CHAPTER 2

LITERATURE SURVEY

2.1 GENERAL

SCC is a newly accepted construction material because of its versatility, availability of raw materials, strength, and durability. SCC can be designed to withstand the harshest environmental conditions while taking on the most inspirational and imaginable shapes. Researchers are continuously working to develop better SCCs from economic, strength, and durability standpoints with the help of innovative chemical admixtures (e.g., HRWR, VMA) and supplementary cementing materials (SCMs). The use of SCMs conserves energy and has environmental benefits due to a reduction in carbon dioxide emissions, as a result of the reduction in the manufacture of Portland cement. Strict air pollution controls and regulations have driven the development of an abundance of industrial byproducts that can be used as supplementary cementitious materials. Typical examples are fly ash, SF, ground granulated blast furnace slag, MK, RHA, and natural pozzolans that can be used to incorporate into SCC as an addition or as partial cement replacement.

This literature review discusses three dominant themes of the research namely the short background of SCC, RHA and MK blended SCC (Fresh, strength, durability properties of SCC) and ternary system in SCC.
2.2 RICE HUSK ASH

The production of RHA is primarily in areas where rice crops are abundant. Fully burned RHA could be gray, purple or white, depending on the impurities present and the burning conditions. In open field burning or in uncontrolled combustion environments, the ash will remain mostly unreactive because of the unfavorable mineralogical composition. Partially burned RHA contains carbon and is, therefore, black in color. The silica in RHA can be amorphous or crystalline, depending on the manner in which it is burned and cooled. If the ash is formed in the open field burning or in uncontrolled combustion environments, it will retain a large proportion of non-reactive silica in the form of cristobalite and tridymite, and would require grinding to develop pozzolanic activity.

RHA reactivity is attributed to its high content of an amorphous silica, and its very large surface area, governed by the porous structure of the particles. Generally, reactivity is favored also by increasing the fineness of the pozzolanic material. However, Mehta (1992) reported that grinding of RHA to a high degree of fineness should be avoided, since it derives its pozzolanic activity mainly from the internal surface area of the particles. The form of silica obtained after the combustion of rice husk depends on the temperature and duration of the combustion of rice husk. Mehta (1992) also reported that amorphous silica can be produced by maintaining the combustion temperature below 500°C under oxidizing conditions for prolonged periods or up to 680°C with a hold time less than 1 min. The RHA can remain in the amorphous form, at combustion temperatures of up to 900°C if the combustion time is less than 1 h, while crystalline silica is produced in 1,000°C with combustion time greater than 5 min. It is also observed that at burning temperatures up to 700°C, the silica is in amorphous form.
2.2.1 Characteristics of RHA

The characteristics of RHA depend on the geological and geographical factors related to the types of the rice plants, soil types, climatic conditions, burning temperature, duration of burning, grinding methods and collecting devices.

According to the ACI committee recommendations, there are primary factors, which will influence the effective use of agro ashes in concretes. These are: chemical and phase composition of the ashes and alkali-hydroxide concentration of the reacting system, the morphology of the RHA particles, the development of heat during the early phase of the hydration process and the changes in the mixing water requirement when using RHA. For effective utilization, it is necessary to know about the characteristics of RHA and their effects on the properties of the blended SCC.

2.2.2 Physical Properties

The physical properties of agro–ashes like density, color, fineness, mean diameter and shape mainly depend upon the burning of the rice husk and grinding time. Little information could be found in literature on the physical properties of the ashes, but it is apparent that the properties are influenced by the condition of preprocessing.

2.2.2.1 Density

The density of RHA depends on the constituents (iron, silica, aluminium and calcium), and higher carbon content tends to lower the density. The compacted unit mass of RHA ranges from 200 to 600 kg/m$^3$ while the values of concrete incorporating RHA ranges from 2000 to 2300 kg/m$^3$. The specific gravity of RHA varies from 2.02 to 2.08.
2.2.2.2 Color

The color of the RHA may vary from white, light tan to gray and almost black depending on the type and temperature of burning and duration of burning. If the preprocessing occurs between 450°C and 550°C, carbon will remain in the ash, and the ash will be black. As the temperature of processing becomes higher, the ash becomes progressively whiter. However, ash recovered from the interior of large masses of burnt husks where air access is restricted, such as in heap burning, is a lilac pink color.

2.2.2.3 Fineness

The fineness of RHA will have an influence on the pozzolanic reactivity and workability of SCC. The use of RHA increases the water demand due to the fineness of these ashes.

Fineness of this ash is normally measured by BET’s nitrogen absorption method or Blaine’s air permeability method in m²/kg. The RHA has specific surface area (Blaine’s) that varies from 300 m²/kg to 2000 m²/kg. The fineness of RHA increases with increase in grinding time for all burning temperatures. In general, for a given grinding time, there is a considerable reduction in the specific surface area of RHA as the burning temperature increased. The influence of fineness, as determined by the Blaine’s air permeability was studied on the compressive strength of mortars and showed that the compressive strength increases as the fineness increases.

2.2.2.4 Shape and size

The shape and size of ash particles mainly depend upon the mineralogical phases and pyroprocessing. Normally the shape of RHA particles is irregular and cellular texture. The analysis of RHA particles using
SEM showed that the ungrounded RHA particles are in a tubular form split longitudinally with the presence of small bristles distributed over the undulated pores. The well-ground ash particles showed the cellular structures. The RHA has a mean particle diameter varying from 1 µm to 50 µm.

2.2.2.5 Amorphous SiO₂

The reactivity of RHA as a pozzolanic material depends on the crystalline / amorphous ratio. Therefore, for characterization of RHA, the evaluation of the amount of amorphous silica becomes very important. For this purpose, there are some specific methods in the literature concerned. The silica phase in RHA is obviously influenced by the incinerating temperature of rice husk, and it is an important factor in the chemical reactivity of silica in RHA.

2.2.3 Chemical Characteristic

RHA is a fine particulate material with the main chemical constituents being SiO₂, Al₂O₃, Fe₂O₃ and CaO which are responsible for its pozzolanic activity. They also contain MgO, K₂O, Na₂O, SO₃ and unburnt carbon. There is a possibility of variation in the composition from mill to mill, place to place and the type of fertilizer used. The general variation in three principal constituents in RHA will be as follows:

RHA - SiO₂ (80 – 98%), Al₂O₃ (0.10 – 0.6%), Fe₂O₃ (0.15 – 0.60 %)

There are some differences in the standard requirements in the case of SO₃ and loss on ignition. RHA has some minor amount of crystalline constituents like quartz, cristobalite and tridymite and free calcium oxide (up to 10%). In the following sections, the significance of each of the chemical constituents of RHA on the behavior of concrete is discussed.
2.3 METAKAOLIN

MK is a pozzolanic material. It is a dehydroxylated form of the clay mineral kaolinite. It is obtained by calcination of kaolinitic clay at a temperature between 500°C and 800°C. Between 100 and 200°C, clay minerals lose most of their absorbed water. Between 500 and 800°C kaolinite becomes calcined by losing water through dehydroxilation. The raw material input in the manufacture of MK (Al₂Si₂O₇) is kaolin clay. Kaolin is a fine, white, clay mineral that has been traditionally used in the manufacture of porcelain. Kaolinite is the mineralogical term that is applicable to kaolin clays. Kaolinite is defined as a common mineral, hydrated aluminum disilicate, the most common constituent of kaolin.

The dehydroxilation of kaolin to MK is an endothermic process due to the large amount of energy required to remove the chemically bonded hydroxyl ions. Above this temperature range, kaolinite becomes MK, with a two-dimensional order in the crystal structure. In order to produce a pozzolan (supplementary cementing material) nearly complete dehydroxilation must be reached without overheating, i.e., thoroughly roasted but not burnt. It can produce amorphous silica, highly pozzolanic state, whereas overheating can cause sintering, resulting in the formation of burnt, non-reactive refractory, called mullite. MK reacts with Ca(OH)₂, and produces calcium silicate hydrate (C-S-H) gel at ambient temperature. MK also contains alumina that reacts with C-H to produce additional alumina-containing phases, including C₆AH₁₃, C₅ASH₆, and C₃AH₆ (Changling et al 1995).

2.3.1 Physical Properties

MK particles are extremely small with an average particle size of 3 \( \mu \text{m} \) to 12 \( \mu \text{m} \) with very less loss on ignition value (usually in the range of 0.5 to 0.2).
2.3.1.1 Density

The density of MK also depends on the constituents (iron, silica, aluminium and calcium) and lower carbon content tends to higher density. The compacted unit mass of MK ranges from 400 to 600 kg/m$^3$ while the values of concrete incorporating MK range from 2300 to 2600 kg/m$^3$. The specific gravity of MK varies from 2.6 to 2.65.

2.3.1.2 Fineness

The fineness of MK will have an influence on the pozzolanic reactivity and workability of SCC. The use of MK also increases water demand due to the fineness of these ashes.

Fineness of this material is normally measured by Blaine’s air permeability method in m$^2$/kg. The MK has specific surface area (Blaine’s) varying from 12000 cm$^2$/g to 30000 cm$^2$/g.

2.3.1.3 Shape and size

Normally, the shape of MK particles is quasi-amorphous. The MK has a mean particle diameter varying from 1 µm to 12 µm.

2.3.2 Chemical Characteristics

Major constituents of MK are silica oxide (SiO$_2$) and alumina oxide (Al$_2$O$_3$). The other components include ferric oxide, calcium oxide, magnesium oxide, potassium oxide, etc. presented. The typical chemical composition of MK is given in Table 2.1.
Table 2.1 Typical chemical compositions of metakaolin

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Chemical Compositions</th>
<th>Typical Range (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>Lime (CaO)</td>
<td>0-1</td>
</tr>
<tr>
<td>2</td>
<td>Silica (SiO$_2$)</td>
<td>51-54</td>
</tr>
<tr>
<td>3</td>
<td>Aluminum oxide (Al$_2$O$_3$)</td>
<td>42-46</td>
</tr>
<tr>
<td>4</td>
<td>Iron oxide (Fe$_3$O$_4$)</td>
<td>1.20-4.60</td>
</tr>
<tr>
<td>5</td>
<td>Magnesium oxide (MgO)</td>
<td>0.10-0.20</td>
</tr>
<tr>
<td>6</td>
<td>Clay content</td>
<td>Nil</td>
</tr>
<tr>
<td>7</td>
<td>Alkali oxides (K$_2$O and Na$_2$O)</td>
<td>0-1.5</td>
</tr>
<tr>
<td>8</td>
<td>Sulphur (SO$_3$)</td>
<td>0-0.05</td>
</tr>
</tbody>
</table>

2.3.3 Hydration Process

In Portland cement concrete, MK reacts at normal temperatures with calcium hydroxide in cement paste to form mainly calcium silicate hydrates (C-S-H), C$_2$ASH$_8$ (gehlenite hydrate), and C$_4$AH$_{13}$ (tetracalcium aluminate hydrate). The formation of secondary C-S-H by this reaction reduces total porosity and refines the pore structure, improving the strength and impermeability of the cementitious matrix (Ramezanianpour & Bahrami 2012).

The optimum replacement percentage of cement with MK is associated with the changes in the nature and proportion of the different reaction products, temperature and reaction time. The hydration reaction depends upon the level of reactivity of MK in terms of the processing conditions and purity of the feed clay. The feed clay (kaolin) should be either naturally pure or refined by standard mineral processing techniques; otherwise the impurities would act as diluents. From the previous studies, it
clearly noted that the reactivity of the MK is much higher when compared to other pozzolanic materials like SF, fly ash, RHA etc. And it is considered as highly reactive pozzolanic materials.

2.4 BACKGROUND OF SCC

SCC is a type of concrete that was developed in the 1980s in Japan, as concrete technologies became widespread across the world. In particular, developments in superplasticizer technology have contributed substantially to the formation and advancement of SCC (Melo & Carneiro 2010).

One of the most critical differences between SCC and conventional concrete is the incorporation of a SCM's material in the form of a filler or cement replacement. Because cement is the most expensive component of concrete, reducing cement content could be an economical solution. In addition, the spaces between aggregates are filled and an impermeable concrete can be produced. Industrial by-products or waste materials, generally, fly ash, GGBFS, RHA, MK, and limestone powder, are used as SCMs in SCC (Felekoglu et al 2007). Thereby, the workability of SCC is modified and the amount of by-products or waste materials that is used can be increased concurrently.

In comparison with plain concrete, SCC can fully self-compact under its own weight (Nanthagopalan & Santhanam 2009). Also it has high flowability and filling rates, reduced blocking in congested reinforced areas, and high segregation resistance, as well as high durability, low permeability, and high compressive strength (Wu et al 2009).
2.5 RHA AND MK BLEND ED SCC

2.5.1 Fresh state property

The fresh state property of SCC is related to the flowability of its binder paste components because fresh concrete consists of an aggregate skeleton and a paste matrix. Therefore, numerous researchers studied the flowing behavior of binder paste to facilitate the design process of SCC (EFNARC 2002; Ravindrarajah et al 2003). The beneficial qualities of HRWR and SCMs can produce the desired flowing ability of binder paste. Using HRWR is essential to achieving an excellent flowing ability in binder paste. HRWR improves the flowing ability of binder paste and, thus, that of SCC by reducing the yield stress and plastic viscosity (Yen et al 1999). However, an excessive dosage of HRWR results in extremely high fluidity, which might cause segregation problems in the form of bleeding. Suitable SCM could be used to improve the segregation resistance along with the beneficial flowing ability in the binder paste, and, thus, in SCC. Numerous renowned SCMs, such as silica fume, fly ash, RHA, MK, and GGBFS have been used in binder paste (Okamura & Ozawa 1995). In comparison, the use of RHA and MK is limited.

The multi-dispersed, micro-porous surface and the irregularly shaped particles of the RHA caused elevated levels of water demand for concrete mixtures containing RHA, which decreased its compressive strength (Rawaid et al 2012). To achieve greater workability and strength, SP should be added to the concrete mixtures that are incorporated in RHA. Eva et al (2011) have studied the properties of SCC that had been mixed with MK (SCC-M). They reported that SCC-M required the addition of larger amounts of water and SP, compared to SCC with slag (SCC-S), to achieve the parameters that were required for the SCC mixtures. Moreover, SCC-M was losing its fluidity relatively quickly over time because of the wider surface
area that the binder shared with MK, thus, displaying higher levels of reactivity.

2.5.2 Strength

The strengths that were developed using the mixes of SCC and RHA were comparable to the control concrete (Shazim et al. 2011). The elevated content of amorphous silica (SiO\(_2\)) in the RHA that displayed substantial reactivity, led to a remarkable increase in the compressive strength of SCC. The compressive and flexural strengths of RHA concrete are comparable to an SF concrete that is produced using the same replacement level, and these strengths are higher than those of the control mixtures (Salas et al. 2009). Rawaid et al. (2012) also stated in their study that the rate in strength gain in the early stages is lower in RHA concrete than in OPC concrete.

RHA has been used as a highly reactive pozzolanic material to improve the microstructure of the interfacial transition zone (ITZ) between the cement paste and the aggregate in SCC. Mechanical experiments on RHA-blended SCC revealed that, in addition to the pozzolanic reactivity of RHA (the chemical aspect), the particle grading (the physical aspect) of cement and RHA mixtures also exerted substantial influence on the blending efficiency. High amounts (up to 30%) of RHA could be blended using cement without adversely affecting the strength and permeability of concrete (Chatveera & Lertwattananuk 2009). The effects of RHA on the physical properties of concrete are linked to its average particle size. Fine particles operate as a refinement on the pore structure, act as a nucleation point for hydration products, and restrict the development of the unfavorable crystals that the hydration process generates (Rodriguez 2006). In addition, the increment in the strength of concrete that is related to physical effects can be justified by the effect of fine particles of RHA in the concrete matrix (Rodriguez 2006).
Increments of MK are proportional to the demand for HRWR in SCC mixtures. The compressive strength of SCC containing MK increased as MK content increased from 0% to 25% (as a partial replacement of cement). Conversely, the optimum percentage of SF’s compressive strength was 8%, and was similar to that of MK’s 8% (both increased the strength of the control mixture by approximately 14%). However, raising the amount of MK from 8% to 25% only enhanced the compressive strength by 7% (Assem et al 2012). Extensive research is reported in the literature on the different properties of MK paste and concrete, such as porosity, pore size distribution, pozzolanic reaction, strength properties of MK concrete (Sabir et al 2001). Brooks & Johari (2001) reported that strength increased in proportion to the MK content. Li & Ding (2003) reported similar results, where concrete achieved the highest strength with 10% MK content.

2.5.3 Durability

Combining RHA with concrete enhances the durability of concrete by retaining its pore structure. The results that were discussed above are similar to those of SF concrete. Producing high performance concrete or SCC using RHA as an SCM is possible (Salas et al 2009). Chindaprasirt & Rukzon (2008) studied the resistance to chloride penetration of blended Portland cement mortar containing palm oil fuel ash (POA), RHA, and fly ash (FA). They found that RHA could be the most effective pozzolan when compare to POA and FA cement. RHA exhibits the formation of a cellular microstructure and an elevated level of pozzolanic activity when rice husks are burnt at temperatures that are lower than 700°C (Ganesan et al 2007). It contains up to 95% of silica content in the form of non-crystalline or amorphous silica. The reactivity of amorphous silica is directly proportional to the specific surface area of ash. The chemical reaction of amorphous silica with Ca2+, OH− ions, and calcium hydroxide during the cement hydration
forms greater quantities of calcium silicate hydrate gel (C-S-H), which is known to contribute to the improvement of the durability properties of concrete (Feng et al 2004).

MK inclusion decreased the absorption and durability related properties of SCC. However, it was more significant at a lower w/b ratio. All the MK mixes showed a low level of absorption (below 3% at 30 min), indicating that the concrete was of “suitable” quality. Including MK also increased the resistivity of SCC by a maximum of 24%, 26%, and 20% for w/b ratios of 0.32, 0.38, and 0.45, respectively (Rahmat & Yasin 2012). The water transport parameters of SCC with MK were much lower than for SCC with slag, as manifested by the measured values of water absorption coefficient and water penetration depth (Eva et al 2011). A sorptivity test also revealed that the addition of 10% of MK produces optimal result when compared to other replacement levels, irrespective of the w/b ratio and testing age. The results of salt ponding and RCPT tests demonstrated that using MK significantly enhanced the resistance to chloride penetration, compared with the OPC concrete. This improvement was augmented as MK content increased. An exponential relationship between chloride permeability and the compressive strength of concrete was exhibited, which indicates that the resistance to chloride penetration of concrete increases with increasing compressive strength. A SEM analysis of cement pastes revealed that the microstructure of the MK cement paste is more uniform and compact than that of the ordinary Portland cement paste (Ramezanianpour & Bahrami 2012).

Erhan et al (2012) have studied the corrosion behavior of concrete using accelerated corrosion tests of concrete containing MK. The principal findings were the following: failure times in chloride-contaminated concrete were shortened as the chloride concentration increased. The shortest failure
time was observed in the control concrete, which contained 3.03% chloride (5 h). However, the most extended period was observed in 15% MK-blended concrete (132 h). They observed that considerable differences existed between the failure values (time) of the plain and MK concrete. This situation implies that MK can be used effectively to enhance the corrosion resistance of concrete (Erhan et al 2012). The minimum current density values of corrosion were measured in 15% MK concrete, irrespective of the chloride contamination level. However, the 5% MK concrete’s corrosion values trended closer to those of the 15% MK concrete. The corrosion rates of the concrete seemed to match the aforementioned findings. The highest corrosion rate was measured as 0.0058 mm/yr in the control concrete by applying 3.03% chloride contamination. However, the use of MK caused the corrosion rate to reduce by approximately 50% (Erhan et al 2012). The mentioned study demonstrated that up to 15% replacement of MK in OPC concrete revealed itself as having properties that are useful for corrosion resistance, water absorption, and resistivity of SCC.

2.5.4 Ternary system

The fresh state properties of SCC are improved considerably in the ternary system by using the mineral admixtures. A total of 28- and 90-day compressive strength developments of the binary and ternary mixtures demonstrated a similar tendency. However, due to the relatively slow hydration reaction characteristics of FA, 28-day compressive strengths of ternary mixes were lower, compared to those of the binary mixtures. Adding limestone filler (LF) provided greater compressive strength for both series of mixtures. Accordingly (Mehmet et al 2012), it can be inferred that LF affects the hydration kinetics of the cement paste, as well as filling ability. All of the binary mixes were determined to have low resistance against chloride penetration, whereas the ternary mixtures displayed extremely low chloride
ion penetration characteristics. The addition of fillers generally improved the chloride penetration resistance of the concrete.

Other research studies lead to conclude that the compressive strength of the concrete in which FA content increased reduced markedly, whereas the concrete that included GGBFS had comparable strength values to that of the control concrete. Conversely, SF and MK concrete had consistently higher compressive strength than the control concrete. The negative effect of FA on the compressive strength was relatively diminished using mineral admixtures in a ternary system (Erhan et al 2010). Through cement conservation, enhanced durability, and environmental protection, such ternary blends contributed to sustainable development (Bhanumathidas & Mehta 2004).

From the literature survey carried out on the RHA or MK or RHA+MK blended SCC, the following observations can be made:

1. Use of RHA in SCC as supplementary cementing material provides economic, energy saving, ecological benefit and improvement in the properties of materials.

2. In many of the studies carried out on the utilization of RHA in SCC, the rice husks were ignited under controlled temperature. The incinerating temperature was in the range of 500°C to 700°C. The duration of incineration was between 1 hour and 2 hour and ground for 1 hour.

3. The amount of water required for standard consistency of cement RHA mortar is always higher than that required to balance against the ash reactivity and to produce a more workable concrete.
4. The size, shape and gradation of the aggregates (Fine and Coarse) greatly influence the fresh state properties of the SCC. Similarly, the type and dosage of the SP also much influenced the fresh and hardened properties of the SCC.

5. There are no standard mix design procedure and testing methods for SCC available like for conventional concrete. Presently, to develop the mix design for SCC and testing of fresh properties, EFNARC 2005 guidelines and previous studies are followed with some modifications.

6. Due to the multi-dispersed with micro porous surface and irregular shaped particles of the RHA, water demand was high for concrete mixtures containing RHA.

7. The main reason of the improvements in mechanical and durability properties of RHA blended concrete, possibly may be attributed to the formation of C-S-H gel and less portlandite.

8. RHA concrete had higher compressive strength at the age up to 180 days than the control concrete. The flexural and splitting tensile strength, modulus of elasticity, drying shrinkage of control concrete and concrete incorporating RHA are comparable.

9. The RHA concrete showed excellent resistance to chloride ion penetration and the charge passed in coulombs was below 1000 both at 28 days and 91 days which were below the control concrete.

10. Partial replacement of cement with MK decreases the slump flow values of the SCC mixtures and increases the water demand like RHA blended SCC.
11. SCC with MK can be produced with proper stability without using a viscosity modifying agent and the presence of MK improved both the early ages and the long-term compressive strength of SCC.

12. MK fineness are a very important factor to optimize the SCC production in terms of w/cm and superplasticizer content.

13. MK blended SCC, significantly improves the compressive strength, tensile strength, water absorption, chloride permeability and corrosion. But the resistance to acid attack is higher for MK cement mixes as compared to the control ones.

14. The combination of RHA and BA allowed to reach a high level of cement replacement without the need for the addition of large amounts of superplasticizer due to the positive effect of particle fineness in the rheological property.

15. The negative effect of FA on the compressive strength was relatively diminished with the ternary and the quaternary use of MK and SF.

16. The use of RHA in ternary blends offers a good solution to enhance the early-age engineering properties of concrete with a high volume of fly ash blended cements. Through cement conservation, enhancement of durability and environmental protection, such ternary blends obviously contributed to sustainable development.

17. The combination of SF and RHA can increase the total cement replacement percentage up to 40% and produce UHPC. There is a synergy effect between SF and RHA on the compressive strength.
2.6 NEED FOR RHA AND MK BLENDED SCC

Thus, very limited information is available on the acid attack, chloride permeability, and corrosion characteristics of SCC containing RHA and MK, especially in their combination. In general, there is a need to specifically study the performance of RHA and MK as reactive pozzolana for strength, chloride permeability, acid attack, and corrosion potential properties in the blended SCC.

It is felt that a more comprehensive and systematic evaluation of RHA blended SCC, MK blended SCC, and RHA+MK blended SCC as cement replacing materials carried out in this report will lead to its widespread application in chemical behavior and corrosion-prone reinforced SCC structures. In addition to reducing demand for Portland cement, reducing its cost and developing self-compatibility and technical benefits are the advantages of using RHA and MK in SCC.