

# Minor Project Report

On

## Hydration Studies of Cement by SEM and XRD Techniques

Submitted in Partial Fulfillment of the Requirement for the Degree of  
M.Sc. Chemistry

Submitted by-  
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Division of Chemistry  
School of Basic and Applied Science

GALGOTIAS UNIVERSITY  
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(Established under Galgotias University Uttar Pradesh Act No. 14 of 2011)

School of Basic and Applied Science

CERTIFICATE

This is to Certify that Ms. Akriti Goswami has carried out her minor project work entitled "Hydration Studies of Cement by SEM and XRD Techniques" under my supervision. This work is fit for submission for the award of Master Degree in Chemistry.

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## CERTIFICATE

This is to certify that the work in the project entitled "Hydration Studies of Cement by SEM and XRD Techniques" has been carried out by me Akriti Goswami from 27 May, 2019 to 27 July, 2019 under my supervision at CSIR-Central Building Research Institute Roorkee, INDIA, for the partial fulfillment of the requirements of the award of degree of Master of Science in Chemistry.

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**Certificate from the organization where you are doing your project**

## **CANDIDATE DECLARATION**

I hereby declare that the dissertation entitled "**Hydration Studies of Cement by SEM and XRD Techniques**" submitted by me in partial fulfillment for the degree of M.Sc. in Chemistry to the Division of Chemistry, School of Basic and Applied Science, Galgotias University, Greater Noida, Uttar Pradesh, India is my original work. It has not been submitted in part or full to this University of any other Universities for the award of diploma or degree.

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Akriti Goswami

## PROJECT SUMMARY

The performance and service life of cement can be improved by understanding its basic hydration mechanism, which is a complex process due to the presence of various kinetic steps and rapidly changing reaction chemistry especially at early stages. Hydration process start as cement comes in the contact of water and forms calcium silicate hydrates (C-S-H) and calcium hydroxide (CH) at room temperature. Hydration process start as the cement a grain come in contact with water and continues till several years. Tricalcium silicate ( $C_3S$ ) and dicalcium silicate ( $C_2S$ ) account for about 75% by weight of modern cement and control the major properties of concrete system such as mechanical strength, durability, permeability, etc. While, tricalcium aluminate ( $C_3A$ ) and tetra calcium aluminoferrite ( $C_4AF$ ) responsible for the setting and hardening of cement at early age of hydration. Precise understanding of hydration process and tuning the composition at molecular/nano level may change the properties that will affect the durability and service life of concrete besides reduction in cost and GHG emission. With advancement in microscopic techniques, it is now possible to understand the morphological changes occurring at nanolevel and thus, tuning the strength, hardness and other basic properties of the material through micro- and nanoscopic phases of the materials. The aim of the present study is to understand the mineralogical and morphological changes occurred during the hydration of Portland cement at different ages of hydration (i.e. at 1, 3 and 7 day of hydration) with Field Emission Scanning Microscopy (FESEM) and X-Ray Powder Diffractometer (XRD).

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# **1. INTRODUCTION**

## **1.1 Cement**

Cement is a well known building material and has occupied an indispensable place in construction work. The cement commonly used is Portland cement, and the fine and coarse aggregates used are those that are usually obtainable, durable and economical concrete mix; it is necessary to understand the characteristics and behavior of the ingredients. Portland cement is an extremely ground material having adhesive and cohesive properties, which provide a binding medium for the discrete ingredients. It is obtained by burning together, in a definite portion, a mixture of naturally occurring argillaceous and calcareous materials to a partial fusion at high temperature.

Several detailed reviews have been written about the mechanisms that are thought to govern the kinetics of hydration[1]. At the time they were published, several important issues – the mechanistic origin of the induction period, the rate-controlling mechanisms during the acceleration period, the most important factors responsible for the subsequent deceleration of hydration, etc. – were addressed but left unresolved due to either lack of data or seemingly equivocal evidence for different viewpoints. But significant strides have been made both in experimental techniques and in theoretical models in the intervening years. Our intention is to focus on these more recent developments, thereby providing an updated picture of the current state of knowledge and identifying the remaining controversies or gaps in understanding. Knowing the chemical composition of the raw materials, of intermediate products and of the final product represents an aspect of major importance in the fabrication and use of a product with expected specifications. The reactions occurring in the cement hydration process have, consequently, been of high interest for the researchers who studied them, among others, by means of the X ray diffraction (XRD) and scanning electron microscopy (SEM) methods[1].

## **1.2 Cement Chemistry**

The use of the mentioned methods allows more accurate information regarding the behavior of the Portland cement paste during hydration, and a more realistic knowledge of the mechanisms that generate new properties such as strength and durability, which are

among the most important in the selection of cement for a specific application. The Portland cement represents a mixture of clinker and finely ground gypsum, where the clinker is made up of four main mineral components at a maximum temperature of up to 1450°C. In the clinker, the calcium silicates represent 75 - 80 %, hence the name of silicatic cements, while calcium aluminates and calcium alumino ferrite form only 20 – 25 % [2].

### **1.3 Components of Cement**

Alite ( $C_3S$ ) is an impure form of tricalcium silicate,  $Ca_3SiO_5$ . The name was given by **Torneborn** in 1897 to a crystal identified in microscopic investigation of Portland cement. In cement Alite is found in the largest ratio (50%), under the form of colourless and equisized grains. This is the calcium silicate with the highest hydrolysis reaction which very easily react with water.  $C_3S$  hydration defines to a large extent the behavior of the cement, though its rate is not constant and not even the rate changes are constant [3].  $C_3S$  rapidly hydrates and hardens the cement slurry and enforces high initial (1-3 days) and final mechanical strength .

Belite ( $C_2S$ ) is an industrial mineral important in Portland cement manufacture. Its main constituent is dicalcium silicate,  $Ca_2SiO_4$ , sometimes formulated as  $2CaO.SiO_2$ . Belite is the mineral component that has three or even four polymorphous forms which easily reacts with water and turns into a hydrated dicalcium silicate. This slowly hydrates and hardens the cement.

The hydration and hydrolysis reactions of the two mineral compounds above also produce hydrosilicates that initially have a gel structure similar to that of the natural mineral called tobermorite[4]. The calcium silicate hydrates form the majority of the hydration products, present a gel structure, where the solid phase is made up of a lattice of microcrystals, initially of angstrom size with eyes filled with a saturated composition of components: in a later stage, the crystals develop, age and strengthen, leading to the increase of the mechanical strengths.

Tricalcium aluminate ( $C_3A$ ) is the mineral component that has the form of crystals in the clinker when slowly cooled down or as vitreous mass, when the clinker is cooled down fast. In this case it fills in the voids between the alite and belite crystals. Pure tricalcium aluminate has a violent reaction with water; the slurry hardens instantaneously, which requires the addition of gypsum ( $CaSO_4 \cdot 2H_2O$ ) when the cement clinker is ground [5]. The amount of gypsum added to the cement clinker should be carefully controlled as a too large an amount leads to expansion and hence, to the damage of the hardened cement paste. The optimal gypsum amount shall be defined by observing the hydration heat

release.

The gypsum also reacts with brownmillerite ( $C_4AF$ ) sulphoferrite hydrate and calcium sulphoaluminate hydrate, whose presence can accelerate the hydration of calcium silicates. The two calcium aluminate hydrates act as flux and diminish the clinker burning temperature[5].

## 2. Literature Review

If construction has a signature material, it's concrete -- the familiar stone-like substance that forms some part of nearly everything we build. And the key to concrete is Portland cement- the fine gray powder that binds sand and gravel into concrete's rock-like mass. It produces by heating a mixture clay, shale and limestone in a kiln at very high temperature  $\sim 1500^\circ\text{C}$ . A series of chemical reactions takes place at this high temperature which converts this powder material into the clinker. This clinker ground to an extremely fine grey powder with the addition of gypsum [6]. This fine grey powder contains four main phases:

Phase	Quantity (%)
Tricalcium Silicate ( $C_3S$ )	60-70
Dicalcium Silicate ( $C_2S$ )	10-20
Tricalcium Aluminate ( $C_3A$ )	5-10
Tetracalcium Alumino Ferrite ( $C_4AF$ )	3-8

Of these compounds,  $C_3S$  and  $C_2S$  are mainly responsible for the strength of the cement due to the formation of major binder phase i.e. calcium silicate hydrates (C-S-H) during hydration. The hydration of  $C_3S$  produces  $\sim 61\%$  C-S-H and  $39\%$  calcium hydroxide (CH), whereas  $C_2S$  produces  $\sim 82\%$  C-S-H and  $\sim 18\%$  CH. High percentages of  $C_3S$  (low  $C_2S$ )

results in high early strength but also high heat generation as the concrete sets. The reverse combination of low  $C_3S$  and high  $C_2S$  develops strengths more slowly (over 52 rather than 28 days) and generates less heat.  $C_3A$  causes undesirable heat and rapid reacting properties, which can be prevented by adding  $CaSO_4$  to the final product.  $C_3A$  can be converted to the more desirable  $C_4AF$  by the addition of  $Fe_2O_3$  before heating, but this also inhibits the formation of  $C_3S$ .  $C_4AF$  makes the cement more resistant to seawater and results in a somewhat slower reaction, which evolves less heat. The balance of the formed compounds versus the performance characteristics required from the cement is a chemically controlled parameter. For this reason considerable efforts are made during the manufacturing process to ensure the correct chemical compounds in the correct ratios are present in the raw materials before introduction of the materials to the kiln.

## 2.1 Tricalcium silicate ( $C_3S$ )

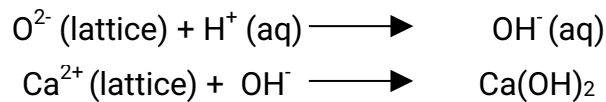
Pure  $C_3S$  undergoes a series of reversible phase transition during heating process at high temperature [7]. First crystal structure of  $C_3S$  was determined by Jeffery (JI). He showed all three polymorphism of  $C_3S$ : triclinic (T), Monoclinic (M) and Rhombohedral (R), these phase transformation are recapitulated below:



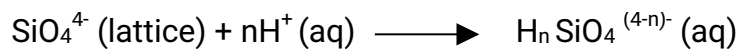
Transformation of these polymorphs is almost partially reversible when cooling: optical data supports the existence of two triclinic forms between 620 and 980°C and two other monoclinic forms between 980 and 1070°C .

Many efforts have been made by the material researchers over the last decades for understanding the hydration chemistry of cement. Understanding of basic hydration reaction is only possible way to changes the properties that will affect the durability and service life of structure besides reduction in cost and gas emission.  $C_3S$  hydration happens over a dissolution-precipitation process that may occur through the formation of each pits where the C-S-H preferentially precipitates; even so, its precipitation rate depends on the

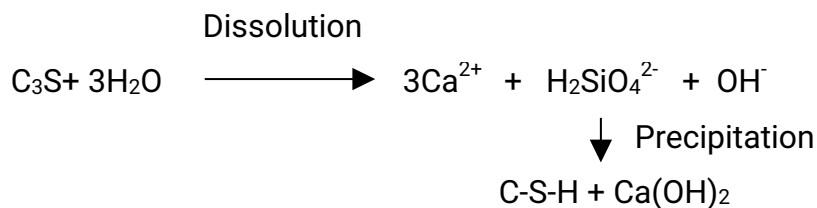
concentration of the components in solution. There are four main stages that occur during the hydration i.e. pre-induction, induction, acceleration and deceleration period [8]. On contact with water, C<sub>3</sub>S undergoes an intense and short-lived reaction, known as the pre-induction period. Oxygen ions from the surface of the C<sub>3</sub>S lattice react with protons in the water and form hydroxide ions, which in turn combine with Ca<sup>2+</sup> leading to form calcium hydroxide (CH).



At the same time, silicate material from the 'C<sub>3</sub>S' lattice surface enters into the liquid phase.



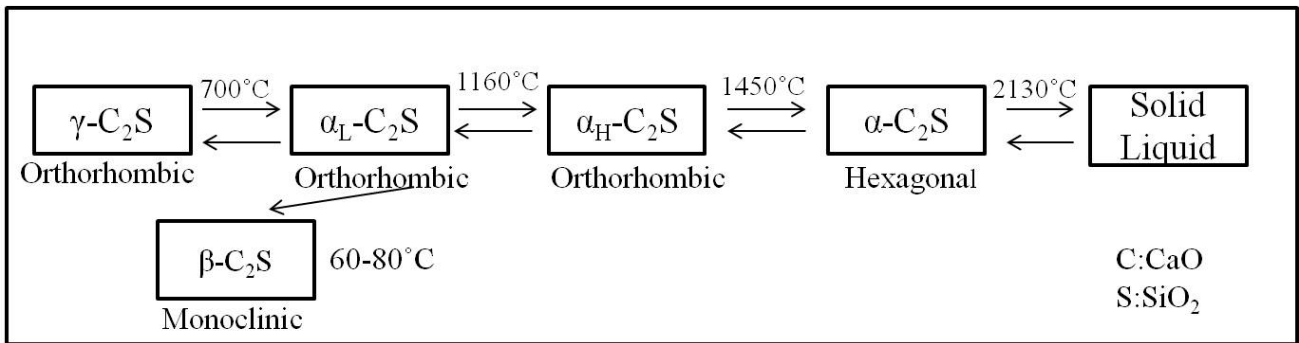
A complete reaction may be represented as:



Hydration of C<sub>3</sub>S suffers a slow down when reaching the so-called induction or dormant period, followed by a rapid increasing on the rate. Stage I is related to the initial dissolution phase. Here the rate of reaction is very high due to the dissolution of the anhydrous phase, and then slows down rapidly running to stage II. This is known as the induction period. After that, in stage III, the rate of reaction increases again reaching a maximum with the massive precipitation of the hydrates; during stage IV, it slows down gradually due to the formation of products and consumption of the reactants.

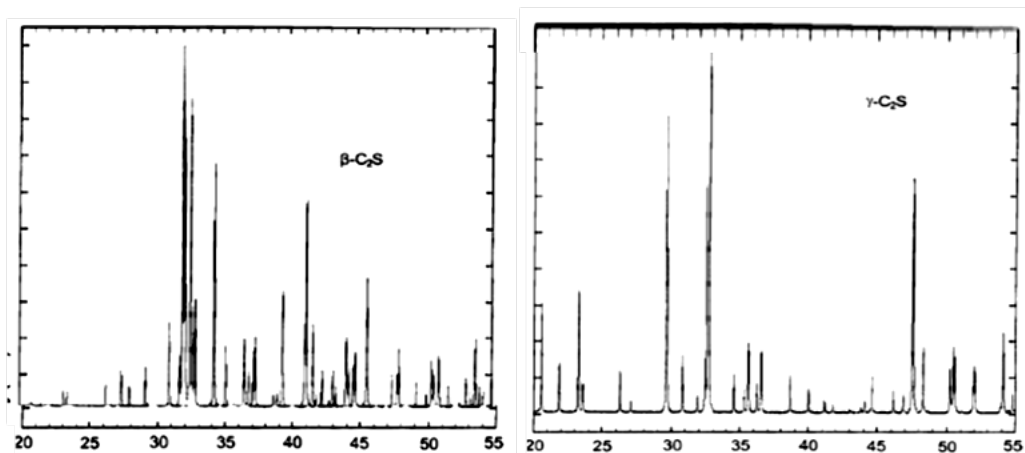
## 2.2 Dicalcium silicate (C<sub>2</sub>S)

Dicalcium silicate (C<sub>2</sub>S) present in five polymorphs known as α-C<sub>2</sub>S, α<sub>H</sub>-C<sub>2</sub>S, α<sub>L</sub>-C<sub>2</sub>S, γ-C<sub>2</sub>S and β-C<sub>2</sub>S during cooling process of cement clinker (Fig. 2.1). Slower cooling process leads to the formation of γ-C<sub>2</sub>S while through the quenching process β-C<sub>2</sub>S is formed. The polymorph of C<sub>2</sub>S present in Portland cement is β-C<sub>2</sub>S, which reacts slowly with water and generate lowest heat of hydration than the other phases present in clinker, responsible for later age strength.



**Fig. 2. 1.** Polymorphs of Belite

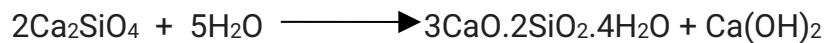
The structures of all of polymorphs of  $C_2S$  are built from  $Ca^{2+}$  and  $SiO_4^{4-}$  ions. The arrangements of these ions are closely similar in the  $\alpha$ - $C_2S$ ,  $\alpha_H$ - $C_2S$ ,  $\alpha_L$ - $C_2S$ , and  $\beta$ - $C_2S$ , but  $\gamma$ - $C_2S$  have different arrangement of ions [9]. The higher temperature polymorphs cannot normally be preserved on cooling to room temperature unless stabilized by foreign ions,  $\gamma$ - $C_2S$  is much less dense than the other polymorphs, and this causes crystals or sintered masses of  $\beta$ - $C_2S$ , to crack and fall to a more voluminous powder on cooling, a phenomenon known as dusting.  $\gamma$ - $C_2S$  is undesirable in Portland cement due to its inferior hydraulic nature and  $\beta$ - $C_2S$  polymorph can be achieved either the quenching process or by using stabilizer. Many of the earlier crystal data reported for the  $C_2S$  polymorphs were based on powder XRD patterns. This structure of  $\beta$ - $C_2S$  belongs monoclinic space group while  $\gamma$ - $C_2S$  orthorhombic space group. Fig. 2.2 shows the comparative of XRD micrographs of  $\beta$ - $C_2S$  and  $\gamma$ - $C_2S$ , showing that all the major phases of  $C_2S$  are overlapped with the  $C_3S$  phase except a distinct peak at  $2\theta$  value  $31.10^\circ$  and  $35.29^\circ$ , while  $\gamma$ - $C_2S$  have a distinct peak at  $2\theta = 29.63^\circ$ .



**Fig. 2.2.** XRD micrograph of  $\beta$ - $C_2S$  and  $\gamma$ - $C_2S$

Dicalcium silicate ( $C_2S$ ) reacts slowly, contributing little to the strength development in

cement at ages less than 28 days. It does, however, contribute substantially to the strength development beyond that time. The hydration of C<sub>2</sub>S is



C<sub>2</sub>S shows slowest hydraulic reactivity than the other compounds present in Portland cement it reacts only 30% in 28 days and 90% at 1 year of hydration. It forms C-S-H initially of low C/S ratio which increases at later ages and low CH content is formed, responsible for the later age strength [11].

### 2.3 Hydration products

The products of the reaction between cement and water are termed "hydration products." In concrete (or mortar or other cementitious materials) there are typically four main types:

**Calcium silicate hydrate:** this is the main reaction product and is the main source of concrete strength. It is often abbreviated, using cement chemists' notation, to "C-S-H," the dashes indicating that no strict ratio of SiO<sub>2</sub> to CaO is inferred. The Si/Ca ratio is somewhat variable but typically approximately 0.45-0.50 in hydrated Portland cement but up to perhaps about 0.6 if slag or fly ash or microsilica is present, depending on the proportions. [12]

**Calcium hydroxide:** (or Portlandite)- Ca(OH)<sub>2</sub>, often abbreviated to 'CH.' CH is formed mainly from alite hydration. Alite has a Ca:Si ratio of 3:1 and C-S-H has a Ca/Si ratio of approximately 2:1, so excess lime is available to produce CH.

**AFm and AFt phases:** these are two groups of minerals that occur in cement, and elsewhere. One of the most common AFm phases in hydrated cement is monosulfate and by far the most common AFt phase is ettringite. The general definitions of these phases are somewhat technical, but for example, ettringite is an AFt phase because it contains three (t-tri) molecules of anhydrite when written as C<sub>3</sub>A.3CaSO<sub>4</sub>.32H<sub>2</sub>O and monosulfate is an AFm phase because it contains one (m-mono) molecule of anhydrite when written as C<sub>3</sub>A.CaSO<sub>4</sub>.12H<sub>2</sub>O. The most common AFt and AFm phases in hydrated cement are:

**Ettringite:** ettringite is present as rod-like crystals in the early stages of reaction or sometimes as massive growths filling pores or cracks in mature concrete or mortar. The chemical formula for ettringite is (Ca<sub>3</sub>Al(OH)<sub>6</sub>.12H<sub>2</sub>O)<sub>2</sub>.2H<sub>2</sub>O or C<sub>3</sub>A.3CaSO<sub>4</sub>.32H<sub>2</sub>O mixing

notations. **Monosulfate:** monosulfate tends to occur in the later stages of hydration, a day or two after mixing. The chemical formula for monosulfate is  $C_3A.CaSO_4.12H_2O$ .

**Monocarbonate:** the presence of fine limestone,[13] whether interground with the cement or present as fine limestone aggregate, is likely to produce monocarbonate ( $C_3A.CaCO_3.11H_2O$ ) as some of the limestone reacts with the cement pore fluid.

### **3. METHOD AND METHODOLOGIES**

#### **3.1. X-RAY DIFFRACTION (XRD)**

Make: Rigaku, Japan

Model: DMax 2200

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the mineralogical composition and crystallographic structure of natural and manufactured materials. XRD is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.



The analyzed material is finely ground, homogenized and average bulk composition is determined[14]. All the experiments were carried out at room temperature using copper radiation( $\text{Cu-K}_\alpha$ ) at 40Kv/mA. Scanning was performed with a step width of  $0.02^\circ$  over an angular range from  $5-80^\circ$  with a scanning rate of  $1^\circ/\text{min}$ .



**Fig. 3.1: Powder XRD system (Make: Rigaku; Model: DMax 2200)**

X- ray tube [Copper (broad focus)]

Wave length,( $1.5404 \text{ \AA}$ ), Divergence slit (Automatic)

Scan speed ( $1^\circ/\text{min}$ ), Range  $2\theta$  ( $5^\circ$  to  $80^\circ$ )

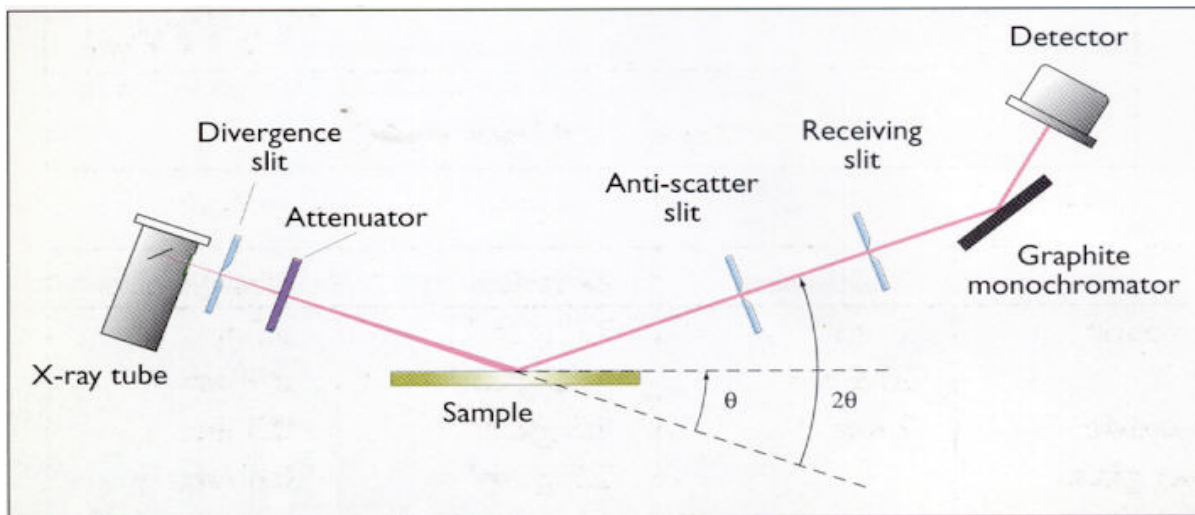
Operating Voltage (40 kV)

filament current (40 mA)

### **3.1.1. Fundamental principles of X-ray powder diffraction**

X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and 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 [15]. 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 to the diffraction angle and the lattice spacing in a crystalline sample [16]. 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 should be attained due to the random orientation of the

powdered material. Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns[17]. A key component of all diffraction is the angle between the incident and diffracted rays.



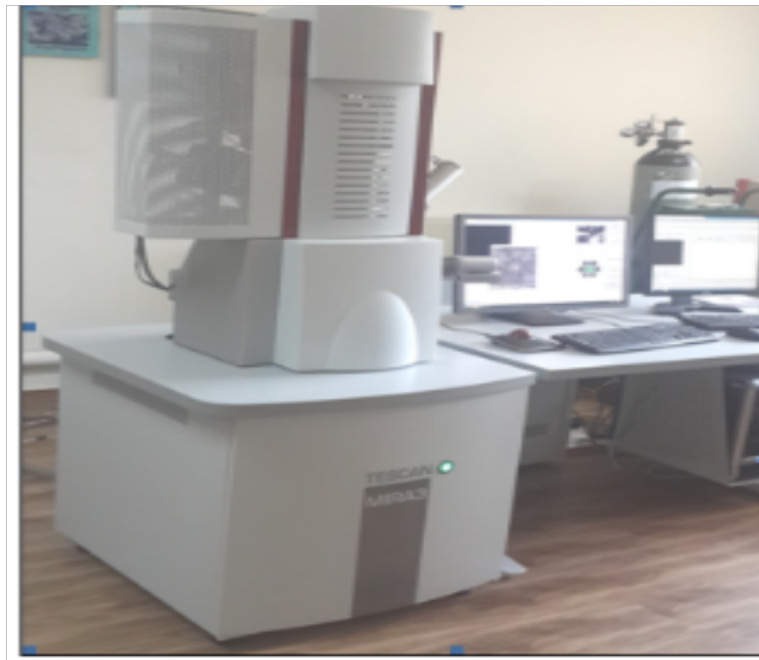
**Fig. 3.2: Diagrammatic presentation of fundamental preparation of XRD**

### **3.2. Scanning Electron Microscope (SEM)**

Make: TESCAN

Model: MIRA3

Scanning Electron Microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons (Figure 3.3). A SEM is used to visualize very small topographic details on the surface or entire or fractioned objects. Researchers in biology, chemistry and physics apply this technique to observe structures that may be as small as 1 nanometer. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture) and chemical composition. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties[18]. The FESEM is also capable of performing analyses of selected point locations on the sample, this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD).



**Fig. 3.3:** Field Emission Scanning Electron Microscope

### 3.2.1. Fundamental principles of SEM

- The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam source is tungsten filament. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample[19]. Once the beam hits the sample, electrons and X-rays are ejected from the sample. Accelerated electrons in an SEM carry significant amounts of kinetic energy and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD) that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays) that are used for elemental analysis and continuum X-rays), visible light (cathodo luminescence--CL), and heat.
- Secondary electrons and backscattered electrons are commonly used for imaging

samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbital's (shells) of atoms in the sample[20]. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive" that is,x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

- The application of the scanning electron microscope (SEM) in [20] morphological analysis of nano structured materials, cementitious materials and concrete microstructure is becoming increasingly common. SEM micrographs provide detailed images of the microstructure that augment from stereo and optical microscopy. The primary advantages are high-contrast images of the microstructure, the high spatial resolution of the images and the ability to perform simultaneous imaging and chemical analysis.
- Normal optimizing parameters for SEM are:
  - Accelerating Voltage (EHT): 10 – 25 kV,
  - Beam Current: 100-250  $\mu$ A,
  - Probe current: 200.00  $\mu$ A,
  - Detector: Secondary Electron Detector (SE),
  - Working Distance: 10-12mm,
  - Magnification: >15,000x for nano structured materials,
  - >3,000x for cementitious system

### **3.3. SAMPLE PREPARATION FOR XRD**

- Oven dry the sample(s) for atleast 12hr before grinding.
- Grind solid samples to a fine talc like powder using one of the following methods:

- Agate mortar and pestle
  - Spex Shatter box
  - Spex Mixture Mill
- Transfer the powdered sample to an appropriate labeled glass bottle.
  - Select the steel, glass or plastic sample holder unless the sample material is very small.
  - Place enough powder from the labeled sample bottle to fill an empty sample holder. Gently press the powder flush with the sample holder using a glass slide. The surface of the powder must be smooth. Remove excess powder from the sample holder edges and carefully place in the appropriate XRD slot.

### **3.4. SEM SAMPLE PREPARATION**

- **Sample Cleaning and Drying**

Before SEM characterization, **sample must be thoroughly greased and dried to eliminate any outgasing from organic contamination and water.** Samples can be cleaned using solvent like acetone or methanol. when cleaned by volatile solvent, samples can be blown dry using a compressed gas. After cleaned by water samples should be dried completely using oven or hot plate. Surface dust are removed using above processes.

- **Handling**

**Gloves must be worn all the time during sample preparation and transfer** do not touch sample holder, samples, sample stubs and sample exchange tool with bare hands.

- **Sample Mounting**

Normally samples are mounted on the holders or stubs using double sided conductive tapes. Only use of vaccum compatible carbon and carbon tapes provided by lab.

- **Powder Samples**

Powder materials are hard to mount and need special handling for sample

mounting. Otherwise they may get loose and fly off the holder in the vacuum and under the beam. For small amount of powder, they can be dispersed in a volatile solvent like Acetone and alcohol, and then drops of the mixture can be dripped onto a clean substrate. After drying the powder particles should be dispersed onto the substrate surface[20]. For large amount of powder, they can be compressed into small disks for sample mounting. Carbon, copper tapes can be used for powder mounting. Sprinkle the powder lightly with a spatula, press lightly to seat. Turn the sample holder upside down and tap it to remove loose material.

- **Less Conductive Samples**

When samples are not very conductive, charge effect will cause image distortion or drift. Low acceleration voltage should be used to reduce the charge effect if samples cannot be coated with a conductive coating. To completely eliminate the charge effect, samples should be coated. SEM lab has sputtering coater for gold coating. The coating thickness could be several nanometer to tens nanometer depending on if the coating interferes with the morphology of your sample. After coating, the sample should be mounted with a conductive "bridge" (e.g. carbon / copper tapes, or silver paint) connected from the top surface of the sample to the sample holder.

- **Please don't expose the vacuum chamber to air for a long time.** Otherwise, it increases the contamination inside and causes carbon deposition on your sample during the imaging. And when the EDS detector is cooled by liquid nitrogen, ice will form on detector and affect its performance. If it takes a while for you to get your samples ready, then vent the chamber only when your samples are ready. There are three different sample holders, each holder has 2-3 different sample plates as shown below. Choose the right holder and plate according to your sample size.
- For the pore-plate, there are two types of stubs: 12.5mm diameter × 5mm height, and 12.5mm diameter × 10mm height.
- Samples can be attached to the flat plates using double-side carbon or copper tapes. Small samples can also be attached onto stubs and then mounted to pore-plates using setscrews.
- Sample plates should be seated in the corresponding sample holder securely, and

fastened with setscrews.

- Using the sample exchange tool to transfer the sample holder into or out of the sample chamber.
- Press the release buttons of the sample exchange tool, and then remove the holder from the hook.

## **4. Result and Discussion**

### **4.1. X ray diffraction(XRD)**

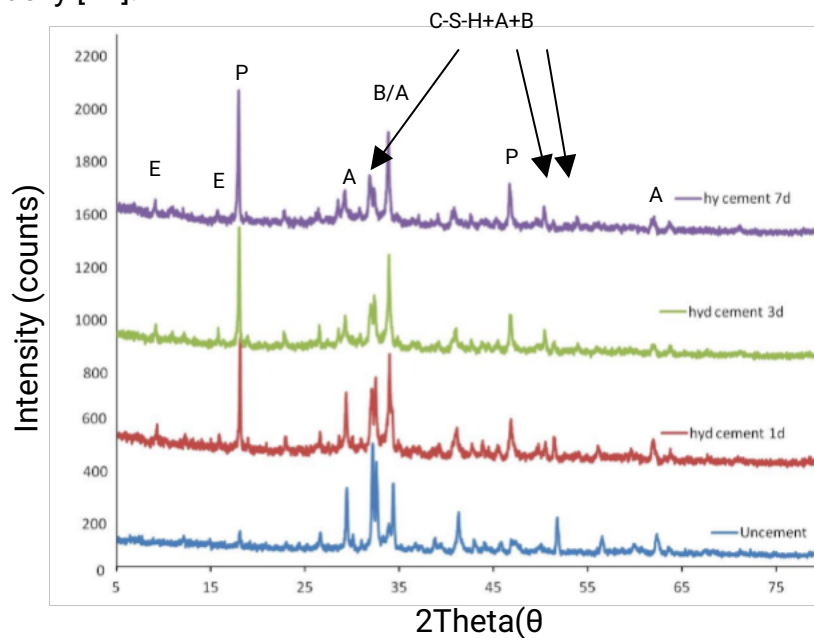
The diffraction spectra show that alite is found mostly in the sample, that part of it is hydrated and the calcium silicate hydrate is produced. Ettringite and Portlandite are present in all hydration stages. In Unhydrated Portland cement diffractometer shows the peak of crystalline compounds present in the sample such as  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$ . Tricalcium silicate is the strongest peak seen at  $51.7^\circ$ ,  $51.3^\circ$ ,  $57.85^\circ$ . Dicalcium silicate is the second most abundant component of Portland its peak appear at  $32.05^\circ$ ,  $32.61^\circ$ ,  $34.40^\circ$ . Tricalcium aluminate peaks can be seen at  $32.72^\circ$ ,  $29.63^\circ$ ,  $47.53^\circ$ . The peaks of Brownmillerite can be seen at  $12.1^\circ$ ,  $24.4^\circ$ ,  $33.7^\circ$ [21]. After one day, peaks of Ettringite and Portlandite are seen at high intensities. After three days, the highest peaks in the diffractogram corresponds to alite and tobermorite gels. After seven days, the spectrum is similar to the spectrum after three days. During the hydration process, values between tobermorite and portlandite phases are seen to diminish both between three and seven days.

### **4.2. Scanning electron microscopy (SEM)**

To analyse the morphological evolution of the Portland cement samples at various time intervals (after 1, 3 and 7days) we used the scanning electron microscope SEM. As the sample microscopic analysis requires samples that are electrically conductive, all the samples were covered by a layer of gold, deposited by spraying. The samples were then broken and the analysis concerned the breaking surface. At 1 day, the surface of cement grain some of the hydration products such as, Calcium silicate hydrate (C-S-H), Calcium hydroxide (CH) crystals and some amount of Ettringite and Portlandite was observed. The brighter part of the image is the calcium hydroxide. The needle like morphology is of ettringite some hexagonal structure of Portlandite were also seen in good quantity. The

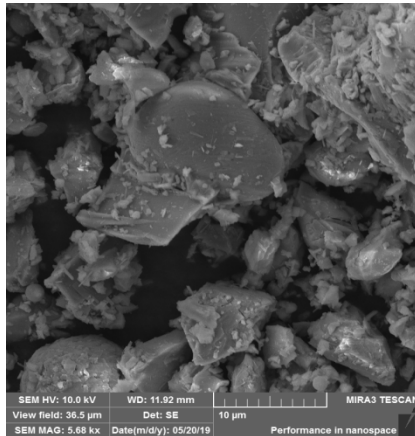
dark part in the image shows that some amount of the hydrated cement remain unhydrated [22]. At 3 day, Portlandite which has hexagonal structure can be identified easily. The C-S-H become more denser and its morphology changes. The black part which is visible is still the unhydrated cement. At 7days a massive image change is observed as compared to 1day and 3 day. On 7 day, as the hydration reaction proceed the amount of voids reduces and a dense microstructure is observed. The amount of ettringite decreases as it covered by C-S-H layer. At 7 day unhydrated content decreases significantly showing the higher rate of product formation. The unhydrated cement mainly have four major components, i.e; C<sub>3</sub>A, C<sub>2</sub>S, C<sub>3</sub>S and C<sub>4</sub>AF.

They are polygonal in shapes and the edges of these compounds are very clear and can be identified easily [22].

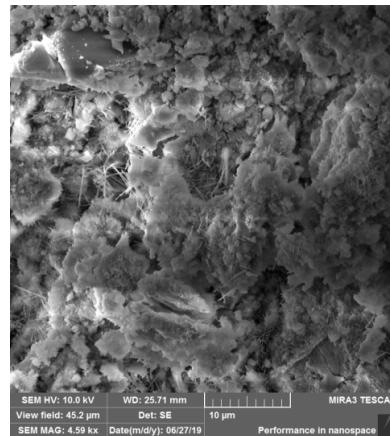


**X-rays pattern of Portland Cement(A-Alite E-Ettringite  
P-Portlandite B-Belite C-S-H -Calcium Silicate Hydrate)**

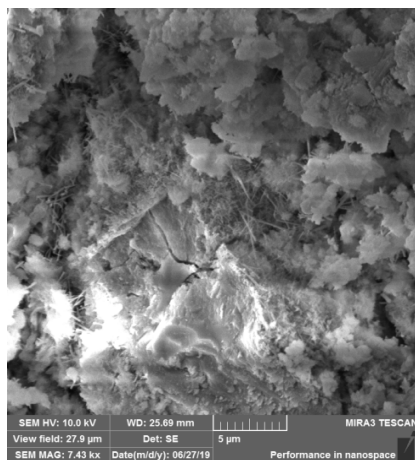




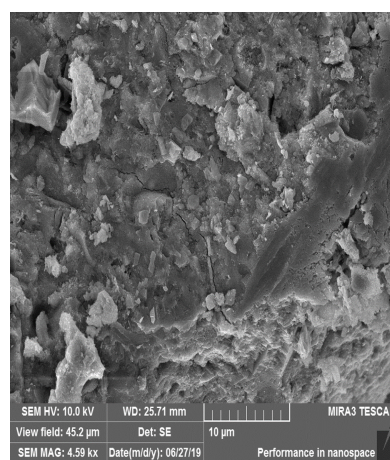
Unhydrated Cement



Hydrated Cement 1 day



Hydrated Cement 3 day



Hydrated Cement 7 day

## SEM Images for Unhydrated and Hydrated Cement

## **5-Conclusion**

By means of two instrumentation techniques namely, XRD and SEM used for the study of hydration process of Portland cement at 1, 3 and 7 days of hydration. Morphological changes were observed in SEM analysis, while mineralogical changes were monitored by XRD technique. The results are as follows:

- XRD results reveal that hydration proceed gradually with the curing age of hydration, as the intensity of CH peak increases from 1 day to 7 day, while intensity of alite and belite phases were decreased.
- SEM results reveal that deposition of hydrated products around the cement grains increases significantly from 1 day to 7 days of hydration. The morphology of C-S-H also observed to change, while ettringite content was visible in a significant amount. However, at 7 day the microstrucure become more dense as compare to 1 and 3 days, while the content of ettringite also reduces as it might get covered by the C-S-H [24].

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