.** Visual appearance of corroded specimens induced by: (a) Wet-dry cycle, (b) Impressed voltage.

3.1 Energy-dispersive X-ray spectroscopy

EDX analysis was performed is several parts of each sample, whilst only the representative findings are exhibited in this section. The findings obtained from EDX conducted on corrosion products are shown in Figure 5. As it can be observed that Iron (Fe) and Oxygen (O) are the main elements found in rust induced under wetting and drying cycles, followed by Sodium and Chloride, and fewer quantities of Silicon, Calcium, Potassium and Manganese. The presence of Fe and O are the main elements found in hydrated iron (the fundamental component exists in rust) with a total ratio of 78.55 wt. %, which in turn transforms into the rust products such as Magnetite (Fe₃O₄), Goethite (α–FeOOH) and Lepidocrocite (γ–FeOOH). The existence of Cl and Na confirms that corrosion is mainly induced due to the penetration of NaCl, occupying about 17.32% of the total ratio of rust elements as shown in Table 2. Similar observations were stated with the rust induced by impressed voltage technique. However, the quantities of Fe and O were observed slightly higher, whilst the amounts of Chloride and Sodium ions were reduced to 33 wt. % and 30 wt. %, respectively, indicating that due to the fast movement of chloride ions during the artificial process of corrosion lower concentrations of Chloride ions are needed for destroying the passive film around steel, and initiating the formation of rust products.
3.2 X-ray Diffraction (XRD)

The rustiness was powdered and sieved to a particle size smaller than 125 μm. The compositions of rust products due to wet-dry and artificial conditions were identified using X-ray powder diffraction (XRD). The angular scanning was measured between 10° and 80° in the 2 theta with a step scan of 0.03° as presented in Figures 5 and 6. It must be noted that the corrosion products can be found either in crystalline forms or amorphous structures [23]. Under wet-dry conditions, it can be noted that Lepidocrocite and Goethite are identified as the main products, followed by Akaganeite, in addition to the presence of Hematite and Magnetite in minor concentrations. The existence of Lepidocrocite and Akaganeite is related to the presence of the high amount of chloride ions in the rust [24]. Similarly, the XRD pattern for rust products that prepared artificially exhibited Lepidocrocite and Goethite are the main phases as shown in Fig. 7. However, the presence of Lepidocrocite seems more pronounced, whereas the appearance of Akaganeite is obviously reduced compared to that induced under wet-dry cycles. Another observation is the disappearance of Hematite under the acceleration test, while it was recognized under wet-dry cycles. This can be explained by the frequent dehydration occurred after absorbing water during wet-dry cycles,
whilst the same situation cannot be found under impressed voltage [25]. According to the literature, it can be generally said that when reinforcement is attacked by chloride ions, the initial corrosion product is Lepidocrocite, which dehydrates and gradually transforms into different products such as Goethite and Hematite ($\alpha$–Fe2O3), whilst Magnetite can be considered as the final phase of iron oxide, especially under aggressive environments where the process of oxidation is being faster [26]. With the diffusion of water and oxygen, new lepidocrocite ($\gamma$–FeOOH) can be regenerated [27]. It is also should be noted that products such as Maghemite ($\gamma$–Fe2O3) have not been recognized through XRD analysis with both types of samples.

**Figure 6.** XRD pattern of corrosion products under wet-dry conditions.

**Figure 7.** XRD pattern of corrosion products under impressed voltage conditions.
3.3 Scanning Electron Microscopy (SEM)

The micrographs obtained from samples exposed to wetting-drying cycles and accelerated corrosion are presented in Figures 8 and 9, respectively. The morphology of rust products formed under wet-dry conditions exhibited the presence of sandy and flowery crystals in different locations, indicating the existence of Lepidocrocite [28] as shown in Figure 8 (a). The appearance of flaky dark areas surrounded in several areas corresponds to Magnetite as illustrated in Figure 8 (b), whilst semi-crystalline cotton-ball structures observed in some locations is likely indicating Goethite as demonstrated in Figure 8 (c). The morphologies of rust products formed under acceleration tests showed almost similar observations with those found under wet-dry conditions, since Lepidocrocite (granular and flowery products) and Goethite (needle-like form) are spotted the main structures observed in the tested samples (Figure 9 (a) & (b)). However, the existence of Magnetite in the form of flat and dark areas was less pronounced compared to rust products induced under wet-dry as shown in Figure 9 (c), while the Hematite and Akaganeite were not recognized by SEM images with both types of corrosion.

![Figure 8. SEM of the corrosion products under impressed voltage conditions.](image-url)
4. Conclusions
In the current paper, investigations on the products of corrosion produced on the surface of reinforcing steel embedded in concrete under two different environmental conditions were performed. The results obtained in this investigation are compared based on the same corrosion level. The following conclusions can be drawn:

- No clear visual differences were observed between rust products formed due to wet-dry cycles and that artificially produced by impressed voltage.
- Even though the main elements found in hydrated iron were mounted in both tested conditions, EDX results exhibited that less concentrations of Chloride ions were needed ions during the artificial process of corrosion to destroy the passive film around steel bars, and initiating the formation of rust products.
- The main rust products detected under the environmental studied were goethite, lepidocrocite, and magnetite.
- Some differences between steel corrosion products produced under the environments studied were observed through XRD tests. The presence of Lepidocrocite seems more pronounced, whereas the appearance of Akaganeite is obviously reduced compared to that induced under wet-dry cycles.
Overall, the impressed voltage test reasonably exhibited a similar trend with that obtained by the wetting drying test. Therefore, the impressed voltage test might be considered as a reliable technique for comparing corrosion activates.

Acknowledgements
The authors would like to thank the department of Science Life in Bradford University for providing the opportunity to carry out the tests required, particularly Mr. Stuart Fox for his helpful advice and support during the experimental investigation.

5. References
[1] Alhawat M, Ashour A and El-Khoja A 2020 Properties of concrete incorporating different nano silica particles Materials Research Innovations 24(30)133-44
[2] Hansson C M 1984 Comments on electrochemical measurements of the rate of corrosion of steel in concrete Cement and concrete research 14(4) 574-584
[3] Mehta P K and Monteiro P J M 1993 Concrete, microstructure, properties and materials Westerville: JP Skalny 113-155
[4] Ahmad S 2003 Reinforcement corrosion in concrete structures, its monitoring and service life prediction—a review Cement and concrete composites 25(4-5) 459-471
[5] Alhawat M and Ashour A 2019 Bond strength between corroded steel reinforcement and recycled aggregate concrete Structures 19 369-85
[6] Zinkaah O H, Ashour A and Sheehan T 2019 Experimental tests of two-span continuous concrete deep beams reinforced with GFRP bars and strut-and-tie method evaluation Composite Structures 216 112-126
[7] Zinkaah, O H and Ashour A 2019 Load capacity predictions of continuous concrete deep beams reinforced with GFRP bars Structures 19:449-462
[8] Zinkaah, O H, Ashour A and Sheehan T 2017 Assessment of strut and tie method for the prediction of shear strength of simply supported concrete deep beams reinforced with FRP bars Advanced Composites in Construction, ACIC2017 September 5-7, 2017, Sheffield, UK
[9] Zinkaah, O H, Ashour A and Sheehan T 2019 2D finite element analysis of GFRP reinforced concrete continuous deep beams with bond modeling Advanced Composites in Construction, ACIC2019 September 3-5, 2019, Birmingham, UK
[10] Cheewaket T, Jaturapitakkul C and Chalee W 2014 Concrete durability presented by acceptable chloride level and chloride diffusion coefficient in concrete: 10-year results in marine site Materials and structures 47(9) 1501-11
[11] Arya C, Vassie P and Bioubakhsh S 2014 Modelling chloride penetration in concrete subjected to cyclic wetting and drying Magazine of concrete research 66(7) 364-376
[12] Cairns J, Du Y and Law D 2008 Structural performance of corrosion-damaged concrete beams Magazine of Concrete Research 60(5) 359-70.
[13] Alhawat M, Khan A and Ashour A 2020 Evaluation of steel corrosion in concrete structures using impact-echo method Advanced Materials Research 1158 147-64

[14] Andrade C and Alonso C 2001 On-site measurements of corrosion rate of reinforcements Construction and building materials 15(2-3) 141-5

[15] Mangat P S and Elgarf M S 1999 Strength and serviceability of repaired reinforced concrete beams undergoing reinforcement corrosion Magazine of concrete research 51(2) 97-112

[16] El Maaddawy T A and Soudki K A 2003 Effectiveness of impressed current technique to simulate corrosion of steel reinforcement in concrete Journal of materials in civil engineering 15(1) 41-7

[17] Alhawat M and Ashour A 2020 Bond strength between corroded steel and recycled aggregate concrete incorporating nano silica Construction and Building Materials 237 117441

[18] Oluwadare G O and Agbaje O 2007 Corrosion of steels in steel reinforced concrete in cassava juice JApSc 7(17) 2474-9

[19] Marcotte T D and Hansson C M 2007 Corrosion products that form on steel within cement paste Materials and structures 40(3) 325-40

[20] Nakayama T, Ishikawa T and Konno, T J 2005 Structure of titanium-doped goethite rust Corrosion science 47(10) 2521-30

[21] BS 4449 2005 British Standard Institution-Carbon steel bars for the reinforcement of concrete—Weldable reinforcing steel—Bar, coil and decoiled product—Specification

[22] Alhawat M, Ashour A and El-Khoja A 2019 Influence of using different surface areas of nano silica on concrete properties AIP Conference Proceedings 2146(1) AIP Publishing LLC

[23] Azad, Abul K., Shamsad Ahmad, and Syed A. Azher. "Residual strength of corrosion-damaged reinforced concrete beams." ACI materials journal 104.1 (2007): 40.

[24] Kui X, Chaofang D, Jiuling L, Xiaogang L and Dan W 2007 Research on atmospheric galvanic corrosion evaluation of magnesium alloy Corrosion science 50(4) 1080-98

[25] Momber A 2012 Colour-based assessment of atmospheric corrosion products, namely of flash rust, on steel Materials and Corrosion 63(4) 333-42

[26] Antunes R A, Costa I and DeFaria D L A 2003 Characterization of corrosion products formed on steels in the first months of atmospheric exposure Materials Research 6(3) 403-8

[27] Vera R, Delgado D and Rosales B M 2008 Effect of unusually elevated SO2 atmospheric content on the corrosion of high power electrical conductors—Part 3. Pure copper Corrosion science 50(4) 1080-98

[28] Antunes R A, Ichikawa R U, Martinez L G and Costa I 2014 Characterization of corrosion products on carbon steel exposed to natural weathering and to accelerated corrosion tests International Journal of Corrosion