CHAPTER 1

INTRODUCTION

1.1 GENERAL

Ordinary Portland Cement (OPC) is becoming an energy exhaustive and pricey constituent in the production of concrete, which is the most widely used construction material. It is expected that the cement requirement will grow threefold to about 3.5 billion tonnes by the year 2015. Although the requirement is vast, the raw materials required for the cement production is relatively less. In addition to the expensive process of cement production, the environmental impact due to the emission of Carbon dioxide (CO$_2$) is alarming, since it is the major source for global warming. Bhanumathidas and Mehta (2001) have estimated that to produce one ton of cement, nearly 1.5 tonnes of earth minerals are consumed and one ton of CO$_2$ is emitted in the atmosphere.

One of the efficient methods to conserve the natural resources and reduce the impact on the environment is to go for SCMs, wherein the quantity of OPC can be saved. Since most of the SCMs are waste materials, which are pollutants when dumped in the lands, blending of them in concrete becomes a safe and effective disposal method. Some of the waste materials which improve the properties of concrete are fly ash, Ground Granulated Blast furnace Slag (GGBS), silica fume, RHA, LP, copper slag and so on.
Most of the SCMs are pozzolanic in nature and hence they are helpful in the increasing the strength and reduce the permeability of concrete with age. Therefore, the blending of cement with SCMs have always resulted in many advantages such as saving in cement, recycling of waste products, increase in physical properties along with increased durability of concrete and reduced impact on the environment through reduced green house gases production. Pozzolana, fly ash, GGBS and limestone are the main materials that are permitted by the European Standards EN 197-1(2000).

1.2 SUPPLEMENTARY CEMENTITIOUS MATERIALS (SCMs)

Blended cement has replaced OPC to a major extent, in lieu of its increased durability and lesser cost. In addition there is reduction in green house gases in the manufacturing of cement, thereby reducing pollution. The new ACI 318-08 Building Code gives the limitation on the quantity of supplementary cementitious materials, expressed as a percentage of the total cementitious materials, as follows:

1. Fly ash or other C618 pozzolans – max: 25 percent
2. Total of fly ash or other pozzolans and silica fume – max: 35 percent
3. Combined fly ash, pozzolan and silica fume – max: 50 percent with fly ash or pozzolan not exceeding 25 percent and silica fume not exceeding 10 percent
4. Ground granulated blast-furnace slag – max: 50 percent
5. Silica fume – max: 10 percent

1.2.1 Binary blending of Fly ash

Fly ash, which was once an environmental pollutant, has now found a good place in the construction industry, mainly in production of blended cement. Fly ash is one of the residues generated during combustion of coal and comprises the fine particles that rise with the flue gases. Fly ash is
generally captured by electrostatic precipitators or other particle filtration equipments before the flue gases reach the chimneys of coal-fired power plants. Depending upon the source of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO$_2$) (both amorphous and crystalline) and calcium oxide (CaO), both being endemic ingredients in many coal-bearing rock strata. It is often used as SCM in concrete production. Owing to its pozzolanic properties, fly ash is used as a replacement for some of the Portland cement content of concrete.

The burning of harder, older anthracite and bituminous coal typically produces Class F fly ash. This fly ash is pozzolanic in nature, and contains less than 20% lime (CaO). Class C fly ash is produced from the burning of younger lignite or subbituminous coal, in addition to having pozzolanic properties, also has some self-cementing properties. In the presence of water, Class C fly ash will harden and gain strength over time. Class C fly ash generally contains more than 20% lime (CaO).

1.2.2 Binary blending of LP

Lime and limestone powder was the oldest material used for construction purpose. It was used as a binding material as well as filler. Lime mortar and concrete was prepared by mixing water with hydrated lime (calcium hydroxide) and aggregate. The setting of lime mortar is caused by loss of water and hardening taking place through the reaction of hydrated lime with atmospheric CO$_2$ to form CaCO$_3$, which is the binding material. Since lime mortar has comparatively low strength properties, lesser durability and retarded setting time, an alternate binding material was sorted for, which was the reason for the emergence of PC.
LP addition to PC causes an increase of hydration at early ages inducing a high early strength, but it can reduce the later strength due to the dilution effect (Ghrici et al 2007). The LP should meet the following three requirements as given by EN 197-1, 2000.

(a) CaCO$_3$ content greater than 75%
(b) clay content, determined with Methylene Blue Test (MBA), less than 1.20g/100g
(c) The Total Organic Carbon (TOC) content shall conform to one of the following criteria:
   • Category I - shall not exceed 0.20% by mass
   • Category II - shall not exceed 0.50% by mass

Portland Limestone Cement (PLC), containing upto 20% limestone, presents satisfactory concrete strength and workability, while the absorption and the chloride permeability seems to be similar to the pure cement concrete (Tsivilis et al 2000). The additional surface area provided by the limestone particles may provide sites for the nucleation and growth of hydration products that leads to further increase in strength (Matschei et al 2007 and Bentz 2006). The increase in the early strength of the mortar due to the addition of limestone and dolomitic limestone can be attributed to their active participation in cement hydration and filler effect of the fine particles of limestone and dolomitic limestone (Voglis et al 2005, Matschei et al 2007). Limestone addition affects the pore structure of the cement paste by increasing linearly the size of capillary pores from 20 nm to 40 nm when the maximum amount (35%) of limestone that is allowed by EN 197-1 is used. On the other hand the threshold diameter decreases exponentially and it is evident that limestone hardened cement pastes have many pores of the same size due to the filling effect that mineral additives have (Pipilikaki et al 2008).
Furthermore Pipilikaki et al (2008) have reported that, limestone decreases the size of gel pores which is related to higher hydration rates. Hence, the use of limestone in cement produces a material that is structurally adequate to be used in construction. It was clearly observed from the visual inspection that the mortar specimens with higher replacement levels of Limestone Filler (LF) suffered more pronounced deterioration in both sulphate solutions, when compared to those without LF (Seung Tae Lee et al 2008). A low proportion (<10%) of LF causes no significant changes in sulphate resistance of parent PC, while a large proportion (>15%) may worsen sulphate performance (Irassar et al 2009). Upto 20% of the cement could potentially be substituted by limestone (or other fillers) to economize on the usage of PC clinker and to reduce the energy and the deleterious emissions associated with its production.

1.2.3 Binary blending of RHA

RHA from the parboiling plants is posing a serious environmental hazard and ways are being thought of to dispose it. This material is actually a pozzolan since it is rich in Silica and has about 85% to 90% silica content. A good way of utilize this material is to use it for making ‘High Performance Concrete (HPC). RHA is a good pozzolans, which increase the durability and strength of concrete with increase in aging.

In the conversion of rice husk to RHA, the combustion process removes the organic matter and leaves the silica rich residue. However, such thermal treatment of the silica in the husk results in structural transformations that influence both the pozzolanic activity of the ash and its grindability. When rice husk is first heated, weight loss occurs up to 100°C due to evaporation of absorbed water. At 350°C, the volatiles ignite, causing further weight loss and the husks commence to burn. From 400°C, to 500°C, the residual carbon oxidizes, and the majority of the weight loss occurs in this
period. The silica is still in an amorphous form. Above 600°C, in some cases the formation of quartz may be detected. As temperature is increased, the conversion to other crystalline forms of silica progresses with the formation of first crystobalite and next at higher temperatures, tridymite. Prolonged heating at temperatures beyond 800°C produces essentially crystalline silica. Uncontrolled combustion of husks as fuel for making clay bricks or for steam generation in parboiling rice plants produces ash, which is not completely amorphous. Due to the crystalline components in the ash, it is referred to as hard burnt ash. In order to obtain ash of acceptable reactivity with lime, it has to be ground for periods as long as seven hours if the ash crystalline ash or, as little as fifteen minutes if the ash is amorphous. The reactivity of the ash is related to its surface area and the amount of amorphous silica.

RHA can be produced with varying pozzolanic activity index depending on the degree of grinding and the burning temperature and upto 40% replacement can be made with no significant change in compressive strength compared with the control mix and effect on volume changes within the limit specified in the American Standard (Moayad et al 1984). However, unlike silica fume, the particles of RHA possess a cellular structure which is responsible for the high surface area of the material even when the particles are not very small in size (Zhang et al 1996). Amorphous silica detected by Scanning Electron Microscopy (SEM) and microanalysis, is concentrated on the interior and exterior surfaces of the uncalcinated husk which may promote a pozzolanic action on the surface of the husk and therefore enable its use in lightweight concrete (Jauberthie et al 2000). RHA is found to be the most effective pozzolan followed by palm oil fuel ash and fly ash. A 95% silica powder could be produced after heat-treating at 700 °C for 6 hours (Della et al 2002).
A linear relationship exists among water absorption, chloride penetration and chloride diffusion by blending cement with RHA (Ganesan et al 2008). The incorporation of the RHA in concrete reduced its porosity and the Ca(OH)$_2$ amount in the interfacial zone (Zhang et al 1996). RHA could be advantageously blended with cement without adversely affecting the strength and permeability properties of concrete (Ganesan et al 2008). Addition of RHA to PC not only improves the early strength of concrete, but also forms Calcium Silicate Hydrate (CSH) gel around the cement particles which is highly dense and less porous and may increase the strength of concrete against cracking (Saraswathy et al 2007).

1.2.4 Ternary and Quaternary Blending

Concrete mix combining two, three or four cementitious materials provides substantial advantages over mixtures containing only Portland or blended cement. Ensuring the proportional use of various SCMs in a manner that positively develops not only strength but also improves the overall durability of the concrete is still a focus for research studies. According to the studies of Isaia (1997), when a less reactive pozzolan is employed in ternary mixtures together with another more reactive mixture such as silica fume or RHA, there is a synergy between these pozzolans, thus the obtained result is higher than those verified in the respective binary mixtures; this result is called synergic effect. Therefore mixing more than one SCM is likely to improve the mechanical and structural properties of the cement matrix.

The pozzolanic effect was stronger in the binary and ternary mixtures prepared with RHA in proportions of 25% or higher (Isaia et al 2003). The amounts of calcium sulphate and ettringite found in the blended cement mortar containing RHA is lesser compared to fly ash (Chindaprasirt et al 2007). Ternary blended pozzolanic material with LP contributes to hydration improving the early age and the long-term compressive and flexural strengths
along with durability which were verified by acid tests and chloride ion penetration tests (Ghrici et al 2007).

The corrosion resistance of ternary blend mortar is higher than that of mortar containing single pozzolan and the use of ternary blend OPC, RHA and fly ash is very effective in reducing chloride induced corrosion of mortar (Chindaprasirt et al 2008). The use of specific mineral like fly ash replacements retards thaumasite formation in limestone cement mortar (Skaropoulou et al 2009). Low-calcium fly ash can be used in the limestone cement matrix to control the volume expansion (Bülent Yılmaz et al 2008).

The quickly cooled RHA resulting from burning rice husk for 12 hours at 500°C has the highest amount of silanol groups and also induced the largest drop in conductivity when added to a saturated calcium hydroxide solution giving an indication of its reactivity towards lime and hence this RHA is the favorable sample to be used as pozzolanic cement additive (Deepa G Nair et al 2008). The use of a blend of equal weight portion of fly ash or RHA and fly ash produces good strength and resistance to chloride penetration. They also require less amount of superplasticizer in comparison to that of normal OPC mortar (Chindaprasirt et al 2008). The significance of the present study therefore rests with characterizing the optimum percentage of quaternary blending of fly ash, RHA, and LP for use as SCMs in concrete based on strength and durability.

1.3 OBJECTIVES OF THE STUDY

Utilization of SCMs for construction shall not only solve waste problems, but also provide a new resource for construction purposes. In this research, use of fly ash, RHA and LP as partial replacement of cement has been tried. The specific objectives of the investigation are as follows
• To study the influence of SCMs on the properties of cement matrix
• To review the existing test methods for evaluating the performance of quaternary blended cement with respect to strength and durability
• To identify the suitable concrete mix in terms of percentage of fly ash, RHA and LP that would satisfy the requirements of the plastic state and that produces the highest strength of concrete in compression, tension and flexure
• To evaluate the mechanical properties and durability of concretes containing SCMs
• To study the microstructure of the concrete mixes and verify the results from strength and durability tests
• To encourage the use of quaternary blended cement in general construction and to realize the potential economic and environmental benefits of this mix

1.4 SIGNIFICANCE OF THE STUDY

Quaternary mixes were developed and evaluated to meet certain strength and durability requirements related to companion control, binary and ternary mixes developed in this investigation. The cement mix systems utilized were obtained from addition of fly ash, RHA, and LP as SCMs to OPC and PPC. Based on the different cement mix systems combining the afore-mentioned SCMs, scores of concrete samples were derived. Mix design variables were taken as the amount of RHA and LP that can be added as replacements to modify two control mixes that were respectively obtained from an ordinary PC and a blended PC. The concrete samples, of various configurations were subjected to a range of test methods to evaluate the feasibility of their performance underscored by the mix system under various strength and durability conditions. The results obtained were ascertained from the micro structural studies of the blended cement matrix. The microstructural characteristics are also evaluated by adapting various surface
analytical studies such as Particle size analysis, X-Ray Diffraction (XRD), SEM/EDAX, Thermo Gravimetric/Differential Thermal Analysis (TG/DTA) and porosity studies.

1.5 SCOPE OF THE STUDY

Basic strength characteristics, such as compressive strength, split tensile strength, flexural strength, density and durability studies of concrete are the main focuses in this research in order to study the influence of blending fly ash, RHA and LP on the quality and performance of concrete. This study also aims at determining the most suitable mix proportion that can produce concrete of desirable strength without compromising on engineering performance and quality. The results of this study will lead to the reduction of the usage of cement, further sustainable development in the concrete industry and reducing harmful impact on the environment.

1.6 ORGANISATION OF THE THESIS

This thesis is divided into five chapters. The introductory chapter contains the background information related to blended cement, the origin, composition, advantages, objective and motivation of this research. Chapter 2 contains the literature review of the research work. Previous research regarding the current topic of research is described. Description of binary, ternary and quaternary blended cement concrete and their properties found in literature are also discussed. Chapter 3 contains the methodology used to carry out the experimental programs, mix proportions, materials and their properties, laboratory tests and the mechanism used to determine the strength and durability. Chapter 4 contains the discussion and analysis of all the results obtained in the experimental program. Chapter 5 contains the conclusion made from the analysis of results and recommendations for future work.