Chapter-2

LITERATURE REVIEW

2.1 GENERAL

This chapter presents a review of literature on subject of this thesis. The review covers the following aspects: i) Studies on High-Performance-Concrete ii) Overview on pozzolanas in concrete iii) Role of supplementary cementitious materials (scms) in High-Performance-Concrete iv) Studies on Superplasticizers v) Studies on Metakaolin vi) Studies on Phosphogypsum vii) Studies on water and its quality viii) Studies on X-ray diffraction and ix) Studies on Scanning electron microscopy (SEM).

2.2 STUDIES ON HIGH-PERFORMANCE-CONCRETE (HPC)

High-Performance-Concrete (HPC) has been defined as concrete that possesses high workability, high strength and high durability. ACI (American Concrete Institute) has defined HPC as a concrete in which certain characteristics are developed for a particular application and environment. Under the ACI definition durability is optional and this has led to a number of HPC structures, which should theoretically have had very long service lives, exhibiting durability associated distress early in their lives. ACI also defines a high-strength concrete as concrete that has a specified compressive strength for design of 6,000 psi (41 MPa) or greater.

A mix of high performance concrete was described by Ozawa et al. (1990), which is defined as a concrete with high filling capacity. It can be filled into all the corners of formwork without using any vibrators. The objective of this study was to investigate the role of chemical admixtures such as superplasticizer and viscosity agents on the deformational and segregation behavior of fresh concrete. The study is important for developing the concrete with high filling capacity. The optimum mix
proportion of superplasticizer and viscosity agent was clarified for the concrete with high filling capacity. It was found that there exists the suitable viscosity of paste for improving not only the deformability but also the segregation resistance, which is highly dependent on the volume of free water in fresh concrete.

Mehta and Aitcin (1990) suggested the term High-Performance-Concrete (HPC) for concrete mixtures that possess the following three properties: high-workability, high-strength, and high durability. Durability rather than high strength appears to be the principal characteristic for high-performance concrete mixtures being developed for use in hostile environments such as seafloor tunnels, offshore and coastal marine structures, and confinement for solid and liquid wastes containing hazardous materials. Strength, dimensional stability, impermeability, and high workability are usually the principal characteristics required of high-performance concrete. In this paper an overview of the composition of concrete and its effect on the properties desired for high performance is given. This overview can be used as a basis for selection of component materials and mix proportioning. A new step-by-step procedure for mix proportioning is described. The calculated mix proportions from this procedure appear to be consistent with the state-of-the-art laboratory and field practice. Also, a brief review is given of concrete production and construction practices essential for making a high-performance end product.

In discussing the meaning of HPC, Aitcin and Neville (1993) stated that "in practical application of this type of concrete, the emphasis has in many cases gradually shifted from the compressive strength to other properties of the material, such as a high modulus of elasticity, high density, low permeability, and resistance to some forms of attack."
HPC was defined by Forster (1994) as "a concrete made with appropriate materials combined according to a selected mix design and properly mixed, transported, placed, consolidated, and cured so that the resulting concrete will give excellent performance in the structure in which it will be exposed, and with the loads to which it will be subjected for its design life."

High-Performance-Concrete (HPC) is a concrete made with appropriate materials combined according to a selected mix design; properly mixed, transported, placed, consolidated and cured so that the resulting concrete will give excellent performance in the structure in which it is placed, in the environment to which it is exposed and with the loads to which it will be subject for its design life. Mix proportions for high-performance concrete (HPC) are influenced by many factors, including specified performance properties, locally available materials, local experience, personal preferences, and cost. With today’s technology, there are many products available for use in concrete to enhance its properties. The primary application for HPC have been structures requiring long service lives such as oil drilling platform, long span bridges and parking structures. HPC still requires good construction practice and good curing to deliver high performance. The Federal Highway Administration (FHWA) has proposed criteria for four different performance grades of HPC (Goodspeed et al., 1996). The criteria are expressed in terms of eight performance characteristics including strength, elasticity, freezing/thawing durability, chloride permeability, abrasion resistance, scaling resistance, shrinkage, and creep. Depending on a specific application, a given HPC may require different grade of performance for each performance characteristics. For example, a bridge located in an urban area with moderate climate may require different performance for strength, elasticity, shrinkage, creep, and abrasion
resistance, compared to performance for freezing/thawing durability, scaling resistance, and chloride permeability.

Concrete is a widely used construction material around the world, and its properties have been undergoing changes through technological advancement. Nima Farzadni et al. (2011) say that with a fast population growth and a higher demand for housing and infrastructure, accompanied by recent developments in civil engineering, such as high-rise buildings and long-span bridges, higher compressive strength concrete is needed. Currently, high-performance concrete is used in massive volumes due to its technical and economic advantages. Such materials are characterized by improved mechanical and durability properties resulting from the use of chemical and mineral admixtures as well as specialized production processes.

2.3 OVER VIEW ON POZZOLANAS IN CONCRETE

Pozzolanas are commonly used as an addition to Portland cement concrete mixtures to increase the long term strength and other material properties. Pozzolana also known as pozzolanic ash is a fine sandy volcanic ash, originally discovered and dug in Italy at “Pozzuoli” in the region around Vesuvius. Pozzzolana is a siliceous and aluminous material which reacts with calcium hydroxide in the presence of water to form compounds, a mix of natural or industrial pozzolanas and Portland cement. Other cementitious materials may also be formed depending on the constituents of the pozzolana. The Pozzolanic reaction is the chemical reaction that occurs in hydraulic cement, a mixture of slaked lime (calcium hydroxide) with amorphous siliceous materials namely, pozzolan or pozzolana, forming non-water-soluble calcium silicate hydrates.

At the basis of the Pozzolanic reaction stands a simple acid-base reaction between calcium hydroxide, also known as Portlandite, or (Ca(OH)₂), and silicic
acid ($H_4SiO_4$, or $Si(OH)_4$). Simply, this reaction can be schematically represented as follows:

$$Ca(OH)_2 + H_4SiO_4 → Ca^{2+} + H_2SiO_4^{2-} + 2 H_2O → CaH_2SiO_4 · 2 H_2O → Eq. No. 2.1$$

or summarized in abbreviated notation of cement chemists:

$$CH + SH → CSH → Eq. No. 2.2$$

The product of general formula ($CaH_2SiO_4 · 2 H_2O$) formed is a calcium silicate hydrate, also abbreviated as CSH in cement chemist notation.

The pozzalanic reaction may be slower than the rest of the reactions which occur during cement hydration and thus the short term strength of concrete made with pozzolanas may not be as high as concrete made with purely cementitious materials. On the other hand, highly reactive pozzolanas, such as silica fume and high reactivity metakaolin can produce “high early strength” concrete that increases the rate at which concrete gains strength. The most commonly-used pozzolan today is fly ash though silica fume high reactivity metakaolin, ground granulated last furnace slag and other materials are also used as pozzolanas.

Pozzolanic materials can be divided into two groups, namely

(i) Natural Pozzolanic

a) Clay and Shales

b) Opalinc Cherts

c) Diatomaceous Earth

d) Volcanic tuffs and

e) Pumicites

(ii) Artificial Pozzolanic

a) Flyash

b) Blast furnace slag
c) Silica fume

d) Surkhi

e) Metakaolin

Most of the pozzolans require grinding to a high degree of fineness to make them suitable for use in concrete except pumicities, which are normally in the finely divided form.

Pozzolans are either naturally occurring or available as waste materials. They mainly contain silica, which becomes reactive in the presence of free lime available in cement when pozzolanic admixtures are mixed with cement. The reactivity varies depending upon the type of pozzolan, its chemical compositions and its fineness. In developing countries like India, pozzolanic materials are mainly available as industrial waste bi-products. Fly ash, silica fume, stone dust, blast furnace slag, rice husk ash etc., are some of the industrial wastes and metakaolin is a quality controlled reactive pozzolana made from purified kaolin which possess pozzolanic properties. Extensive research work has been carried out on the use of pozzolanas in construction materials. Out of the above pozzolanic admixtures, metakaolin made from purified kaolin, is not an industrial waste product, and can be used along with cement to derive enhanced properties for concrete in special situations.

Admixture is defined as a materials other than water, aggregate and cement that is added as an ingredient of concrete or mortar either immediately before or after during the process of mixing to modify certain desired properties of the normal fresh or hardened concrete or mortar or the grout. The most common reason for adding admixtures is to alter the workability, improve the rate of gain of strength, and increase the strength itself, and improve the impermeability and durability and also to improve the appearance. Sometimes many admixtures affect more than one property
of concrete and they affect the desirable properties adversely. Therefore one must be cautious in the selection of admixture and in predicting the effect of the admixture in concrete.

There are wide variety and very large number of admixtures available in the construction market. The admixtures are classified mainly into 17 groups according to the type of materials constituting the admixture or characteristic effect of the use.

- Air-Entraining Agents
- Accelerators
- Air-Detraining Agents
- Alkali aggregate expansion inhibits
- Bonding Agents
- Coloring Agents
- Corrosion inhibiting Agents
- Damp proofing and permeability reducing Agents
- Fungicidal, germicidal and insectal Agents
- Gas forming Agents
- Grouting Agents
- Pozzolanas
- Pumping
- Water-Proofing Agents
- Workability Agents
- Super Plasticizers
- Miscellaneous
2.4 ROLE OF SUPPLEMENTARY CEMENTATIOUS MATERIALS IN HPC

Supplementary cementitious materials (SCMs) are must to produce High-Performance Concrete along with a cost efficient chemical admixture. The use of some mineral and chemical admixtures like metakaolin, Phosphogypsum and Super plasticizer enhance the strength, durability and workability qualities to a very high extent. HPC contains one or more of cementitious materials such as metakaolin and phosphogypsum and usually a super plasticizer. Among the SCMs, metakaolin and phosphogypsum are two such materials, which can significantly improve the performance as well as strength of Portland cement based concrete.

2.5 STUDIES ON SUPERPLASTICIZERS

Superplasticizers are widely used in concrete processing to increase the rheological properties of hardened pastes. Super plasticizers are chemical admixtures which can maintain an adequate workability of fresh concrete at low water/cement ratio for a reasonable period of time, without affecting the setting and hardening behaviour of the cementitious system. Superplasticizers are introduced in concrete like many other admixtures to perform a particular function, consequently they are frequently described according to their functional properties. Super plasticizers have been classified as high range water reducers (HRWR) to distinguish them from other categories of less effective water reducers.

Franklin (1976) stated that, super plasticizers are organic polyelectrolytes, which belong to the category of polymeric dispersants. The performance of super plasticizers in cementitious system is known to depend on cement fineness, cement composition mode of introduction to the mixture etc., as well as on the chemical composition of super plasticizers.
For many years, it was not possible to reduce water/cement ratio of concrete below 0.40 till the advent of super plasticizers. The super plasticizers were first used in concrete in 1960s and their introduction occurred simultaneously in Germany and Japan (Meyer and Hottori, 1981). At first, the super plasticizers were used as fluidizers than water reducing agents. By using large enough super plasticizer, it was found possible to lower the water/binder ratio of concrete down to 0.30 and still get an initial slump of 200mm. Reducing the water/binder ratio below 0.30 was a taboo until Bache reported that using a very high dosage of super plasticizers and silica fume, water binder ratio can be reduced to 0.16 to reach a compressive strength of 280MPa (Bache, 1981).

Aitcin et al. (1991) reported, that by choosing carefully, the combination of Portland cement and superplasticizer, it was possible to make a 0.17 water/binder ratio concrete with 230mm slump after an hour of mixing which gave a compressive strength of 73.1MPa at 24 hours but failed to increase more than 125MPa after long term wet curing.

During 1980s, by increasing the dosage of super plasticizers little by little over the range specified by the manufacturers, it is realized that super plasticizers can be used as high range water reducers (Ronneberg and Sandvik, 1990).

Super plasticizers can be used for three different purposes or a combination of these:

- To increase workability without changing the composition of the mix.
- To reduce the mixing water and the water/cement ratio in order to increase strength and improve durability.
- To reduce both water and cement in order to reduce creep, shrinkage and thermal strains caused by heat of cement hydration.
However, there are two main practical limits in using these chemical admixtures.

- The method of addition affects the slump increase effect.
- Slump loss may reduce the beneficial effect at the time of placing (Cellopardi, 1994).

Ozkul and Dogan (1999) studied the effect of an N-vinyl copolymer super plasticizer on the properties of fresh and hardened concretes. Workability of concrete was measured by slump flow test and in situ tests were undertaken to find out the pumping ability of super plasticized concrete. The coarse aggregate was crushed stone with the maximum size of 25 mm. By using this chemical admixture, which was a little bit different from the conventional ones, the ability of water reduction was increased along with the retention of high workability for a longer time.

In situ test results obtained by Ozkul and Dogan (1999) demonstrated that the superplasticized concrete could be pumped easily from a height of about 13 m and the filling capacity was greater than 85%. The pumping pressure was the same as for normal pumpable concrete and no segregation was observed. For mixtures with water-cement ratios between 0.3 and 0.45, the slump diameters were between 500 mm and 740 mm and the compressive strength varied between 53 MPa and 68 MPa at 28 days of age. In their work, Roncero (1999) et al. evaluated the influence of two super plasticizers (a conventional melamine based product and a new-generation comb-type polymer) on the shrinkage of concrete exposed to wet and dry conditions. Tests of cylinders with embedded extensometers have been used to measure deformations over a period of more than 250 days after casting. In general, it was observed that the incorporation of super plasticizers increased the drying shrinkage of concretes when compared to conventional concretes, whereas it did not have any significant influence
on the swelling and autogenous shrinkage under wet conditions. The melamine-based product led to slightly higher shrinkage than the comb-type polymer.

It must be realized that the introduction of super plasticizer in concrete involves a new chemical component in a complex hydraulic binder system, which already contain several added chemicals. Due to variety of admixture formulations, it is difficult to provide the concrete industry with simple rules specifying proper use of super plasticizers in the presence of other admixtures. However the Marsh Cone test is popularly used to evaluate the characteristics of different pastes, in order to select the optimum dosage of super plasticizers (Giaccio 2002).

2.6 STUDIES ON METAKAOLIN

Metakaolin is manufactured from pure raw materials to strict quality standards. It is not a by-product. Other pozzolanic materials are currently available, but many are by-products, which are available in various chemical compositions. They may also contain active components (such as sulphur compound, alkalis, carbon, reactive silica) which can undergo delayed reactions within the concrete and cause problems over long time periods. Metakaolin is obtained by calcinations of pure or refined kaolintic clay at a temperature between 650°C and 850°C, followed by grinding to achieve a fineness of 700 to 900m²/kg. The resulting materials have high pozzolanicity.

Metakaolin is a high quality Pozzolanic material, which is blended with Portland cement in order to improve the durability of concrete and mortars; it removes chemically reactive calcium hydroxide from the hardened cement paste. Metakaolin reduces the porosity, densifies, thickness of interfacial zone, this improving the adhesion between the hardened cement paste and particles of sand or aggregates.
Zhang and Malhotra (1995) also noted an increased demand for air-entraining admixture comparable to a silica fume concrete. Metakaolin is beneficial in reducing drying shrinkage when compared to silica fume concrete. Optimum ranges for metakaolin addition depend upon desired properties. The optimum dosage was found out to be 15 to 25% for compressive strength.


High-reactivity metakaolin (HRM) is a more recently developed supplementary cementitious material. It is a reactive aluminosilicate pozzolan formed by calcining purified kaolinite at a specific temperature change. Chemically, HRM combines with calcium hydroxide to form calcium silicate and calcium aluminate hydrates. It has been shown that HRM in powder form is a quality-enhancing mineral admixture that exhibits enhanced engineering properties comparable to silica fume slurry (Caldarone et al., 1994; Khatib and Wild, 1996; Khatib and Wild, 1998; Curcio et al., 1998; Frias and Cabrera, 2000).

Brooks et al. (2000) studied about the effect of silica fume, Metakaolin, fly ash and ground granulated blast furnace slag on the setting times of high strength concrete. They observed that the general effect of silicon, metakaolin, fine aggregate and GGBS is to retard the setting time of high strength concrete. In high strength
concrete containing metakaolin there was increase in the retarding effect up to 10% replacement level and at higher replacement level of 15%, the retarding effect appears to reduce.

Concrete property improvements include the following: increased compressive strength and improved sulfate resistance. (Ramlochan et al., 2000) and reduced permeability. Through research, Frias and Cabrera (2000) noted increased heat of hydration when incorporating metakaolin. The researchers noted that heat of hydration curves for metakaolin concrete can be obtained to closely match heat of hydration curves for PCC when the metakaolin is incorporated at amounts less than 10% by weight.

Metakaolin is a processed pozzolan that can be combined with calcium hydroxide in solution to form calcium silica hydrate. The modern use of metakaolin dates back to 1962 when it was used to supplement Portland cement during construction of the Jupia Dam in Brazil (Pera 2001). During heating, adsorbed water is driven off at 100°C, and the kaolinite decomposes at about 500°C. At 500°C, the hydroxyl groups are lost in the form of water. At temperatures of greater than 900°C, the metakaolin undergoes further reactions forming crystalline compounds of free silica and mullite (Pera 2001; Sabir et al., 2001). The use of metakaolin in concrete tends to increase the water demand requiring a larger dosage of water-reducing admixture (Zhang and Malhotra, 1995; Sabir et al., 2001).

Quian and Zongjinli (2001) presented the stress-strain relationships (tension and compression) for concrete containing 0%, 5%, 10%, and 15% of metakaolin. The results indicated that the tensile, flexure and compressive strengths of concrete increase with the increasing metakaolin content. The compressive elasticity modulus of concrete showed only small increase with the increase in metakaolin content.
However, experiment was carried out only up to 15% replacement. To get a clear picture experiments are to be conducted with higher content of metakaolin i.e. above 15%.

Poon et al. (2001) investigated about the rate of pozzolanic reaction of metakaolin in High-Performance-Concrete. Hydration progress in metakaolin blended high performance concrete with age was studied from the compressive strength, porosity and pore size distribution properties. The results were compared with concretes containing silicafume, flyash and Portland cement. They reported the rates of pozzolanic reaction and calcium hydroxide consumption in the metakaolin blended cement concretes. The higher pozzolanic activity results in a higher rate of strength development and pore structure reinforcement for the cement concrete at earlier ages.

Roy et al. (2001) studied about the effect of Metakaolin, silica fume and fly ash on chemical resistance of concrete. Mortars were prepared with various proportions of OPC, silica fume and Metakaolin/low calcium fly ash (0-30% weight replacement). Chemical resistance was found to increase in the order of SF to Metakaolin to Fly Ash and decreased as the replacement level is increased from 0-10% weight replacement to 15 – 30% weight level. They finally concluded that it is important to evaluate a particular concrete formulation before predicting its performance in a special acid environment.

Poon et al. (2001) studied about the rate of Pozzolanic reaction of metakaolin in high performance cement mortars. Hydration progress in metakaolin blended high performance cement paste with age was studied from the compressive strength, porosity and pore size distribution properties. The results were compared with pastes containing silica fume, fly ash and Portland cement. They reported the rates of Pozzolanic reaction and CH (calcium hydroxide) consumption in the metakaolin
blended cement pastes are higher than that in the silica fume or fly ash blended cement pastes. The higher Pozzolanic activity results in a higher rate of strength development and pore structure reinforcement for the cement pastes at earlier ages.

Gruber et al. (2001) investigated metakaolin and PFA mortars for heat of hydration. In this study 5-15% metakaolin was replaced with Portland cement and investigated the replacement effect on heat of hydration. The result showed that heat of hydration was higher in metakaolin-portland cement mortars when compared to reference Portland cement mortar. The increased heat of hydration was attributed to combined effect of Portland cement hydration and metakaolin pozzolanic reaction. Further, the study showed that heat of hydration of PC (Portland cement) - PFA (pulverised fuel ash) mortars was lower than that in equivalent Portland cement mortars. The decreased heat of hydration in PC-PFA was explained that dilution of Portland cement with PFA and negligible pozzolanic activity of PFA in the initial hours.

Jian-Tong Ding and Zongjin Li (2002) studied about the effect of metakaolin and silica fume on properties of concrete. Seven concretes were cast at a water/binder ratio of 0.35 with 0, 5, 10 and 15% cement replaced by metakaolin or silica fume. They concluded that metakaolin offer better workability than silica fume. The incorporation of both metakaolin and silica fume in concrete can reduce the free drying shrinkage and restrained shrinkage cracking width. But the initial cracking appeared earlier in silica fume and metakaolin modified concrete. The incorporation of metakaolin or silica fume in concrete can reduce the chloride diffusion rate significantly.

Badogiannis et al. (2003) studied the effect of metakaolin on concrete properties. They used poor Greek Kaolin, which was thermally treated at defined
conditions and a commercial metakaolin of high purity. The investigation concluded that the poor Greek kaolin exhibited similar behavior to that of commercial metakaolin with respect to the strength development.

Jin and Li (2003) presented the study on the effects of mineral admixtures such as silica fume, slag, fly ash and metakaolin on the mechanical behavior of young concrete under uniaxial compression or tension. They reported that different admixtures have different influences on the properties of young concrete. They also reported that metakaolin showed the best enhancement on the mechanical properties of young concrete.

Cement or some form of cementing material is an essential ingredient of building materials. Cement is the vital binding agent in concretes and mortars. Since its invention in the first half of the 19th century, Portland cement has become the most widely available cementitious material, is relatively expensive to produce and is often in short supply in many developing countries. In comparison, replacement cements can be produced locally on a small scale and at a much lower cost. However, replacement cements are not capable of replacing Portland cement totally, but they can be used in the construction where they have applications. The major advantages of replacements to Portland cement are that they are usually cheaper to produce and requiring no or less imported technology and equipment. They can also be produced in different scale depending on the local market at reduced transportation costs. Pozzolanas can be mixed with lime and/or Portland cement and can improve quality and reduce costs of concretes made from both materials. Clays and shales after some treatment like heat are also used as pozzolanic materials and show adequate pozzolanic activity of the products.
In the recent times, the importance and use of metakaolin in concrete has grown so much that it has almost became a common ingredient in concrete, particularly for making high strength and High-Performance-Concrete. Extensive research has been done all over the world on the benefits that could be accrued in the utilization as a supplementary cementitious material. High volume Metakaolin is a subject of current interest all over the world.

Secondly, cement is the backbone for global infrastructural development. It was estimated that global production of cement is about 3.06 billion tons in 2009. Production of every tone of cement emits carbon dioxide to the tone of about 0.87 ton. Expressing it in another way, it can be said that 7% of the world’s carbon dioxide to the environmental pollution is due to cement production alone. Also due to the high consumption of natural resources like limestone etc. we can not go on producing more and more cement. There is a need to economize the use of cement. One of the practical solutions to economize cement is to replace cement with supplementary cementitious materials.

There are two ways that the metakaolin can be used one way is to intergrind certain percentage of Metakaolin with cement clinker at the factory to produce Portland pozzolana cement (PPC) and the second way is to use the Metakaolin as and admixture at the time of making concrete at the site of work. The later method gives freedom and flexibility to the user regarding the percentage addition of metakaolin.

Metakaolin is manufactured from pure raw material to strict quality standards. Metakaolin is a high quality pozzolanic material, which blended with Portland cement in order to improve the strength and durability of concrete and mortars. Metakaolin removes chemically reactive calcium hydroxide from hardened concrete paste. It reduces the porosity of hardened concrete. Metakaolin densifies and reduces the
thickness of the interfacial zone, thus improving the adhesion between the hardened cement paste, sand and aggregate.

The durability of concretes modified with metakaolin was investigated by Luccourd et al. (2003). Cement was replaced on a mass basis of 5-20% of metakaolin. The transport properties and chemical behavior were analyzed by means of chloride diffusion tests and sulfate immersion. The study concluded that the 10-15% replacement is optimum for workability, the best mechanical performance and the inhibition effect on the chloride diffusion and sulphate attack. For 20% metakaolin no diffusion is observed after one year.

Poon et al. (2006) related the mechanical and durability properties of high performance metakaolin and silica fume concretes to their microstructure characteristics. They reported that metakaolin concrete has superior strength development and similar chloride resistance to silica fume concrete.

Fabien Lagier et al. (2007) investigated the reactivity of two metakaolins, which vary principally in their surface area, and Portland cements of varying composition were examined via isothermal calorimetry for pastes at water-to-cementitious materials ratio of 0.50 containing 8% cement replacement by weight of metakaolin. Both metakaolins examined appear to have a catalysing effect on cement hydration. Calorimetry showed accelerated hydration, a slight increase in cumulative heat evolved during early hydration, and – for some cements examined – apparently an increased intensity of the heat evolved, particularly during the period typically associated with hydration of calcium aluminates. Metakaolin with higher surface area had a greater effect. It is proposed that the presence of metakaolin may enhance dissolution of cementitious phases and/or provide additional, well-dispersed sites for nucleation of hydration products, in addition to increasing the early age concentration.
of solubilized aluminium (due to metakaolin dissolution). The increased intensity of some of the calorimetry data also suggests that some additional exothermic reactions are occurring, which may be related to an increased reactivity of calcium aluminate phases in the cement as well as the reaction of the metakaolin. This effect is apparently increased as the cement equivalent alkali content increases.

2.7 STUDIES ON PHOSPHOGYPSUM

Nowadays the manufacture of cement involves the consumption of valuable natural materials like lime, gypsum etc., in huge quantities. Phosphogypsum is a byproduct of the processing of phosphate ore; mainly in the production of fertilizers. Phosphate ore typically contains naturally occurring radioactive elements, which become concentrated in phosphogypsum as they are removed from the ore during the processing. Phosphogypsum refers to the gypsum formed as a by-product of processing phosphate ore into fertilizer with sulfuric acid. Phosphogypsum is produced from the fabrication of phosphoric acid by reacting phosphate ore (apatite) with sulfuric acid according to the following reaction:

$$\text{Ca}_5(\text{PO}_4)_3\text{X} + 5\text{H}_2\text{SO}_4 + 10\text{H}_2\text{O} \rightarrow 3\text{H}_3\text{PO}_4 + 5\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{HX} \quad \rightarrow \text{Eq.No.2.3}$$

where X may include OH, F, Cl, or Br

Phosphogypsum has become a material of special attraction, because of its suitability for construction activities. At the same time a lot of Phosphogypsum is produced as an industrial waste and its disposal presents a lactic problem to the environment as well as to the industry itself.

Any system is more efficient if the outcome of the process is effectively consumed and utilized in another process. Here comes the use of Phosphogypsum in the manufacture of concrete instead of cement to an extent of 20 to 40%.
Majority of phosphogypsum in India is produced by the dehydrate process due to its simplicity in operation and lower maintenance as compared to other processes. Approximately, 30 million tons of Phosphorous Pentoxide is currently produced annually worldwide, that is about 120-150 million tons per annum of phosphogypsum is being produced currently. For a country like India, this process has an attraction as it helps in saving the foreign exchange towards the import of Sulphur and thus can solve any shortage of cement in the country.

The lack of adequate sources of locally available rock materials has prompted County Commissioner, Columbia County, to take the initiative in finding alternate material for building roads (William C. Kenley, 1984; Ronald W. Williams, 1984). The history of development of this technology is quite interesting as the embargo imposed on supply of sulphur and pyrites from Spain to Germany during the world war I was primarily responsible for the development of a process for the production of cement with mineral gypsum. In 1915 W.S. Mueller invented the process and was transformed into industrial scale by H.H. Kuhne. The process involves roasting of attired Calcium Sulphate, clay and coke / low volatile carbon at 1450° C in rotary kiln. Research in the use of phosphogypsum in place of natural gypsum or anhydrite began around 1965. This led to the construction of two plants at Austria and South Africa with capacities of 350 tons per day of Sulphuric acid each for a total consumption of 0.42 million tones per year of phosphogypsum. Some of the Muller Kuhne’s smaller plants at Comecon have also partly converted to use phosphogypsum so that the world wide use of phosphogypsum has been increased to 100 million tons in this way. The restriction over the level of impurities is required in this process. The upper limits of the Phosphorous pentoxide and Flourine should not exceed 0.5 and 0.15%. This process has immense scope in the Indian context to
increase the production of Sulphuric acid as well as cement for ever growing construction activities in developing India.

In the field of construction activities, Florida Institute for Phosphate Research (FIPR) elected to investigate the use of phosphogypsum in wallboard and other related products. While it is recognized that phosphogypsum is one of the better gypsums that have been used for this purpose and was being used for wallboard production in large number of countries, the economics for using phosphogypsum for this purpose in this country is such that phosphogypsum can not compete with Flue Gas Desulfurization (FGD) gypsum from power plant stack scrubbing. The primary research thrust was to use phosphogypsum for roadbed construction, and the plan was to build a secondary road and test it for both environmental and operating characteristics.

Mehta and Brany (1977) reported that two secondary roads were constructed, one in Polk Country in central Florida and a second in Columbia, a Country in north Florida. Both were subjected to environmental testing. Testing revealed that the physical strength of the Polk Country roadbed increased with time and use. The road needed fewer repairs than similar roads in the area.

Marcelo and Alexandre (1982) investigated the properties of cement-stabilized phosphogypsum mixes as potential materials for base and sub-base construction, as well as seeking a non pollutant alternative to discard large quantities of the material. They discussed the physical characterization of phosphogypsum, and the influence of cement content, curing time, and compaction, moisture content on its unconfined compressive strength and initial tangent modulus. The laboratory results indicate that cement-stabilized phosphogypsum mixes have potential applications as road base and sub-base materials.
Adnan Cloak lan (1988) studied the effect of phosphogypsum – Portland cement – natural pozzolan ratios on the physical mechanical and durability properties of gypsum. The results indicate that the setting time of these pastes decrease with the increase of gypsum content in the mixture ranging from 8 to 11 minutes. The addition of super plasticizers increase the setting time from approximately 11 to 35 minutes. This increase is greatly dependent on the plasticizer admixture dosage. These blends show a kinetic of capillary water absorption very similar to that of the Portland cement binder. The gypsum-Portland cement blends themselves possess good water resistance which is further enhanced by the addition of natural pozzolan and super plasticizer. The water cured blends with the composition of 41:41:18 gypsum Portland cement: Natural Pozzolan offers compressive strength of approximately 20 MPa at room temperature. These blends give excellent properties retention after again in water at 20 degree for 95 days.

In order to investigate the possibility of using phosphogypsum in construction, a comprehensive experimental program has been carried out by Mohammad Akour (1993). Various mixtures were made by using two types of sands, namely, crushed limestone and natural river sands, and two types of cements namely; pozzolanic portland cement and ordinary portland cement. In one group of mixes, crushed limestone sand was used with two types of cements, while natural river sand was used in another group. Second group of mixes was repeated by using treatment of phosphogypsum (with washing and without washing by water and calcination at different temperatures). The highest values of compressive strength obtained in the first and second stage were 27.82 MPa (84%), and 32.6 MPa (92.85%), (of the 0.0% replacement of phosphogypsum by cement) for 10 % replacement of phosphogypsum in the moist curing conditions, receptively, and 22.53 MPa (80.14%), 26.03 MPa
(99.9%) at air dry curing condition for 10% replacement of phosphogypsum. The short-term properties of these mortar mixes have been obtained and discussed. The results of the two sands and cements used before and after treatment of phosphogypsum have been analyzed and compared. The information obtained, related to compressive, tensile, and flexural strengths, effect of phosphogypsum, and cement types, setting times, soundness, chemical composition and X-Ray diffraction, and strength gained with age.

Wissa Anwar, (1993) stated that the industry developed first in Europe and due to a number of circumstances, phosphogypsum disposal of any type did not create a problem. While some of the earlier plants in Florida practiced water disposal, most of the phosphogypsum produced here has been piled on land again. It must be remembered that plant size (capacity) was a big factor in determining if there was a Phosphogypsum problem. Smadi et al. (1999) investigated the influence of phosphogypsum on the times of setting and soundness of cement pastes. In this study, cement paste mixtures were made using ordinary Portland cement and Pozzolanic Portland Cement at a constant water to cement ratio of 0.6 with Phosphogypsum content varying between 0 and 100 percent. In general both initial and final time of setting increased with increasing Phosphogypsum content. The initial time of setting ranged between 100 to 560 minutes and 120 to 710 minutes for pastes containing Ordinary Portland Cement and Pozzalonic Portland Cement, respectively. The corresponding final time of setting ranged between 250 to 1440 minutes and between 270 to 1440 minutes.

Smadi et al., (1999) conducted experimental study to investigate the potential use of phosphogypsum in concrete. This was accomplished by preparing concrete mixes at a water/cement ratio of 0.6 using two types of cement, ordinary Portland
cement and pozzolanic Portland cement, and two types of fine aggregate, natural river sand and lime stone. These mixes were prepared at different replacements (by weight) of phosphogypsum and purified phosphogypsum ranging from 10-100%. The purified phosphogypsum was obtained by calcining phosphogypsum (washed in water and not washed) at temperatures of 170, 600, 750, 850 and 950°C. The compressive, tensile and flexural strength of different hardened concretes were obtained following 3, 7 and 28 days of curing in air and in a moist room. In addition, the setting time and the soundness of cement pastes prepared using Ordinary Portland Cement and Pozzolanic Cement at a water/cement ratio of 0.6 and at different replacements of phosphogypsum, were evaluated. At a particular phosphogypsum percentage of replacement, the results indicated an increasing trend in strength gain over curing time. The strengths of concrete, cured for a specific time, shown a decrease in the strength with further replacement with phosphogypsum. The purification process, by heating phosphogypsum up to 900°C, has resulted in improving the strengths of the concrete mixes. The highest percentage increase in strength was found to be for phosphogypsum calcined at temperatures of 850 and 900°C. The incorporation of phosphogypsum in the cement paste has dramatically increased its initial and final setting times and has increased the percentage elongation of paste prisms used to evaluate the soundness. The improvement in strength upon calcinations is primarily due to the formation of anhydrate at higher temperatures, which subsequently hydrates to gypsum; the latter has some cementing value.

With the advent of 300, 500, 1000 and even 4000-5000 tons per day Phosphorous pentaoxide plants, the Phosphogypsum disposal problem took on new aspects (Manjit Singh, 2002). While most of the rest of the world looked at Phosphogypsum as a valuable raw material and developed process to utilize it in
chemical manufacture and building products, the country Florida is blessed with abundant low-cost natural gypsum-piled the phosphogypsum rather than bear the additional expense of utilizing it as a raw material. It should be noted that during most of this time period the primary reason for not using phosphogypsum in for construction products in this country was because it contained small quantities of fluorine and Phosphorous pentaoxide as impurities and fuel was required to dry it before it could be processed. It has only been in recent years that the question of radioactivity has been raised and this question now influences every decision relative to its potential use in building products in this country. Phosphogypsum utilization has evolved along three broad use groupings:

1. Chemical raw material
2. Agricultural applications
3. Construction materials

Some attempts have been made to utilize phosphogypsum as a base and fill materials in the form of cement-stabilized phosphogypsum mix) in the construction of highways, railways etc (Lopez, Roger (1992)). In other attempts, phosphogypsum was recycled for manufacture of fibrous gypsum boards, blocks, gypsum plaster, composite mortars using Portland cement, masonry cement and super sulphate cement (Gupta (1998)). In some other attempts phosphogypsum was also used as a soil conditioner for calcium and sulphur deficient-soils as it has fertilizer value due to the presence of ammonium sulphate (Bhattacharyya et al., (2004); Eiichi et al., (2006)). Recently, the effect of phosphatic and fluoride impurities present in waste phosphogypsum on the setting time, strength development and morphology of selenite gypsum plaster have been studied (Manjit S. (2003)). Also, the techno-economic feasibility of beneficiating phosphogypsum has been studied where in the beneficiated
phosphogypsum was used for making Portland cement and Portland slag cement, and the results favoured use of phosphogypsum as an additive to cement clinker in place of natural gypsum (Manjit, Mridul (2002)). However, a very few attempts have been made to study the usability of phosphogypsum as partial replacement to cement, whose use in cement and concrete, will be a significant achievement in the development of concrete technology in the coming few decades [Manjit et al. (2002); Mehta et al. (1977); Smadi et al. (1999); Chang et al. (1989); Mulla et al. (2003); Manjit et al. (1995)].

According to Kelly Rusch et al. (2002), Phosphogypsum (PG, CaSO₄·H₂O), a solid byproduct of phosphoric acid manufacturing, contains low levels of radium (²⁶⁶Ra), resulting in stackpiling as the only currently allowable disposal/storage method. PG can be stabilized with class C fly ash and lime for potential use in marine environments. An augmented simplex centroid design with pseudo-components was used to select 10 PG: class C fly ash: lime compositions. The 43 cm³ blocks were fabricated and subjected to a field submergence test and 28 days salt water dynamic leaching study. The dynamic leaching study yielded effective calcium diffusion coefficients (Dₑ) ranging from 1.15×10⁻¹³ to 3.14×10⁻¹³ m² s⁻¹ and effective diffusion depths (Xₑ) ranging from 14.7 to 4.3 mm for 30 years life. The control composites exhibited diametrical expansions ranging from 2.3 to 17.1%, providing evidence of the extent of the rupture development due to ettringite formation. Scanning Electron Microscopy (SEM), microprobe analysis showed that the formation of a CaCO₃ on the composite surface could not protect the composites from salt water intrusion because the ruptures developed throughout the composites were too great. When the PG: class C fly ash: lime composites were submerged, saltwater was able to intrude throughout the entire composite and dissolve the PG. The dissolution of the PG
increased the concentration of sulfate ions that could react with calcium aluminum oxides in class C fly ash forming additional ettringite that accelerated rupture development. Effective diffusion coefficients and effective diffusion depths alone are not necessarily good indicators of the long-term survivability of PG: class C fly ash: lime composites. Development of the ruptures in the composites must be considered when the composites are used for aquatic applications.

Mulla et al. (2003), conducted has done typical analysis of phosphogypsum applications in cement concrete and proved that the major constituent of phosphogypsum is gypsum and the other constituents are in minor quantities. At 5 percent replacement of cement (by weight) with phosphogypsum there is gain in strength as compared with percentile replacements.

Siva Sankar Reddy et al. (2010) investigated the compressive, tensile and flexural strength characteristics of partially cement replaced phosphogypsum concrete using 0., 10, 20, 30 and 40% replacement with different water-binder ratios of 0.40, 0.45, 0.50, 0.55, 0.60 and 0.65. The strength characteristics are studied by casting and testing a total of 450 specimens, which consists of 270 cubes, 90 cylinders and 90 beams for 7, 28 and 90 days. It is shown that a part of Portland cement can be replaced with phosphogypsum to develop a good and hardened concrete to achieve economy; above 10% replacement of phosphogypsum in concrete lead to drastic reduction not only in the compressive strength but in the split-tensile strength also; the flexural strength decreases as width and number of cracks increases significantly at replacement above 10% of cement with phosphogypsum at different water/binder ratios.

The above studies reveal the use of phosphogypsum as a waste material which can be better utilized in the production of concrete for road applications and soil
stabilization. Continuous search is going on around the Globe to further investigate and highlight the application of phosphogypsum in concrete for high strength applications and economical usages of concrete. In future, the continual improvement of this material and its properties are expected to come up from various researches. It is beyond doubt that it contributes for the reduction of environmental pollution.

2.8 STUDIES ON WATER AND ITS QUALITY

Sea water has a total salinity of about 3.5% (78% of the dissolved solids being NaCl and 15% MgCl₂ and MgSO₄), and produces a slightly higher early strength but a lower long term strength; the loss of strength is usually not more than 15% (Abrams (1924)) and can therefore often be tolerated. However, in practice it is generally considered not advisable to use sea water for mixing unless this is unavoidable (Lea (1956)).

When reinforced concrete is permanently under water, either sea or fresh, the use of sea water in mixing seems to have no defects (Shalon and Raphael (1959)). Brackish water contains chlorides and sulphates. When chloride does not exceed 500 ppm, or SO₃ does not exceed 1000 ppm, the water is harmless, but water with even higher salt contents has been used satisfactorily (Building research station London (1956). The appendix to BS 3148-1980 recommends limits on chloride and on SO₃ as above, and also recommends that alkali carbonates and bicarbonates should not exceed 1000 ppm. Somewhat less severe limitations are recommended in American literature McCoy (1956).

Water containing large quantities of chlorides (eg: sea water) tends to cause persistent dampness and surface efflorescence. Such water should, therefore not be used where appearance of the concrete is important, or where a plaster-finish is to be applied (Lea (1956) & Anderson et.al (1985)).
Sand dried out in sea water may contain a large amount of salt, but if sand dredged from the sea water and it allowed to drain and fresh water is used as mixing water, then the salt content represents no more than 1% of the total weight of water (National Sand and Gravel Association, (1959) & Cohen and Mather (1991)). The British code of practice for the structural use of concrete CP110: 1972 specifies the maximum total chloride ion content (as a percentage weight of cement) arising from all sources including aggregate is as follows: 0.1 for prestressed concrete made with sulphate resisting or super sulphate cement and 0.35 for all other concrete containing metal. American Concrete Institute suggests the following limit to the total (i.e. from all sources) soluble chloride ion concentration as a percentage of weight of cement to 0.06 for prestressed concrete, and 0.10 to 0.15 for other concretes. Only concrete that will be permanently dry is exempted from this limitation. In view of the above rules, it is necessary to determine the chloride content even of those admixtures in which calcium chloride is only a minor component.

Natural waters that are slightly acidic are harmless, but water containing humic or other organic acids may adversely affect the hardening of concrete, such water, as well as highly alkaline water, should be tested. The effects of different ions vary, as shown by Steinour (1960).

Impurities in water may interfere with the setting of the cement, may adversely affect the strength of the concrete or cause staining of its surface and may also lead to corrosion of the reinforcement. For these reasons, the suitability of water for mixing and curing purposes should be considered. Clear distinction must be made between the effects of mixing water and the attack on hardened concrete by aggressive waters. Some of the latter type of water may be harmless or even beneficial when used in mixing (Steinour, 1960).
Some tests suggest the sea water slightly accelerates the setting time of cement, others (Thomas and Lisk (1970)) a substantial reduction in the initial setting time but not necessarily in the final setting time. Generally the effects on setting are unimportant if water is acceptable from strength consideration.

Since it is undesirable to introduce large quantities of silt in to the concrete, mixing water with a high content of suspended solids should be allowed to stand in a setting basin before use; a turbidity limit of 2000 ppm has been suggested US Bureau of Reclamation, (1975). However, water used to wash our truck mixers is satisfactory as mixing water, provided of course, that is satisfactory to begin with as ASTM standard C 94-78a allows the use of wash water. Clearly, different cements and different admixtures should not be involved.

An investigation of the deteriorated concrete specimens showed a large amount of gypsum formed at the expense of the cementitious constituents normally present in hydrated Portland cement pastes Mehta (1976). The sulphate content of the ground water, entirely due to alkali sulphates, was up to 10,000 mg/l Berman (1978). Similar cases of sulphate deterioration were reported from the prairie soils in Western Canada, which contain as high as 1.5 percent alkali sulphates (ground water here frequently contains 4000 to 9000 mg/l of sulphate). Typically, as a consequence of the sulphate attack, concrete was rendered relatively porous or weak and eventually reduced to a sandy (non-cohesive) mass. Obviously, such occurrences of sulphate expansion can be avoided by a thorough survey of environmental conditions, and by using sulphate free water for mixing and curing and also providing suitable protection against sulphate attack when necessary.

While the use of potable water is generally safe, water not fit for drinking may often also be satisfactorily used in making concrete. As a rule, water with pH of 6.0
to 8.0 (Mc Coy, 1978), which does not taste saline or brackish is suitable for use, but dark color or bad smell do not necessarily mean that deleterious substances are present (Mc Coy, 1956). These can’t be removed by ordinary conventional water treatment systems.

In many specifications, the quality of water is covered by a clause saying the water should be fit for drinking. Such water very rarely contains dissolved solids in excess of 2000 ppm, and as a rule less than 1000 ppm. For a water/cement ratio of 0.5, the latter content corresponds to a quantity of solids representing 0.05 percent of the weight of cement, and any effect of the common solids would be small. There is, however, one situation when drinking water is unsuitable as mixing water; this is when there is a danger of alkali aggregate reaction and the water has a high concentration of sodium or potassium.

Figg (1981) discovered that concrete of the val-de-la-Mare dam in the United Kingdom was affected by alkali-silica reaction, possibly as a result of a crushed diorite rock containing veins of amorphous silica as coarse aggregate. Extensive remedial measures were needed to ensure the safety of the dam. Palmer (1981) extensively studied the evidence of concrete deterioration attributed to alkali-silica reaction which was found in 23 structures of 6 to 17 years old, located in Scotland, the Midlands, Wales, and other parts of southwestern England. Many of the structures contained concrete made with inadequately washed sea-dredged aggregates.

De Ceukelaire (1992) reported that the effects of hydrochloric acid on concrete are multiple. The changing mineralogy due to the leaching processes causes a loss of strength. Kosmatka and Panarese (1995) & Cebeci and Saatci (1989) reported that a thumb rule is that if water is portable, it is suitable as mixing water for
cement mortar and concrete for the construction and other purposes. This does not appear to be a true statement for all conditions.

Besides loss of strength, leaching of calcium hydroxide from concrete may be considered undesirable for aesthetic reasons. Frequently, the leachate interacts with CO2 present in air and results in the precipitation of white crusts of calcuim carbonate on the surface. This phenomenon is known as efflorescence.

\[
\text{Ca (OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad \text{Eq.No.2.4}
\]

The country as a whole at present has an average amount of about 2200m\(^3\) of water available per capita per year, while Rajasthan gets only 500 m\(^3\), which is less than 24\% of the country’s average. If the availability of water in any place is more than 1700 m\(^3\) per capita per year, people do not face any problem to satisfy needs. When it is available less than this, then water stress is felt by the people. The magnitude of this stress depends upon the increase in pollution, irrigation, energy, industries domestic and other needs. The regions having less than 1000 m\(^3\) of water available per capita per year are certainly under water stress (Kshirsagar (2000)). The United Nations report says that about \(\frac{1}{3}\) of the world’s population is living in countries facing moderate to high water stress. In India, six basins are under water stress and 40 to 70\% of the basins have less than the average country per capita availability of water (Kshirsagar (2000)). In addition to the problem of increased demand for water, the availability of quality water is again getting diminished every year all over the world and particularly in the developing countries, on account of the discharging of untreated and treated wastewaters of different industries in to the environment, which are polluting the surface and subsurface sources of water. The rapid growth of industrial activities leading to the generation of large quantities of waste water results in the adverse pollution of various segments of the environment.
Han-young moon et al. (2004) made detailed study on the process of deterioration and the formation of reactants by chemical reaction of ordinary Portland cement mortars and pastes exposed to 5% sodium sulfate solution. From the results of variation of engineering properties such as visual rating, compressive strength loss and expansion, it can be confirmed that water – cement ratio may be a key to control the deterioration of cement matrix during sodium sulfate attack. The capability for higher absorption of sulfate ions into the cement matrix with a high water – cement ratio may explain the severe deterioration of the cement matrix. More importantly, micro structural observations such as XRD and DSC revealed that the deterioration of the cement matrix resulted from the formation of ettringite, gypsum and Thaumasite. However, more detailed investigations on the structural difference between ettringite and Thaumasite are needed in the future. In practice, the results of XRD analysis with immersion period confirm that calcium hydroxide content must be reduced in the cement matrix for further improving durability against sodium sulfate attack. Conclusively, the mechanical and micro structural deterioration of ordinary Portland cement matrix was a result of the formation of products containing SO$_4$ ions. These products eventually led to the expansion, strength reduction and cohesiveness loss in the cement system.

Pengfei Haung et al. (2005) reported that the damage resulted from HCl corrosion is dangerous for safe application of concrete structure, especially when the structure is subjected to tensile or bending load. After HCl corrosion, the flexural strength loss of the high strength concrete is larger than that of the normal strength concrete, which indicates that the sensitivity to HCl corrosion increases with increasing concentration.
Turkel et al. (2007) investigated the influence of various acids on the properties of Pozzolanic cement mortars. Low concentrations of hydrochloric acid and nitric acid caused higher deterioration compared to sulfuric acid during the testing period. It should be noted that the sulfuric acid produced least soluble calcium salt and least damage on test specimens in terms of both strength and weight loss. The better performance of mortars against sulfuric acid attack can also be attributed to the low content of $\text{C}_3\text{A}$ cement.

As water being precious natural resource for environmental considerations it may be required to understand the properties of concrete with waste water. Reddy Babu (2009) studied effect of metal ions in industrial waste water on fresh and hardened properties of concrete and reported that on comparison with control specimens, test samples prepared with treated waste water of electroplating industry did not show loss of strength, though their setting time has increased.

The presence of dissolved inorganic substance in ground waters is mostly through mineral origin and would be expected in varied concentrations geographically. Literature on the quality of different waters indicates that the water may contain salts of Sodium, Potassium, Calcium and Magnesium.

Thus, the role of chemical compounds present in the water is very deleterious even in hydrolysis. Hence the need to study the role of chemical compounds in the mixing and curing water on hydration of cement and thus on the properties of concrete is more pronounced now. Particularly with the use of mineral admixtures in concrete.

2.9 STUDIES ON X-RAY DIFFRACTION

Laue discovered that X-rays can be diffracted by crystals in the same way as light by a diffraction grating as a two-dimensional representation of a lattice. When a
beam of X-radiation is incident upon a substance, the electrons constituting the atoms of the substance become small oscillators. These on oscillating at the same frequency as that of incident X-radiation, emit electromagnetic radiations in all directions at the same frequency as the incident X-radiation. These scattered waves come from electrons, which are arranged in a regular manner in a crystal lattice and then travel in certain directions. If these waves undergo constructive interference, they are said to be diffracted by the crystal plane. Every crystalline substance scatters the X-rays in its own unique diffraction pattern producing a finger print of its atomic and molecular structure. Bragg’s law governs the conditions for diffraction and the diffracted beams are often referred to as reflections. Constructive interference of the reflected beams emerging from two different planes will take place if the difference in the path lengths of two rays is equal to whole number of wave lengths.

An alternative technique to Laue’s was developed by Peter Debye and Paul Scherrer (1916) and independently by Albert Hull (1917) who used monochromatic radiation and a powdered sample. The powder method is widely used for all samples especially metals and alloys, and for other substances, which are not, obtained as single crystals. The finely powdered sample taken in a walled glass tube or coated on a piece of hair is exposed to a beam of monochromatic X-rays. The diffracted rays are allowed to fall on a strip of photographic film arranged in a circular camera with the crystal at its center. In modern diffractometer the sample is spread on a flat plate and the diffraction pattern, together with the intensities of the reflections, is monitored electronically.

Taylor (1964) reported that the X-ray diffraction techniques employed for cement provide (i) analytically for the identification of unknown compounds and
sometimes – quantitative estimation of the phases present in mixtures and (ii) structurally – to give information about the composition of individual compounds.

Powder diffraction techniques are used to identify a sample of solid substances by comparison of the diffraction lines and their intensities with a large data bank (The powder diffraction file, which is maintained by the Joint Committee on Powder Diffraction Standards, JCPDS, and contains information on over 4 million substances). The powder data obtained on cement samples are provided widely in the literature (Taylor, 1964). Powder diffraction data are also used to determine phase diagrams for different solid phase result in different diffraction patterns, and to determine the relative amounts of each phase present in a mixture. The technique is also used for the initial determination of the dimensions and symmetries of unit cells.

As already known, all solid matter is composed of atoms, ions or molecules condensed together in a coherent mass in which the individual atoms have, in general, only limited capacity for motion relative to each other; that is, they are in more or less fixed positions. If these positions repeat at regular intervals in all directions in space, the substance is said to be crystalline; if they show no long-range order, as in glass, the substance is said to be amorphous.

X-rays, which are electromagnetic radiation with wavelengths of about 100 pm (picometer = 10^{-12} m), may be produced by bombarding a metal with high-energy electrons. The electrons decelerate as they plunge into the metal and generate radiation with a continuous range of wavelengths called Bremsstrahlung (Bremse is German for brake, Strahlung for ray). Superimposed on the continuum are a few high-intensity, sharp peaks. These peaks arise from collisions of the incoming electrons with the electrons in the inner shells of the atoms. A collision expels an electron from an inner shell, and an electron of higher energy drops into the vacancy,
emitting the excess energy as an X-ray photon called characteristic or monochromatic radiation (Warren, 1980).

In the sample, the crystallites are oriented at random, but some of them will have their 100 faces and other faces like 110 and 111 faces oriented at suitable glancing angles so as to satisfy Bragg’s equation. Thus, in a single exposure, diffraction maxima corresponding to all the crystal faces are obtained. If the incident angle is $\theta$, the reflected beam makes an angle $2\theta$ with the incident beam. The crystallites are oriented in all possible directions, and this may be considered to be equivalent to rotating the crystal about the incident beam at a constant glancing angle. The reflected beam will travel over the surface of a cone, whose semi-vertical angle is $2\theta$. For each set of planes, the reflected beams outline a cone of scattered radiation. Such cones cut the photographic film at two places to produce two areas about the central spot. The photographic film when taken, developed and stretched consists of a series of areas. A pair of lines equidistant from centre spot is due to reflection from a particular plane. The distance of each line from the central spot are determined by measuring lengths and halving them (Kuriacose & Rajaram, 1988).

When a monochromatic beam of X-rays is allowed to fall on the powder of a crystal, then the following possibilities may happen.

i. There will be some particles out of the random orientation of small crystals in the fine powder, which lie within a given set of lattice planes (marking the correct angle with the incident beam for reflection to occur).

ii. Another fraction of the grains will have another set of planes in the correct position for the reflections to occur and so on.

iii. Also, the reflections are possible in the different order for each set.
iv. All the like-orientations of the grains due to reflection for each set of planes and for each set.

All the like-orientations of the grains due to reflection for each set of planes and for each order will constitute diffraction cone whose interaction with a photographic plate gives rise to a trace. The crystal structure can be obtained from the arrangement of the traces and their relative intensities.

**2.10 STUDIES ON SCANNING ELECTRON MICROSCOPY (SEM)**

Scanning electron microscopy (SEM) has been a primary tool in the investigation of the complex internal structure of concrete and hydrated cement paste for many years. While the internal architecture of concrete can be studied by various techniques such as transmission electron microscopy (for nano scale details) or pictographic microscopy (for practical examination of field concretes), no other technique can provide the depth and breadth of information as available with SEM.

Most SEM instruments provide for the simultaneous utilization of both techniques, i.e. image examination and study of microstructural details and at the same time, qualitative or quantitative analysis of the chemical composition of any deserved future in the image.

Concretes are peculiar engineering materials. Their properties depend on their internal structures, and very tremendously the microstructure changes with cement used, age, water cement ratio, curing incorporation of chemical admixture, incorporation of mineral admixtures, quality of mixing water, and many other variables. Further more, many concretes in service or subject to deterioration by various chemical and physical process, all of which can modify their internal structures as well as their end use properties. Thus, at least a nodding acquaintance with the internal architecture of cement pastes and other features within concretes
would seem to be an essential tool in the armament of all who deal with concrete properties and with concrete behavior in service.

Paul Stuzman (2004) illustrated that Portland cement, itself, is far from a simple material and SEM images can be usefully applied to both qualitative and quantitative characterization of cement clinkers.

One of the important parameters of any concrete is its water cement ratio. Sahu et al. (2004) provided a novel backscatter SEM based technique for determination of water cement ratio in mature concrete.

Paul Brown et al. (2004) reported on the changes induced in various concretes exposed to concentrated sodium sulfate solutions and on the differences between effects induced by sodium sulfate and magnesium sulfate exposures by SEM.

Anna maria Fernandez et al. (2004) illustrated the power of secondary electron mode SEM examination (of fracture surfaces) and also of transmission electron microscopy in their investigations of alkali activated fly ash pastes being developed for waste immobilization. Corr et al, (2004) studied more conventionally hydrating cement pastes, by using SEM technique.

Escalante – Garcia and Sharp, (2004) investigated the detailed microstructural and chemical characteristics of ordinary Portland cement pastes and of various cement pastes hydrated under a variety of conditions were investigated by using SEM. The hydration of cement in pastes and mortars was also investigated by Igarishi et al, (2004) who used SEM to measure the contents of residual anhydrate cement and pores in samples of varying water cement ratios, age and mineral admixtures.

Finally review of above works reveal the importance of SEM and justifies that SEM is a perfect tool to understand the internal structures of concrete or mortar, and some indications of the wide range of applications that also can be pursued by SEM.
2.11 CLOSURE

From the review of literature presented in this chapter, it can be observed that metakaolin and phosphogypsum are potential materials for partial replacement of cement in construction Industry. Very little research work has been carried out in our country for utilization of metakaolin and phosphogypsum in the production of sustainable concrete and high performance concrete. Hence, there is an urgent need to study the strength and workability behavior of High-Performance-Concrete produced with phosphogypsum and metakaolin admixtures.

The detailed review reveals that very limited work has been carried out to study the effects of quality of water on properties of HPC. Though some of the researchers investigated on some of the aspects mentioned above, their work was limited to study the strength and setting properties of cement mortar and ordinary concrete only. However now a days there is need to use HPC instead of ordinary concrete for complicated structures and for durability. Hence, there is need to study the effects of quality of water on strength properties of HPC. The present work aims to investigate the effect of quality of water on three types of HPC namely HPC with only OPC, HPC with Phosphogypsum and HPC with metakaolin. The results will be analysed and recommendations will be made on the proper usage of water in the preperation of HPCs.