Chapter -1

INTRODUCTION

1.1. Cement – Scenario – History

Cement in general termed as Ordinary Portland Cement (OPC), and is used as a perfect binding material across the world. It will also commonly available for material for general use around the globe, an ingredient to mortar, stucco and grout [1]. Cement is produced from limestone by grinding, calcining then grinding to produce a fine powder, which intern is mixed with gypsum to retard setting time.

The basic cement clinker is a hydraulic mass composes two third mass of calcium silicate ($CaO.SiO_2$), and the rest consists of aluminum and iron associates and other materials [1], with the ratio of CaO to SiO_2 to be not less than 2, and magnesium oxide to be not more than 5% by mass. These are the norms proposed by German Standards, published in 1909.

The reacted mass (calcined mass) basically forms nodules like materials of approximately one inch diameter, which acquires the properties of binding, and in order to increase the rate of reaction of binding, surface area is increased by grinding in a ball mill. According to ASTMC 150, the cement posses the properties of hardening as well as water resistance. The nature of hardening retards when grounded calcium silicates present in multiple forms. Nature is gifted with lime stone and is extensively available as a natural resource by way of rocks. During the advent of technological developments cement has been considered to be the best material to be used in construction [2].

The basic cement nodule (clinker) is produced by heating calcined limestone to an approximate temperature of 1300^{o}C. Iron oxide and aluminium oxide appear as flum and are responsible for strength of cement.

There are special cements available like Low Heat and Sulfate Resistant type, which require to control the composition of tricalcium aluminate ($3CaOAl_2O_3$), for which lime stone which is used as a conventional raw material for production of clinker substitute alumino silicate, in general practice less pure limestone which contain clay with SiO_2 is being used [1]. The percentage of such lime stones may be in the order of 80% and next addition of raw materials depends on percentage purity of limestone. Some of the materials being used include shale, clay, iron ore, sand, fly ash, bauxite and slag. When coal is burned in the kiln, ash generated acts as an essential ingredient to cement. The so called Portland cement was developed first from natural cements of Great Britain during early period of nineteenth century and its anonymous nature of Portland stone, which is in general a type of rock which was excavated beside Portland in the desert of England [2].

A brick layer Aspidin [1] invented production of Portland cement in the year 1811, and was patented in the year 1822, and was called 'British Cement'. The entitled name of Portland cement was also published in the year 1823, as was associated with William Lockwood, Date Stewart, and others [3]. The production of Portland cement was patented in the year 1824 [2].

During 1826, James Frost had constructed a manufacturing unit for producing the cement [4], and in 1843, Aspidin's ward William [1] reported to have improved the quality of cement and was named 'Patent Portland Cement', though he doesn't possess the patent. In the year 1848, William Aspdin improved the quality, furthermore and in 1853, shifted to Germany and started cement production [3]. William Aspidin produced the cement, which was called meso-Portland cement mixture of Portland cement and hydraulic lime [5]. During 1859, John Grant of Metropolitan Boards laid requirements for cement for the requirement of London sewer project, which had become a set specification for Portland cement. During 1860, the Hoffman kiln gave perfect control. The Hoffman 'endless' kiln gave perfect control in combustion and proved to produce better grade cement. The cement produced at Portland cement fabric was been the first to use a Hoffman Kiln[6], which was then considered to be the first modern plant, after wards the association of German Cement manufacturers laid the standards of Portland Cement in the year 1878 [7].

Cement has the ability of quick setting upon addition of water, and in order to retard the setting time a quantity of 2-8% of calcium sulphate is added to clinker and then grounded in a ball mill to produce final cement. The ball mill grinding is controlled to produce a particle size distribution as 15-18% of total mass to contain 5 micro meters, and 5-7% of particles above 45 micro meters [8]. Fineness is measured by 'specific surface area' which gives surface area of cement. The initial reactions of cement upon addition of water is faster and depends on fineness, general values of cement surface area is about 320-380 m^2/kg and 450-650 m^2/kg for fast hardening cements [9-10]. Transportation of cement is done by pneumatic mechanism for shorter distance and for longer distance specially designed containers are used, which manages the compactions of vibration during transportation. Cement plants have the silos to store the production of 1-20 weeks, and is delivered to customers by bags and containers.

1.2. Constituents of Ordinary Portland cement

Tricalcium silicate $(CaO)_3.SiO_2$	C_3S	45-75%
Dicalcium silicate $(CaO)_2.SiO_2$	C_2S	7-32%
Tricalcium aluminate $(CaO)_3.Al_2O_3$	C_3A	0-13%
Tetracalcium alumino ferrite $(CaO)_4.Al_2O_3.Fe2O_3$	C_4AF	0-18%

Gupsum $CaSO_4.2H_2O$ 2-10%

Where, C_3S, C_2S, C_3A, C_4AF are the notations of cement chemists

1.3. Setting and hardening of cement

Cement when mixed with proper proportion of water starts setting hard due to series of complex reactions and so far the reactions are partly understood. The constituents present in cement causes slow interactions and interlinking yielding crystalinity and intern strength. During initial reactions carbon dioxide is slowly released and converted to Portlandite ($Ca(OH)_2$) into insoluble calcium carbonate, after the initial setting, the material is subjected to curing in warm or normal water where the reactions speeds up intern accelerating hardening. Gypsum is mixed in clinker to inhibit rate of reaction [1].

In conventional practice cement is extensively used to prepare concrete which in turn used in construction. For production of concrete which consists of gravel, water, sand and cement [1]. The material to be constructed can be casted to any desired shape and upon hardening becomes a structural product, which withstands loads. Taylor made structures are also produced in the cement plant based on the requirement by the customer.

When water is mixed with Portland cement, the mass sets in few hours and hardens over a period of about few weeks. This processes varies widely with the parameters like curing temperature, humidity but in general concrete sets within 6 hours and builds a compressive strength of about 9-15 Mpa in a day, then develops to 20-24 Mpa in 3 days, then develops to 30-35 Mpa in 7 days and then develops to 40-60 Mpa in 28 days [1].

The Pozzolona Cement (PPC) is a kind of cement, produced when fly ash is blended with Ordinary Portland Cement (OPC), to a maximum percentage of 35. The process of blending is done in a ball mill with Ordinary Portland Cement, gypsum and fly ash, in order to produce homogenous quality of cement.

Pozzolona occurs naturally as well as from thermal power plants, where huge volumes of coal is combusted to produce heat, in turn steam to run the turbine and in turn coupled to alternator to produce electricity. Pozollona processes siliceous and aluminous material, which is very reactive with Ordinary Portland Cement, to produce cementious compounds [11]. Finer the silica in Pozzolona leads higher cementious properties of producing calcium silicates. Pozollanic materials available in nature are volcanic ash, calcined clay, fly ash and silica fumes.

1.4. Types of cement

The demand to produce different types of cement based on the utility had been increasing over decades, and scientists are successful in producing different types of cement as demand arises. Following are the types of cements:

1. Ordinary Portland Cement (OPC)
    a. 33 grade cement
    b. 43 grade cement
    c. 53 grade cement
2. Portland Pozzolona Cement (PPC)
   (on par with 33 grade cement)
3. Portland Blast Furnace Slag Cement
4. Oil Well Cement
5. Rapid Hardening Portland Cement
6. Sulphate Resisting Portland Cement
7. White Cement

Amongst the above types PPC and OPC had been widely used in practice as common cement. Portland Pozzolona Cement is produced by grinding pozolonic (fly ash) material with clinker.

During current times good quality of fly ash is available from thermal power plants, which are being used in the production of PPC, cement without the presence of PPC is termed OPC [11].

The benefit of PPC in comparison to OPC is that, pozzolana associates with lime and alkali in cement upon addition of water and forms a product which infers to strength, impermeability, and sulfate resistance. It also infers to workability, reduces and controls destructive expansion from alkali-aggregate reaction [5]. It also reduces heat of hydration liberated during the process, which causes thermal strain resulting cracking. When water is mixed with Portland cement, the product sets in few hours and hardens over a period of few weeks. The processes of curing vary widely depending on the mix used and the conditions of curing.

In general the compressive strength of any cement continues to rise slowly as long as it is in contact with water for hydration. Setting and hardening of Portland cement happens by the formation of water containing compounds, and as a result of reactions between cement components and water.

Upon addition of water to Portland Cement, a brief and intense hydration starts which is called pre induction period, Calcium sulphate and alkalies dissolve completely, then short, hexagonal and needle like crystals form at the surface of the clinker particles as a response of reaction between calcium and sulphate ions with tri calcium aluminate [1]. Furthermore, calcium silicate hydrates in colloidal shape caused by formation of a thin layer of hydrated products on the clinker surface, and then first hydration period ceases.

Once hydration period ceases, and the induction period starts, in which time no reaction takes place. The initial hydrated products are very feeble to couple the gap between the clinker particles and do not form a consolidated microstructure [1]. Furthermore the movement of the cement particles in accordance to one other is slightly affected [1]. The setting starts after one to three hours, when initial calcium silicate hydrate forms on the surface of the clinker particles, which are finely grounded in the beginning. After completion of hydration of clinker further more an intense hydration takes place.

The next level of curing starts after four hours and ends within 24 hours. During this period a basic micro structure forms consisting C-S-H needles and leafs, calcium hydroxide and ettringite $((Ca))6(Al_2O_3)(SO_3)3.32H_2O)$ crystals which grows in longitudinal shape [1].

As the crystal grows, the gap between the cement particles tends to bridge. Furthermore, the hardening process steadily increases, but with a decreasing rate. The density of microstructure increases and pores get filled. The pores filling takes place with respect to time and the hydration process increases the compressive strength of cement [1].

Celik [12] studied in the year 2009, about the effect of particle size distribution, and found the increment in compressive strength of cement upon addition of fractions of 20 and 30 μm particles, in a stipulated range.

Zhang and Napieer-Munn [13] studied in the year 1995 about effect of particle size distribution and developed models pertaining to compressive strength of cement.

Lot of research work had been done by scientists and engineers in the area of increasing the parameters, one after the other, and studying its response. It had been acknowledged that, upon increasing fineness of cement, the compressive strength of cement in all the days found to be increasing [12].

Likewise upon increasing different chemical constituents what is the response had been studied. Similarly the fly ash fineness had been grounded further and the response was studied. With a different perspective researchers had also tried with selected proportion of cement particle size towards yielding higher compressive strengths.

It had been studied that the quality of cement depends on combination of all constituents' interaction, with in a stipulated range. According to research reports no single parameter/constituent can be labeled as a significant parameter for maintaining good strength. Eg. Many researchers acknowledge that upon maintaining higher cement fineness, strength can be increased, but there are instances where fineness is more and quality was found to be very feeble. It is also found to be certain that upon increasing the fineness of final cement, strength can be increased.

In view of the above, the present thesis is aimed to study the effect of different constituents and find out feasible constituents. It is also aimed to use waste constituents and find the compatibility as a cementing material. The major objectives of the thesis is outlined in the following section.

1.5. Objectives

1. The effect of single as well as multiple constituents (physical - <10, <30, <53 µm particles and chemical – LOI, IR, SO_3) and its response in terms of compressive strength. Towards this objective different commercially cement samples were aimed to procure (approximately 100 samples) from local market, then analyze for physical and chemical constituents,

2. Developing an equation between physical & Chemical constituents and 1,3,5 & 28 days strength using John's Macintosh Program (JMP) statistical software,

3. Measuring the physical parameters (bulk density, tapped density, Husner's ratio and specific surface area) of all the commercial samples procured and to analyze the impact of these parameters on compressive strength

4. Establishing range of values of constituents (Physical & Chemical) and physical parameters towards producing higher

quality cement. Validation of range of constituents/model developed by JMP software.

5. To use waste materials like granite waste, plastic waste and effluent slate mine waste water as cementing material by mixing these materials with cement and assess the consistency as a binding material with cement, and also validation of range of constituents/model developed by John's Macintosh Program (JMP) software.