Corrosion resistance of zeolite coated mild steel in chloride environment

H.B. Pande & P.A. Parikh*

Chemical Engineering Department, S.V. National Institute of Technology, Surat 395007, India.

[E-mail: pap@ched.svnit.ac.in]

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Corrosion resistance of as-synthesized ZSM-5 coating on mild steel sheet in 3.5 wt% NaCl solutions was studied by weight loss method as well as electrochemical method. The first method monitored the extent of corrosion as a function of time (up to 9 days), whereas the latter was performed for 3 h. Results revealed the zeolite coating to be offering superior inhibition of corrosion. It provides an alternate choice of material selection to other environmentally harmful coating materials.

[Keywords: Zeolite, Coatings, Material Selection, Corrosion, Sea Water, Marine Environment]

Introduction

Mild steel (MS) has a versatile use in the industrial as well as in social life due to its cost effective mechanical properties. For many years MS is extensively used in chemical process industry as material of choice to manufacture drums for handling various chemicals, for fabrication of equipment used in waste water treatment,1 in gas and oil industry,2 etc. In coastal environment saline humidity causes high rate of corrosion of mild steel.3,4 Corrosion of MS occurs chiefly during process of transportation and handling of chloride containing mediums.5 Such environments are encountered in petroleum, marine vehicles, waste treatments plants, etc. Zeolites are emerging as corrosion resistant materials.6,7 Zeolites are porous and crystalline aluminosilicate with channels of uniform cross-section of 0.3 nm to 1.2 nm size.8 They find largest applications as catalysts and adsorbents in petrochemical and petroleum refining processes.9 Low silica zeolites are used for last many years as a hydrophilic and antimicrobial coating in industry.10-12 Cheng et al.13 had reported the applicability of zeolite as a corrosion resistance coating material on aluminum alloy. The un-calcined zeolite contains a structure directing agent (used as a template for zeolite synthesis) trapped within the channels of zeolite, which acts as a as barrier between the substrate and the corrosive medium. Beving et al.,14 Chen et al.,15 and Valtchev et al.16 reported that pre-treatment of metal substrate plays a crucial role on the quality of film formed. Earlier similar conclusion was reached17,18 demonstrating the outcome of efficient pretreatment results in successful application of high silica zeolite coating on Aluminium and SS-304 substrates. In addition to corrosion resistance coating, applications of zeolite coating include, biocompatible implant of zeolite coated titanium alloy,19 and as an insulator for computer chips and Al alloy in zero or micro gravity environment.20 Processes, such as, sol gel synthesis,21 deposition layer by layer,22 and hot pressing method 23 have been reported for coating of zeolitic materials. Easy and safe zeolite coating by ionothermal synthesis of zeolite film on Al alloy 24 gives alternative to hazardous chromium conversion coating 25 by regular and several thickness of zeolite coating.26 Despite widely employed these techniques are, they are more suitable for laboratory experimentation. When a coating needs be applied on large areas as that of ships, external surface or chemical process reactors, conventional coating techniques such as spray, or paint coating would be preferable.

A survey using any scientific search engine would make it clear that very few reports deal with coating the MS with zeolite as a corrosion resistance material against a chloride containing solution. Though, corrosion resistance against single acid and single alkali solutions of single concentration at a single temperature of 298 K has been reported.26 In the present study experiments were performed to fill in this gap which should help the applications which encounter the saline and humid air/solutions. Since sea water typically contain 3.5 wt% NaCl,27 the same concentration
was chosen for the present work. Due to the intended applications of the corrosion protecting coating on large surface areas, zeolite powder was coated resembling to paint coating.

**Materials and Methods**

As synthesized zeolite ZSM-5 (Si/Al = 25), kindly provided by Sud-Chemie India Pvt. Ltd., was used in this work to coat the MS sheet. Corrosion inhibition of the zeolite coated MS sheet was studied in stagnant condition for 3.5 wt% NaCl solution at ambient temperature and atmospheric pressure following the mass loss method and electrochemical method (potentiodynamic polarization method measurement). NaCl was purchased from Finar Chemicals Ltd., India. Required concentrations were obtained by using double distilled water, 0.08 μs/cm conductivity, generated by Millipore (Elix(3), India). Zeolite adhesion on MS sheet was ensured by using one of the adhesives available in the open market.

The size of MS sheet specimens used in weight loss study was 2×1.5×0.3 cm. The sheets were filed by rough and smooth files and then polished with grit sandpaper progressively from grade number 120 up to 1000 mesh followed by cleaning with distilled water, methanol and acetone, in this sequence. This bare or uncoated metal was then used to examine the extent of corrosion. The metal block used for coating, was polished by low grade grit sand paper (grade number 60 and then 120), to roughen the surface which affords a stable and denser zeolite deposition. These samples were dried at room temperature overnight and then stored in desiccators.

A thin layer of adhesive (available in the Indian market by the name Quickfix) was spread on MS sheet and zeolite powder was sprinkled uniformly, taking care that all the faces were completely covered by zeolite and pressed with a clean spatula of stainless steel. This zeolite coated sheet was kept in drier at 60 °C for over-night. Loose zeolite particles were disengaged by subjecting the sheet to ultra-sonication for 1 min. After removal of loose particles, the sheet was dried at 60 °C for 4 h. When zeolite coated MS sheet was subjected to temperature of about 150 °C, the zeolite layer completely disengaged from the metal surface. This may be due to the limitation of the adhesive’s low thermal stability.

Elemental composition of MS sheet was detected by optical emission spectroscopy OES, (ARL 3460, Thermo Scientific). Crystal morphology was examined with a scanning electron microscope (LEO series VP1430, Carl-Zeiss) operated at 18 kV equipped with Oxford Instruments EDX facility, having a silicon detector under a pressure of 1.34 x 10⁻² Pa. Surface of bare MS sheet, zeolite coated MS Sheet and cross-sectional view of zeolite coating to measure thickness was performed on an SEM (S-3400N, HITACHI). The accelerating voltage was 15 kV. Crystallinity of zeolite powder sample was determined by X-ray powder diffractometer (Philips X’pert MD system, The Netherlands) using Cu Kα radiation (λ = 1.5405 Å). Zeolite sample was scanned in a 2θ range of 0-70° at a scanning rate of 0.4°/s. Contact angle between zeolite coated surface and water droplet was determined by using Kruss-DSA 100 equipment with DSA 3 software. Contact angle was determined by the sessile drop method (6.0 μL volume) and Laplace-Young fitting. Solution pH was measured using the pH meter (CL 54+, Toshcon Industries Pvt. Ltd., India) at room temperature and stagnant condition of 3.5 wt % NaCl medium before and after the immersion of substrate in to solution.

Corrosion inhibition was evaluated by weight loss method. In 250 mL glass beaker 3.5 wt% NaCl solution in water was taken and into this the MS sheet sample with zeolite coating was fully dipped. The mass losses were recorded in both the cases after 1, 3, 6 and 9 day/s at 30 °C. After respective time both the sheets were subjected to the ultrasonication. Masses of the sheets were noted after drying. Difference in mass losses in case of bare and coated samples with reference to mass loss in case of bare sample is defined as corrosion inhibition efficiency. At least one third of experiments were repeated two more times and the mass losses were found to be within ± 5% of the average. Electrochemical analyzer model CHI608C (CH Instruments Inc., USA) was used to monitor corrosion inhibition by electrochemical method. It consists of three electrode cell system, Pt as the counter electrode, saturated calomel as the reference electrode and MS sheet as a working electrode with and without zeolite coating (1 cm x 1 cm x 0.3 cm in size dipped into a salt solution). This system tracked the rate of corrosion of the metal bars. This method was employed only at room temperature. The observations were recorded
for 3 h. Polarization resistance measurement were performed with the scan rate of 0.01 V/s at -10 to +10 mV against corrosion potential (E_{corr}) of the working electrode.

Results and Discussion

Elemental analysis indicated the MS sheet used in this work contained 98.6 wt% Fe, 1.06 wt% Mn, and 0.15 wt% Si, S, Cr, Mo, Ni, etc. were present in very small quantities. SEM image (not shown here) confirmed a crack-free zeolite coating completely covering the surface of MS sheet. Cross-sectional view of the zeolite coating on MS surface indicated a minimum 145 µm of coating thickness, though the coating thickness did vary to some extent across the length of the MS sheet. EDX analysis confirmed the presence of zeolite element on the surface of MS sheet. Zeolite coated MS sheet identified the presence of Si, Al, and O as the chief elements. In case of bare metal sheet, Fe was observed as a main element on surface, which was not observed in zeolite covered MS sheet. Angle formed by a water drop on coated sheet was found to increase up to 116.7° from 85±2°. Independently, water was observed not to adsorb/spread on the zeolite surface at the time of experiment. It demonstrates hydrophobic nature of the surface maybe due to presence of structure directing agent (template) in the zeolite crystals.

Observed corrosion resistance in this report has been attributed to the zeolite layer. In fact there is a layer of the polymeric adhesive beneath the zeolite layer. This inner organic layer maybe thought of affording the corrosion resistance. However, in a control experiment the adhesive layer was observed to peel off in pure water at slightly elevated temperature making the substrate MS sheet exposed to corrosive media, whereas in case of zeolite coated substrate the layer did not peel off. In light of this the attribution for corrosion resistance to the zeolite powder is justified.

Extent of corrosion in terms of weight loss was measured by weight loss (gravimetric method) shown in Equation (1) and Table 1 lists the corrosion inhibition efficiencies, E_w as observed from the mass loss method.

\[
E_w \% = \left( \frac{W_2 - W_1}{W_2} \right) \times 100
\]

Where W_2 and W_1 are weight loss of bare and zeolite coated MS sheet before and after immersion in test solution.

It is pertinent to note that about 90-95% of inhibition could be achieved for a period of exposure of 1 to 9 days using ZSM-5 coating. Zeolite coated MS sheet reduced the corrosion by more than an order of magnitude. It was noticed that inhibition decreased with duration. However, rate of the fall in efficiency was only little as would be evident from Fig. 1. The decrease in corrosion rate has been ascribed to the formation of corrosion product causing a protective layer on metal surface.

Weight loss results clearly show that zeolite prevents the contact between corrosive medium and the MS sheet, leading to corrosion resistance. Values of pH at room temperature after immersion of bare and zeolite coated MS sheet in the salt solution as a function of exposure duration are shown in Fig. 2.

It is evident that pH of the solution has always remained less in case of zeolite coated MS than that for the uncoated MS. This may be due to formation of OH^- ion to a higher extent at bare metal surface. Since increase in pH indicates corrosion, it would be obvious that zeolite coating has imparted the corrosion resistance. Also, it is clear from the Fig. 2 that after higher rate of pH increase (upto 72 h), this rate remained constant and lower value than that with the bare MS sheet.

Electrochemical polarization study

Polarization curves yielded the values of corrosion current density (I_{corr}), corrosion potential (E_{corr}), resistance polarization (E_{Rp}), and anodic (ba) and cathodic (bc) Tafel extra-plots, Fig. 3. Values of various parameters are shown in Table 2. Intersection of cathodic and anodic extrapolates gives corrosion current density of bare and zeolite coated MS sheet. Extent of corrosion inhibition efficiency deduced from current, E_I and polarization resistance E_{Rp} were calculated by Equations 2 and 3.

\[
E_I \% = \left( \frac{I_{corr}(coated)}{I_{corr}} \right) \times 100
\]

\[
E_{Rp} = \left( \frac{R_p(coated)}{R_p} \right) \times 100
\]
where, $I_{\text{corr}}$ and $I_{\text{corr(coated)}}$ are corrosion current densities in absence and presence of zeolite coated MS sheet, respectively, $R_p$ and $R_{p(coated)}$ polarization resistances values in absence and presence of zeolite coating on MS sheet, respectively.

Values of $E_1$ and $E_{R_p}$ (Table 2) suggest that current density in case of coated metal was many times less than that for uncoated metal which bespeaks of corrosion retarding process. The same has been reflected in the relative values of resistance polarization in two cases. Similar observation and inference had been reported in the literature. $E_{\text{corr}}$ values shift toward positive value indicating higher potential to resist corrosion in case of coated material. Electrochemical method suggests the corrosion inhibition exceeding 99%. Poorqasemi et al. reported variations in corrosion inhibition as determined by mass loss method and electrochemical method, as is the case with the present study, and had attributed this difference to variation in immersion time for which the metal samples were dipped in salt solution in two different methods.

**Conclusions**

Corrosion inhibition performance of the zeolite ZSM-5 coated MS sheet was compared with that of the bare MS sheet in 3.5 wt% NaCl aqueous solutions at room temperature for the duration up to 9 days. The mass-loss method indicated the inhibition up to 95%, whereas the electrochemical method showed it to be up to 99%. The corrosion resistance had been reflected in different patterns of rise in pH values with exposure duration.

Performance of the as-synthesized zeolite ZSM-5 as corrosion resisting material maybe visualized as due to the presence of the organic template present within the zeolite channels which prevents the diffusion of the corrosive medium and thus contact between metal and corrosive medium.

**Acknowledgments**

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**Table 1** Corrosion inhibition efficiency (E_w) of ZSM-5 (Si/Al = 25) coating in NaCl aqueous solution.

<table>
<thead>
<tr>
<th>Time (Day)</th>
<th>Weight loss (g)</th>
<th>E_w (%)</th>
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<tr>
<td></td>
<td>Un-coated</td>
<td>Coated</td>
</tr>
<tr>
<td>1</td>
<td>0.0028</td>
<td>0.000156</td>
</tr>
<tr>
<td>3</td>
<td>0.0068</td>
<td>0.000460</td>
</tr>
<tr>
<td>6</td>
<td>0.0120</td>
<td>0.000905</td>
</tr>
<tr>
<td>9</td>
<td>0.0166</td>
<td>0.001350</td>
</tr>
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**Table 2** Results from electrochemical polarizations studies

<table>
<thead>
<tr>
<th>Sample</th>
<th>-Ecorr (V)</th>
<th>k_b (mV decade(^{-1}))</th>
<th>I_corr (mA cm(^{-2}))</th>
<th>R_p (Ω cm(^{2}))</th>
<th>E_l (%)</th>
<th>E_Rp (%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ba</td>
<td>bc</td>
<td></td>
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</tr>
<tr>
<td>Uncoated</td>
<td>0.6347</td>
<td>117</td>
<td>536</td>
<td>29.92</td>
<td>140</td>
<td>99.58</td>
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<tr>
<td>Coated</td>
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<td>194</td>
<td>209</td>
<td>0.1254</td>
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References