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Corrosion Rate Assessment of Nanoparticles Admixed Cement Slurry Coated Steel

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Abstract—*The effect of ordinary Portland cement (OPC) slurry coating and carbon nanotube (1%, 3% and 5% by weight of cement) admixed OPC slurry coating on the corrosion properties of steel exposed under saline water (3.5% NaCl) was investigated. After 90 days of exposure under saline environment, the potentiodynamic polarization (cyclic sweep) and weight loss measurements were performed in order to evaluate the corrosion rate of bare steel (BS) and differently coated steel systems. It was observed that the coating systems containing carbon nanotube exhibited higher corrosion inhibition as compared to OPC slurry coating system. It was also observed that an increase in the dosage of carbon nanotube resulted in a decrease in corrosion rate. Moreover, the scanning electron micrographs of cement paste containing carbon nanotube confirmed that the nanoparticles act as filler and thus improved the micro-structural properties of cement paste.*

1. INTRODUCTION

Steel reinforced concrete is one of the most extensively used materials for the construction of buildings, bridges, etc. in the world. However, steel corrosion has been identified as the main weakness of reinforced concrete which shortens the life of infrastructures. Although, Concrete is a highly alkaline material (pH ranging from 12.6 to 13.8), primarily due to its calcium, sodium and potassium hydroxide content. Under these pH conditions, the embedded steel spontaneously forms a passive film (γ-$Fe_2O_3.H_2O$) which, while only a few nanometers thick, affords it protection [1-3]. This film can be destroyed by aggressive agents such as chloride ions or CO_2. The chloride ions continuously enter through tiny pores of concrete and accumulate on the surface of steel and thus destroy the protective film as indicated in equation (1) and (2). The CO_2 reacts with pore water and cement hydration product $Ca(OH)_2$ to produce calcium carbonate, which reduces the concrete alkalinity as shown in equation (3) and (4).

$$Fe^{2+} + 2\,Cl^- \longrightarrow FeCl_2 \quad (1)$$

$$FeCl_2 + 2\,H_2O \longrightarrow Fe(OH)_2 + 2\,HCl \quad (2)$$

$$CO_2 + H_2O \longrightarrow H_2CO_3 \quad (3)$$

$$H_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2H_2O \quad (4)$$

In fact, concrete-embedded reinforcing steel corrosion is an electrochemical process in which one part of steel acts as an anode and other parts acts as a cathode; and the pore water of concrete acts as an electrolyte. The anode governs oxidation, which involves a loss of electrons, while during the cathodic reaction; the electrons generated in the anode combine with certain ions in the electrolyte. This electron gain constitutes reduction [4-7]. This process set up a redox reaction, given in equation (5) and (6).

$$\text{Anodic Reaction: } 2Fe \longrightarrow 2Fe^{2+} + 4e^- \quad (5)$$

$$\text{Cathodic Reaction: } 4e^- + 2H_2O + O_2 \longrightarrow 4OH^- \quad (6)$$

With the corrosion process underway, the reinforcing steel oxidizes to form ferric oxide hydrate ($Fe_2O_3 \bullet H_2O$) or rust. The process is expressed by the equations (7), (8) and (9). The hydrated ferric oxide ($Fe_2O_3 \bullet H_2O$) may have up to ten times the volume of the consumed steel that it replaces. This substantial volumetric increase causes pressure in the concrete, which leads to cracking, spalling and delamination of the concrete cover

$$2Fe^{2+} + 4OH^- \longrightarrow 2Fe(OH)_2 \quad (7)$$

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3 \quad (8)$$

$$2Fe(OH)_3 \longrightarrow Fe_2O_3 \bullet H_2O + 2H_2O \quad (9)$$

Thus the corrosion process can be controlled by controlling one of the above reactions. Further, there are various methods of prevention or mitigation against corrosion of embedded steel which includes the selection of corrosion-resistant steel, use of coatings, addition of concrete sealers, use of thicker concrete cover, addition of supplementary pozzolanic materials, addition of corrosion inhibitors and cathodic protection [8-16].

Particularly, additions of pozzolanic materials such as silica fume, fly ash contribute to lowering the permeability and consequently enhance the mechanical and durability properties of steel reinforced concrete. These properties can be further improved with the use of nanoparticles in the cementitious composite. In particular, carbon nanotube (CNT) is known to

be the materials of the 21st century and is currently receiving a lot of interests due to its extremely high mechanical properties. Applications of carbon nanotubes seemed to be endless varying from electronic, biological, chemistry right to multi-functional composites. CNT is reported to have 100 times more strength than steel but yet 6 times lighter than steel [17-27]. Its Young's modulus and tensile strength are observed to be as high as 1 TPa and 200 GPa, respectively. CNT have been used in several composites in order to strengthen the matrix owing to its high mechanical properties. Also, it is reported that CNT act as filler and thus improving the microstructure cementitious composite [28-34].

The present investigation deals with the corrosion rate assessment of ordinary Portland cement slurry coated steel and CNT incorporated cement slurry coated steel. The corrosion rates of all the specimens were determined using potentiodynamic polarization test (cyclic sweep) and weight loss measurements after 90 days of exposure under saline environment. Three replications were used for each category of the specimen. Also, microstructure of CNT-cement paste was studied with the help of scanning electron micrographs.

2. 2. EXPERIMENTAL PROCEDURES

2.1. Coating systems

Four types of coatings were prepared using Portland cement with particle sizes in the range of 1-100 μm; multi-walled carbon nanotubes (CNTs) with average diameter of 50 nm and around 500 nm length. The first coating contains only ordinary Portland cement (OPC) slurry (SC). The other coatings contain OPC with 1% (CNT1), 3% (CNT3) and 5% (CNT5) carbon nanotubes by weight of OPC. In order to formulate these coatings, first of all carbon nanotubes were dispersed using ultrasonic with some part of the mix water for 10 min then mixed with OPC slurry and stirred up to 6 minutes in a magnetic stirrer. Thereafter, coatings were applied on the steel surface as shown in Fig. 1 and then air dried for 24 hours. Also for comparison purposes bare steel (BS) specimens of equal size were prepared. Then all the specimens were exposed under saline (3.5 % NaCl) water for 90 days.

Fig. 1: Coated steel specimens

2.2. Cyclic sweep measurements

The cyclic sweep measurements were performed using the Gill AC Potentiostat supplied by ACM (Applied corrosion monitoring) instruments. The most common three-electrode electrochemical cell was used in which the specimens were served as the working electrodes (WE), a saturated calomel electrode (SCE) and Platinum electrode were served as the reference electrode (RE) and the counter electrode (CE) respectively. A working sense (WS) was also connected to working electrode. The saline water was used as an electrolyte of the cell. In this electrochemical cell, the working and counter electrode carry the current; and the working sense and reference electrode measure potential (voltage). The cyclic sweep measurements was carried out at the exposure duration of 90 days with start potential -250 mV, reverse potential 250 mV and scans rate 200 mV/minute. Then, the corrosion kinetic parameters such as corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (B_a, B_c), corrosion current density (I_{corr}) and corrosion rate were determined by means of Tafel extrapolation of the polarization curves. Then the inhibition efficiency (IE) in percentage was estimated by the following relationship.

$$IE\ (\%) = \frac{(CR)o-(CR)i}{(CR)o} \times 100 \qquad (10)$$

Where $(CR)_o$ and $(CR)_i$ are corrosion rates of the bare and coated steel respectively.

2.3. Weight loss measurements

The weight loss measurements were performed in accordance with ASTM G1-90 after 90 days exposure duration. The weight of mild steel specimens were taken by electronic balance after removing the coating and the corrosion products, washed with distilled water and ethanol, and then dried at room temperature. Then the weight losses were calculated by subtracting the final weight from initial weight of the specimens. Then the corrosion rate in mils per year (mpy) was obtained by the following relationship:

$$\text{Corrosion rate (mpy)} = \frac{K \times W}{D \times A \times T} \qquad (11)$$

Where: W = weight loss in grams, K = constant (5.34×10^5), D = density in g/cm^3, A = area (inch^2), t = time (hours)

2.4. Scanning electron microscopy

In order to investigate the interaction of the carbon nanotubes clearly, paste sample (10 mm diameter and 20 mm length) containing 5% CNTs using water to cement ratio of 0.5 was prepared and cured for 28 days, then crushed and dried in an oven at 60°C for 24 h. After that, the samples were attached to a stub with carbon tape and then coated with Au film about 30 s for conducted samples. Microstructural analysis of samples was characterized using scanning electron microscopy (SEM).

3. RESULTS

3.1. Cyclic sweep measurements

The polarization curves (plot of cell potential versus current density) of the bare, OPC slurry and CNT-admixed cement slurry coated mild steel exposed under saline water for 90 days are shown in Fig. 2 and corresponding corrosion kinetic parameters are listed in Table 1. It can be seen that the corrosion current density decreases with increasing the dosage of CNTs in the coating system.

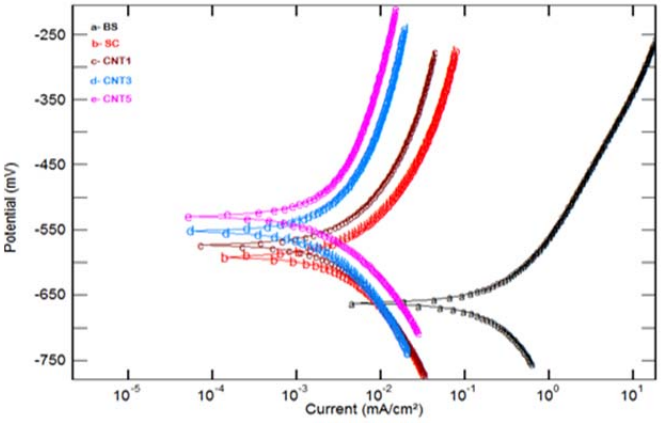

Fig. 2: Polarization curves

Table 1. Corrosion kinetic parameters

System	E_{corr} (mV)	I_{corr} (mA/ cm^2)	C.R (mpy)	I.E (%)
BS	-662.94	0.7922897	361.52	-
SC	-594.63	0.0115708	5.2797	98.54
CNT1	-573.21	0.0062911	2.8706	99.21
CNT3	-551.46	0.0032284	1.4731	99.59
CNT5	-525.14	0.0023365	1.0661	99.71

The corrosion inhibition efficiency of SC, CNT1, CNT3 and CNT5 with respect to the BS was found as 98.54%, 99.21%, 99.59% and 99.71% respectively. Moreover, the corrosion inhibition efficiency of CNT1, CNT3 and CNT5 with respect to the SC was found as 45.63%, 72.10% and 79.81% respectively. Hence, it was observed that inhibition efficiency of OPC slurry coating system was considerably improved with the incorporation of CNTs.

3.2. Weight loss measurements

From the weight loss measurement, the corrosion rate (mpy) of BS, SC, CNT1, CNT3 and CNT5 was observed to be 347.95, 4.62, 2.45, 1.27 and 0.96 respectively. Hence, the corresponding corrosion inhibition efficiency of SC, CNT1, CNT3 and CNT5 with respect to the BS was found as 98.67%, 99.30%, 99.64% and 99.73% respectively. Furthermore, the corrosion inhibition efficiency of CNT1, CNT3 and CNT5 with respect to the SC was found as 46.97%, 72.51% and 79.44% respectively. Thus, it was observed that inhibition efficiency of OPC slurry coating system was significantly enhanced with the addition of CNTs.

3.3. Scanning electron microscopy

Fig. 3a and b shows the SEM micrographs of ordinary Portland cement and multi walled carbon nanotubes respectively. Fig. 4a and b shows SEM micrographs at different magnitudes of ordinary Portland cement paste after curing for 28 days. Hydration products of ordinary Portland cement with water - small fibers of calcium silicate hydrate (C-S-H), calcium hydroxide (C-H) and calcium sulfoaluminate hydrate (ettringite) can be seen. Fig. 5a and b shows SEM micrographs at different magnitudes of ordinary Portland cement paste with 5 wt.% CNTs, after 28 days curing, which clearly exhibits the interfacial interactions between the hydration products and multi-walled carbon nanotubes; this can be observed from the insertion of multi-walled carbon nanotubes (arrows) between the hydration products.

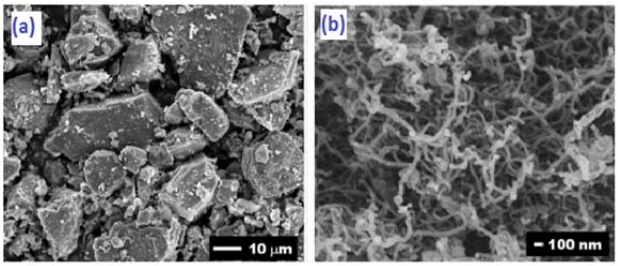

Fig. 3. SEM micrographs of (a) OPC and (b) CNTs

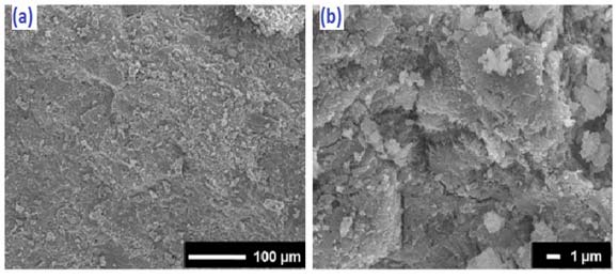

Fig. 4. SEM micrographs of OPC paste at 28 days: (a) 200x and (b) 5000x

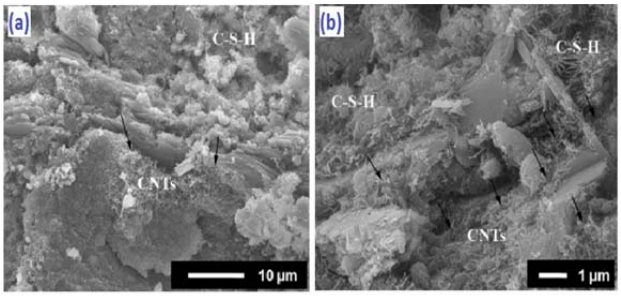

Fig. 5. SEM micrographs of OPC containing 5 wt.% CNTs mix at 28 days: (a) 2000x and (b) 10,000x

4. DISCUSSION

The corrosion rate was found to be considerably decreases with increasing the amount CNTs in the OPC slurry coating system. Thus the corrosion inhibition efficiency of OPC-CNTs slurry coated steel was enhanced as compared to bare steel. As it is evident from the SEM micrographs of OPC paste containing 5 wt.% of CNTs, the additional CNTs appear to densely fill in the places between the C-S-H phase and CH phase. In this way, the additional multi-walled carbon nanotubes can reduce the porosity of these Portland cement paste, thus restrict the ingress of aggressive agents such as chloride ions.

5. CONCLUSIONS

The effect of different contents of CNTs admixed OPC slurry coatings on the corrosion rate of steel was investigated. All the coating systems were exposed under saline water for the duration of 90 days. The potentiodynamic polarization test (cyclic sweep) and weight loss measurements were performed to investigate the corrosion inhibition mechanism of these coating systems. Moreover, microstructure of CNT-cement paste was studied with the help of scanning electron micrographs. The corrosion inhibition efficiency was found to be significantly increased with increasing the amount CNTs in the OPC slurry coating system. This fact can be explained with the help of scanning electron micrographs, which clearly showed excellent interaction between CNTs-OPC paste and carbon nanotubes performing as filler resulting in a denser microstructure when compared to the OPC paste without CNTs. Thus, the corrosion resistance of steel was appreciably improved by blocking the tiny pores of OPC paste and reducing the ingress of aggressive agents.

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