4.1 Preamble

This chapter deals with the preparation of cement samples for characterization towards the evaluation of constituents and phases present in it. The synthesis, study of polymers as inhibitors for concrete corrosion and evaluation of their physical nature by using XRD will be presented. The procedure for simulation of pore solution as reference and simulation of different environment such as pore solution contaminated with chloride and iodide will also be presented. The hydration study of cement in the presence and absence of polymeric inhibitors, experiments related to setting of cement and electrochemical studies to evaluate corrosion rate will be discussed.

4.2 XRF Studies of Cement

The oxides present in the cement samples will be detected qualitatively as well as quantitatively from XRF results. The X-ray Fluorimeter used in this study is Brucker’s S8 TIGER model. The XRF studies involve the following stages.

i. Sample preparation

ii. Recording of XRF spectrum

iii. Analysis of XRF spectrum

4.2.1 Sample preparation for XRF

This method requires the sample surface to be kept flat and pure, meaning no contaminants. 6.0 grams of lithium borate-lithium bromide and 1 gram of cement were mixed in a crucible. The crucible was then placed into a fusion instrument, which is
operated according to the manufacturer’s recommendations. The fused sample should appear disk shaped and be clear in color.

4.2.2 Recording of XRF spectrum

The prepared sample wafer is placed into the XRF machine individually and a scan is performed. The resultant XRF spectrum will be analyzed in chapter VIII further to detect the oxides composition.

4.3 XRD Studies of Cement

Cement clinker phases have been quantified by using Bogue, microscope or X-ray diffraction (XRD) methods. The Bogue method is a reconstruction of the chemical analysis based on an equilibrium system, while microscope counting is tedious and time consuming\(^1\). The summary of the status of the accuracy and precision of phase quantification in Portland cement by the above three basic techniques were given by Aldridge and it was mentioned that the XRD method has a greater potential for quantification than Bogue or microscope methods\(^2\). Bogue’s calculation gives inaccurate results, because the phases do not have the compositions that are assumed\(^3\). But conventional methods require that standard data should be acquired for every phase present in the mixture to be analyzed. The Rietveld method of quantitative analysis minimizes or eliminates many of these problems and therefore provides numerous advantages over conventional quantitative analytical methods\(^4\). By using this method, the quantitative data of four main phases present in the cement such as Tricalcium Silicate (C\(_3\)S), Dicalcium Silicate (C\(_2\)S), Tricalcium Aluminate (C\(_3\)A), and Tetracalcium Alumino ferrite (C\(_4\)AF) can be obtained.
The phase identification and the influence of polymer during cement setting and crystalline nature of the samples have been analyzed through XRD. Brucker’s D2-Phaser, a desk top XRD have been used for analysis of sample. The scans were performed with 2θ ranging from 5-70° at a rate of 0.01° per minute. All spectra were analyzed by using EVA software for qualitative analysis and Rietveld refinements were carried out by using pattern analysis software, namely, TOPAS (Total Pattern Analysis Software). Copper Kα radiation (λ=1.5418Å) was used and the power of X-ray generation is 30KV and 10mV. The sample preparation method for XRD studies is discussed below.

4.3.1 Sample preparation and recording of XRD

The cement sample is finely ground using mortar and pestle and then passed through 25micron sieve, in order to avoid preferred orientation. Sample preparation is a main key step for quantitative analysis for obtaining the sharp signal of related XRD of indented sample. The cement sample is prepared in such a manner to ensure the specimen is a representative of the material and is homogeneous. This was then placed in the sampling tray, where the surface was smoothed to eliminate surface irregularities.

4.3.1.1 Effects of Sample preparation

In order to obtain accurate results, numerous instrumental and sample-related problems must be addressed; these include particle statistics, primary and secondary extinction, microabsorption, preferred orientation, separation of overlapping and broad reflections, variation in standard data with composition, availability of pure standards and detection of amorphous and trace phases. Sample preparation is a main criterion to study the material property. The following are the requirements of the sample preparations.
i) An ideal powder sample should have many crystallites in random orientations.

ii) The crystallites should be distributed equally among all orientations.

iii) Crystallites should be <10mm in size to get good powder statistics, otherwise the measured diffraction pattern will not agree with that expected from an ideal powder.

iv) The crystallites should not be large in number since it will lead to imperfect diffraction pattern.

In the present investigation, the studies related to identification of phases present in the cement, effect of polymers during cement setting and alteration of mineralogical phases due to polymer inclusion have been conducted by using XRD technique.

### 4.4 SEM Studies on Cement

The surface morphology and microstructure of the cement is studied by using SEM. The SEM used in this research is a JEOL JSM 840. All images were scanned at 15 kV acceleration voltages. A location of particles was chosen such that it accurately represented the powder as a whole. The presence of $\text{C}_3\text{S}$, $\text{C}_2\text{S}$, $\text{C}_3\text{A}$, and $\text{C}_4\text{AF}$ will be discussed based on this study. Further, the influence of polymer on cement phases will also be studied by using this method. The sample preparation and recording of SEM are discussed below.

#### 4.4.1 Sample preparation and recording of SEM

First the samples were hand fanned to achieve an even dispersion of the cement powder. A sample pedestal was prepared by placing double sided carbon tape on the top surface of aluminum stubs. This surface was then gently placed onto the dispersed cement powder. This method ensures that the powder that adhered to the tape was evenly spread as near as possible to a single layer of particles. The gold sputtering was performed to prevent charging of the cement powder specimens.
In the present studies, the morphological studies related to identification of phases present in the cement, effect of polymers during cement setting and alteration of mineralogical phases due to polymer inclusion have been conducted by using SEM analysis. Further, surface examination of the mild steel with and without inhibitor has also been studied using SEM analysis.

4.5 FT-IR Studies on Cement

Identification of functional moieties present in the cement is analysed by the FT-IR technique. Perkin Elmer FT-IR 8000 spectrometer Model RX-I is used for the present study. The sample preparation and recording of FT-IR spectra are given below.

4.5.1 Sample Preparation for FT-IR spectra

To prepare the sample for FT-IR analysis, 100 mg of KBr powder is mixed with 1mg of the cement powder sample. Thorough mixing is essential to ensure a homogenous mixture. After the two powders are mixed thoroughly and completely, they are placed into a die and pressed at 10,000 psi under vacuum for approximately 5 minutes. This process forms a pellet which is then ready to be placed in FT-IR sample holder to be scanned.

In the present study, FT-IR spectral investigation is exploited to derive the functional groups present in the cement sample.

4.6 Synthesis of Polymers

The synthetic routes for the polymers employed in the current investigations have been discussed at length in the Chapters V, VI and VII.
4.6.1 XRD studies on polymers

The synthesized polymer samples are characterised by using XRD to study mainly nature of polymer and the extent of crystallization. Crystallinity is a measure of amount of crystalline region in polymers and their properties like hardness, tensility, stiffness, crease and melting points. The scans are performed with 2θ ranging from 5-70° at a rate of 0.01° per minute.

4.6.2 Calculation of % Crystallinity

It is calculated from the intensities of lines (area) in the XRD spectrum. Total intensity of XRD lines is separated into crystalline intensity (I_c) and amorphous intensity (I_a). Then crystallinity or percentage of crystallinity (%X_c) is calculated using the relation,

\[ \%X_c = \frac{I_c}{I_c + I_a} \times 100 \]

where \( I_c + I_a = \) Total intensity of lines in XRD spectra.\(^5\)

Distributions of amorphous and crystalline regions of polymers are shown in Fig 4.1.

![Fig 4.1 Distribution of amorphous and crystalline regions in polymers](image)
4.7 Studies on Cement Setting Time

Stepwise procedure for studying the setting time of cement as per I.S.4031 is discussed below.

4.7.1 Preparation of test block

i. 400 gm of cement is taken.

ii. A neat cement paste is prepared by gauging the cement with 0.85 times water required to get a paste of standard consistency.

iii. The stop watch is started at the instant when water is added to the cement. The gauging time should not be less than 3 minutes nor more than 5 minutes.

iv. The Vicat mould is filled with cement paste, the mould resting on non-porous plate. The surface of the cement paste is leveled with the top of the mould with a trowel.

4.7.2 Determination of initial setting time

i. The mould is placed together with the non-porous plate under the rod bearing the initial setting time needle. The needle is adjusted, so that it touches the surface of test block.

ii. The needle is released quickly allowing it to sink in the cement paste in the mould. The penetration of the needle in the paste is noted.

iii. This procedure is repeated after every 2 minutes, until the needle fails to penetrate the block up to about 33 to 35 mm from the top of block.

iv. The time shown by the stop watch at this instant is noted as the initial setting time.
4.7.3 Determination of final setting time

i. The needle of Vicat apparatus is replaced by the needle with an annular attachment.

ii. The needle is released gently to touch the surface of the test block. The procedure is repeated until the needle makes an impression, while the attachment fails to do so.

iii. The time shown by the stop watch at this instant is noted as final setting time.

4.8 Hydration Study of Cement in the presence of Polymeric Inhibitor

The addition of corrosion inhibitors is one of the corrosion prevention methods used in order to delay the corrosion process. Corrosion-inhibiting additives should not change the concrete characteristics, such as mechanical resistance and dimensional stability. These properties arise from the mineralogical phases of cement such as $\text{C}_3\text{S}$, $\text{C}_2\text{S}$ and $\text{C}_3\text{A}$. During hydration, C-S-H gel will be formed which should not undergo any kind of chemical alteration by the addition of additives, since it will be reflected in strength property of concrete at early as well as later stage.

In order to study these effects, experiments related to cement hydration have been conducted. Cement samples having w/c ratio of 0.40 in the presence and absence of polymeric inhibitors have been used for hydration studies. The samples (with and without addition of polymeric inhibitors) are collected at regular time intervals such as 1 hr, 3 hr, 5 hr and 24 hr during the hydration process. Further, the samples collected have also been analyzed by using XRD and SEM to evaluate the interaction of polymer (organic matrix) with cement (inorganic matrix).
4.9 Simulation of Pore Solution

Simulated pore solution without sodium chloride (0.5M KOH + 0.1M NaOH) is used as reference. The pH of the blank pore solution is maintained at 12.5. In Chapter 5, the simulated pore solutions contaminated with chloride ions have the composition of 0.5M KOH + 0.1M NaOH + 0.5M NaCl. The pH of this electrolyte is 11. In Chapter 6, the simulated pore solutions contaminated with chloride ions have the composition of 0.5M KOH + 0.1M NaOH + 1M NaCl. The pH of this electrolyte is 10. In Chapter 7, the simulated pore solutions contaminated with chloride ions have the composition of 0.5M KOH + 0.1M NaOH + 1M NaCl. The simulated pore solutions contaminated with iodide ions have the composition of 0.5M KOH + 0.1M NaOH + 1M KI and the pH of this electrolyte is 10.5. In concrete corrosion, chlorides play a major role, particularly at coastal zone. Hence, the presence of chloride ions in the pore solutions will definitely influence the corrosion rate. The presence of iodide ions will also influence the corrosion rate of steel. Hence, in the present study, the pore solutions have been simulated by using halide ions in such a way that they simulate an environment similar to that of coastal zone to study the inhibitor efficiency towards corrosion.

4.10 Electrochemical Techniques

Electrochemical techniques are now widely used in evaluating inhibitors, since corrosion is mainly an electrochemical phenomenon arising from the current flow between anodic and cathodic areas on a metal surface. The effect of inhibitor will be to reduce this current. The corrosion behaviour of the steel samples with and without inhibitor in pore solution (with and without chloride or iodide) as electrolyte has been evaluated by electrochemical impedance spectroscopic (EIS) and potentiodynamic polarisation studies.
using potentiostat/galvanostat/ frequency response analyzer of ACM instruments (Model: Gill AC).

i) Electrode used

For electrochemical studies a cylindrical mild steel rod, which is used in construction purpose with an exposed area of 1 cm$^2$ is used. The composition of the steel used in this study is Fe 98.59 %, C 0.30 %, Mn 0.94%, P 0.05% and S 0.04%.

ii) Electrode surface preparation

The steel sample is abraded using successive grit size of SiC-coated abrasive papers (60, 100, 220, 320, 400 and 600). The abrasion is continued with 0.3 µm alumina paste to a mirror finish: It is finally rinsed with deionised water and acetone.

iii) Electrode cell assembly

Electrochemical measurements are carried out in a 100 ml glass vessel. The steel sample having a mirror finished surface forms the working electrode, while a saturated calomel electrode (SCE) and platinum electrode were used as the reference and auxiliary electrodes, respectively. These electrodes are placed within a flat cell in such a way that only 1 cm$^2$ area of the working electrode is exposed to the electrolyte solution (Pore solution with various concentration of inhibitor with chloride or Iodide). The working electrode is exposed to pore solution for 10-15 minutes before electrochemical measurements.

iv) Electrochemical impedance spectroscopy (EIS)

Impedance measurements are carried out at the open circuit potential by using computer controlled potentiostat. After immersion of the specimen, prior to the impedance measurement, a stabilization period of 30 min is observed, for $E_{oc}$ to attain a stable value. The AC frequency extends from 0.1 Hz to 10 KHz with signal amplitude of 10mV at the corrosion potential. The measurements were automatically controlled by Z-view software.
and the impedance diagrams are given in the Nyquist representation \((Z_{\text{real}} \text{ vs } Z_{\text{imaginary}})\). From the Nyquist plots, electrochemical parameters such as \(C_{\text{dl}}\) and \(R_{\text{ct}}\) are calculated.

**v) Polarisation measurements**

The Tafel polarisation measurements are made after EIS studies in the same cell set-up, for a potential range of -200 mV to +200 mV with respect to open circuit potential, at a scan rate of 1 mV /sec. From the plot of \(E\) vs \(\log i\), the corrosion potential \(E_{\text{corr}}\), corrosion current \(I_{\text{corr}}\), Tafel slopes \(b_a\) and \(b_c\) are obtained in the absence and in the presence of inhibitors at various concentrations for various environment.

**vi) Evaluation of inhibition efficiency**

**a) Potentiodynamic polarisation method**

The inhibition efficiency can be calculated from the value of \(I_{\text{corr}}\) by using the formula,

\[
\text{Inhibition efficiency (\%)} = \frac{I_{\text{corr}} (\text{blank}) - I_{\text{corr}} (\text{inh})}{I_{\text{corr}} (\text{blank})} \times 100
\]

where \(I_{\text{corr}} (\text{blank})\) is the corrosion current in the absence of inhibitor and \(I_{\text{corr}} (\text{inh})\) is the corrosion current in the presence of inhibitor.

**b) AC impedance method**

The inhibition efficiency can be calculated from the value of \(R_{\text{ct}}\) by using the formula,

\[
\text{Inhibition efficiency (\%)} = \frac{R_{\text{ct}} (\text{inh}) - R_{\text{ct}} (\text{blank})}{R_{\text{ct}} (\text{inh})} \times 100
\]

The \(R_{\text{ct}} (\text{inh})\) is the charge transfer resistance in the presence of inhibitor and \(R_{\text{ct}} (\text{blank})\) is the charge transfer resistance in the absence of inhibitor.
c) Surface coverage from polarisation method

The surface coverage of the inhibitors can be calculated using the formula

\[
\theta = \frac{I_{\text{corr}}(\text{blank}) - I_{\text{corr}}(\text{inh})}{I_{\text{corr}}(\text{blank})}
\]

4.11 Summary

This chapter discussed about the preparation of cement samples for characterization and the evaluation of their constituents and phases present. Synthesis of polymers as inhibitors for concrete corrosion have been mentioned and evaluation of their physical nature by using XRD has been discussed. The procedure for simulation of pore solution as reference and simulation of different environments such as pore solution contaminated with chloride and with iodide has been presented. The hydration study of cement in presence and absence of additives, experiments related to setting time of cement, and electrochemical techniques to evaluate corrosion rate have been discussed.
4.12 References

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