CHAPTER 2
LITERATURE SURVEY

Cement is a glue that binds the aggregate and filler materials in concrete. Cement being one of the major constituent it affects the performance and durability of concrete. Basically the oxide composition of Portland cement is 60-70% CaO, 17-25% SiO₂, 3-8% Al₂O₃, 0.5-6% Fe₂O₃ and small amounts of MgO, K₂O, Na₂O which may also be present.

2.1 INFLUENCE OF WATER

Water is essential in cement chemistry. The chemical reactions between cement and water are more complex than simple conversions of anhydrous compounds into the corresponding hydrates. Each component of cement produces a range of hydration products with intermesh and interleave to produce a dense and strength developing solid.

Water acts both as a solvent for clinker ions and as an important constituent of hydration products. These products are called as hydrates since they contain water molecules. [2]

**Alite**: Tri Calcium Silicate (C₃S)₃CaO·SiO₂

Alite is the most important constituent of clinker. This constitutes 50-70% of the mass of clinker. It reacts very quickly with water and determines short term strength and setting time. The reaction of C₃S is the fastest and generates most of the heat, but it’s contribution to the final strength is little. About 70% of C₃S reacts in 28 days and hence is most important at aging of 28 Days.
\[ C_3S + H_2O \rightarrow C-S-H + Ca(OH)_2 \] (2.1)

**Belite:** Di Calcium Silicate (C\(_2\)S)\(_2\)CaO.SiO\(_2\): This constitutes 15-30% of the whole of clinker. Belite reacts slower than alitethus it contributes to the long term strength development.

\[ C_2S + H_2O \rightarrow C-S-H + Ca(OH)_2 \] (2.2)

**Aluminate:** (C\(_3\)A) 3CaO.Al\(_2\)O\(_3\): Aluminate in cement is twofold. It is beneficial in the cement manufacturing, where it forms a liquid during clinkering and thus facilitates the formation of belite and alite in the cement kiln. However, the presence of aluminate in the final product is undesired, since it may react rapidly with water and cause unwanted rapid setting. This can be suppressed by adding a sulfate containing set-controlling agent (usually gypsum) to the cement. Otherwise, the products formed during the hydration of aluminate will interfere with the desired products and decrease the final strength of cement.

\[ 2C_3A + 18H_2O \rightarrow C_2AH_8 + C_4AH_{10} \] (2.3)

\[ 2C_3A + 32H_2O + 3(Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow C_6AS_3H_{32} \] (2.4)

\[ C_6AS_3H_{32} + 2C_3A \rightarrow C_4ASH_{12}[3] \] (2.5)

**2.1.1 Reaction Products**

When anhydrous cement is mixed with water several exothermic reactions take place simultaneously and consecutively. When Alite and Belite undergo hydration it forms calcium hydroxide (CH) and solid calcium silicate hydrate(C-S-H) that consists of varying composition of calcium, silica and water. Calcium hydroxide is the crystalline phase formed during cement hydration.
2.1.2 Water in Hardened Cement Paste

Water can exist in hardened cement paste in different forms. The classification of water into several types is based on the degree of ease or difficulty with which it can be removed from the (hcp).

![Diagrammatic model of the types of water associated with the calcium silicate hydrate](Source: P.K. Mehta)

1. Capillary Water: This is located in capillary and layer pores (>5nm) and is free from the influence of the attractive forces of solid surfaces. Water in larger voids can be considered as free water as it’s removal does not result in any overall volume change.

2. Adsorbed water: This is the water present close to the solid surface and is under the influence of surface attractive forces. The maximum thickness of this layer of water is 1.3nm. The loss of this water is the main contributing factor to drying shrinkage.

3. Interlayer water: This is the water present in gel pores narrower than about 2.6nm. This is the water between layers of C-S-H which are held by hydrogen bonding. It can be removed only by strong heating at elevated temperature. The loss of this water results in considerable shrinkage because the vanderwaals forces are able to pull the solid surfaces close together.

4. Chemically bound water: This is the water that has combined with fresh cement and is an integral part of microstructure of cement hydration products. This is not lost on drying but is only evolved when the paste decomposes in excess of 1000 °C [4].
2.2 BEHAVIOUR OF CEMENT PASTE IN CONCRETE AT ELEVATED TEMPERATURE DEHYDRATION

The basic effect of high temperature exposure on cement paste is removal of water by evaporation and dehydration. Due to this a complex physic-chemical transformations takes place and an irreversible change in cement structure occurs. These changes in microstructure or nano structure influences the macro properties concrete. Dehydration takes place when temperature rises above the decomposition temperature of mineral or hydrate. Each cement component dehydrates at different temperature and are hence discussed separately.

2.2.1 Dehydration of Calcium Silicate Hydrate

The properties of hydrated Portland is determined by the presence of calcium silicate hydrate (C-S-H). the dehydration can be given by the following equation

\[(\text{CaO})_x\text{SiO}_2(\text{H}_2\text{O})_y \Leftrightarrow \text{CaO}_x\text{SiO}_2(\text{H}_2\text{O})_{y-x} + x \text{H}_2\text{O}\] (2.6)

The dehydration of C-S-H and the evaporation of water are the main reasons for the weight loss of cement paste in the temperature range 105-1000 °C. During the dehydration of C-S-H water is released causing the arise of vapour pressure in the micro pores, when the temperature rises to 700 °C, C-S-H mainly dehydrates to β-C2S.

2.2.2 Dehydration of Calcium Hydroxide (CH) Portlandite

The dehydration of calcium hydroxide takes place in the temperature range 450-550 °C causing a rapid weight loss of cement paste.

\[\text{Ca(OH)}_2 \Leftrightarrow \text{CaO} + \text{H}_2\text{O}\] (2.7)

The dehydration produces calcium oxide (CaO) and water vapour.

**De-carbonation:** During the curing of cement paste, carbonation takes place and produces calcite (CaCO3) when cement is heated to temperatures above 650 °C, de-carbonation takes place. The calcite decomposes into lime and carbon dioxide.
CaCO₃ ⇌ CaO + CO₂  \hspace{1cm} (2.7)

**Recrystallization:** When the cement paste are heated to temperature above 700 °C, recrystallization of amorphous C-S-H to β C₂S takes place [5].

### 2.3 STRENGTH OF CONCRETE AT ELEVATED TEMPERATURE

Lea and Stradling in 1922 explored the factors that can influence the strength of concrete at elevated temperatures. They were probably the first to appreciate the potentially destructive role of thermal incompatibility of aggregate and cement paste. They also discovered that the decomposition of Ca(OH)₂ into lime (CaO) and water during heating can lead to serious damage to the concrete after cooling as lime expands on heating. They showed that there is significant loss in compressive strength for test temperature above 300 °C for Portland cement paste. At 500 °C the residual strength of cement paste containing 100% OPC is approximately 50% of initial strength and as low as 35% of original strength at 600 °C [6].

Generally the trends in strength for temperature above 200 °C were similar for cement paste and concrete although different in magnitude relative to initial cold strength [7].

Different researchers found similar results regarding the effect of elevated temperatures on the properties of concrete. One of effects of high temperatures on concrete structures was the reduction in Compressive Strength of Concrete. The first effect of temperature rise, in concrete occurs between 100-200°C when the evaporation of free moisture occurs. As the temperature rises to 250°C, the loss of evaporable water occurs. The strength loss at 300°C is in the range 15-40%. At 550 °C the reduction in compressive strength is 55-70% of its original value. The effects of temperature on mechanical properties of most of the concrete is similar [5, 8, 9].

On exposure to elevated temperature the strength of concrete increases between 100–200 °C. This is due to increased surface forces in cement gel due to removal of absorbed moisture. The gel like hydration products decompose at
400°C. Between 600 to 800°C de-hydroxylation of calcium hydroxide begins, which is accompanied with decomposition of calcium carbonate causing collapse of structural integrity and thus loss of compressive strength [10]. Yuzer et. al., found that decreases in compressive strength of Portland cement mortars started at 600°C in air cooled samples. Xiao J. and Koni G. stated that compressive strength of ordinary concrete started to decrease drastically when the temperature reached between 400 to 800°C. The loss in strength is nearly 80%. The loss is nearly 55% at 900°C [11, 12].

Savva et al observed that only 7 to 25% of the initial strength is left at a temperature over 600°C. Below 500°C the role of aggregates in strength loss is not significant [13].

2.4 MICROSTRUCTURE OF CEMENT PASTE AT ELEVATED TEMPERATURE

The dehydration such as the release of chemically bound water from calcium silicate hydrate becomes significant above 110°C. Micro cracks start to appear at around 300°C. The internal stresses caused by the dehydration of C-S-H and thermal expansion of aggregates induce the formation of micro cracks. High temperatures in the range 400°C to 600°C activate a series of reactions in the cement paste. These reactions begin with the complete desiccation of pore system followed decomposition of hydration products and destruction of C-S-H gel. The calcium hydroxide Ca(OH)₂ dissociates at around 530°C resulting in shrinkage. The fire is generally extinguished with water and CaO turns into Ca(OH)₂, causing cracking and crumbling of concrete[14].

In their study on the effect of elevated temperatures on ordinary portland cement paste, J Piasta et al., observed an increase in compressive strength at 100°C due to internal autoclaving in cement pastes. This results in additional hydration of cement grains, this is indicated by decrease in C₃S and C₂S phases. In the temperature range 200-500°C there is liberation of water from cement paste and decomposition of calcium hydroxide. Above 600°C calcium carbonate begins to decompose. Due to these transformations, there is formation of micro cracks in the temperature range 300-500°C and a rapid increase in porosity in the temperature range of 600-700°C [15], Wei-Ming
Lin, T.D. Lin and L.J. Powers Couche studied the microstructure of concrete. The microstructure was investigated using scanning Electron Microscopy (SEM) and polarized light microscopy for the better understanding of the mechanical behaviors of concrete. Before exposure to high temperatures the C-S-H gel is in the form of spine, prism, rod shaped honey comb shaped structure. Calcium hydroxide appears as thin hexagonal plates. Ettringite forms long rods or needles with parallel sides that have no branches. The concrete loses its absorbed water in the temperature range of 65 to 800 °C and interlayer water in the 80 to 100 °C range with the increase in temperature between 100 to 200 °C, the cement paste begins to lose its material property. Chemical bonds before hydration are in the form of hydroxyl silanol groups (Si-OH), HO-Si). Therefore loss of water contributes to the shrinkage and strength reduction. The chemical decomposition and loss of bonded water causes significant changes in cement paste. They affect the primacy chemical bonds secondary cohesive forces, porosity and pore size distribution [16].

Handoo et al reported the results of an experimental investigation on concrete cubes made from ordinary Portland cement OPC. The specimens were exposed to high temperature up to 1000 °C in steps of 100 °C for a period of 5 hours. The mineralogical changes due to elevated temperatures were established using XRD, DTA/TGA and SEM. Ultra pulse velocity was used to study the determination of compressive strength with increase in temperature. Reduction in compressive strength of concrete beyond 500 °C is quite rapid. The decomposition of portlandite at the surface beyond 700 °C and beyond 900 °C at the core results in the deterioration of concrete. These changes in morphological is shown by SEM studies. In samples exposed to 600 to 800 °C, the microstructure mainly consisted of micro cracks with increased number of voids, deformed calcium hydroxide crystals and disrupted C-S-H phase boundaries. The complete decomposition of portlandite beyond 700 °C, at surface and beyond 900 °C, at the core results in total deterioration of concrete [5].

G.F Peng and, Z.S. Huang studied the micro structural changes in hardened cement paste of High Performance concrete when exposed to elevated temperature. They reported that pores structure coarsening is responsible for strength in HPC rather than decomposition of C-S-H at temperatures below 400 °C. The decomposition of
Ca(OH)$_2$ and calcium carbonate which takes place from 430-600 °C is responsible for additional strength loss at 600 °C [17].

The microstructural investigation of structure of heated Portland cement paste using various done by Qi Zhang (2013) indicate that the microstructure of cement paste hardly changes at temperatures between 105-400 °C. From 500-800 °C micro cracks start to appear due to the dehydration of C-S-H. At 600 °C there is formation of pores. The total porosities as obtained from MIP increases with increase in temperature. The porosities increases dramatically beyond 400 °C [18].

Omer Arizo (2007) reported that on exposure to elevated temperature the reduction in compressive strength begins at 100 °C and continues to do so till 1200 °C up to 800 °C there is a gradual reduction but above 800 °C there is a drastic reduction. He also reported that the effect of water /cement ratio of the mixture on the relative strength was insignificant for all types of aggregates. The effect of elevated temperatures on concrete containing river gravel aggregates was greater than other aggregates. This was attributed to the siliceous composition of the river gravel [19].

2.5 MINERAL ADMIXTURES

Mineral admixtures are finely divided siliceous materials that are added to concrete in range of 20 to 70% by mass of the total cementitious material. Natural pozzolans in the raw state or after thermal activation are being used as admixtures. Many industrial by products have now become a primary source of mineral admixtures due to environmental and economic considerations. Cements containing mineral admixtures are referred to as blended cements.

The detrimental effects of Ca (OH)$_2$ can be eliminated by the use of mineral admixtures such as fly ash (FA), ground granulated blast furnace slag (GGBFS), silica fume(SF), metakaolin (MK), nano silica (ns), pumice, etc. These are also known as pozzolanic materials. They are incorporated as active addition or as substitutions to ordinary Portland cement due to their capacity for reacting with lime which originates during the hydration of Portland cement. Due to the reaction between Ca(OH)$_2$ and reactive silica from these mineral admixtures additional hydrated products are formed.
along with decrease in Ca(OH)₂ content resulting in formation of dense matrix. Thus the mechanical and physical properties, durability of concrete increases on exposure to elevated temperatures.

Fly ash the major constituents of fly ashes are Silica (SiO₂), Alumina (Al₂O₃), ferric oxide (Fe₂O₃) and Calcium Oxide (CaO). The other minor constituents are MgO, Na₂O, K₂O, SO₃, MnO₂ and TiO₂. Fly ashes are classified as class F fly ash and class C fly ash, depending upon the total percentage of SiO₂, Alumina and Ferric oxide. If their percentages exceed 70%, then it is called as siliceous fly ash or class F fly ash. This is obtained by burning bituminous coal. If the percentage is equal or more than 50% and reactive calcium oxide is not less than 10%, fly ash is called as Calcareous fly ash or Class C fly ash. This is obtained by burning bituminous coal.

2.5.1 Effect of Fly Ash on Cement

The important reaction in a flyash and cement mixture is between reactive silica and calcium hydroxide from the cement and water reaction to form calcium silicate hydrates

In the pozzolan-lime reaction, OH⁻ and Ca²⁺ react with the SiO₂ or Al₂O₃-SiO₂ framework to form calcium silicate hydrate (C-S-H), calcium aluminate hydrate (C-A-H), and calcium aluminate ferrite hydrate:

Tobermorite gel: SiO₂ + Ca(OH)₂ + H₂O → CaO.SiO₂.H₂O

Calcium aluminate hydrate:
Ca(OH)₂ + H₂O + Al₂O₃ → Al₂O₃.Ca(OH)₂.H₂O

Calcium aluminate ferrite hydrate:
Ca(OH)₂ + Fe₂O₃ + Al₂O₃ + H₂O → Ca(OH)₂.Al₂O₃.Fe₂O₃.H₂O

The crystallized compound of C-S-H and C-A-H, which are called cement gel, hardened with age to form a continuous binding matrix with a large surface area and are components responsible for the development of strength in the cement paste [20].
Additionally, the alumina available from the fly ash can also produce a variety of hydrates including calcium aluminate hydrates (C₄A₉H₉) gehlinite (C₂ASH₈) ettringite C₃A.₃CS.H₃₂ and calcium-monosulfo aluminate hydrate C₃A, CSH₁₂. In the presence of gypsum monosulfoaluminate may be written as.

The rates at which pozzolanic reacts occur are dependent upon the total concentration of calcium, alkali, sulfate silica, aluminate in the solution both from fly ash and the cement.

Debate exists as to when the pozzolanic reactions begin. Some research has reported no reaction occurs until 28 days, other research reports reactions at early ages. The discrepancy is likely due to different techniques measuring reactivity.

Work by Maage has found that the pozzolanic reactions to be more sensitive to temp than to characteristic of the Portland cement. Pozzolanic reactions begin earlier at high temperatures [21].

The use of fly ash especially class-F, as replacement of cement has a significant effect on the early strength and later age strength gain. These changes in properties are closely related to concrete’s microstructure. This is affected by fly ash both physically and chemically [22]. In a review article by kokubn concluded that the main effect of fly ash was the finely divided powder effect. The fly ash increases the available space in the flow structure created by cement particles and thus enhancing the cement hydration [23].

Mechanism in which fly ash absorbs Ca²⁺ and provides the precipitation sites for cement hydration products such as ettringite and calcium hydroxide, so that C₃A hydration is accelerated under OH⁻, the fly ash glass phase dissolves and reacts to form plate or fibrous C-S-H phases that link the particle. Diamond pointed out that in the fly ash cement paste the fly ash particles often covered with a layer of fibrous hydrates termed as duplix film, because of its similarity to that which develops on the aggregate surface of concrete. The fly ash particles act as nucleation sites for cement hydration leading to the deposition of cement hydration products like CH and C-S-H.
phase and thus forming the duplex film. Xu, Sarkar in their study on effect of fly ash on microstructure of cement mortar observed the formation of hydration products such as stratlingite ($C_2ASH_8$) aluminate hydrates, $C_2AH_{13}$, $C_4AH_{13}$ along with hydration products such as C-S-H(II) and C1.5S3.5H$_x$ form in the fly ash pastes both in bulk &aggregate-paste interface. The addition of fly ash reduces amount of CH in the paste. EDAX studies showed that the hydration products near the fly ash contain more Al than those near the cement grains indicating dissolution and reaction of Al from fly ash particles. The replacement of cement by fly ash also lowers the initial porosity [24].

The results of the experiments conducted by Prinya Chindaprasirt, Chai Jaturapitakkul, Theerwat Sinsiri on the effect of fly ash fineness on the micro-structure on the blended cement paste demonstrated that greater the fineness of the fly ash, the more effective it is for reducing the pore diameter of the paste. The blended cement paste containing fly ash than portland cement this is due to the gradual filling of large pores from factors such as hydration reaction, nucleation effect, packing effect and pozzolanic reaction of fly ash particles, the smaller particles of the fly ash can be easily dispersed into the blended cement paste and makes it more homogenous. The unreacted fly ash particles fill up the voids and allow dense packaging of materials and matrix phase. There is a greater decrease in calcium hydration content also due to enhanced pozzolanic reaction of fewer fly ash particles [25]. Masslehuddin et al., carried out investigations to evaluate the compressive strength development and corrosion resisting characteristics of concrete mixes in which fly ash was used as admixture. Concrete was made with fly ash additions of 0%,20% and 30% and water cement ratios of 0.35,0.40,0.45 and 0.50 was used. It was concluded that the addition of fly ash as an admixture increases the early age compressive strength and longtime corrosion resisting characteristics [26]. Rafat Siddique carried out experiments to evaluate the mechanical properties of concrete mixtures in which fine aggregate (sand) was partially replaced with class-F Fly ash in five percentages (10%, 20%, 30%, 40% and 50%). It was observed that the mix with 50% fly ash content had the maximum compressive strength, flexural strength and modulus of elasticity at all ages[27].

In the studies conducted by Drazan Joic and others on the setting time, compressive strength development and drying shrinkage of cement mortars in which fly
ash was used as replacement (0-40% by mass) to ordinary Portland cement it was found that all the percentages of replacement by fly ash increases the setting time. The increased addition reduces the early strength of cement mortars. The increased addition significantly reduces the formation of cracks and thus improves the resistance to drying shrinkage and durability of composite material [28].

Namagga (2009) conducted experiments with varying proportions of fly ash (0-50%) as partial replacement of cement and tested for 3, 7, 14, 28 days strength and found that as the percentages of fly ash increased the, the early strength gain decreased. This is due to existence of reaction of free lime during the curing process. Concrete with 25-35% fly ash had the best compressive strength [29]. Sata et al., (2007) performed experiments to find out the variation of compressive strength of fly ash concrete containing 10%, 20%, and 40% fly ash as replacements. They observed that the mixes had lower early strength and the concrete attains the age of the mix design with age [30].

Prinya Chindaprasirt et al., conducted investigations on the effect of fineness on compressive strength of cement paste fly ash of two fineness. An original fly ash of particle size 19.1 μm and a classified fly ash of particle size 6.4 μm were used at replacement levels 20%, 40% by weight, Test results showed that the cement paste with classified fly ash had better compressive strength [31]

Islam and Islam conducted experiments with mortars of OPC and fly ash replacements mortars by 10%, 20%, 30%, 40%, 50%, and 60%. It was reported that the 3 days and 28 days of OPC was higher than that of fly ash blended mortars. The 60 days compressive strength for 20%, 30%, 40%, fly ash replacements mortars were 1%, 2%, 7% higher than no fly ash motors. The maximum compressive strength was exhibited by 30% and 40% replace mortars [32].

Ozlem Celik, Erdem Damci, characterized and studied the effects of fly ash on compressive strength of OPC. They found that addition of 15-35% of fly ash to cement clinker caused a decreasing effect on the compressive strength of mortars. The most important parameter is particle size distribution. The pozzolanic reaction and thus compressive strength increases with fineness of fly ash [33].
2.6 EFFECT OF ELEVATED TEMPERATURE ON BLENDED CEMENTS

Sazzad et al., (2003) discussed the effect of elevated temperature on hand and compressive strength of cement mortar. The study showed that the compressive strength and bond strength decreased with increase of temperature and the bond strength of cement mortar completely vanished at 800 °C [34].

T.U., Ahmed et. al., concluded that compressive strength and bond strength of cement up to a definite temperature and after that it decreases with increase of temperature. The behaviors Fly ash cement concrete is similar to plain cement concrete. With increase in temperature up to 250 °C, as far as decrease in 28 day compressive strength is concerned, the replacement of fly ash up to 20% performed better under compression when exposed to elevated temperatures of 250 °C [35].

The behaviour of fly ash composite concrete under sustained elevated temperature was investigated by Viswanath et al., (2012). OPC was replaced by 35%,40% and 45 % and the concrete specimens were subjected to 200 °C and 300 °C for 2 hours and 4 hours. For a moderate temperature rise of 200 °C, the addition of fly ash did not cause a significant change in compressive strength. The concrete with higher levels of fly ash performed better for longer duration of exposure [36].

Huai-Shuai Shang et al., in an experimental study of high performance concrete with characteristic compressive strength of 50MPa and 60 MPa at 20 °C found that these concrete had 99.1% and 93.2% of their original strength between 400-500°C the strength dropped to 80.4, 80.4% and 81.5% respectively[37]. Pavel Padevet in their experiments showed that water saturated specimens of cement paste with fly ash achieved better performance at temperatures greater than 200 °C [38].

Sarshar R. and, Khoury G.A. stated in their experiments on material properties that cement paste containing 100% OPC loses significant compressive strength above 300 °C. Replacement of cement with both PFA and SF improved the residual compressive strength considerably [39]. It has been observed (Potharaju et al., 2001) with the increase in temperature up to 250 °C, the behaviour of fly ash concrete is similar to the no fly ash concrete as far as the decrease in residual compressive strength
at 28 days is concerned. The replacement by fly ash up to 20% resulted in a better performance under compression when exposed to a temperature up to 250 °C [40].

In an study on the effect of elevated temperature on physic chemical and microstructural properties of blended cements by Mohammed Heikal (2008). It was conclude the blended cement paste containing (70% OPC + 10% WCS + 10% GCB + 10% SF) had higher compressive strength than cement paste containing other proportions of the silica fume (SF), ground granulated blast-furnace slag (WCS) and ground clay bricks (GCB). It was confirmed by SEM and XRD that the increase in compressive strength was due to the presence of to be rmorite which did not decompose at 500 °C. The loss of strength at 800 °C was due to the decomposition of hydrated products to C₂S and C₃S [41].

The effect of elevated temperature on mechanical properties and microstructure of silica flour concrete was investigated and studied (Morsy. M.S. et al., 2010) using Ordinary Portland Cement (OPC) and Silica Flour (SF) in percentages varying from 0.5 to 20% with water/binder ratio of 0.5. After 28 days of curing, the specimens were exposed to 100 °C to 800 °C. The specimens were tested for compressive strength and indirect tensile strength. The phase decomposition study was monitored using differential scanning calorimeter (DSC) analysis and identification of the changes in the microstructure of the specimens using the scanning electron microscope (SEM). The above investigation reported that the exclusion of water at 100 °C resulted in a reduction of residual compressive strength. Between 100 and 400 °C, it was reported that silica flour concrete unlike control concrete resulted in increase in compressive strength due to hydrothermal interaction of the silica flour particles liberating free lime. Further increase in temperature beyond 400 °C, the compressive strength of blended concrete has decreased [42].

The effect of elevated temperature on the mechanical properties of concrete specimens obtained by substituting cement with finely ground pumice and silica fume was studied (Bahar Demirel et al., 2010). They also studied the effect of addition of silica fume to cement with finely grounded pumice (FGP) in proportion of 5% to 20% by weight. Specimens were subjected to elevated temperature of 400, 600 and 800 °C for
The compressive strength and ultrasonic pulse velocity, sorptivity and weight loss was determined. The microstructure analysis of the specimens were performed using scanning electron microscope (SEM). Greater amounts of FGP not only resulted in a decrease in compressive strength and ultrasonic pulse velocity values of the concrete but also increased the porosity and sorptivity values. This occurred in the concrete with FGP, a greater reduction occurs in as the FGP content increases. The highest weight loss occurred in specimens with FGP plus SF that were subjected to 800 °C. The reduction in the compressive strength of concrete was significantly larger for samples exposed to temperatures higher than 600 °C. This result is due to the lost water caused by crystallization resulting in a reduction of the Ca(OH)\(_2\) content, in addition to the changes in the morphology and the formation of micro cracks. of Ca(OH)\(_2\) and C-S-H gels, especially at 800 °C, resulted in the total deterioration of concrete. This study demonstrates concrete specimens containing FGP or FGP and SF is are stable up till 600 °C because all the hydrated phases including C-S-H and Ca(OH)\(_2\) appeared to have amorphous structures at this temperature instead of their characteristic crystal structures. the decomposition of Ca(OH)\(_2\)and C-S-H gels, especially at 800 °C, resulted in the total deterioration of concrete. The drastic reduction in ultrasonic pulse velocity values between 400 and 800 °C indicates that the physical state of the concrete samples deteriorated rapidly beyond 400 °C. SEM investigations conducted on the specimens confirmed the deformation of well-developed Ca(OH)\(_2\) crystal sand the C-S-H gel at temperatures beyond 600 °C [43].

The effects of high temperature on the mechanical properties of cement based mortars containing pumice and fly ash was carried out by Serdar Ayudin(2007). The specimens were exposed to elevated temperatures between 300-900° in increments of 300 °C for a period of 3 hours. It was observed that the incorporation of fly ash in pumice mortar had a positive effect at a high temperature of 900 °C. XRD analysis revealed the formation of gehlenite in mortars containing 60% fly ash. It was also observed that the thermal conductivity decreased in the presence of fly ash and pumice. This made the material suitable as a thermal insulation material [44].

Hager I., et al., (2013) carried out studies on the effects of fire on the properties of concrete and mortars. The specimens were exposed to elevated
temperatures. The author also suggested that the color changes in the specimens can be used to assess the extent of damage caused due to exposure to fire [45].

The residual performance of Portland cement concretes was analyzed Tolentino et al. (2002) after being thermally treated at (600) C and cooling down to room temperature. The 28 days compressive strength of concrete was studied. Researchers observed a decrease of residual compressive strength and modulus of elasticity, with the raise of heat treatment temperature, as a result of heat-induced material degradation. The results also indicated that the microstructural damage increased steadily with increasing temperature. Based on the results of this experimental work they concluded that residual mechanical properties of concrete are dependent of their original non heat-treated values [46].

Mohammed Heikal et al., (2013) studied the effect of nano-silica (NS) on physicochemical, compressive and flexural strengths of OPC-granulated slag blended cement pastes and mortars after 3, 7, 28 and 90 days of hydration. The compressive and flexural strengths of cement mortars containing NS are higher than those of control OPC mix. The results obtained were analyzed using XRD, DTA, IR and SEM techniques. XRD patterns of the blended cement paste hydrated up to 90 days. Shows that the main hydration products are mainly calcium silicate hydrate (CSH) with various C/S ratios and portlandite (CH). As the hydration proceeded, the peak intensity of CSH increased, where as those peaks of CH decreased; this is due to pozzolanic reaction of the active silica and alumina of the GBFS with the released portlandite during OPC cement hydration. FTIR study on OPC cement hydration indicated a small peak located at about 3650 cm\(^{-1}\) due to Ca(OH)\(_2\). The intensity of this peak decreased with curing time, due to the pozzolanic activity of slag. The broad bands located at 3400 cm\(^{-1}\) and 1640 cm\(^{-1}\) are as a result of stretching and bending vibrations of water lattice present in CSH, CAH and CASH hydrates. The band that appeared around 950 cm\(^{-1}\) is attributed to CSH. Its intensity increased with curing time, due to the continuous hydration of OPC phases as well as the pozzolanic reaction of slag portion with free portlandite. The observed band at 1475 cm\(^{-1}\) is due to the stretching vibration of CO\(_2\) which results from the carbonation of hydrated products [47].
Abd. El. Aleem et al., (2014) studied the effect of replacement of OPC with nanosilica (NS) on the hydration kinetics, microstructure of OPC and also the behavior of these composites at elevated temperature. The presence of NS improved the physicochemical and mechanical properties both at ambient temperature and at elevated temperatures between 250-800°C. The improved strength is due to the pozzolanic reaction that occurred at 250-450° that leads to the formation of additional CASH and C-S-H and gehlenite like hydrate. The presence of these hydrates was confirmed by XRD analysis. It was also seen that the cement matrix with NS possessed a homogeneous, dense and compact microstructure. This is due to increased number of nucleation sites by the presence of NS [46, 48].

Khander M. Anwar Hossain (2006) studied the strength and durability characteristics of high strength volcanic ash concrete (HSVAC) at elevated temperatures. The experimental programme was carried out on blended concrete containing 20% volcanic ash. It was reported that the 28 days compressive strength decreased with increasing VA content. The HSVAC lost 4-15% of its original strength from 200-400°C. Even though the strength loss in the range 400-600 was high the concrete containing VA did not undergo spalling and were thus able to retain a better strength than the control specimens. This was explained by the increased pozzolanic reaction and reduction in volume expansion [49].

2.7 REFRACTORY OXIDES AND ITS APPLICATIONS

Zirconium dioxide (ZrO₂):- Zirconium dioxide sometimes known as Zirconia is a white crystalline oxide of Zirconium. Zirconia as a pure oxide does not occur in nature but it is found in baddeleyite and zircon (ZrSiO₄) which form the main source of material. Pure ZrO₂ has monoclinic crystal structure at room temperature and at increasing temperature there is a transition to tetragonal and cubic structure. Zirconium dioxide is an important engineering ceramic for various applications, as electrolytes of solid oxide fuel cells, high-temperature structural ceramics, and thermal barrier materials. Zirconia has three polymorphs. The transitions between different phases of zirconium oxide have been widely investigated. In general, the monoclinic form is the stable phase at room temperature. At elevated temperatures (>1170 °C), the tetragonal p hase becomes stable, followed by the cubic phase at even higher temperatures >2370 C
Zirconia (ZrO₂) is used extensively as a refractory material in furnaces and crucibles, in ceramic glazes and in gas mantles. Zirconia-Alumina composites are of high strength, toughness, wear-resistance and thermal-shock resistance hence used for manufacturing cutting tools and rocket nozzles. Zirconia finds a major use in bio ceramic applications as in dental prosthesis, bone replacement, bio ceramic scaffolds. Tetragonal ZrO₂, also finds application as catalyst, catalyst support due to several positive characteristics of Zirconia in such as bio compatibility, colour and mechanical properties, it is suitable for use in modern dentistry [52, 53, 54].

Porous ZrO₂ with non-uniform microstructure has higher thermal conductivity than ZrO₂ with uniform microstructure. Hence uniform microstructure is important for porous ZrO₂ with low thermal conductivity for thermal barrier coating applications[55]. Sintered Zirconia ceramics play a very important role as a refractory material in development of new-high tech materials, because of their high strength, good thermal shock stability and high resistance against oxidation[56].

Ceramic membranes manufactured using ZrO₂ composites have high thermal and chemical stability, long life and good de-fouling properties in their applications and they have catalytic properties [57, 58].

When 20% more ZrO₂ was added to TiO₂-ZrO₂ composite membrane, it retains a crack-free microstructure even up to a temperature of 800°C. When Zirconium alloys are used in nuclear power plants hydride precipitation may occur when the hydrogen solubility limit is reached. This is due to the good reversibility of hydrogen absorption reaction of Zirconium [59]. A single-phase monoclinic Zirconia, the thermodynamically stable modification up to a temperature of 1170°C has been prepared by gel precipitation followed by calcination at 450°C. It has high surface area. It was found that the specific surface area and pore volume of monoclinic Zirconia both decreased markedly on increasing calcination temperature. The thermal stability of monoclinic Zirconia can be improved significantly by addition of various oxides like CaO and MgO. This led to an improvement in the thermal stability up to 900°C [60].
The Zirconium based amorphous alloys exhibit good engineering properties of high tensile strength, high elastic modulus, relatively high impact fracture energy, high corrosion resistance and good soft magnetic. Zirconium thermal-barrier coating when applied to engine reduces the operating temperature and extends the life of the engine. As the thickness of the thermal-barrier coating increases, total conductivity decreases. Thermal conductivity of Zirconia thermal-barrier coating appears to decrease slightly with increasing temperature [61].

In recent years great progress has been achieved in the creation of high-strength ceramics based on ZrO$_2$. ZrO$_2$ differs from other refractory oxides of ionic-covalent type in that it has a higher electrical conductivity, which increased substantially with temperature. Due to the additional stabilization of high-temperature ZrO$_2$ phases by nitrogen improvement was seen in electrical properties ZrO$_2$. Because of its properties, ZrO$_2$ is widely used in the production of heat-insulating materials, solid oxide fuel cells, gas sensors, ceramics, catalyst supports and sorbents Zirconia ceramic-thermal-barrier coating has high thermal conductivity and hence these coatings are used in gas turbine engines and reciprocating heat engine [62].

Zirconium-di-oxide is used in ceramics and high temperature batteries [63]

Aluminum Oxide: Alumina is the most cost effective and widely used material in the family of engineering ceramics. The raw materials from which this high performance technical grade ceramic is made are readily available and reasonably priced, resulting in good value for the cost in fabricated alumina shapes. With an excellent combination of properties and an attractive price, it is no surprise that fine grain technical grade alumina has a very wide range of applications. Aluminum oxide, commonly referred to as alumina, possesses strong ionic inter atomic bonding giving rise to its desirable material characteristics. It can exist in several crystalline phases which all revert to the most stable hexagonal alpha phase at elevated temperatures. Weight loss in vacuum ranges from $10^{-7}$ to $10^{-6}$ g/cm$^2$.sec.α-Phase (Corundum) of Aluminium oxide is used in plasma spray application due to its high corrosion resistance and hardness Aluminum Oxide Nano fluids are a promising candidate for advanced heat transfer applications such as microelectronics cooling [64].
Aluminum Oxide ceramics have been used as heat conducting substrates of hybrid integrated circuits [65].

N.C. Biswas et al studied the physical chemical, mechanical and thermal properties of Zircon-Mullite, Alumina-Zircon composites and found that Alumina-Zircon composites had better above said properties.[66]

The lining of thermal heating equipment are exposed to temperatures between 1100 °C -1200 °C. These lining are made of refractory concrete with alumina cement. Recent experiments have shown that materials having micro additives such as Aluminum hydroxide or Aluminum silica have thermal properties similar to that of refractories with alumina cement[67].

Titanium Di Oxide: Its most widely used application is as a pigment, where it is used in powder form, exploiting its optical properties, as photocatalyst, corrosion resistant, oxygen sensor, and Antimicrobial Coatings. But its ability to withstand higher temperature is not very much exposed in present scenario. Hence following literature study is made to exploit the refractive property of TiO₂ TiO₂ residues from a sulfate method are used in metallurgical processes or as a component of fireproof materials. In order to reduce wear on refractory linings due to corrosion and the infiltration of slags and molten metals, particulate materials containing TiO₂ are added to the refractory products consisting of a mixture of aggregates and binding agents. The use of the particulate materials containing TiO₂ is suitable both as an additive for refractory products whose aggregates consists substantially of Al₂O₃, SiO₂ and aluminum silicates, and as an additive for refractory products whose aggregates are substantially magnesia, dolomite, chrome magnesia, chromium ore and spinel, and for refractory products which contain silicon carbide, silicon nitride, Zirconium silicate, Zirconium oxide, borates and boron oxide. For many years it has been known to use materials containing TiO₂ to reduce wear and to repair damaged areas in the hearth of blast furnaces[68]. The positive effect of TiO₂ addition on the magnesite chrome refractory brick structure has been reported in the literature. Thus, 1, 3, 5, and 7 wt.% TiO₂ ratios were used in the blend, and the refractory properties were positively affected by the
3% TiO₂ addition. A dense chrome refractory material has been produced comprising from 85 to 98% chromic oxide, from 1 to 10% Zircon and from 0.5 to 5% of a titanium compound, possesses very low porosity, has high corrosion resistance to molten glass, and in addition, has good resistance to thermal cracking during firing[69]. Yttrium-titanium oxide particles (10 to 20 nm) in a ferrite steels provide very good high temperature strength[70].

Silicon Carbide is the only chemical compound of carbon and silicon. It was originally produced by a high temperature electro-chemical reaction of sand and carbon. Silicon carbide is an excellent abrasive and has been produced and made into grinding wheels and other abrasive products for over one hundred years. Today the material has been developed into a high quality technical grade ceramic with very good mechanical properties. It is used in abrasives, refractories, ceramics, and numerous high-performance applications. Silicon Carbide has been recognized as a high performance material for structural ceramics because of its unique combination of properties, such as high mechanical properties maintained at high temperature, high wear resistance, high thermal conductivity and its low electrical resistivity[71]. The material can also be made an electrical conductor and has applications in resistance heating, flame igniters and electronic components. Structural and wear applications are constantly developing. Silicon carbide is not attacked by any acids or alkalis or molten salts up to 800°C. In air, SiC forms a protective silicon oxide coating at 1200°C and is able to be used up to 1600°C. The high thermal conductivity coupled with low thermal expansion and high strength gives this material exceptional thermal shock resistant qualities. Thermal conductivity is measured on structural Silicon Carbide and high thermal conductivity Silicon Carbide ceramics. These ceramics possess conductivity maxima, the values of which are 4 W/cm⁻¹k⁻¹ at 100K for high thermal conductivity Silicon Carbide and 0.6 W/cm⁻¹k⁻¹ at 150K for structural Silicon Carbide. These have good electrical insulation properties. Silicon Carbide is considered to be a useful structural material at high temperature because of its mechanical strength is greater than Aluminium Oxide. Silicon Carbide ceramics are suitable material for high electrical insulation and high thermal conductivity[72]. Silicon Carbide is one of the few crystals that can be classed as high thermal conductivity solids. In order to fabricate Silicon Carbide ceramics of high thermal conductivity, a sub micrometer size β – Silicon Carbide powder doped
with various amounts of combinations of $Y_2O_3$ and $Ca_2O_3$ as sintering additives was hot pressed at 2000°C under 40MPa for 2h in Ar and some hot-pressed specimens were subsequently annealed at 1900°C for 4h in Ar. By adding 1 mol% or more additives, full densification was achieved and materials had thermal conductivities in excess of 166W/m/K. The thermal conductivities further improved to over 200W/(mK) after annealing. The improvement of thermal conductivity of Silicon Carbide ceramics will broaden their applications as structural and functional materials[73].

2.8 EFFECT OF REFRACTORY OXIDES IN CEMENT

Inert materials like quartz, calcite, titanium dioxide ($TiO_2$), alumina, Zirconium dioxide ($ZrO_2$) enhance the cement hydration and thus improve the thermal resistance. The nano particles are uniformly distributed in the cement paste. As the hydration begins, the hydrated particles diffuse and envelop the $ZrO_2$ particles as kernels. These kernels promote cement hydration. This makes the cement matrix more compact and homogeneous. Thus the structure of concrete is improved by the decrease in pore size. The nano materials in such instances not only act as fillers but also as an activator to promote hydration and thus improve the microstructure[74]. The presence of small quantity of $TiO_2$ (0.5%) is known to increase the hydraulic activity of cement because of the distortion of the belite and alite crystal lattice as a result of the substitution of the $Si^{4+}$ ion by the $Ti^{4+}$ ion and formation of corresponding solid solutions. In the CaO $TiO_2$ system there is formation of CaO $TiO_2$ and 3CaO $TiO_2$, which possess hydraulic properties[75]. Although $TiO_2$ enhances the early hydraulicity of alite the clinkers have shown slow initial setting. However, 1% $TiO_2$ clinker have roughly 20% higher, 3 and 90-day strengths. Introduction of $TiO_2$ into $C_3S$ affects the hydration behaviour of tricalcium silicate by (a) modifying the polymorphism of $C_3S$ and (b) forming a CaO $TiO_2$ compound that affects the hydraulicity of $C_3S$. $TiO_2$ has an inhibiting effect on the early hydration reaction of $C_3S$ but only up to 2%. With 1% $TiO_2$ in $C_3S$, the extent of hydration becomes least, up to 1 day. The concentration of up to 2% $TiO_2$ slows down the hydration process for approximately 2 days and thereafter picks up to exceed the degree of hydration of undoped $C_3S$. Concentrations of more than 2% $TiO_2$ have an accelerating effect on the hydration process from the initial period to the decay period. The effect of the addition of nano-sized $TiO_2$ particles on the early hydration reaction of cement was studied by Jayapalan A.R.. It was reported the hydration
reaction was accelerated and the rate of hydration increased when the size of the TiO$_2$ particles was reduced. The increase in the rate of reaction was proportional to the percentage of the TiO$_2$. Heterogeneous nucleation effect was found to be dominant compared to the effect of dilution when inert TiO$_2$ particles were added to cement[76]. The use of industrial wastes, such as waste tyres, non-ferrous metal slag or waste sand in cement manufacture has led to the presence of several transition metal oxides(such as ZrO$_2$ and TiO$_2$)in cement clinker or hydrated cement. Their presence cases a delay in first two days but the hydration is accelerated after 28 days [77]. In another study Kakali (1989) concluded that the presence of ZrO$_2$ in 1-1.5% in the clinker causes a considerable delay in setting time and development of strength. But Blaine et al. (1966) indicated that smaller ZrO$_2$ additions increased the early compressive strength [78].

Ali Nazari investigated the changes in compressive strength and workability of concrete by partial replacement of concrete with different percentages of nano-TiO$_2$. The results obtained from the study showed that the nano TiO$_2$ blended concrete had significantly higher compressive strength than the control without the nano particles [79, 80]. Ali Nazari also studied the effect of nano TiO$_2$ in concrete containing GGBFS the addition led to increase in tensile and flexural strength up to 3% TiO$_2$. The nano particles acted as fillers and nucleating agents thereby promoting the hydration of cement. This causes formation of dense cement matrix by the refinement of pores [81] in a similar investigation with nano Al$_2$O$_3$, it was found that the cement could be advantageously replaced with nano-Al$_2$O$_3$ particles up to maximum limit of 2.0% [82].

Hu Li et al investigated the properties of blended cement mortars with nano particles such as NS, nano Fe$_2$O$_3$.The strength of mortars containing NS increased along with the % of NS. But the inclusion of nano Fe$_2$O$_3$ decrease the strength of the mortars. The increase strength was explained based on the fact that when nano particles are dispersed in cement paste, the hydrate products deposit on the nano particles. The nano particles located inside the cement paste act as nucleus and accelerate and promote the hydration reactions resulting in improvement of pore structure [83]. The incorporation of fillers in polymer in terms of improving mechanical properties and
wear performance was studied by Rajesh Chandra et al., (2013). The addition of nano fly ash and ZrO$_2$ to polyimide composites, enhances its mechanical properties[84].

In their investigations Masoud Neghdary found that the addition of Zirconia nano particles improves the structure of concrete by decreasing the pore size. Cement paste, which is replaced with 0.5% Zirconia, showed on improved split tensile and flexural strength. This is due to the rapid consumption of portlandite formed during the hydration of Portland cement [85].