CRYSTALLOGRAPHY STUDY OF REINFORCING STEELS IN SIMULATED CONCRETE PORE SOLUTION

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Abstract

Constituents elements are strongly influence the corrosion rate of metals and materials. The chemistry of reinforcing steels controls the corrosion rate. The studies performed in many countries have indicated that corrosion rate is strongly influenced by the constituent elements. The role of constituent elements on corrosion rate of different type of reinforcing steels exposed in different SPS solution. In this paper we are reporting the corrosion behavior of two types of steels namely S and T were exposed in SPS solution. The corrosion rates of steels are observed to increase with passage of time. T is exhibited higher corrosion rate than S. This is attributed to the formation of non-porous and protective oxide layers on S. The results are confirmed by Raman spectroscopy and XRD studies. To understand the causes and establish the mechanism, laboratory studies on exposed samples have been performed. Raman spectroscopy and XRD studies have been carried out to understand the mechanism of deterioration of different grade of steels.

Keywords:

Reinforcing Steel; Raman spectroscopy; XRD; SPS solution

I. Introduction

Reinforced Steel is a very important material for construction of building, bridge, road and so many things. Steels are using because of its durability, strength and long life. Steels are the main constituent of the earth by which any country economy maintains. When steels are exposed in any environment firstly it forms iron oxide on the surface. Formation of oxide layer is depending upon type of oxides [1-3]. During the atmospheric corrosion of steels different types of oxide are formed on the surface i.e. lepidocrocide (γ-FeOOH), goethite (α-FeOOH), akaganeite (β-FeOOH) and feroxyhite (δ-FeOOH) [4, 5]. The nature of oxide is depending upon chemistry and atmospheric constituents. When steels are exposed in concrete environment it forms protective layer on the surface which contain adherent and non-porous oxides are called passive layer. Corrosion is not occurring in concrete environment because of formation of passive layers. This passive layers are mainly contain goethite (α-FeOOH) and maghemite (γ-Fe$_2$O$_3$) on the surface [3,6].Our objective is to perform this study because when steels are exposed in simulated concrete pore solution in a laboratory, they form different types of oxide which may be protective or unprotective, by predicting the corrosion rate and life span of steels.

II. Experimental details

Two grades of reinforced steels (S and T) have been used in this study. The steels coupons of size 20 mm diameter - 10 mm height were cut from bar. The surfaces of the steels were belt polished and degreased in acetone before to fixing them on sps solution. The chemical compositions of the steels used for this study are given in Table 1.

Table 1: Chemical compositions of reinforced steels used in the this study

	Wt% of alloying elements										
Steels	C	Mn	Si	S	P	Ni	As	Cu	Cr	Sn	Fe

S	0.264	0.79	0.19	0.003	0.03	0.02	0.016	0.017	0.051	0.014	Balance
T	0.238	0.73	0.17	0.002	0.01	0.04	0.006	0.003	0.010	0.001	Balance

The laboratory experiments were performed on same steels with 3.5% NaCl. For assessing the corrosion behavior of steels, two type of crystallography studied after corrosion test. The first sets of experiments were the exposure of samples in simulated concrete pore solution. Procedure for the atmospheric exposure tests were followed as described in ASTM G50-76[7] .The rust on the exposed specimens was cleaned in acid solution as recommended in ASTMG1-90[8]. A few grams of rusts from the steel surface were scrapped out and kept for the other studies. The average data for the two sets of specimens have been incorporated in the paper.

III. Results and discussion
Raman Spectroscopy Studies

A vast difference in corrosion rate of steels and adherence of rusts to their surfaces in different types of test electrolytes (different pH solutions) was quite an interesting observation and led us to investigate this further by determining the nature of rusts and their morphology. Rusts collected from different samples after completions of the experiments were subjected to Raman spectroscopy and spectra are shown in Figure 1 to 4. In order to have better clarity, the major peaks extracted from the spectra of the figures with their attribution are inserted in form of table. It is important to mention here that certain structures of iron oxides are recognized more protective than the others. Thus, lepidocrocite (γ-FeOOH), akaganeite (β-FeOOH), iron hydroxide (FeOOH), etc. are reported unstable and non-protective oxides [9, 10]. Due to their instability (tendency to transform to other stable forms of oxide) and pores morphology, they act as cathodic depolarizers and reservoir for moisture, oxygen and polluting gases. On the other hand some other phases of oxides such as maghemite (γ- Fe_2O_3), goethite (α-FeOOH), etc. are quite stable and bear a compact morphology [10]. It is seen from the Raman shifts recorded in Figure 1 and 3 that for steel S, the majority of peaks at are attributed to α-FeOOH (goethite) and γ -Fe_2O_3 (maghemite) [11,12]. This is more pronounced in both solution of different with high alkalinity and salinity, Figure 4 where very strong peaks of the above stated phases of rusts are observed. As stated above these phases of rusts are known to be quite stable, adherent to the surface and impede the corrosion reaction at the steels' surface. In contrast to this, the rusts formed on steel T are mostly γ -FeOOH (lepidocrocite) [13].These phases of rusts are unstable and porous in nature and transform to other form of oxides with passage of time and depolarize the cathodic reactions [9, 14]. It is to be noted that the strongest peak of a particular oxide is observed only at very low power (<0.1 mW) of the illuminating laser. Since we are dealing with mixed oxide phases contaminated with other compounds, a very low laser power (<1 mW) resulted in noise in Raman spectrum. To avoid this, laser power was maintained between 1 and 1.5 mW.
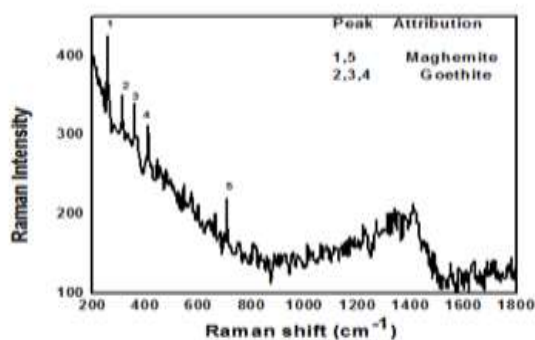

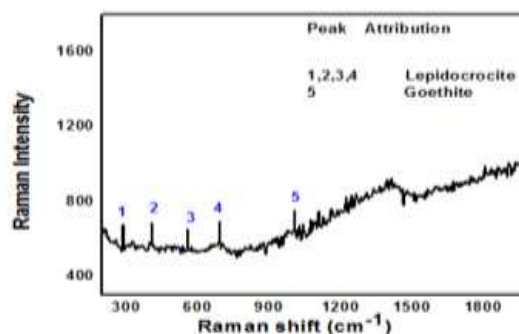Figure 1: Raman spectra of Steel rebar S surface immersed in the SPS solution

Figure 2: Raman spectra of Steel rebar T surface immersed in the SPS solution
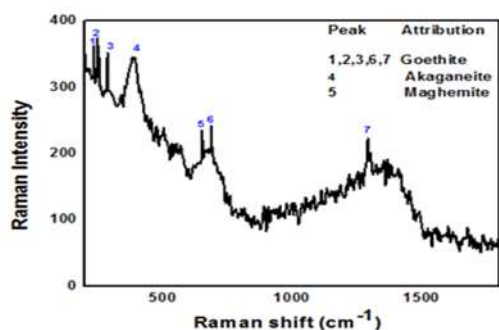
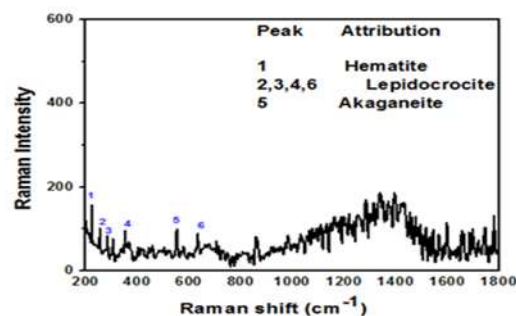Figure 3: Raman spectra of Steel rebar S surface immersed in the SPS solution Contaminated with 3.5 % NaCl

Figure 4: Raman spectra of Steel rebar T surface immersed in the SPS solution Contaminated with 3.5 % NaCl

X-ray diffraction studies

The study of rusts by Raman spectroscopy as described above has provided important clue about the nature of rusts formed on steels' surfaces exposed under different conditions. Unfortunately, the Raman shifts of many compounds are either very closer or tally with each other. For example, Oh et al. reported strongest peak of maghemite at 670 and 486 cm^{-1} [15].

Jubb and Allen attributed this peak to magnetite [16]. Ohtsuka et al. on the other hand reported the Raman peak at 670 cm^{-1} corresponding to ferroxyhite [17]. This occurs as many compounds bear identical bond polarizability, crystal symmetry and the exciting wave length resulting in the same Raman shift.

Further, the Raman peaks in the range of 1300–1314 cm^{-1} exhibit different iron oxides phases. Thus depending only on one characterization technique may lead to an erroneous conclusion. It was therefore necessary to use technique other than Raman spectroscopy to arrive at a definite conclusion about the phases present in the corrosion products.

In view of this X-ray diffraction studies of the generated corrosion products were performed and diffraction patterns are shown in Figure 7 to 10. The major peaks with their attribution are inserted in figures in form of table. It is evident from the diffractograms that the rust of steel S invariably exhibit very strong peaks of α -FeOOH (goethite) and γ -Fe$_2$O$_3$ (maghemite) in test solutions of all pH. For Steel T, however, stronger peaks of γ -FeOOH (lepidocrocite) are noted. This is in conformity with the results recorded by Raman spectroscopy.
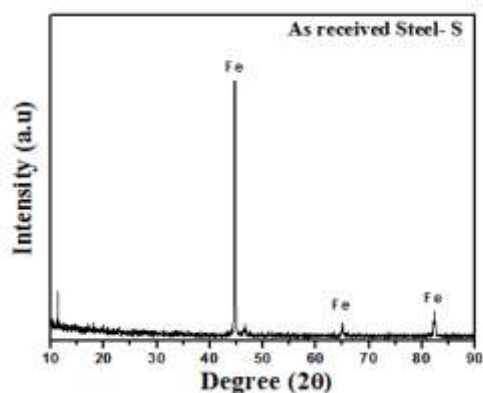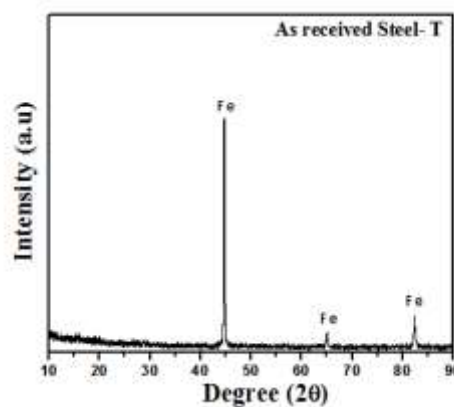

Figure 5: XRD image of Steel rebar S

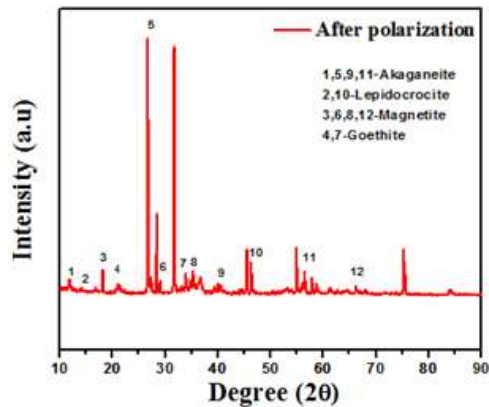Figure 6: XRD image of a Steel rebar T

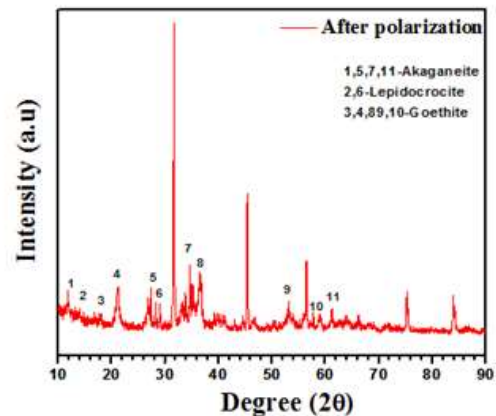Figure 7: XRD image of a Steel rebar S surface immersed in the SPS solution

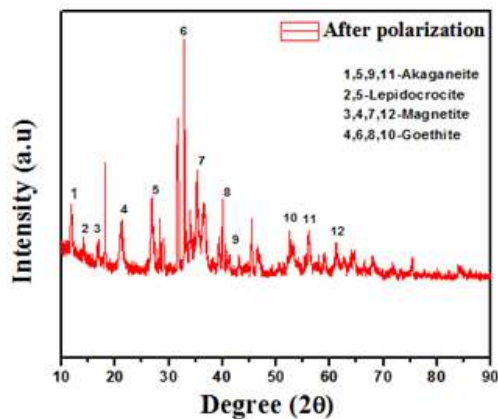Figure 8: XRD image of a rebar T surface immersed in the SPS solution

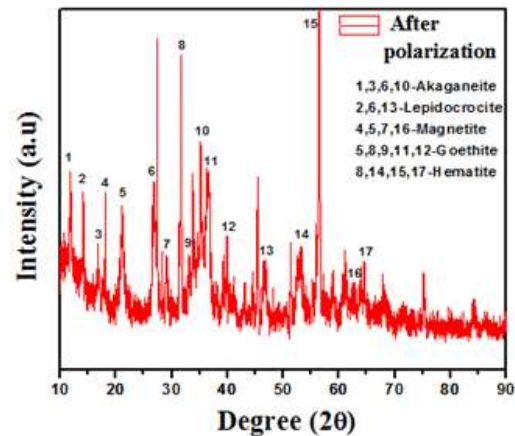Figure 9: XRD image of a Steel rebar S surface immersed in the SPS solution contaminated with 3.5 % NaCl

Figure 10: XRD image of a rebar T surface immersed in the SPS solution contaminated with 3.5 % NaCl

IV. Conclusion

From the above studies it has been concluded that:

i. Corrosion rate of T is higher than S during all period of exposure;

ii. The corrosion rate of S is less because of alloying elements i.e. Cu, Cr, P and Si are present in more amount than T;

iii. On S steel very protective, non-porous and adherent oxides while on steel T non-protective, porous and non-adherent oxides are formed.

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