2.1 Purpose of the Analytical Investigations

The main objective of this research program is to understand the deposition of Sb during the chemical decontamination process on carbon steel (CS) surface and on the magnetite surface over CS and devise suitable modifications in the formulation to prevent its deposition. Hence all experiments were carried out under the conditions, which are followed for chemical decontamination of iron rich oxide surfaces. A combination of organic acids and chelating agents in reducing condition at 85±1°C was used as the experimental medium. Reducing environment was achieved by continuous purging of inert Argon gas throughout the course of the experiment and the purity of Argon gas was 99.995%.

i. In studies on kinetics of dissolution of different Sb species (oxidation states) in aqueous medium, experiments were performed to find out the stable soluble species of antimony under the working conditions. In Sb deposition and inhibition experiments, specimens were exposed to the solution in batch mode with intermittent solution sampling. Liquid phase analysis (for Fe and Sb) was carried out to understand the changes in the composition of the solid phases. As there is corrosion process occurring during either Sb deposition or release (during chemical decontamination), there is a need to quantify the concentrations of Fe and Sb at different levels during the experiments. Hence, UV-Vis spectrophotometry (UV), Atomic Absorption Spectrometry (FAAS), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) were employed depending upon their suitability.
ii. Surface characterization is needed to know the changes in crystal structure and phase due to deposition and release of Sb either on metal or on ferrite. X-ray Photoelectron Spectroscopy (XPS) was used extensively to explore the possible mechanism in antimony deposition and its inhibition over 100 Å thickness.

iii. Surface morphology was studied with Scanning Electron Microscopy (SEM) and energy dispersive x-ray microanalysis (EDX). X-ray diffraction (XRD) was used to find out the formation of any new crystalline compound during the exposure process. Magnetite powder samples were analyzed by Fourier transform Infrared spectroscopy (FT-IR) to identify the interaction of magnetite with antimony and chelating agents.

iv. As some of the surfaces (metal or metal overlaid with oxide) get altered either due to Sb deposition or release, a study made by using electrochemical techniques (like potentiodynamic anodic polarization - PDAP and electrochemical impedance spectroscopy - EIS and Tafel plot) will throw light on the changes taking place at the surface/ interface.

Hence the above mentioned techniques are employed during the investigations carried out in this work.

2.2 Experimental Setup for Dissolution and Deposition Studies

A glass setup was used to perform all the experiments as shown in Fig. 2.1. The glass setup was the combination of 1 liter round bottomed flask, condenser, thermometer, Ar gas purging glass tube and a heating & stirring mantle. All types of experiments viz. dissolution, deposition, inhibition etc. were performed with this glass setup. One neck of
the round bottomed flask was used to collect liquid samples with pipette and during sampling the Ar gas purging rate was increased to avoid air ingress.

Fig. 2.1: Glass set-up for static experiments.

2.3 Experiments

2.3.1 Dissolution

All the chemicals were used either of AR or GR grade and Millipore water (Resistivity> 18 MΩ.cm) was used in the solution preparation. Dissolution experiments were carried out by taking known quantities of antimony powder (Sb⁰) or antimony trioxide (Sb(III)) or potassium antimonate hexahydroxide (Sb(V)). These experiments were carried out with a 900ml volume of sample at 85±1°C in medium containing Nitrilo
Tri Acetic Acid (NTA), Ascorbic Acid (AA) and Citric Acid (CA) (300 ppm each) under de-aerated condition. The mixture of organic reagents is called “NAC formulation”. Solution samples were taken at pre-determined intervals and analyzed for antimony by AAS and UV-spectrometer.

2.3.2 Antimony Adsorption on Metal Surfaces

Experiments related to the adsorption of Sb(III) and Sb(V) on CS surface were carried out on CS specimens with the dimension of 1cm x 1cm x 0.2cm. The CS specimens were polished with 400 grade silicon carbide paper. The polished specimens were cleaned with acetone and washed with Millipore water. The solution samples were taken at predetermined intervals and were analyzed by Atomic Absorption Spectrometry and UV spectrometer or Inductively Coupled Plasma – Atomic Emission Spectroscopy.

The exposed specimen surfaces were further characterized by different techniques.

2.3.3 Antimony Adsorption Inhibition on Carbon Steel

The experiments for inhibition of antimony adsorption on CS were carried out in batch mode. Organic inhibitors viz. Rodine 92B, Thio-urea, and Di-phenyl thio urea were tried to quantify their inhibitory effects on Sb(III) adsorption on CS in the presence of NAC formulation. Similarly, different passivators viz. MoO$_4^{2-}$, SeO$_3^{2-}$, PO$_4^{3-}$, and AsO$_2^{-}$ were also tested for their inhibition power on Sb adsorption on CS in 5mM Citric Acid. Inhibition experiments were carried out in citric acid medium only for better understanding of the adsorption process in the absence of complexing agents (NTA).
2.3.4 Ultrasonic Treatment of Exposed Carbon Steel Coupon

After the exposure of CS coupons to decontamination formulation, the coupons were observed to contain loosely bound material. Ultrasonic bath was used to separate out the loosely bound material from the coupons. While ultrasonic treatment removed only loosely held material, the inherent oxide on the carbon steel specimens remained undisturbed. The samples were kept in an ultrasonic bath (Model Life Care Fast Clean Ultrasonic Cleaner, 60Watt, 33±3KHz, India) for about twenty minutes and subsequently the detached materials from samples were filtered out on Millipore filter paper of 0.22µm pore size. Both loosely bound material and ultrasonically treated specimens were used for subsequent characterization.

2.3.5 Antimony Adsorption and Its Inhibition on Magnetite Surface

In general, CS surfaces are covered with a thick magnetite layer developed during normal operation of nuclear plants. So it is mandatory to get a thorough understanding of Sb adsorption on magnetite surfaces also. Hence adsorption studies were carried out extensively on magnetite powder. In adsorption experiments, 250 ml high purity water was heated and de-aerated. Subsequently organic acids were added in the required quantities in water followed by the addition of 10ppm Sb(III) (solution of Sb₂O₃). Magnetite powder (1.0g) was added into the solution after one hour of the addition of the Sb₂O₃ solution.

Antimony(III) adsorption studies were carried out with different complexing organic acids and these complexing organic acids were selected based on their complexing capability with Fe and Sb. Subsequently, some adsorption experiments were performed to assess the effects of cations such as Mn²⁺, Mg²⁺; oxyanions like MoO₄²⁻, PO₄³⁻; organic compounds viz. Rodine 92B, Pyrogallol Red, Phenanthroline
on Sb(III) adsorption. Surface modification of magnetite was also attempted by using Lauric acid and Benzoic acid at 85±1°C for 5 hours to minimize further adsorption of Sb(III) in Tartaric Acid. During the course of those experiments, solution samples were taken at predetermined intervals and the samples were analyzed using ICP-AES to determine the concentration variation of iron and antimony in solution. Adsorption process was evaluated using the following equation,

\[ A = \frac{[(C_i - C_x)/C_i]}{W} \]  

Where

\( A \) = Adsorption Fraction per unit mass of magnetite or cm\(^2\).  
\( C_i \) = Initial concentration of Sb(III) before magnetite powder addition  
\( C_x \) = Sb(III) concentration at sampling time  
\( W \) = weight of un-dissolved magnetite powder*  

* In some CS related experiments ‘W’ was the exposed surface area in cm\(^2\).

Details of these studies are given in the subsequent chapters.

2.4 Instrumental Techniques

2.4.1 Ultraviolet/Visible Spectroscopy

In ultraviolet-visible spectroscopy, the molecule absorbs ultraviolet/visible light (200nm to 800nm) and as a result valence electrons are excited from ground electronic state to an excited electronic state. In general, valence electrons stay in \( \sigma \) bonding orbital, \( \pi \) bonding orbital and non-bonding orbital. Transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) require the least amount of energy and therefore usually the most important. The electronic transition follows certain selection rules. UV absorptions are generally broad because
vibrational and rotational levels are “superimposed” on top of the electronic levels. For this reason, the wavelength of maximum absorption ($\lambda_{\text{max}}$) is usually reported.

![Schematic of a UV/Vis. Spectrometer instrument.](image)

**Fig. 2.2:** Schematic of a UV/Vis. Spectrometer instrument.

The ultraviolet visible spectra of compounds are usually obtained by passing light of a given wavelength (monochromatic light) through a dilute solution of the substance in a non-absorbing solvent. As light absorption is a function of the concentration of the absorbing molecules, hence the absorption of light as reported by the Beer-Lambert Law is,

$$\text{Absorbance} = -\log(I/I_0) = \varepsilon cl \quad \cdots \quad (2.2)$$

Where:

- $I$ = intensity of transmitted light
- $I_0$ = intensity of incident light
- $\varepsilon$ = molar absorptivity
- $c$ = molar concentration of solute
- $l$ = length of sample cell (cm)
2.4.1.1 Instrumentation

A schematic diagram of uv/vis spectrometer is shown in Fig.2.2. A hydrogen or deuterium discharge lamp is used in the ultraviolet range and a tungsten/halogen lamp is used in the visible range. The white light passes through a grating monochromator. In the double beam instrument, a light beam is spilt by a half-silvered mirror, which transmits about 50% and reflects the other 50%. One beam passes through the sample and then to a photovoltaic cell; simultaneously other beam passes through the solvent to a similar transducer. The spectrum is produced by comparing the currents generated by the sample and the reference beam. The comparison is carried out with null detector.

The UV/Vis. instrument used is made from M/s Thermo model evolution 500. The instrument was used to differentiate Sb(III) and Sb(V) species in the solution with Pyrogalol red complexing agent.

2.4.2 Flame Atomic Absorption Spectrometry (FAAS)

FAAS is a spectro analytical procedure for the qualitative and quantitative determination in trace and ultra trace level of chemical elements. Atomic absorption spectroscopy uses the absorption of light to measure the concentration of gas-phase atoms. Hence in FAAS, the analyte usually in liquid phase is vaporized inflame into the gas phase. The ground state atoms adsorb ultraviolet or visible light and make the transition to higher electronic energy levels. The amount of light adsorption corresponds to analyte concentration [2]. Application of the Beer-Lambert law directly is difficult in FAAS due to variation in the atomization efficiency from the sample matrix, and non-uniformity of concentration. Usually, concentration determination is carried out after calibrating the instrument with standards of known concentration.
2.4.2.1 Instrumentation

A schematic diagram of a FAAS is shown in Fig. 2.3. The light source is usually a hollow-cathode lamp of the element that is being measured. In FAAS, flame burner is used for desolvation, vaporization and atomization of liquid sample at higher temperature (2100 – 2800°C). Sample solutions are usually aspirated with the gas flow into a nebulizing/mixing chamber to form small droplets before entering the flame. FAAS uses monochromator and detectors for UV and visible light. The main purpose of the monochromator is to isolate the adsorption line from background light due to interference. Usually in dedicated instruments monochromator is replaced with a bandpass interference filter. Photomultiplier tubes are the most common detectors for FAAS [3]. The technique encounters some chemical and physical interference.

![Schematic of a FAAS instrument.](image)

**Fig. 2.3:** Schematic of a FAAS instrument.

The FAAS instrument used in this study was from M/s GBC model 902. In all the measurements in this study the standard solutions were prepared along with organic acid employed in the study to counter the possible interference effects.
2.4.3 Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES)

An inductively coupled plasma spectrometer is a tool for detection of metals in solution in the concentration range percentage to ultra trace level. A schematic diagram of ICP-AES is similar to FAAS as shown in Fig. 2.3. The only difference in ICP-AES is the light source and sample atomizer. In plasma torch, liquid sample is injected into argon gas plasma contained by a strong magnetic field generated by RF generator. The plasma generates a temperature of approximately 8000°C. At this temperature all elements become thermally excited and the electrons emit light at their characteristic wavelengths as they return to ground state. This light is collected by the spectrometer and passes through a diffraction grating that serves to resolve the light into a spectrum of its constituent wavelengths. Within the spectrometer, this diffracted light is then collected by photomultiplier tubes as detector and amplified to yield an intensity measurement that can be converted to an elemental concentration by comparison with calibration standards. This technique is also known as inductively coupled optical emission spectrometer (ICP-OES), is a very sensitive technique for identification and quantification of elements in a sample [4]. Most of the ICP-AES instruments are designed to detect a single wavelength at a time (monochromator) and this can be done in sequential scanning. Since an element can emit at multiple wavelengths and this wavelength can be captured simultaneously with polychromator. Detection limits typically range from parts per million (ppm) to sub parts per billion (ppb), depending on the element and instrument.

The ICP-AES from HORIBA JOBIN YVON model ULTIMA 2 was used for elemental analysis. The instrument has sequential scanning based on Czerny Turner monochromator with 1 meter focal length and a high frequency 40.68 MHz RF generator. The instrument gives resolution <10 pm up to 430 nm and < 18 pm up to 430 -800nm.
The relative standard deviation was less than 1.5% for elements analyzed by the technique.

2.4.4 Powder X-Ray Diffraction (XRD)

XRD is a non-destructive technique that reveals phase and unit cell dimension information of a crystalline material. The powder XRD technique is used for the powder sample consisting of fine grains of single crystalline material and also for particles in liquid suspensions or polycrystalline solids (bulk or thin film materials). Powder diffraction data can be collected using either transmission or reflection geometry. Both methods yield the same data. The reflection mode is used usually for solid sample while transmission mode is used for the liquid sample.

X-ray diffraction is based on constructive interference of monochromatic X-rays from a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg’s Law ($n\lambda=2d\sin\theta$). This law relates the wavelength of electromagnetic radiation ($\lambda$) to the diffraction angle ($\theta$) and the lattice spacing ($d$) in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of $2\theta$ angles, all possible diffraction directions of the lattice attain due to the random orientation of the powdered material. Scanning of the sample with the diffraction angle is done with the goniometer. It is a mechanical assembly that makes up the sample holder, the detector arm and associated gear. In a conventional X-ray diffractometer, 0-20 (Bragg-Brenatano) goniometer is used. Here the X-ray tube is stationary, the sample moves by the angle $\theta$ and the detector simultaneously moves by the angle 20. Angle conversion of the
diffraction peaks to d-spacings allows identification of the material because each material has a set of unique d-spacings. The peak position and the relative intensity of the lines are indicative of a particular phase and material thus providing “fingerprint” for comparison [5].

A qualitative phase analysis of unknown sample was carried out by matching the XRD pattern with a library of standard. Limitations of the technique are that only crystalline materials can be characterized and the detection limit is 2wt% of the sample.

Glancing angle XRD (M/S STOE, Germany make X-ray θ–θ mode) was used with Cu Kα (8.047 KeV) as the incident X-ray source. Specimens from the antimony deposition and inhibition were characterized for finding new phases. Some of the powder samples were extracted from the loosely bound specimens by ultrasonic treatment.

### 2.4.5 Scanning Electron Microscopy (SEM)

SEM is an electron microscopic method for high-resolution imaging of surfaces. SEM is similar to light microscope but uses electrons instead of visible light. It gives a much higher magnification (>100,000X) and greater depth of field up to 100 times compared to light microscopy [6].

The high energy incident electrons interact elastically and in-elastically with the sample’s surface and near-surface material and produce various types of electrons and X-rays. SEM uses secondary electrons (SE) and backscattered electrons (BSE) for imaging. SE is lower-energy electrons emitted resulting from inelastic scattering. The SE can be formed by collisions with the nucleus where substantial energy loss occurs or by the ejection of loosely bound electrons from the sample atoms. The energy of secondary electrons is typically 50 eV or less. Similarly, BSE is beam electrons or primary electrons that are reflected from the sample by elastic scattering. Composition related information
is obtained from an energy dispersive x-ray emitted from the sample bombarded with a high energy electron and the technique called energy dispersive spectroscopy (EDS).

### 2.4.5.1 Instrumentation

A schematic diagram of an SEM is shown in Fig. 2.4. In SEM, electron gun is used to produce a high energy electron beam situated as column above the sample chamber. Electron gun produces electrons by a thermal emission source, such as a heated LaB₆ filament, or by a field emission cathode. A series of electromagnetic lenses is used in SEM to focus the electrons into a small beam as small as about 10 Å. The focused beam is directed and positioned onto the sample surface with the help of scanning coils near the end of the column. The beam can also be focused at a single point or scanned along a line for x-ray analysis for composition analysis.

![Schematic of an SEM instrument.](image-url)
Two electron detector types are predominantly used for SEM imaging. Scintillator type detectors (Everhart-Thornley) are used for secondary electron imaging. Detectors for backscattered electrons can be scintillator types or a solid-state detector.

The SEM column and sample chamber are maintained at a moderate vacuum to allow the electrons to travel collision free from the electron beam source to the sample and then to the detectors. High-resolution imaging is done by the chamber at higher vacuum in the range of $10^{-5}$ to $10^{-7}$ Torr. Imaging of nonconductive, volatile, and vacuum-sensitive samples can be performed at higher pressures.

### 2.4.5.2 Image Formation and Magnification

Image formation of surface was carried out by the scanning of the electron beam in a raster pattern. The interaction of high energy electron that emits electrons is detected for each position in the scanned area by an electron detector. The intensity of the emitted electron signal is displayed as brightness on a computer monitor. By synchronizing the scan of the incident electron beam with computer monitor scan, the computer monitor displays the morphology of the sample surface area scanned by the beam. Magnification of the computer monitor image is the ratio of the image display size of the sample to the area scanned by the electron beam [7].

The SEM from CAMSCAN model 3200 was used for high-resolution imaging of our exposed CS surfaces. The quantitative elemental information on the surfaces were carried out with EDS made from OXFORD model INCA.

### 2.4.6 X-ray Photoelectron Spectroscopy (XPS)

XPS is a spectroscopy of photoelectrons generated from atom due to X-ray hitting the materials and these photoelectrons provide both elemental and chemical information
from all kinds of solid material. XPS is a surface sensitive technique due to inelastic scattering losses of photoelectrons as a result only photoelectrons from top few atomic layers are detected.

Fig. 2.5: Schematic of an XPS instrument.

2.4.6.1 Principle of XPS

Bombarding a sample in ultra high vacuum with soft X-ray (~1.5 KeV) gives rise to the emission of photoelectrons from core shells. If the energy of monochromatic X-rays is known (hv) and the kinetic energy of the emitted photoelectrons Ke is measured with an electron spectrometer then the binding energy (Be) of the atomic orbital from which the electron originates can be calculated by means of the equation

\[ B_e = h\nu - K_e - \phi \quad \ldots \ldots (2.3) \]

In this equation, \( \phi \) is the work function of the spectrometer. The work function is the minimum amount of energy an individual electron needs to escape from the surface.
and detected by the spectrometer. The typical value of the spectrometer work function is around 4.5 eV.

Each element produces a unique set of electrons with specific energies. An XPS spectrum is obtained by measuring the number of these electrons as a function of binding (or kinetic) energy. With the exception of H and He, all elements can be detected.

**2.4.6.2 Instrumentation**

Like any optical spectroscopic instrument electron spectrometers are also made up of various components and these are a Source, a sample holder, an analyzer, a detector, signal processor and readout. Figure 2.5 shows a typical arrangement of these components. Electron spectrometer works under the ultra high vacuum in the range of 10^-10 Torr.

**Vacuum and Vacuum pumps**

In XPS equipment vacuum is required to avoid loss of energy of photoelectrons due to scattering by gas molecules and also to avoid surface contamination due to adsorption of gas molecules from the measurement chamber during the course of the experiment. In XPS, ultra high vacuum (UHV) lower than 10^-9 Torr is maintained by vacuum pumps. The transition of the vacuum from atmospheric pressure to UHV is beyond the pumping characteristics of any single pump. Hence, two or more different pumps are needed to achieve the required vacuum. The most common pumps used for preliminary pumping are rotary pumps and turbomolecular pumps. The ion pumps are used to reach UHV level with auxiliary titanium sublimation pumps.

As XPS works under UHV, the materials used for construction must not degas under UHV. Most of UHV vessels are stainless steel while in places where there is
magnetic screening requirement mu-metal is used instead of stainless material. The other metals and material for small-scale fabrication in UHV viz. sample mounts, sample heating, electrical connections, seals etc. are copper, nickel, platinum, molybdenum, tantalum, tungsten and borosilicate glass [8].

**Source**

Soft X-ray tube is used as a source in table top XPS. The energy of x-ray and full width half maxima (FWHM) must be optimized to cover the whole range of elements and their chemical information. Al and Mg Kᵋ is mostly being used as a source. Al kα x-ray energy is 1486.6 eV and FWHM is 0.85 eV while for Mg kα x-ray energy is 1253.6 eV and FWHM is 0.75eV.

Synchrotron source gives the continuous tunable x-ray source of high intensity of all the required energies. In principle synchrotron can produce high photo-ionization cross-section of all core levels.

**Analyzer**

Most photoelectron spectrometers use hemispherical type electron analyzer. In hemispherical analyzer electron beam is deflected by an electrostatic magnetic field, which is generated in between the two hemispherical plates. The deflection of electron beam follows the curved path and the radius of curvature depends on the kinetic energy of electron and the magnitude of an electrostatic field. Scanning of various kinetic energy electrons is carried out by focusing them at the detector by varying the field strength. The analyzer is maintained at or below 10⁻⁵ Torr pressure [9].
Transducer

Channel electron multipliers (CEM) are used as transducers in electron spectrometer which consist of glass tube that have been doped with lead or vanadium. In CEM several kilovolts potential is applied across the end as a result of which a single incident electron multiplies into $10^6$ to $10^8$ electrons and generates a pulse. The pulses are counted electronically.

2.4.6.3 Information from XPS Peaks

Electron spectroscopy for chemical analysis provides qualitative and quantitative information about the elemental composition and oxidation states of elements of solid surfaces. It also often provides useful structural information [8]. A low resolution, wide-scan of XPS spectra gives the elemental composition of samples. A high resolution scan peaks provide information about the chemical shift, Valence band structure, and Auger chemical shifts etc.

Photo-Electron Chemical Shift

The peak position of a photo electron (BE) is found to change with the variation in the chemical environment of the atom. The variation may be in the number of valence electrons and the type of bonds they form that influence the binding energies of core electrons. The change in the valence electrons (oxidation state) can be observed in terms of change in the binding energy. Usually more positive oxidation state gives higher binding energy due to more attraction of core electrons through the nucleus of an atom.
**Auger Chemical Shift**

Auger peaks also shift with changes in the chemical environment similar to photoelectron chemical shift. The magnitude of the Auger chemical shift is often significantly greater than that of the photo-electron chemical shift. The difference in Auger and photo-electron chemical shifts is due to the difference in final-state relaxation energies between chemical states. It is defined as a modified Auger parameter ($\alpha$) as follows:

$$\alpha = E(KKL) + E_B(K) \ldots \ldots(2.4)$$

Where $E(KKL)$ is the kinetic energy of the most intense Auger peak and $E_B(K)$ is the binding energy of the most intense photo-electron peak. The value of Auger parameter is useful for characterizing the charging samples or in identifying the chemical states where chemical shift is very low (below resolution limit).

**Valence Band Structure**

Valence levels are low binding energy (0-20 eV) electrons occupied levels and are involved in de-localized or in bonding orbitals. The spectrum in this region consists of many closely spaced levels giving rise to a band structure. The spectrum gives the information about the electronic structure of materials and in checking the accuracy of band structure calculations.

XPS (Model VG ESCALAB MK200X) was used with Al $k\alpha$ as an X-ray source and 150 mm hemispherical analyzers at 20 eV pass energy was used for collecting the photoelectrons. The instrument was calibrated with Au 4f7/2 line at 84.0 eV with 1.6 FWHM [10]. Carbon 1s peak at 285.1 eV was used as an internal standard for charge correction in the case of insulating samples. The data acquisition and deconvolutions of the spectra were carried out using dedicated software ‘Eclipse V2.1’ supplied along with
the instrument. The component spectra were fitted with a Gaussian-Lorentzian peak functions on a Shirley background.

### 2.4.7 Fourier Transform-Infrared Spectroscopy

Fourier Transform-Infrared Spectroscopy (FTIR) is a powerful technique to identify types of chemical bonds of organic/inorganic materials. The technique measures the absorption of infrared radiation (IR) by the sample material versus wavelength. Absorption of infrared radiation in the material usually excites molecules into a higher vibrational state. The wavelength of absorbed IR is a function of the energy difference between the at-rest and excited vibrational states of the particular molecules. Adsorption bands in the range of 4000-1500 wavenumbers (cm\(^{-1}\)) typically belong to functional groups viz. –OH, C=O, N-H, CH\(_3\) etc.

The FTIR spectrometer uses an interferometer to modulate the wavelength from a broadband IR source. A detector is used to measure the intensity of transmitted or reflected light as a function of its wavelength. The detector provides signal in the form of the interferogram, which is transformed into a single-beam infrared spectrum by applying Fourier transforms. The FTIR spectra usually plotted as intensity versus wavenumber (in cm\(^{-1}\)). Wavenumber is reciprocal of the wavelength. The intensity of FTIR spectra can be the percentage of light transmittance or absorbance [11].

Infrared spectra of magnetite powder after different treatment were recorded by using a BOMEM MB-100 FTIR spectrometer with a spectral resolution of 1 cm\(^{-1}\).

### 2.4.8 Electrochemical Techniques

Corrosion is an electrochemical oxidation (anodic) and a reduction (cathodic) process. The anodic reaction is as follows
Fe → Fe^{2+} + 2e^- \ldots (2.5)

Several cathodic reactions are possible depending on the reducible species present in the solution which are as follows [12]:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \ldots \ldots (2.6) \]

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \ldots \ldots (2.7) \]

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \ldots \ldots (2.8) \]

At equilibrium, both oxidation and reduction rates are equal giving rise to a zero net current and the corresponding potential and current represents the ‘corrosion potential (E_{corr})’, ‘open circuit potential (OCP)’, and ‘corrosion current (I_{corr})’ respectively. The corrosion rate (milli inches per year) can be calculated by the following equation:

\[ \text{Corrosion Rate (mpy)} = (0.13 \times I_{corr} \times \text{E.W.}) / (A \times D) \ldots \ldots (2.9) \]

Where:

- E.W. = equivalent weight (in g/equiv.)
- A = area (in cm$^2$)
- D = density (in g/cm$^3$)
- 0.13 = metric and time conversion factor

$I_{corr}$ at $E_{corr}$ can be determined by polarizing the specimen away from its equilibrium by imposing a potential other than $E_{corr}$ in a systematic manner and measuring the resulting current. When the applied potential is positive (with reference to $E_{corr}$), it is anodically polarized while negative potential signifies cathodic polarization. The degree of polarization is a measure of anodic and cathodic reaction rates retarded by various environmental and/or surface processes. Passivation, pitting or other slow processes can be accelerated by applying a potential to the specimen.
2.4.8.1 Tafel Plot

A Tafel plot is a curve of applied potential vs. logarithm of current density generated by stepwise increases in potential (0.1 mV/Sec) about 250 mV anodically and cathodically from the corrosion potential as shown in Fig.2.6 [12]. The corrosion current ($I_{corr}$) can be calculated directly by the intersection of extrapolated linear Tafel region at $E_{corr}$. Tafel constants are calculated by measuring the slope of these extrapolated lines. Anodic linear region gives anodic Tafel constant ($\beta_a$) and cathodic linear region gives the cathodic tafel constant ($\beta_c$).

Fig. 2.6: A typical Tafel plot.

Fig. 2.7: A typical potentiodynamic anodic polarization plot.
2.4.8.2 Potentiodynamic Anodic Polarization (PDAP)

This technique is used to find out the active/passive characteristic of a given metal-solution system [12, 13]. The specimen is scanned in the positive potential from $E_{corr}$ and the current is measured. The plot showing different regions is shown in Fig. 2.7.

In active region metal loss by dissolution increases rapidly with increase in potential, in passive region corrosion rate is negligible and in transpassive region the corrosion again increases due to the oxidative dissolution of passive films. Passive region current density and transpassive region's potential give information about the degree of passivation and the stability of passive films. Lower current density in the passive region indicates a higher degree of passivation and higher transpassive potential means greater stability of the passive film. The anodic current required to transform active to passive behavior is known as critical current density ($i_{cc}$) and corresponding potential is called primary passivation potential ($E_{pp}$).

2.4.8.3 Electrochemical Impedance Spectroscopy (EIS)

EIS provide information on electrochemical mechanisms, reaction kinetics and detection of localized corrosion of the system. In the EIS, a small amplitude ac sine wave signal (10 mV) is applied to the system and hence it is a non-destructive method [14]. EIS consists of response of the electrochemical processes taking place at the interface between the electrode and the solution to the voltage and frequency perturbations. Nyquist plot is a curve of real and imaginary components of impedance at a number of frequencies to describe the electrochemical system. The equivalent circuit representing various resistances, impedances corresponding to the electrochemical processes is mathematically fitted to the frequency response data. The $R_{p2}$ [15] value of the metal/solution interface is taken and compared with the corrosion rate from Tafel plot.
The resistance depends on the ionic concentration, type of ions, temperature and the geometry of the area in which the current is carried.

Fig. 2.8: A typical test cell used for corrosion measurements.

2.4.8.4 Test Cell and Instruments

Since all voltage measuring devices measure a potential difference, $E_{corr}$ of the metal-solution interface can be measured indirectly by comparing with the reference system's potential. The test cell used in a typical electrochemical experiment is shown in Fig. 2.8. It is a conventional three-electrode glass cell with a platinum foil as counter electrode, saturated calomel electrode through a luggin capillary as reference electrode and the metal specimen (CS) as a working electrode. The experiments were performed with test solutions containing organic acid, antimony and inhibitors at 85°C in deaerated environment using an Eco Chemie Autolab PG STAT 30 system. The samples were allowed to attain the stable open-circuit potential (OCP) before starting the electrochemical measurements. The potentiodynamic anodic polarization (PDAP) behaviors of the samples were obtained by polarizing the working electrode from $-1\text{V}$ to $+1.5\text{V}$ with respect to corrosion potential ($E_{corr}$) at a scan rate of 0.5 mV/sec. The corrosion current ($I_{corr}$) was determined from the intersection of anodic and cathodic Tafel lines or from that of $E_{corr}$ with the suitable Tafel line. The magnitude of the corrosion
current was taken to be representative of the corrosion resistance of the composite material. Impedance spectra for different samples were recorded at OCP by applying a sinusoidal voltage of ± 10mV in the frequency range of 10^4– 0.005Hz.

2.5 References


