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Corrosion resistance system for the steel liner of Hydro-Electric plant in acidic medium

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ABSTRACT-

The Kopili Hydro-Electric Project (KHEP) of North Eastern Electric Power Corporation Limited (NEEPCO) is one of the pioneering Hydro-Electric Projects in the North Eastern Region (NER) of India. In recent years, it has been found that the low pH of the reservoir water has damaged plant equipment and metallic parts in KHEP due to corrosion. These parameters were tested according to the standard procedure of APHA (American Public Health Association). The metal parts used in power plant was characterized by field emission scanning electron microscopy (FESEM) energy dispersive X-Ray (EDX). The FESEM-EDX observation of the metal surface confirmed that the boiler quality (BQ) steel of ASTM (American society for testing and materials) grade A537 are used in the power plants. The corrosion rates were measured in sulfuric acid solution of different pH and molarity by potentiodynamic curves or Tafel extrapolation method. After that the metal surface was coated with silicon based super hydrophobic coating which has superior water-repelling effects and has received increasing attention as a promising solution to corrosion of metallic materials. The contact angle of super hydrophobic coating was more than 140º. The corrosion rate of coated BQ metal plate was measured by Tafel extrapolation method and it had been observed that corrosion rate was reduced to more than 80 times compared to uncoated metal.

Keywords: Corrosion resistance; Tafel extrapolation; super hydrophobic coating; steel liner; contact angle

INTRODUCTION

The Kopili Hydro-Electric Project (KHEP) of North Eastern Electric Power Corporation Limited (NEEPCO) is one of the pioneering Hydro-Electric Projects in the North Eastern Region (NER) of India. In recent years, it has been found that the low pH of the Kopili River water has damaged plant equipment and metallic parts in KHEP due to corrosion. The main reason for low pH is due to inappropriate mining of coal.

The coal in Meghalaya has high content of sulfur in it and when it comes in contact with water (rain water), sulfuric acid is formed and the pH of river water decreases to a low value. This low pH is not desirable for the aquatic environment and metal parts of the hydroelectric plant.

Acidic environment enhances the corrosion behavior of metals. As the metals are electro-positive in nature and so they are good electron donors. So, when an acid comes in contact with the metal surface high proton concentration increases oxidation of metal. This elevated oxidation of metals is the main cause behind the corrosion of metal.

Due to their superior water-repelling effects, superhydrophobic surfaces have received increasing attention as a promising solution to corrosion of metallic materials [1]. This present work is based on the principle of superhydrophobicity. Many review articles covering different aspects of superhydrophobicity have been published [2-6].

The surface morphology has a crucial role on effective wettability in superhydrophobic surface. Roughening a surface can not only enhance its hydrophobicity due to the increase in the solid–liquid interface [7,8] but also air can be trapped on a rough surface between the surface and the liquid droplet. Since air is an absolutely hydrophobic material with a contact angle of 180°, this air trapping will amplify surface hydrophobicity [9,10]. Hierarchical micro- and nanostructuring of the surface is thus responsible for superhydrophobicity.

EXPERIMENTAL PROCEDURE

MATERIALS

Boiler quality (BQ) steel (ASTM A-537 grade B) and Stainless steel 304 (SS 304) were provided by by NEEPCO. Ag/AgCl,reference electrode and Platinum wire as counter electrode were purchased from Metrohm, India. Emery papers of grade 320, 600, 1000, 1200 grade were purchased from CUMI Co.Sulfuric acid, hydrochloric acid and acetone were purchased from Merck, India. The hydrophobic coating purchased from Rust-Oleum®.

METHODS

Analysis of water parameter

The water samples were collected from Kopili reservoir. The water parameters namely pH, ionic conductivity, turbidity, sulfate ion concentration, salinity, total dissolved solid (TDS) were measured by pH meter, ionic conductivity /TDS meter, turbidity meter, salinity meter respectively according to APHA (American Public Health Association)

Preparation of metal (steel liner) coupon

SS304 and SS316 were cut by electrical discharge machining (EDM) to make circular plates (blank) of 20mm diameter. BQ plates were firstly processed to reduce the thickness by milling machine. Then it was cut into circular plates (blank) of 20mm diameter by CO_2 laser cutting. After that the plates were polished by emery paper of grade 320, 600, 1000, 1200 subsequently.

Artificial corrosive environment

1 molar of H_2SO_4 was prepared to make the acidic solution. From that, the other pH solutions of various pH ranges were prepared.

Hydrophobic coating on Steel liner

The metal coupons were coated with hydrophobic coating. Firstly, the coupons were coated with base coating which works as primer, then it was kept for 40 minutes at room temperature for drying. After that it was coated with liquid repellent top coat and kept for 10 hours at room temperature for drying**.**

Corrosion Study

A corrosion cell (400 ml) was designed which has a provision to connect reference electrode, counter electrode and working electrode. This cell used to fill up with acidic solution and all the electrodes were inserted to the cell keeping in contact with acidic solution. The electrodes were connected to the connector of potentiostat. Then the experiments were run by the command given by software of system of potentiostat. Counter electrode and reference electrodes were used as platinum and $Ag/AgCl_2$ respectively. The effective area of working electrode is $1cm^2$.

RESULTS

ANALYSIS OF WATER PARAMETER

Table 1: Parameters of acidic water collected in 28th OCT, 2016

Date of sampling	Name of Samples	pH	Ionic Conductivity (mS/cm)	Turbidity (NTU)	SO_4^{2-} concentration (mg/L)	Salinity (mg/L)	TDS (mg/L)
28/10/16	Umrong	3.74	0.18	0.2	65.07	147.7	98.7
	Khandong	3.79	0.19	0.1	61.31	146.1	96.9

The water parameters were measured and it has been observed that pH is effectively low for Kopili reservoir which indicates water is still acidic in nature. Ionic conductivity is low. But sulfate concentration is not negligible so the TDS. The sulfate ion and TDS which are present in the water are due the coal washed water. Water which washes coal and mixed to water of reservoir. Series of chemical reaction are involved for production of sulfate and H^+ ion when water comes in contact with coal.

CHARACTERIZATION OF THE STEEL LINER

The materials which were collected from NEEPCO power plant were characterized by FESEM-EDX instrument to check the elemental composition and it was compared with standard composition of ASTM. Two materials were analyzed which are boiler quality steel (ASTM A-537 grade B) and stainless steel 304. For each materials three spectrums were obtained.

Characterization of BQ plate:

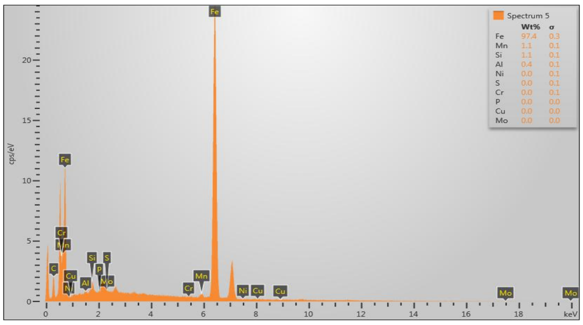

Figure 1: EDX analysis of for BQ plate

Table 2: Comparison of composition between ASTM standard and experimental data for BQ A-537

Components of BQ plate	Weight Percentage			
	ASTM Standard	Spectrum-1	Spectrum-2	Spectrum-7
Iron (Fe)		97.4	97.1	96.7
Manganese (Mn)	0.7-1.72	1.1	1.1	1.2
Silicon (Si)	0.13-0.5	1.1	1	1.5
Copper (Cu)	0.38(max)	0	0.4	0.3
Sulphur (S)	0.025(max)	0	0	0
Phosphorous (P)	0.025(max)	0	0	0
Molybdenum (Mo)	0.09	0	0	0
Chromium (Cr)	0.29	0	0	0
Carbon (C)	0.24	0	0	0
Nickel (Ni)	0	0	0	0.2
Aluminum (Al)	0	0.4	0.4	0.4

After characterization of steel liner by FESEM-EDX it has been observed that the amount of elements present in BQ A-537 is quite similar to that of ASTM standards.

Characterization of SS 304

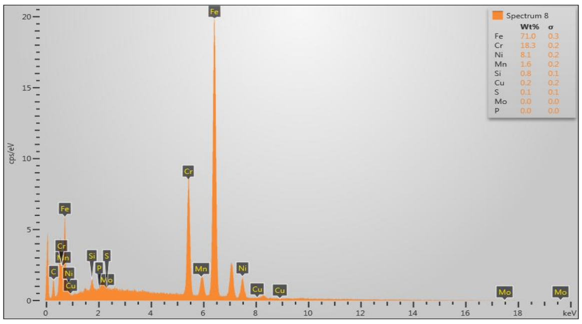

Figure 2: EDX analysis of spectrum 8 for SS 304

Table 3: Comparison of composition between ASTM standard and experimental data for SS304 plate

Components	Weight Percentage			
	ASTM Standard	Spectrum-1	Spectrum-2	Spectrum-3
Iron (Fe)		71	70.4	69.8
Chromium (Cr)	18-20	18.3	18.2	18.2
Nickel (Ni)	8-12	8.1	7.6	7.6
Manganese (Mn)	2	1.6	1.7	1.9
Silicon (Si)	1	0.8	1.1	1.2
Sulphur (S)	0.03	0.1	0	0.2
Carbon (C)	0.08	0	0	0
Phosphorous (P)	0.045	0	0	0
Copper (Cu)	0	0.2	0.4	0.3
Aluminum (Al)	0	0	0	0.8

After characterization of steel liner by FESEM-EDX it has been observed that the amount of elements present in SS 304 is quite similar to that of ASTM standards.

HYDROPHOBIC COATING ON STEEL LINER

Figure 3: Hydrophobic coating on BQ plate

The coupons were coated with base coat and top coat. The base coat mainly contains hydrocarbons and titanium dioxide which are used to protect the metal from sun and UV lights. The top coating is used for hydrophobicity and corrosion resistance. This coating contains mainly silicone derivatives and alkane hydrocarbons.

Table 4: Composition of top coating and base coating

Base Coating		**Top coating**	
Name of Chemicals	**Weight percentage range**	**Name of chemicals**	**Weight percentage range**
Propane	10-25	Acetone	50-75
Naphtha, Petroleum	10-25	Propane	10-25
Methyl Acetate	10-25	n-Butane	2.5-10
Titanium Dioxide	10-25	Silicone Derived Proprietary Ingredient	1.0-2.5
Methyl Isobutyl Ketone	2.5-10		
n-Butane	2.5-10		
n-Butyl Acetate	2.5-10		
Ethyl Acetate	2.5-10		
Methanol	0.1-1.0		
bis(1,2,2,6,6-Pentamethyl-4-Piperidinyl) Sebacate	0.1-1.0		

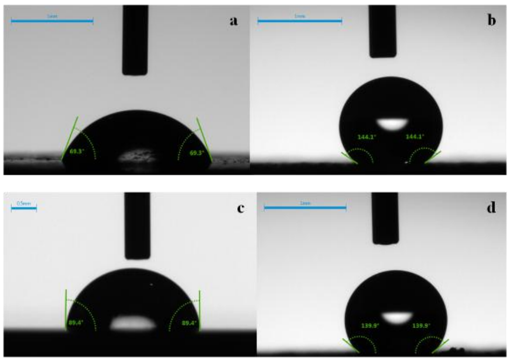

Figure 4: Contact angle of bare BQ and SS304 (a,c) and coated BQ and SS304 (b,d) steel liners

To observe the hydrophobicity contact angle was measured. It has shown in the figure 4 that the contact angle of coated material is higher than the non-coated material. Higher contact angle means higher hydrophobicity. The contact angle on coated surface is 139°- 144° whereas on bare metal the contact angle is 69.3°- 89.4°.

ASSESSMENT OF THE CORROSION FOR STEEL LINER

Electrochemical tests

Calculation of corrosion rates

The corrosion rate depends on the kinetics of both anodic (oxidation) and cathodic (reduction) reactions. According to Faraday's law, there is a linear relationship between the metal dissolution rate or corrosion rate, R_M, and the corrosion current, i_{corr}.

$$R_M = \frac{M}{nF\rho} i_{corr} \qquad \textbf{Eq. 1}$$

Where *M* is the atomic weight of the metal, *ρ* is the density, *n* is the charge number which indicates the number of electrons exchanged in the dissolution reaction *F* and is the Faraday constant, (96.485 C/mol). The ratio M/n is also sometime referred to as equivalent weight.

Calculation of corrosion currents

Calculation of corrosion rates requires the determination of corrosion currents. When reaction mechanisms for the corrosion reaction are known, the corrosion currents can be calculated using Tafel Slope Analysis. The relationship between current density and potential of anodic and cathodic electrode reactions under charge transfer control is given by the Butler-Volmer equation:

$$i = i_{corr}\left(e^{2.303\frac{\eta}{b_a}} - e^{2.303\frac{\eta}{b_c}}\right) \qquad \textbf{Eq. 2}$$

$$\eta = E - E_{corr} \qquad \textbf{Eq. 3}$$

In the above equation *E* is the applied potential and *i* the measured current density. The overpotential, *η*, is defined as the difference between applied potential and the corrosion potential E_{corr}. The corrosion potential, E_{corr} is the open circuit potential of a corroding metal. The corrosion current, i_{corr}, and the Tafel constants b_a, and b_c can be measured from the experimental data.

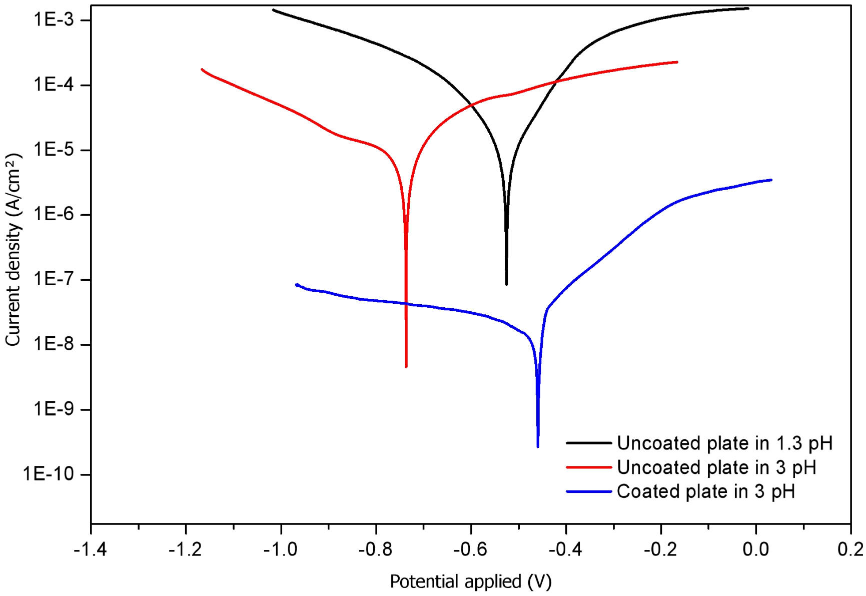

Figure 5: Tafel plots of coated and uncoated BQ plates in different pH solution of sulphuric acid

Table 5: Values of different variables used to find the corrosion rate

Sl. No.	Parameters	Uncoated BQ Steel		Coated BQ Steel in pH Value '3'
		pH 1.33	pH 3	
1	b_a (V/dec)	0.108	0.317	-1.003
2	b_c (V/dec)	0.115	0.119	0.218
3	E_{corr}, Calc (V)	-0.526	-0.74	-0.479
4	E_{corr}, Obs (V)	-0.526	-0.737	-0.459
5	j_{corr} (A/cm²) $*10^{-8}$	1120	694	8.010
6	i_{corr} (A) $*10^{-8}$	1120	694	8.010
7	Polarization resistance (Ω)	2164	5408	1510000
8	E Begin (V)	-0.589	-0.999	-0.781
9	E End (V)	-0.459	-0.647	-0.309
10	χ^2 $*10^{-14}$	3810.000	259000.000	8.480
11	Corrosion rate (mm/year) $\times10^{-4}$	1303.1	806.99	9.31

Three experiments were done. At first the corrosion rates were measured in 0.01 M sulfuric acid solution of 1.33 pH and then corrosion rate was measured in sulfuric acid solution of pH 3. Then the corrosion rate was measured for coated BQ plate in the acidic solution of 3 pH. It has been observed that the corrosion rate in higher in higher acidic solution and it is 1303.1×10^{-4} mm/year (Table 5.5). In lower acidic solution, the (pH 3) the corrosion rate is 806.99×10^{-4} mm/year. The corrosion has been reduced from 806.99×10^{-4} mm/year to 9.31×10^{-4} mm/year after applying of coating in solution of same pH. The E_{corr} and the OCP has increased after coating (Figure 5). So the resistance has increased. All the variables of corrosion study are given in Table 5.

CONCLUSIONS

It has been observed that the pH of the reservoir water is consistently low. That means this condition is optimum for corrosion. The dissolved iron concentration is very low which indicates that the iron has formed complexes and precipitates as iron hydroxides. After applying the hydrophobic coating it was observed that the corrosion rate reduced from 806.99×10^{-4} mm/year to 9.31×10^{-4} mm/year. The corrosion rate was decreased about 80 times in the same acidic condition after applying coat. E_{corr} and the OCP has increased after coating from -0.74 to -0.479, which indicates the resistance of coating in acidic media.

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REFERENCES

1. Mohamed, A.; Abdullah, A. M.; Younan, N. A. CorrosionBehavior of Superhydrophobic Surfaces: a Review. Arabian J. Chem. 2015, 8, 749−765

2. Bhushan, B., Jung, Y.C. Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction. Prog. Mater Sci. 2011, 56 (1), 1–108

3. Ma, M.L., Hill, R.M. Superhydrophobic surfaces. Current Opinion & Colloid Interface Sci. 2006, 11 (4), 193–202

4. Nakajima, A., Hashimoto, K., Watanabe, T. Recent studies on super-hydrophobic films. Monatsh. Chem. 2001, 132 (1), 31–41

5. Roach, P., Shirtcliffe, N.J., Newton, M.I. Progress in superhydrophobic surface development. Soft Matter 2008,4 (2), 224–240

6. Xue CH, Jia ST, Zhang J, Ma JZ. Large-area fabrication of superhydrophobic surfaces for practical applications: an overview. Sci. Technol. Adv. Mater. 2011, 11 (3)

7. Wenzel, R.N. Resistance of solid surfaces to wetting by water. Ind. Eng. Chem. 1936, 28 (8), 988–994.

8. Wenzel, R.N. Surface roughness and contact angle. J. Phys. Chem. 1949, 53 (9), 1466–1467

9. Ogihara, H., Xie, J., Saji, T. Factors determining wettability of superhydrophobic paper prepared by spraying nanoparticle suspensions. Colloids Surf. 2013, A 434, 35–41.

10. Sun T, Feng L, Gao X, Jiang L. Bioinspired surfaces with special wettability. Acc. Chem. Res. 2005, 38 (8), 644–652.