CHAPTER-3

EXPERIMENTAL
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Corrosion is an electrochemical interaction between metal and its environment and essentially affected by both the factors. So it is essentially to control the factors associated with the corrosion of the metals. The testing methods to control the corrosion must be established that the tests should be informative and reproducible. So to this, it is necessary that due to care of exercised in selecting an experimental method for corrosion testing, and in correlated laboratory tests with actual service conditions. Thus it is obvious that no universal corrosion testing procedure is available which would cover all aspects of corrosion. Detailed information is provided by various authors as per requirement and specification [1-9].

Jelinek [10] and Borgman [11] suggested the use of two or more different methods to avoid any criticism associated with a single experimental procedure. Reproducibility of the results in corrosion testing depends upon the type of attack and is much greater if the attack is uniform than when it is localized. According to Evan, it is desirable to perform all the experiments in duplicate or triplicate. According to ASTM [3] efforts should be made to have a large surface to mass ratio and small ratio for edge to total surface area. It is desirable to expose a large number of specimens so that a certain number can be removed after definite intervals rate with time. According to Champion, a thickness of 0.036 inch is convenient for many purposes while the Garman specification recommends the specimen’s dimensions with less than 5 x 2 cm. Mayer [12] discussed the considerable detailed pre cleaned and degreased. Speller suggested that in the initial stages of corrosion erratic results are usually obtained and the initial rate of corrosion is usually much greater than that after the action has proceeded for some time. Wesley states that a constant corrosion rate is frequently encountered in total immersion tests.
If the rate of corrosion is higher the testing period must be kept shorter.
In laboratory tests the duration “need not be longer than the number of
hours calculated by dividing the corrosion rate in mdd into 10000”.
Evan, Champion and Speller pointed out that the in tests where
corrosion is assessed by weight loss, it is necessary to remove the
corrosion products from the specimens after exposure and that also
without any loss of the base metal. It is desirable, therefore that before
applying any methods of cleaning, its effects in dissolving the base metal
should be predetermined.
The corrosive medium is another important factor in corrosion studies.
Champion present a general discussion of corrosive media based on the
literature. Wesley and ASTM [3] suggest that each specimen should be
tested in a separate container and such containers and specimen
supports should be used which do not affect the corrosion process.
Temperature control of the corrosive medium is another important factor to
be considered. Champion suggests that temperature control to ±0.1°C is
generally adequate for many corrosion tests.
Champion and Uhlig have reviewed and discussed the various methods
used for the measurements of corrosion effects on the metal and
medium. The visual observation of the specimen on removal from the test
solution provides valuable information regarding the nature of attack as
Fontana [13]. For studying the growth of the tarnish and the thickness of
the surface film optical interference method has been described by
Booker and Benzamin [14].
Winterbettem [15] and Lustman [16] have used computer to carry out
extensive calculations involved in the methods. Chatterjee and Thoms
[17] monitored the dissolution process by two methods: by specular to
measurements and the relating the drop in specular to the weight of the
metal removed. Microscopic methods are used in determining the kind of
attack, e.g. intergranular or transgranular, the measurement of the
depth of the pits, and to determine the constituents of the metal that are especially capable of initial attack. 

According to Ailor, the oxidation products should be examined their composition and their morphology. Evan and Bannister [18] measured the quantity of electricity required to chemically reduce the surface film. A related but different technique of the anodic polarization of the oxide has been used by Dignam [19-20] to characterize high temperature oxides on aluminum.

Change in physical properties such as tensile strength, ductility, resistance and hardness of the metal can be used to evaluate their deterioration. It is not possible, however, to evaluate the damage due to each type of attack separately. Loss in weight is useful to determine the extent and rate of uniform corrosion, but the method is subject to error if the corrosion products are completely removed.

Rhodes and Berner [21] have used the volume of the hydrogen evolved as measure the extent of the corrosion measurement of oxygen adsorption is useful in tests where corrosion takes place mainly with the absorption of oxygen. Like hydrogen evolution, this method also fails to determine the distribution of attack. Measurements of depth of pit by methods other than microscopic are useful in determining the serviceability of the metals used as containers of fluids or as roofing materials.

In the present work, as the corrosion products was completely removed by cleaning solution, the loss in weight method was considered to be reliable one to collect corrosion and inhibition data. Here duplicate experiments were performed for weight loss measurements and the mean value of the weight loss has been recorded. However, to derive a reliable value of the blank weight loss large number of replicates was made in 0.5M and 1.0M trichloroacetic acid.
3.1 Steel

Steel is an alloy of Iron and carbon as primary elements, the carbon content varies between 0.002% and 2.1% by weight which modifies the characteristics of the steel. The additional elements present in the alloys of Iron are nickel, chromium, molybdenum, boron, titanium, vanadium, and niobium [22] manganese, phosphorus, sulfur, silicon, and traces of oxygen, nitrogen, and aluminium. Mild steel is also known as low-carbon steel or Plain-Carbon steel. It is the most common form of steel. The amount of the carbon content is controlled by the heat treatment of the mild steel. The relative amounts of constituents are found using the lever rule. The following is a list of the types of heat treatments possible: Spheroidizing, Full annealing, Process annealing, Isothermal annealing, Normalizing, Quenching, Martempering, Quench and tempering and Austempering [23-24]. Today, steel is one of the most common materials in the world, with more than 1.3 billion tons produced annually. It is a major component in buildings, infrastructure, tools, ships, automobiles, machines, appliances, and weapons.

3.2 Characteristic of the selected metal

(Specification given by the company)
Name: Essar Steel
Certificate number: ESH/TC/D/HR/60/2009/047116
Cast number: B59747
Grade: SRGENP6
Steel Quality: IS 2062 E 250 (Fe 410 W) B: 2006
Composition of the above mentioned steel is as

<table>
<thead>
<tr>
<th>Element</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.160</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.980</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.009</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.013</td>
</tr>
</tbody>
</table>
Silicon 0.007
Aluminium 0.040
Carbon equivalent 0.328

Yield strength 292 MPa (MPa = 1N/mm$^2$ = 0.102Kgf/mm$^2$)
Ultimate tensile strength 448MPa

3.3 Material used

All reagents used are of A.R. grade. All solutions prepared in conductivity water and standardized by different methods [22]. Water bath used is Equitron 14LSS Model No. 8414.AJG106 having accuracy up to 0.01°C.

Balance used was of Reptech.

Chemicals used

1. Trichloroacetic acid S D fine
2. Isoniazid Himedia
3. 3, 4-dimthoxybenzaldehyde S D fine
4. 4-hydroxybenzaldehyde S D fine
5. Benzaldehyde S D fine
6. Anisaldehyde Merck
7. Carbon tetrachloride S D fine
8. Acetic acid Rankem
9. Methanol S D fine
10. Acetone S D fine
11. EDTA S D fine
12. Perspex
13. Hydrochloric acid S D fine
14. Phenolphthalein S D fine
15. Sodium hydroxide Rankem
Their purities are checked by noting their melting points, solubility and crystallization method [23]. The required quantity of the chemicals were weighed through Reptech balance and mixed with methanol then added into the trichloroacetic acid solution. Conductivity water was used throughout the work. Conductivity water was redistilled over potassium permagnate. The distilled water was boiled to expel carbon dioxide and stored in airtight Pyrex aspirator. The pH of the water was found to be ~6.8 and conductivity was $1.5 \times 10^{-5}$ mhos. This water was used for preparing solution of reagents.

3.4 Preparation of Stock Solutions

Trichloroacetic acid solution:

0.5M and 1.0M trichloroacetic acid solutions were prepared by dissolving required amount of pure trichloroacetic acid into conductivity water. The solutions were standardized by titrating against sodium hydroxide solution of known concentration using phenolphthalein as indicator. From the weight of sodium hydroxide and the volume of trichloroacetic acid required, the strength of acid was maintained as 0.5M and 1.0M [24].

3.5 Preparation of metal specimens for test solution

In the present work two types of specimens were used for different type of methods of study.

(i) For weight loss studies rectangular specimens of dimensions 6cm x 3cm (thickness 2mm) with a small hole of about 2mm diameter just near the one end of the specimen for suspension have been used. The specimens were polished with the different grades of ambry. Each specimen was washed with distilled water and dried. Then the specimens were degreased by carbon tetrachloride. The specimens then immersed into the test solution of the specific concentration.
For polarization studies the specimens were of circular shape having the diameter of 2.8cm with a handle 3cm long and 0.5cm wide. The specimens were washed with distilled water then with acetone and dried. The back of the specimen as well as handle of the specimen were coated with first with paraffin then with Perspex (Poly(methyl methacrylate)) from ethyl acetate solution, leaving only circular portion having apparent surface area of the mild steel coupons exposed to the corrosive medium.

3.6 Synthesis of Schiff Bases and their characterization

The schiff bases were prepared according to the reported methods [25] Schiff bases N’-(3,4-dimethoxybenzylidene)pyridine-3-carbohydrazide, N’-[(E)-(4-hydroxyphenyl)methylidene]pyridine-3-carbohydrazide, N’-[(E)-phenylmethylidene] pyridine-3-carbohydrazide and N’-[(E)-(4-methoxy phenyl) methylidene]pyridine-3-carbohydrazide were prepared by mixing equimolar (1:1 molar) methanolic solutions of Isoniazid and 3,4-dimethoxybenzaldehyde, benzaldehyde, 4-hydroxybenzaldehyde and 4-Methoxybenzaldehyde respectively. The mixtures were refluxed with constant stirring by using the Remi magnetic heating plate. After refluxing the mixture was poured to the ice cold water and he solid was separated by using watman filter papers.

The crystalline powder formed was washed several times with lot of cold distilled water and recrystallized from ethanol. The pH was maintained by adding adequate amount of glacial acetic acid solution. The schiff bases were characterized by FT-IR, Mass and NMR spectroscopic method [26-29] and purity was checked by melting points, Thin Layer Chromatography and Thermo Gravimetric Analysis. The mass spectrum are given in figures 3.1.1 to 3.1.4, the IR spectrum in figures 3.2.1 to 3.2.4 and NMR spectrum of schiff bases in figures from 3.3.1 to 3.3.4 respectively. The CHNS data of synthesised schiff bases are reported in table 3.1.
The characterization parameter like IR, NMR and mass of synthesized compounds is explained as under:

- **The N’-(3,4-dimethoxybenzylidene)pyridine-3-carbohydrazide (SB-I)**, Yellow crystals; mp 196-199°C; IR (KBr): \( \nu \text{ cm}^{-1} = 3178 \) (-NH), 3045 (-CH), 1646 (amide C=O), 1598 (imine C=N), and 1204 (O-CH\(_3\)); 1H NMR (DMSO): \( \delta \text{ ppm} = 8.89-8.92 \) (d, pyridine 2H), 8.11-8.15 (d, pyridine 2H), 8.22 (s, CH), 8.48 (s, NH), 7.5-7.8 (d of d, aromatic 2H), 6.92 (s, aromatic 1H), and 3.92-4.12 (m, O-CH\(_3\)). The mass spectrum shows the base peak of m/z at 285 which show the formation of the Schiff base.

- **The N’-[(E)-(4-hydroxyphenyl)methylidene]pyridine-3-carbohydrazide (SB-II)** The mass spectrum shows the base peak of m/z at 241 which show the molecular mass of the Schiff base. Yellow powder; mp 264-268°C; IR (KBr): \( \nu \text{ cm}^{-1} = 3344 \) (-OH), 3207 (-NH), 3068 (-CH), 1658 (amide C=O), and 1608 (imine C=N); 1H NMR (DMSO): \( \delta \text{ ppm} = 11.5 \) (s, OH), 8.8-8.5 (d, pyridine 2H), 8.4-8.3 (d, pyridine 2H), 7.8 (s, CH), 8.0 (s, NH) 7.5-7.3 (d, aromatic 2H), and 7.0-6.8 (d, aromatic 2H).

- **In N’-[(E)-phenylmethylidene] pyridine-3-carbohydrazide (SB-III)**, White crystals; mp 218-221°C; IR (KBr): \( \nu \text{ cm}^{-1} = 3160 \) (-NH), 3025 (-CH), 1692 (amide C=O), 1598 (imine C=N); 1H NMR (DMSO): \( \delta \text{ ppm} = 8.88-8.91 \) (d, pyridine 2H), 7.99-8.05 (d, pyridine 2H), 8.32 (s, CH), 8.65 (s, NH) 7.79-7.80 (d, aromatic 2H), and 7.50-7.51 (d, aromatic 2H). The mass spectrum shows the base peak of m/z at 225 which show the formation of the Schiff base.

- **In case of N’-[(E)-(4-methoxy phenyl) methylidene]pyridine-3-carbohydrazide (SB-IV)**. The mass spectrum shows the base peak of m/z at 255 which show the molecular mass of the Schiff base. Yellow crystals; mp 185-188°C; IR (KBr): \( \nu \text{ cm}^{-1} = 3176 \) (-NH), 3037 (-CH), 1656 (amide C=O), 1606 (imine C=N), and 1257 (O-CH\(_3\)); 1H NMR (DMSO): \( \delta \text{ ppm}=8.89-8.92 \) (d, pyridine 2H), 8.11-8.15 (d, pyridine 2H),
8.22 (s, CH), 8.48 (s, NH), 7.5-7.8 (d of d, aromatic 2H), 6.92 (s, aromatic 1H), and 3.92-4.12 (m, O-CH₃).

### Table 3.1
Elemental analytical data of the schiff bases

<table>
<thead>
<tr>
<th>Schiff base</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>S</th>
<th>Decomposition Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB-I</td>
<td>63.62</td>
<td>5.289</td>
<td>15.09</td>
<td>16.001</td>
<td>0.0</td>
<td>315</td>
</tr>
<tr>
<td></td>
<td>(63.11)</td>
<td>(5.29)</td>
<td>(14.72)</td>
<td>(16.81)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SB-II</td>
<td>64.81</td>
<td>4.636</td>
<td>17.66</td>
<td>12.894</td>
<td>0.0</td>
<td>330</td>
</tr>
<tr>
<td></td>
<td>(64.72)</td>
<td>(4.60)</td>
<td>(17.42)</td>
<td>(13.26)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SB-III</td>
<td>69.71</td>
<td>4.947</td>
<td>18.96</td>
<td>6.383</td>
<td>0.0</td>
<td>345</td>
</tr>
<tr>
<td></td>
<td>(69.32)</td>
<td>(4.92)</td>
<td>(18.66)</td>
<td>(7.10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SB-IV</td>
<td>61.58</td>
<td>5.506</td>
<td>15.57</td>
<td>17.344</td>
<td>0.0</td>
<td>330</td>
</tr>
<tr>
<td></td>
<td>(65.87)</td>
<td>(5.13)</td>
<td>(16.46)</td>
<td>(12.53)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.7 Protocols used

(i) **Weight loss measurements**

The washed, degreased and dried rectangular coupon of mild steel weighed with the help of Reptech balance. Then one specimen was suspended in the 200mL of test solution with the help of glass hook in beaker, the solution being open in air at 35±0.1°C for various immersion periods (1, 2, 3, and 4 hours). After the test the coupon was cleaned with saturated ammonium acetate solution [30-31]. But in the present work only distilled water was used to remove the corrosion products of mild steel in trichloroacetic acid.

The method was used at different temperatures (35, 40, 45, 50 and 55±1°C) and different concentration of acid and inhibitors. For maintaining the temperature constant the water bath of Equitron was used.
Even though this method is universally accepted, it leads to erroneous results, particularly when corrosion rate is low. The specimens cleaning procedure after the exposure to the corrosive environment to remove the corrosion products are the principal source of error for this method. The results obtained are always representative of exact conditions in spite of best precaution taken to simulate the same. Mostly the weight loss os not uniform with time hence an average weight loss reported depends upon the duration of exposure. Actual rate of corrosion at any instant can’t be known by this method. The value obtained by this method is only important and significant, when the corrosion undergoes uniform type at attack. For localized corrosion, the method provide misleading picture. Furthermore, it does not provide any information regarding the mechanism of protection [45].

(ii) Polarization Measurements:
For polarization studies, the coupons were of circular design and the circular coupons were coated with perspex leaving only circular portion of the apparent surface area. It acts as working electrode. The other electrode was platinum of the same dimension and called auxiliary electrode. For these measurements, H-type Pyrex glass cell with porous partition to separate the two compartments was used. It also contains a built in capillary to make connection with reference saturated calomel electrode. In each compartment, the volume of corrosive media was 80mL. Arrangement of apparatus for cathodic polarization measurement is shown in fig. 3.1

(iii) Potential measurement
For potential measurement, single cell of pyrex glass was used which have the volume of corrosive media was 80mL. Two electrodes in this measurement used were platinum and the test coupon and the potentiometer was used to measure the voltage.
Fig. 3.1: Arrangement of apparatus for cathodic protection
The proposed structures of the Schiff bases are as follows:

**SCHIFF BASE-I**

\[ \text{N'-(3,4-dimethoxybenzylidene)pyridine-3-carbohydrazide} \]

**SCHIFF BASE-II**

\[ \text{N-[(4-hydroxyphenyl)methylene]pyridine-3-carbohydrazide} \]

**SCHIFF BASE-III**

\[ \text{N'-(\text{(E)-phenyl)methylidene]pyridine-3-carbohydrazide}} \]

**SCHIFF BASE-IV**

\[ \text{N'-(\text{(E)-(4-methoxyphenyl)methylidene]pyridine-3-carbohydrazide}} \]
Fig. 3.1.1: Mass spectrum of Schiff Base-I

Fig. 3.1.2: Mass spectrum of Schiff Base-II
Fig. 3.1.3: Mass spectrum of Schiff Base-III

Fig. 3.1.4: Mass spectrum of Schiff Base-IV
Fig. 3.2.1: IR spectrum of Schiff Base-I

Fig. 3.2.2: IR spectrum of Schiff Base-II
Fig. 3.2.3: IR spectrum of Schiff Base-III

Fig. 3.2.4: IR spectrum of Schiff Base-IV
Fig. 3.3.1: NMR spectrum of Schiff Base-I

Fig. 3.3.2: NMR spectrum of Schiff Base-II
Fig. 3.3.3: NMR spectrum of Schiff Base-III

Fig. 3.3.4: NMR spectrum of Schiff Base-IV
Fig. 3.4.1: TGA and DSC Curves of Schiff Base-I

Fig. 3.4.2: TGA and DSC Curves of Schiff Base-II
Fig. 3.4.3: TGA and DSC Curves of Schiff Base-III

Fig. 3.4.4: TGA and DSC Curves of Schiff Base-IV
References