

**COMPARATIVE STUDY ON EFFECT OF PARTICLE SIZE
AND SILICA CONTENT OF RICE HUSK ASH ON
PROPERTIES OF SELF-COMPACTING MORTAR SYSTEMS**



By

MUHAMMAD ALI JANJUA

(2014-NUST-MS-Str-16)

This thesis is submitted in partial fulfilment of
the requirements for the degree of

Master of Science

in

Structural Engineering

National Institute of Civil Engineering (NICE)

School of Civil & Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

Islamabad, Pakistan

2017

This is to certify that Thesis entitled

**COMPARTIVE STUDY ON EFFECT OF PARTICLE SIZE AND
SILICA CONTENT OF RICE HUSK ASH ON PROPERTIES OF
SELF-COMPACTING MORTAR SYSTEMS**

Submitted by

MUHAMMAD ALI JANJUA

Has been accepted towards the partial fulfillment of

the requirements for award of degree of

Master of Science in Structural Engineering

Thesis Supervisor

(Prof. Dr. Ing. Syed Ali Rizwan, PhD) NUST Institute of Civil
Engineering (NICE)

School of Civil and Environmental Engineering (SCEE) National University of
Sciences and Technology (NUST)

Islamabad Pakistan

ACKNOWLEDGEMENTS

All praise to Almighty Allah who gave the courage and power to the author for completing this research work.

I am heartily thankful to my supervisor Prof. Dr. Ing. Syed Ali Rizwan, HoD Structural engineering department, NUST Institute of Civil Engineering (NICE), for giving me time and support from initial stages till the completion of this work.

I appreciate the support provided to me by my parents and by my family as this research work would not have been completed without their prayers and whole hearted encouragement and support.

I must not forget the supporting role of my friends and especially Engr. Siraj ud din, Engr. Hasnian Khan, Engr. Haseeb Taj and Engr. Sufian Ahmed, Capt. Noor Khan student of Ms. Structural engineering at NICE, NUST and laboratory staff at NICE Engr. Fawad and Mr. Ismail, for providing the technical assistance and cooperation during the reported research work.

Special thanks to DAAD for providing F-Cal 8000 Field Calorimeter and Modified Schwindriner Shrinkage Apparatus to NICE/NUST under an International Research Project, for funding the author's trip to Germany for research and for providing materials.

ABSTRACT

This research work reports the manufacturing procedure of local Rice Husk Ash (RHA), its use in Self-Compacting Mortar (SCM) systems and the comparison of locally made RHA with another source to study the effect of particle size and silica content of RHA on the properties of SCM systems. Local RHA was used in SCM systems in two states i-e as made (without milling, D_{50} = 84 microns, SiO_2 = 88.5%) and reduced particle size (milled RHA, D_{50} =21 microns, SiO_2 = 88.5%) while RHA for comparison was brought in from Germany courtesy Technical University Freiberg (RHAG, D_{50} =81 microns, SiO_2 = 94.5%). All three RHAs were found to be amorphous and have been used in SCM systems to study the effect of particle size and SiO_2 content of RHA on fresh and hardened properties of SCM systems. Four partial replacement levels 0, 10, 15, 20% with respect to cement weight and two w/b ratio 0.4 and 0.5 were used.

Addition of RHAP-21 and RHAG-81 in SCMs showed increased strength at 28 days of age, better early age volumetric stability and delayed hydration kinetics as compared to control mix with larger particle size showing better volumetric stability delayed hydration peaks. RHAP-84 however showed lower strength values compared to control mix and RHAP-21 as well as RHAG-81 however showed better volumetric stability than its counterparts. For RHAP-21 and RHAG-81, 15% cement replacement showed best strength results of SCMs while for RHAP-84 it was observed that increasing the amount of ash in SCM systems decreased the strength. It appears that larger particle size make the systems more viscous, increases flow times and SP demand to overcome internal friction and entrains more air compared to finer particle size with same w/b ratio and RHA content.

SiO_2 reactivity has been determined in terms of electrical conductivity drop and XRD on hardened paste samples. RHAP-21 and RHAG-81 gave almost same strength level, though other properties are quite different, confirming indirectly the lower particle size with lower SiO_2 may be considered equivalent in performance to bigger particle size and higher SiO_2 of RHA in self-compacting systems and makes the role of SiO_2 prominent in the absence of fine size of particles. This study confirms that the role of SiO_2 in strength gain is

more important than the particle. RHAP-84 and RHAG-81 have comparable particle sizes but different silica content and the performance of RHAG-81 is comparable to control mix in terms of strength gain which confirms the role of silica content. Locally made RHA had to be milled in order for it to be made usable in SCM systems as the performance of local RHA when used without any processing is poor. It was also observed that RHAG-81 was useable without any post processing

Contents

List of Tables	6
List of Figures	7
List of Notations	8
CHAPTER 1: INTRODUCTION.....	9
1.1 General	9
1.2 Self-Consolidating Concrete (SCC).....	10
1.3 Secondary raw materials (SRMs).....	10
1.4 Rice Husk Ash (RHA)	11
1.5 Objectives of the study.....	12
CHAPTER 2: LITERATURE REVIEW	13
2.1 General	13
2.2 Self-Compacting Concrete	13
2.2.1 Background	13
2.2.2 Effect of w/c and SP.....	13
2.2.3 Environmental effect.....	15
2.2.4 Advantages.....	15
2.3 SRMs.....	16
2.3.1 Physical packing effect.....	16
2.3.2 Pozzolanic chemical effect.....	17
2.3.3 Need of SRMs in SCC	17
2.3.4 Advantages	18
2.4 RHA	18
2.4.1 Composition and nature of RHA.....	19
2.4.2 Burning Regime/Combustion of RHA.....	20
2.4.3 Effect of surface area of RHA.....	21
2.4.4 Reactivity of RHA.....	21
2.4.5 Unburnt Carbon in RHA	22
2.4.6 Particle size of RHA.....	22
2.4.7 Production of RHA in Pakistan.....	23
CHAPTER 3: MATERIALS AND METHODOLOGY	24
3.1 General	24

3.2 Materials.....	24
3.2.1 Cement	24
3.2.2 Fine Aggregate	24
3.2.3 Super Plasticizer.....	25
3.3 Water	26
3.4 Rice Husk Ash.....	26
3.4.1 Rice Husk Ash Pakistan-RHAP-21 and RHAP-84	26
3.4.2 Burning Regime	27
3.4.3 Rice Husk Ash Germany	27
3.5 Mixing Regime.....	29
3.6 Sample preparation and curing.....	30
3.7 Strength testing.....	30
3.8 Storage of materials.....	31
3.9 Formulations Studied	32
CHAPTER 5: EXPERIMENTAL RESULTS	33
5.1 General	33
5.2 Characterization Results.....	33
5.2.1 Amorphous States of RHAs	33
5.2.2 Physical and Chemical properties of powders	34
5.3 Water Demand.....	35
5.4 Setting Times.....	37
5.5 Air Content.....	37
5.6 Super Plasticizer Demand of SCM Formulations for Target Flow	39
5.7 Flow Values.....	39
5.8 Strength Data.....	41
5.9 Viscosity Measurements of SCP Formulations.....	41
5.10 Calorimetry of SCM Formulations	43
5.11 Shrinkage Measurements of SCM Formulations	45
5.12 Electrical Conductivity of Saturated Ca(OH) ₂ Solution with RHAs	48
5.13 XRD for drop in Ca(OH) ₂ Content.....	48
5.14 Electrical Conductivity of Hardened SCM Formulations containing RHA.....	49
5.15 Thermal Conductivity of Hardened SCM Samples containing RHA	50

CHAPTER 6: DISCUSSION.....	51
6.1 General	51
6.2 Characterization	51
6.3 Water Demand.....	51
6.4 Setting Times.....	52
6.5 Air Content	52
6.7 Super Plasticizer Demand of SCM Formulations for target Flow	53
6.8 Flow Values.....	53
6.9 Strength Test	53
6.10 Viscosity Measurements of SCP Formulations.....	54
6.11 Calorimetry of SCM Formulations	54
6.12 Shrinkage of SCM Formulations.....	54
6.13 Electrical Conductivity Drop of Saturated Ca(OH) ₂ Solution Containing RHAs	55
6.14 XRD for drop in Ca(OH) ₂ Content.....	55
6.15 Electrical Conductivity of Hardened SCM Formulations containing RHA.....	55
6.16 Thermal Conductivity of Hardened SCM Samples containing RHA	56
CHAPTER 7: CONCLUSION	57
References.....	58

List of Tables

Table 1: Physical properties of rice husk.....	12
Table 2: Silica content in plants	20
Table 3: Properties of Melflux 2651 F.....	26
Table 4: Burning Regime of RHA.....	27
Table 5: Mixing Regime.....	29
Table 6: Mix Design of SCM formulations.....	32
Table 7: Physical and Chemical Properties of powders.....	35
Table 8: Strength data of SCM formulations.....	41
Table 9: Variation in electrical conductivity of saturated Ca(OH) ₂ Solution.....	48
Table 10: Absolute intensities corresponding to 2theta angle of 18.035°.....	49
Table 11: Electrical Conductivity of Hardened SCM Samples Containing RHA.....	49
Table 12: Thermal Conductivity of Hardened SCM Samples Containing RHA.....	49

List of Figures

Figure 1: Effect of SP and SRMs on development of dense microstructure	14
Figure 2: SEM image of RHA Particle	19
Figure 3: SEM of CEM 1 cement particle (MS thesis Maj. Aftab, NUST).....	24
Figure 4: Oven used for drying fine aggregate	25
Figure 5: Melflux 2651 F	26
Figure 6: RHAG-81 (Left) and RHAP-21 (Right) powders	28
Figure 7: RHAP-84	28
Figure 8: Hobart Mixer	29
Figure 9: Curing Tank.....	30
Figure 10: Controls 5000 KN-Compression Machine	31
Figure 11: XRD patterns of RHAP-21 sample	33
Figure 12: XRD patterns of RHAG-81 sample.....	34
Figure 13: XRD patterns of RHAP-84 sample	34
Figure 14: Water Demand of Paste systems containing RHAP-21, RHAP-84 and RHAG-81.....	36
Figure 15: Vicat apparatus used for calculating water demands of paste systems	36
Figure 16: Setting times of paste formulations containing RHAP-21, RHAP-84 and RHAG-81	37
Figure 17: Air content of SCM formulations containing RHAP and RHAG	38
Figure 18: Luftporengehalt apparatus used to calculate air content of SCM formulations containing RHAP and RHAG	38
Figure 19: SP Dosage of w/b ratio 0.4 for SCM formulations	39
Figure 20: SP Dosage of w/b ratio 0.5 for SCM formulations	39
Figure 21: Flow times of SCM formulations.....	40
Figure 22: Haggerman's cone for measure the spread of SCM formulations	40
Figure 23: Apparent viscosity of SCP systems containing RHAP-21	42
Figure 24: Apparent viscosity of SCP systems containing RHAG-81	42
Figure 25: Apparent viscosity of SCP systems containing RHAP-84.....	43
Figure 26: Calorimetry response of SCM systems containing RHAP-0.4 w/b	43
Figure 27: Calorimetry response of SCM systems containing RHAG-0.4 w/b.....	44
Figure 28: Calorimetry response of SCM systems containing RHAP-0.5 w/b	44
Figure 29: Calorimetry response of SCM systems containing RHAG-0.5 w/b.....	45

List of Notations

SCC	Self-Compacting Concrete
SCM	Self-Compacting Mortars
SRMs	Secondary Raw Materials
RHA	Rice Husk Ash
SF	Silica Fume
FA	Fly Ash
LSP	Lime Stone Powder
MSP	Marble Stone Powder
VEAs	Viscosity Enhancing Agents
HRWR	High Range Water Reducers
AEAs	Air Entraining Agents
GGBFS	Ground Granulated Blast Furnace Slag
ITZ	Interfacial Transition Zone
CSH	Calcium Silicate Hydrate
ASR	Alkali-Silica Reaction
MPS	Mean Particle Size
PCSIR	Pakistan Council of Scientific and Industrial Research

CHAPTER 1: INTRODUCTION

1.1 General

Construction has evolved and so have the materials used in construction. Man has used heat treated lime and limestone as pre-historic materials for binding. It wasn't till 1824, the advent of portland cement, that true evolution in construction started. Construction marvels before the advent of Portland cement did exist however Portland cement couple with super plasticizers took the industry to a whole new level. Self-compacting concrete (SCC) is the result of such advancements in concrete technology and in the modern era SCC is on its way to replace the conventional concrete. The recipe of this modern concrete is made up of many elements as opposed to few ingredients in old days. Today secondary raw materials (SRMs) such as rice husk ash (RHA), silica fume (SF), fly ash (FA), limestone powder (LSP), marble stone powder (MSP) etc along with various chemical admixtures such as viscosity enhancing agents (VEAs), super plasticizers (SP), high-range water reducers (HRWR), air entraining agents (AEAs) etc are regular ingredients of modern concrete. Chemical admixture play a vital role in achieving smooth flow, good viscosity and optimum porosity while mineral admixture add to the strength and durability to concrete [1].

In other countries various SRMs are used for making SCC. In Pakistan however, not all materials are easily available for use in SCC. Most of these mineral admixtures are by products of various industries and since Pakistan lags in industrial advancement as compared to the first world countries and absence of technologies like fluidized bed combustion, it is hard to produce controlled by-product. The result of this is in manifestation of non-availability of variety of SRMs and low quality product.

RHA holds more potential for use in an agricultural country than any other SRM due to easy availability of raw materials. Pakistan is an agricultural country and is ranked 11th in the world with production of 6 million tons of rice every. The husk from this rice is not being used for any technical application rather is serving trivial non- technical purposes. This husk has a lot of potential if put to proper use. At present the husk is mostly used in collection of chicken litter in poultry farm or for small scale uncontrolled burning but if burnt under a very

specific pyro-processing regime the husk makes it way to produce ash which is inert in itself but reacts in the presence of certain elements and moisture to precipitate hydration products. Being an agricultural country Pakistan can put to use this ash in making SCC. This research uses this husk and through a specific pyro-processing regime converts the husk into ash which is then used as a partial replacement for cement in self-consolidating mortar systems (SCMs). 100 kg of rice husk produces 20 kg of rice husk ash (RHA) i-e 1/5th of quantity of husk[2], for this study after burning 100 kg of husk a total of 18.7 kg of ash was obtained which is comparable.

1.2 Self-Consolidating Concrete (SCC)

ACI committee 237 in there publication “237R-07 Self Consolidating Concrete” define self-consolidating concrete (SCC) as

“Highly flow-able, non-segregating concrete that can flow into place, fill the formwork and encapsulate the reinforcement without any mechanical consolidation”

“Flows and consolidated under its own weight and without vibration, passes between reinforcement and spaces to completely fill the formwork while simultaneously avoiding segregation and maintaining its stable composition” [3, 4]

SCC has proven itself across the world as a very useful technology in numerous projects and especially in concrete placement where conventional concrete is rather hard to place or where it offers hindrance for the labor to reach for placement or vibration and even where vibration is uneconomical. Application includes tunnels, long span modern bridges, pre-stressed member and columns of high rise buildings etc. For proper application of SCC it is imperative that the mix should be balanced in terms of flow and ability to resist segregation. Other special uses may require pumping long distances which should be addressed in the mix design. Further discussion on SCC will be done in chapter 2 of this report.

1.3 Secondary raw materials (SRMs)

Secondary Raw Materials (SRM) are mineral admixtures which are have little or no reactive cementitious value but when in very finely grinded form and in presence of moisture

they react with calcium hydroxide precipitated from cement hydration to yield hydration products which are similar to that of cement [5]. They not only advance the hydration of cement but also improve the hydration products. SRMs are used in high performance concrete (HPC)/ high strength concrete (HSC) to decrease the use of cement content and improved microstructure and to reduce the effective water content resulting in denser microstructure. With a view to make environmental friendly concrete, SRMs are used as partial replacements of cement which not only is the most expensive constituent of concrete but also, the ingredient of concrete which is the most non-friendly towards the environment. Cement production accounts for 5% of total CO₂ emission and its production is expected to increase to 3.7-4.4 billion tons by 2050. Calcination in the production of cement accounts for major portion of CO₂ emission. SRMs are usually by products of different industries hence are relatively economical than cement and seldom require any further pyro-processing once retrieved from industry. Some of the SRMs include silica fume (SF), fly ash (FA), lime stone powder (LSP), marble powder (MP), rice husk ash (RHA) and ground granulated blast furnace slag (GGBFS). For this study, as enunciated above, RHA from different sources has been incorporated as partial replacement of cement. RHA as well as other SRMs are known to impart desirable properties to concrete in both fresh and hardened state.

1.4 Rice Husk Ash (RHA)

Pakistan being an agricultural country produces rice in abundance. Basmati rice is being acknowledged as quality rice throughout the world and is liked for its taste and aroma. Punjab province has major share in production of rice especially district Sheikhpura, Faisalabad, Multan and Vehari. One ton of rice yields almost 200 kg of husk and 40 kg of RHA [6]. The potential for rice husk to be converted into a value added commodity is immense. Amorphous rice husk ash (RHA) is used in this project which is a highly pozzolanic material and imparts higher strength derived mainly from its physical packing effect and chemical pozzolanic effect.

Parameter	Nature/Value
Color	Golden
Length	4.5 mm (average)
Hardness	6 Mohr's Scale
Bulk Density	96-100 kg/m ³
Thermal Conductivity	3.3 K Cal-cm/°C
Angle of Repose	35° (ungrounded)
Fuel Value	2800-3700 K-Cal/kg

Table 1: Physical Properties of Rice Husk [7]

1.5 Objectives of the study

The study aims at achieving the following objectives:

- To find the best burning regime reported by researchers and apply it to local rice husk to produce pozzolanic active amorphous RHA.
- Characterization of both RHA from both the sources to see the nature of RHA produced.
- Study the effect of particle size and SiO₂ content on self-compacting mortar systems (SCMs)
- To study the effects of RHA from different sources on fresh and hardened properties of self-compacting mortar systems

CHAPTER 2: LITERATURE REVIEW

2.1 General

The literature review will cover different aspects of the research that have been studied in detail. SCC, SRMs and RHA and the action of SP will be discussed in detail.

2.2 Self-Compacting Concrete

2.2.1 Background

The concept of self-consolidating concrete was given by Prof. Okamura at Ouchi University, Japan. This SCC, which is now termed as first generation of SCC, was mostly restricted to special applications and it was characterized mostly by use of higher quantities of cementitious material coupled with high dosage of superplasticizers. This added to the total cost of the system and it was due to this relatively higher cost that the use was limited and widespread commercialization of SCC was not possible. The modern recipe for such systems however comprise of many ingredients which include cement, sand, coarse aggregate, SRMs, water, super plasticizer, viscosity enhancing agents (VEAs), air entraining agents (AEAs) and high range water reducers (HRWR) etc. It was due to the advent of SP that the strengths of concrete reached where they stand today as they allow the use of low w/b ratios. Super plasticizer also imparted the flowing ability of the concrete or mortar systems mostly due to particle to particle repulsion. Prior to the advent of SP in the early 1980s the concrete strength were mostly to 25 MPa in 1940s to 34 MPa in 1950s [7]. It was due to the advent of superplasticizers in Germany and Japan that engineers were able to make use of high strength concrete.

2.2.2 Effect of w/c and SP

The high strength is mostly contributed to lower water to cement ration (w/c) and denser micro-structure which is reflected as total porosity of the system. The porosity can be controlled by use of fines such as cement but this increases the cost of the system therefore, SRMs are integrated into the systems for enhanced micro-structure, lower porosity and better hydration products which in term reflect a higher strength concrete. However, with lower w/c comes the problem of poor workability as the mix is dry and cannot be properly placed.

Extensive external work would be needed in such cases but the use of SP tackles this problem and gives the SCC a nice smooth flow. SP dosage have to be found specific to the mix. For SCC systems, workability is not a problem due to use of SP however the use of fines such as SRMs at times increases the SP dosage and the water demand of the SCC system. If the dosage is too high for a mix it effects on hydration is detrimental and the setting times are delayed, very high dosage could even result in no setting of the mix. The recommended dosage usually is about 1-1.5% of the cementitious material used in the mix.

There is no specific formula to find the optimum mix. Trial and error method with multiple attempts often leads to finalizing the quantities of different ingredients in the SCC mix. One reason for this is the effect of different ingredients on each other. For example when SRMs are added into the mix, as enunciated above, they tend to increase the SP dosage but they also impart better viscous behavior into the mix. Addition of super plasticizers on the other hand tends to make the flowability of the SCC good due to better dispersion of binder particles and prevention of deflocculation in fresh state of concrete but simultaneously SP is known to delay the hydration kinetic slightly. Following table give an overview.

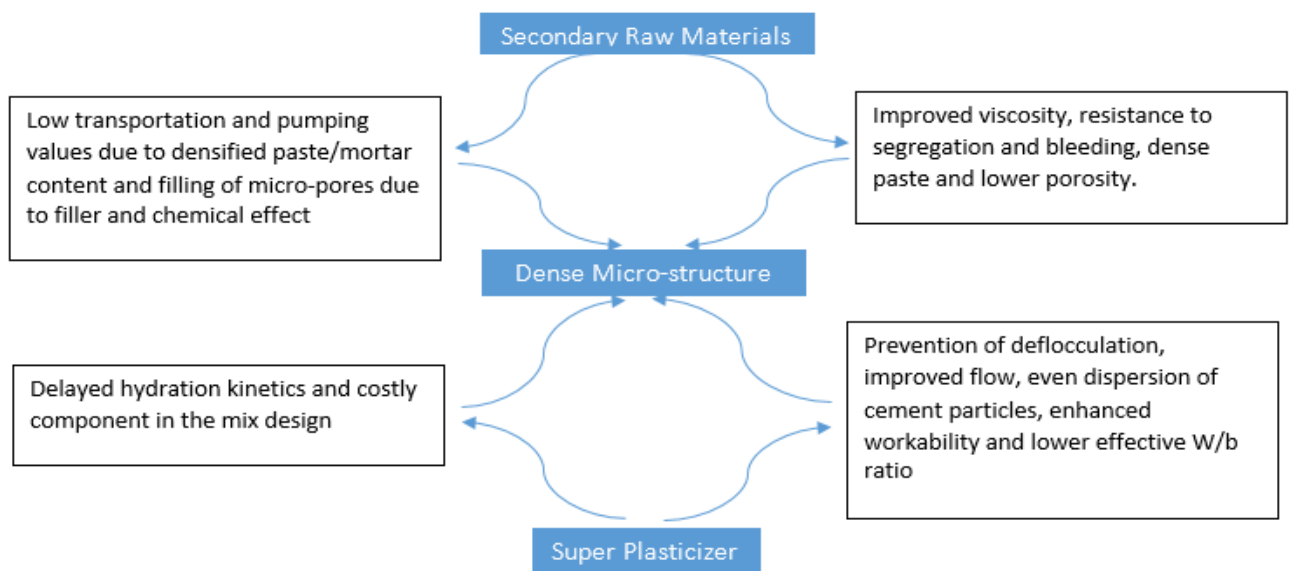


Figure 1: Effect of SP and SRMs on development of dense microstructure

2.2.3 Environmental effect

The manufacturing process of cement is energy intensive and non-friendly to the environment. One ton of cement requires 4 GJ of energy/tons and usually produces around 1-1.3 tons of CO₂ gas which is a greenhouse gas and is adding to the greenhouse effect, the cause of global warming and climate change. Technological advances have allowed countries to expand at an exponential rate. In the whole 20th century, United States of America (USA) used 4.5 gigatons of cement and constructed its majority skyscrapers and other infrastructure. China, on the other hand has managed to use 6.6 gigatons of cement in just three years (2011-2013) [8]. Other countries such as Russia, Brazil, Mexico and even Pakistan is manufacturing cement in abundance for both local use and for export. This mass scale manufacturing of cement is at the detriment of the environment and use of SCC is one very effective way to make the concrete environmental friendly. First generation SCC systems had high contents of binder however today SCC is no longer of the sorts. Content of cement is managed effectively and use of SRMs is very common in SCC. However, SRMs are mostly used as partial replacements but even at lower replacement percentages of such huge quantities of cement can have a very huge effect on the environment. SCC integrated with SRMs also address the detrimental effect of cement on environment as well the carbon footprint indirectly[9].

2.2.4 Advantages

SRMs impart many useful properties on to the concrete and improve the overall quality of the mix system. Some of the advantages of SRMs are as follows

- Little or no labor and vibration is needed for the placement of SCC.
- Finished level of SCC requires less or at time no screeding
- Construction speed is also increase due to easy placement of the concrete
- Effective against congested placements or high reinforced members such as tunnels, bridges and columns of high rise
- Excellent finishes
- Extensive use in precast member industry

2.3 SRMs

SRMs have been termed with a variety of names in literature like secondary cementitious materials (SCMs), pozzolanic powders, powders and mineral admixtures depending on the role they play in concrete matrix. SRMs are materials with either inherited or latent cementitious properties and require little or no pyro-processing for their use as partial replacement of cement. These type of materials are used to make concrete mix more economical, increase the strength, reduce total internal porosity and permeability and influence other fresh and hardened properties of concrete that suits the nature of need of the user. However, one must be careful in selecting the type and amount of SRMs to be used as they bring about dramatic changes in properties of SCC [5] and in some cases the uniformity of such materials may be questionable [10]. Most of the SRMs used as cement replacements have no or little value attached to them and are used for non-technical trivial uses as they are by products of industrial processes. Two basic effects are responsible for imparting desirable properties once SRMs are integrated into the SCC or any other type of concrete namely filler effect and chemical effect.

2.3.1 Physical packing effect

One of the two major operation of SRMs on concrete systems is the packing effect which is very helpful in reducing the total porosity of the system as the particles of SRM fill the micro pores in the mix. Total porosity of the system as stated earlier is one of the factor that helps in increasing the overall strength and durability of the concrete and can be catered only by filling the pores either by physical or chemical effect. SRMs not only decrease the total porosity of the whole mix but also result in lower porosity and smaller pores at interfacial transition zones (ITZ) [11]. Silica fume is known to improve the quality of bond at ITZ[12] and latest research has confirmed that RHA is a very effective replacement of silica fume [13, 14]. By controlling the overall porosity of the concrete one can also successfully reduce the permeability of the concrete and the resulting concrete has a denser micro-structure and is of high strength.

Finer particles are more reactive than larger particle size having same silica content. Addition of SRMs of any kind provides nucleation sites for the hydration products which

results in faster and better hydration. Silica fume is characterized as a good SRM mainly due to its very fine particle size and high silica content. Limestone powder and quarry dust being finer act as nucleation centers and also adsorb more SP to overcome friction between its particles[7]. Particle size plays an important role in controlling the total porosity of the system and hence providing better chemical durability and mechanical strength [15].

2.3.2 Pozzolanic chemical effect

SRMs are not very reactive themselves but in finely divided form they react with calcium hydroxide Ca(OH)_2 in the presence of moisture to form calcium-silicate-hydrate CSH gel [16]. This pozzolanic activity of SRM precipitates hydration products which are similar to that of cement. It is this chemical activity of SRM that improves the hydration products, makes the micro-structure denser and gives higher strengths to the concrete. The reaction of Portland cement and pozzolans progresses like acid-base type reaction of lime coupled with alkalis with the oxides ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) present in the pozzolan [17]. This reaction leads to two things, first being the gradual decrease in total quantity of free Ca(OH)_2 content and second being the increase in formation of CSH gel resembling to the precipitation of cement reaction hydration.

2.3.3 Need of SRMs in SCC

Other than the environmental friendliness, SRMs tend to improve the overall performance of concrete. Today, SRMs are becoming a must constituent in making of SCC because they impart desirable properties on to concrete. However, SRMs may have positive or negative effects on water demand, temperature rise, strength development, freeze thaw resistance, chemical attack resistance, reduce chloride ion penetration [18, 19] alkali-silica and alkali-carbonate reaction control [10]. Many SRMs are by-products and hence can be made available with ease and at very low cost. Many countries are manufacturing cement including Pakistan for both domestic use and for exporting it thus depleting natural resources. SRMs are used as partial replacements and hence reduce the total quantity of cement required.

2.3.4 Advantages

Following are the advantages in integration SRMs in concrete systems

- a. Use of SRM can lead to achievement of desired properties in concrete with lesser amounts of cement in both fresh and hardened state.
- b. Use of SRM will reduce cement content which is expensive constituent of concrete.
- c. Filler and chemical effect of SRM give better mechanical properties like compressive and flexural strengths with improved microstructure.
- d. SRMs are finer than cement hence they give better packing and better volume stability.
- e. Use of SRMs leads to an environmental friendly concrete systems

2.4 RHA

Rice produced in Pakistan is of supreme quality specially basmati rice which is famous throughout the world. Rice husk is the outer covering of rice and comprises of two halves joined together at the base and open at the top and is not edible therefore it is removed. This rice husk is obtained as a by-product of rice milling industry and is usually disposed-off. The husk is either burned or used for small scale burning for non-technical purposes. This agro-based waste is abundantly available in Pakistan and holds tremendous potential to be converted into a value based product. In developing countries the husk is burned to produce electricity through steam generators and the remainder burnt ash is used as a SRM in SCC.

Once the husk is put through a specific burning regime in controlled environment the resulting ash, if in amorphous form, results as good SRM and has been used by in SCC to induce properties in the concrete that improve the overall quality of the concrete systems. Through physical packing/filler effect and pozzolanic chemical effect RHA imparts desirable properties which include improved strength and durability[20], better resistance against chloride ion penetration [21], better response against freeze and thaw conditions, improvement in resistance to salt scaling [22] and reduction in Alkali Silica Reaction (ASR) expansion and it reduces the unit weight of the concrete as well [23] while providing a better response against chemical attacks [24].



Figure 2: SEM image of RHA Particle

2.4.1 Composition and nature of RHA

Of all plant residues, rice plants contains highest proportion of silica[25]. RHA is made up of both organic and inorganic matter where organic matter consists of cellulose, hemi cellulose, lignin, some proteins, vitamins and the inorganic matter mostly made up of silica. This silica is taken up from the soil in the form of monosilic acid by the plant through roots and it eventually makes it way up to the outer portion of the rice i-e husk of the rice where it forms cellulose silica membrane[26]. Once the burning takes place the organic matter is decomposed leaving behind ash rich in silica. However it is important to note that the overall composition of rice husk depends upon a number of factors which include geographical factors, use of fertilizers[27], crop season and relative humidity[28, 29] to name a few.

Plant	Part of Plant	Ash%	Silica%
Rice Husk	Grain Sheath	22.1	93
Wheat	Leaf Sheath	10.5	90.5
Sorghum	Leaf Sheath epidermis	12.5	88.8
Rice Straw	Stem	14.6	82
Breadfruit tree	Stem	8.6	81.8
Bagasse	-	14.7	73
Corn	Leaf Blade	12.1	64.3
Bamboo	Nodes(inner portion)	1.5	57.4
Sunflower	Leaf and Stem	11.5	25.3
Lantana	Leaf and Stem	11.2	23.3

Table 2: Silica Content in Plants[7]

2.4.2 Burning Regime/Combustion of RHA

Burning regime is probably the most important parameter controlling the amorphous state, surface area and overall quality of RHA. The burning regime can be roughly divided into three main factors namely temperature, hold time and the environment of burning. The equipment used define the level of control on temperature. Research has reported fluidized bed reactors to be the best form of equipment to fully utilize the fuel value of rice husk[30] and the same technology offers higher probability of resulting amorphous RHA as the temperatures in fluidized bed reactors are kept below the crystalizing temperatures for silica content[31]. Higher temperatures ranging up to 1000°C turn the silica into crystalline form[32] which is not a reactive form of RHA and possesses poor pozzolanic property [1, 7, 14]. 402°C is the minimum temperature required to completely burn the organic matter[33] while ranges of up to 500-600°C produce amorphous RHA with high silica content [34]. RHA produced after burning is usually grey in color while black color may indicate partial burning[35].

The other important factor is the hold time for producing good quality RHA. The temperature also plays it part in determining the hold time. For instance at high temperature such as even at 900°C the silica in RHA can remain amorphous if the combustion time is less than one hour but combustion at 1000°C for over 5 mins produces crystalline SiO₂ [32].

Other research reports that burning at 500°C for 6 hours does not completely decompose the organic matter where as combustion at 700°C for 6 hours also produces ash with little or no organic matter[25]. Semi-oxidizing environment should be provided for combustion as it ensures flow of oxygen for good combustion. Excess of oxygen or inadequate supply results in poor quality of RHA.

2.4.3 Effect of surface area of RHA

RHA has a cellular structure and as enunciated before contain cellulose lignin matrix. When rice husk is put through combustion, the organic matter decomposes making way for a porous silica skeleton which has high surface area when ground finely. The silica in RHA reacts with lime to form calcium silicate hydrate (CSH) gel however the level of reactivity is surface assisted (depends on surface area) and is a function of temperature at which the RHA is burned[36]. The reactivity of RHA depends greatly on the surface area of particles which is effected by the combustion temperature. A study shows change in the surface area of RHA with change in temperature[37]. The same research indicates that the surface area reaches its maximum value of 170 m²/g at 500°C however higher values of surface area of 261 m²/g after acid-treatment have been reported [38]. A group of researchers boiled RHA with water, washed it and then later dried the RHA. For constant combustion duration of 3 hours, an increase in surface area from 200 to 271 m²/g has been reported for temperature range of 500-600°C. Above 600°C the surface areas decreased [39-41].

2.4.4 Reactivity of RHA

Reactivity of RHA depends on amount of amorphous silica content in RHA as crystalline form of the silica is not very reactive and the surface area as well as pore volume. The silica in RHA reacts with calcium hydroxide that results from cement hydration to produce CSH gel. This additional CSH gel densifies the microstructure and gives good strength gain. The surface area also assists the reactivity of RHA and this surface area and pore volume may be reduced by rigorous milling. A study confirms that this CSH gel is formed through dissolution-precipitation process as silica in RHA reacts with Ca(OH)₂ in high pH saturated solution of calcium hydroxide and subsequently Ca_{1.5}SiO_{3.5x}H₂O is formed[16].

2.4.5 Unburnt Carbon in RHA

The unburnt carbon in RHA has very high surface area which result in ash that have high water demand. Presence of more quantities of unburnt carbon in RHA results in lower quality ash as this unburnt carbon increases the water demand due to its high surface area and porosity and also decreases the silica content[42]. If the loss on ignition of a given ash is high, it reflects on a higher SP dosage for that ash as compared to an ash with lower loss on ignition[7].

2.4.6 Particle size of RHA

Particle of RHA is also of consequence for the reactivity of the ash. RHA is more reactive in fine particle size as compared to a larger particle size however the reactivity of RHA is also effected by the surface area. Reducing the particle size is detrimental towards surface area. Milling regime is very crucial to obtain an optimized particle size with enough surface area to offer good pozzolanic activity. Lower surface area in order to reduce the particle size can decrease the reactivity of RHA. It has been found through research that a considerable drop in particle size can be observe with up to 1 hour of milling however after the first hour the particle size seems to more or less remain comparable and reaches a plateau in terms of particle size[7].

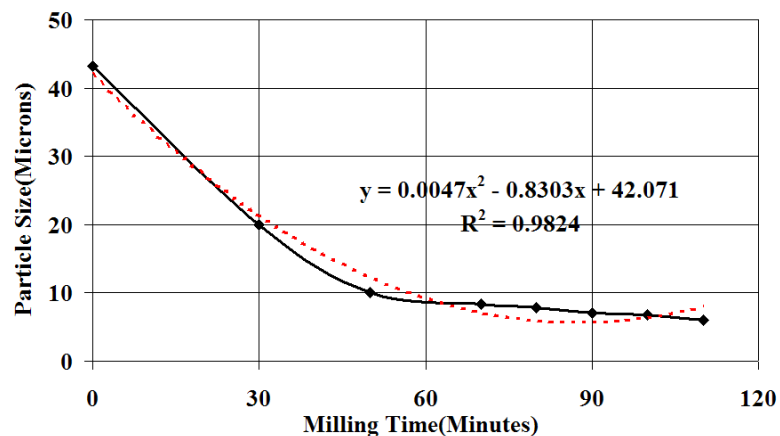


Fig 2.3: Particle size and milling time relationship

2.4.7 Production of RHA in Pakistan

PCSIR, Peshawar made a drum type incinerator to produce ash from rice husk. The same drum type incinerator was used by a researcher in Delft University to produce RHA[42]. However the capacity of the drum incinerator was increased to 1m³. The drum and the chimney was made from galvanized iron sheets and were light weight, enough for two persons to carry and move it around. Ignition was made by waste paper or some wood and required no control afterwards. Temperature up to 780°C have been recorded. Using the facilities of PCSIR, Peshawar another researcher made RHA however the product was crystalline and showed poor reactivity[7]. In this research using the facilities of PCSIR, Lahore the author has managed to produce amorphous RHA.

CHAPTER 3: MATERIALS AND METHODOLOGY

3.1 General

This chapter gives details of materials used in the research. Description of the material used and details pertaining to them will be discussed in detail. This chapter will also discuss the methodology adopted for carrying out the research and preparation of samples and other important parameters.

3.2 Materials

3.2.1 Cement

For the research ordinary portland cement (OPC), Bestway grade 53 was used. The cement was stored in an air tight container to prevent exposure to the moisture in the air. Cement bags were brought in when needed and transferred in to the containers. Cement is the binder and all other ingredients constitute the matrix of concrete which include water, coarse and fine aggregate. Cement is the most expensive constituent of concrete and in order to economize concrete, one preferable option is to reduce its content.

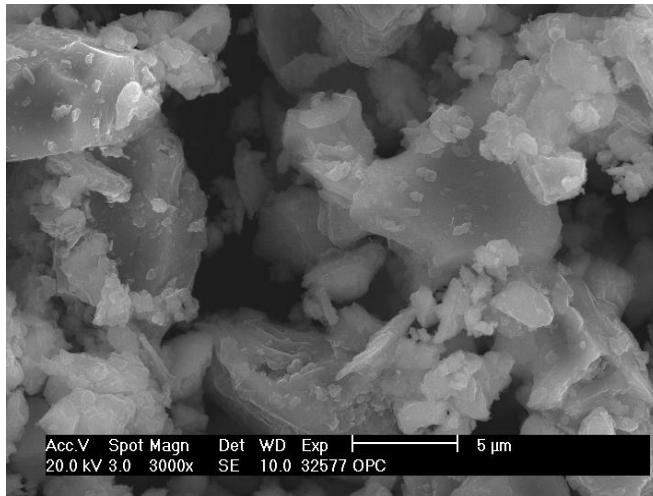


Figure 3: SEM of CEM 1 cement particle (MS thesis Maj. Aftab, NUST)

3.2.2 Fine Aggregate

Locally available sand with particles greater than 2 mm was used with a fineness modulus of 2.09. Since the project mostly focuses on mortar systems therefore coarse aggregate was not used. Mortar in the concrete matrix is most important due to its vital role

in strength, workability, pumpability, finishability, durability, wearability and the cost [43]. Certain additional parameters kick in while using mortar instead of paste such as vigorous adjustment of SP, moisture state of fine aggregate and type and source of fine aggregate that effect the overall system. SP dosage usually needs more attention in mortar than in pastes as ratio of sand used in the mix dictates the amount of cement particles present in the system for grafting. Higher quantities of sand leads to higher dosage of SP. If however the sand is lessened, and cement increased, better flows can be achieved using lesser super plasticizer. The mix included cement, sand, water and SP. The fine aggregate was oven dried for 24 hours at $140^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and then allowed to cool at room temperature for 24 hours. A ratio of 1:1.667 was used for cement and sand.



Figure 4: Oven used for drying fine aggregate

3.2.3 Super Plasticizer

Melflux 2651F was used for this project which is in powder form. The plasticizer was used once some the mixing had already been done (for mixing regime see section 3.2.1). Melflux 2651F is manufactured using the latest techniques and technology and has side chains of polyethylene glycol and it is a free-flowing spray dried powder of a modified polycarboxylic ether. The SP used is manufactured by BASF. Basic properties are listed below in Table 3.

Physical shape	Powder
Appearance	Characteristic, yellowish to brownish
Drying loss	Max. 2.0%
Bulk density	300-600 kg/m ³
Dosage recommendation	0.05-1.50% by weight of cementitious material
pH value at 20°C, 20% solution	6.5-8.5

Table 3: Properties of Melflux 2651 F



Figure 5: Melflux 2651 F

3.3 Water

Tap water was used for this research. The water was used as is without any processing. The quantities of water were measured as per mix design using a weight balance. The pH of the water was recorded as 8.2.

3.4 Rice Husk Ash

Rice husk ash from two sources was used in this research. Both sources will be separately discussed here.

3.4.1 Rice Husk Ash Pakistan-RHAP-21 and RHAP-84

RHAP-21 and RHAP-84 were prepared using the facilities of Pakistan Council for Scientific and Industrial Research, Lahore (PCSIR). The raw material, rice husk, was bought from Sheikhupura district and then transported to Lahore. Glass annealing furnace was used

for firing the raw rice husk at Glass and Ceramic department, PCSIR. A total of 100 kg was burned in 10 batches of 10 kg each using the burning regime reported below. First three burnings were done and tested using XRD to see whether the ash produce was amorphous or crystalline. Once it was confirmed that the parameters can be maintained and replicated the remaining firings were done to ensure uniformity in production of the ash. The ash produced was then transported to Germany where it was milled using rotatory milling machine to a finer particle of 21 microns (RHAP-21) while the ash without milling was labelled RHAP-84 and had a particle size of 84 microns.

3.4.2 Burning Regime

Following three parameters were given to PCSIR for the combustion of rice husk. The temperature was controlled manually by fluctuating the gas flow of the furnace. Thermometer attached with a rod was used to constantly check the temperature of the furnace. For providing semi-oxidizing environment, a small window in the furnace was kept half open to allow cross ventilation and ensuring oxygen for combustion.

Burning temperature	500-550°C
Retention time	5 hrs
Burning environment	Semi-oxidizing

Table 4: Burning Regime of RHA from Pakistan

3.4.3 Rice Husk Ash Germany

RHAG was attain courtesy of Technical University Freiberg and was acquired from an industry as a waste byproduct material. Such sources provide RHA readily for use and requires little or no pyro-processing [32, 44]. For this research RHAG was used as provided with absolutely no processing at all.



Figure 6: RHAG-81 (Left) and RHAP-21 (Right) powders



Figure 7: RHAP-84

3.5 Mixing Regime

Mixing regime for the research was chosen such that it gave optimum results in terms of SP dosage. The mixing water was divided into 80 and 20% with respect to weight. 80% water was added first and after some mixing 20% water with SP was added and this yields the best results [7]. Effective mixing was done using Hobart mixer to better activate the SP. A total of 4.5 minutes were chosen for mixing. Since the mix included RHA which usually has very high surface area values and demand more water to wet the surface, therefore the mixing regime was selected to supplement the SP so that less dosage would give better flow. Different regimes were tried prior to the selection of the following mixing regime.

0-30 sec (0.5 min)	Dry mixing (Cement + Sand + SR quantities as per the mix design)
30-60 sec (0.5 min)	Addition of 80% water and then slow mix
60-120 sec (1 min)	Fast mixing
	Mixing stopped and hand mixing to clean wall of the bowl
120-300 sec (3 mins)	20% water + SP addition and fast mixing

Table 5: Mixing Regime



Figure 8: Hobart Mixer

3.6 Sample preparation and curing

Once the mixing was done in accordance with the selected mixing regime, the mix was then poured into prisms for 2, 7 and 28 day strength data. Standard prisms were used to cast the samples and covered with plastic sheets to avoid any transfer or moisture. After 24 hours the prisms were demoulded and the samples were put in curing tank as per dates for testing.



Figure 9: Curing Tank

3.7 Strength testing

Samples were tested for flexure and compression at 2, 7 and 28 days. Control 5000 KN machine was used for flexure and compression. The samples were positioned appositely so that the loading is applied in the center of the sample. If proper centering is not done, the samples are subjected to stress concentrations on either side. Strength test for flexure was done first which split the sample into two, the smaller portions of the sample were then used to test for compression. Therefore, from one sample, one strength measurement for flexure while two compression values were obtained. Averages were taken to get the final result.

Before the measurements, the sample were taken out of the curing tank and dried using a simple cloth and measurements were taken. Once the samples were dried they were

weighed and dimensions, width and height, of the sample were measured and recorded and the length of the sample was taken as 160 mm. The measurements were taken using a digital Vernier caliper and a weighing balance. These measurements were taken for two reasons. First, to record this data and secondly the weight, width and height was also required as an input in the strength machines.



Figure 10: Controls 5000 KN-Compression Machine

3.8 Storage of materials

The materials used for this were stored in air tight containers to avoid contact of moisture and to eliminate the effect of external environment. Cement, sand and ashes were originally stored in the storage shed and incase of need of material were brought into the lab in relatively smaller quantities. In the lab, air tight containers were used as well. Special care was taken while using the material to minimize the contact of moisture. Cement can be rendered useless for research purpose if exposed to moisture for longer periods of time. Therefore, when a bag of cement was brought in from the storage, some of it was transferred to a small container while the remaining was sealed and wrapped in plastic bags to avoid detrimental effect of environment.

3.9 Formulations Studied

For this research, 20 SCM formulations were studied. The mix composition of these formulations weighing one kg is shown in Table 6.

Formulation Number	System	w/b	Cement (g)	SRM (g)	Sand (g)	Water (g)	SP(% Cement)
01	CEM1-0-0.5	0.5	375	-	625	188	0.29
02	RHAP-21-10-0.5	0.5	337.5	37.5	625	188	0.37
03	RHAP-21-15-0.5	0.5	318.75	56.25	625	188	0.72
04	RHAP-21-20-0.5	0.5	300	75	625	188	1.05
05	RHAG-81-10-0.5	0.5	337.5	37.5	625	188	0.42
06	RHAG-81-15-0.5	0.5	318.75	56.25	625	188	0.84
07	RHAG-81-20-0.5	0.5	300	75	625	188	1.16
08	RHAP-84-10-0.5	0.5	337.5	37.5	625	188	0.78
09	RHAP-84-15-0.5	0.5	318.75	56.25	625	188	1.52
10	RHAP-84-20-0.5	0.5	300	75	625	188	2.33
11	CEM1-0-0.4	0.4	375	-	625	150	0.56
12	RHAP-21-10-0.4	0.4	337.5	37.5	625	150	0.71
13	RHAP-21-15-0.4	0.4	318.75	56.25	625	150	0.94
14	RHAP-21-20-0.4	0.4	300	75	625	150	1.36
15	RHAG-81-10-0.4	0.4	337.5	37.5	625	150	0.78
16	RHAG-81-15-0.4	0.4	318.75	56.25	625	150	1
17	RHAG-81-20-0.4	0.4	300	75	625	150	1.48
18	RHAP-84-10-0.4	0.4	337.5	37.5	625	150	1.08
19	RHAP-84-15-0.4	0.4	318.75	56.25	625	150	1.8
20	RHAP-84-20-0.4	0.4	300	75	625	150	3.2

Table 6: Mix design of SCM formulations

A typical formulation RHAP-21-10-0.5 means that RHAP having particle size 21 microns was used as ten percent cement replacement at w/b ratio of 0.5. All other formulations can now be understood accordingly

CHAPTER 5: EXPERIMENTAL RESULTS

5.1 General

This chapter will discuss the tests done and the results retrieved from those test chosen for the research. Discussion on the results would be done alongside.

The first objective of the research was to produce local RHA using best suited burning regime as recommended by literature. The burning regime reported earlier was provided to PCSIR for firing of rice husk. The nature of the product was verified using X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) to see the state, whether amorphous or crystalline, and the silica content.

5.2 Characterization Results

5.2.1 Amorphous States of RHAs

To check the state of RHAs XRD was performed on the samples utilizing the facility available at School of Chemical and Materials Engineering (SCME), NUST using the machine STOE Germany which uses Cu K α radiation as a source. XRD patterns of sample show that the ashes have a presence of α -Cristobalite at 2θ angle of 22° and RHAP-21/RHAP-84 has traces of possibly sylvite which is a crystalline form of quartz at 2θ angle of 27° .

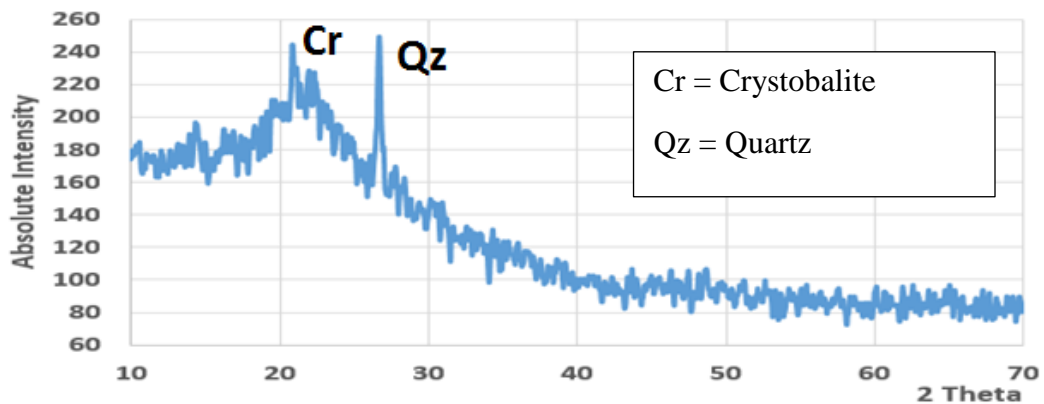


Figure 11: XRD patterns of RHAP-21 sample

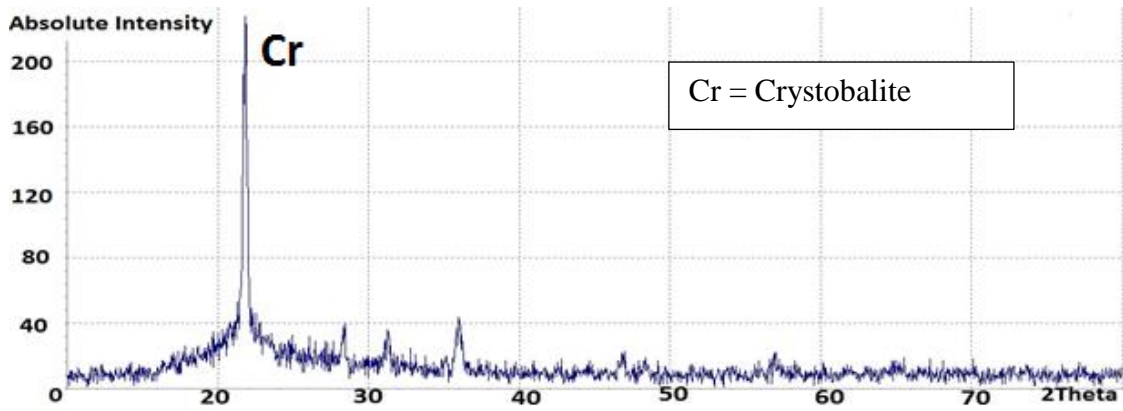


Figure 12: XRD patterns of RHAG-81 sample

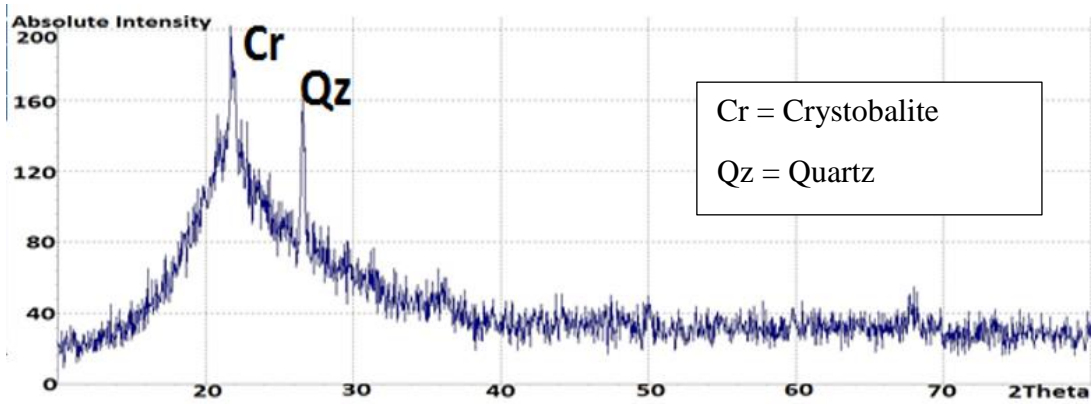


Figure 13: XRD patterns of RHAP-84 sample

5.2.2 Physical and Chemical properties of powders

For chemical composition of the powders XRF was performed on both ashes and cement. Following table reports the chemical composition along with particle size and BET surface area values.

Systems	CEM1	RHAP-21	RHAG-81	RHAP-84
SiO ₂	19.19	85.15	94.50	88.51
TiO ₂	0.29	0.26	0.16	0.19
Al ₂ O ₃	4.79	4.44	4.32	4.97
Fe ₂ O ₃	3.27	7.85	0.82	2.92
MnO	0.04	0.66	0.73	0.27
MgO	2.23	0.32	0.21	0.25
CaO	65	1.98	1.97	2.99
Na ₂ O ₃	0.58	0.29	0.34	0.28
K ₂ O	0.51	1.7	1.98	4.4
P ₂ O ₅	0.08	-	-	-
LOI	3.84	2.45	3.04	2.45
D ₅₀ , Microns	16.4	20.33	81.83	84.10
BET m ² /g	1.1	21.20	15.98	25.62

Table 7: Physical and Chemical Properties of Powders

5.3 Water Demand

Water demand was calculated using Vicat apparatus. 500 g of system was prepared for the test with 0, 10, 15 and 20% replacement levels. It was important to check the water demand to fully understand the behavior of RHAs. Paste formulations were used instead of mortar for this specific test to study behavior of RHAs. The results are shown in figure below.

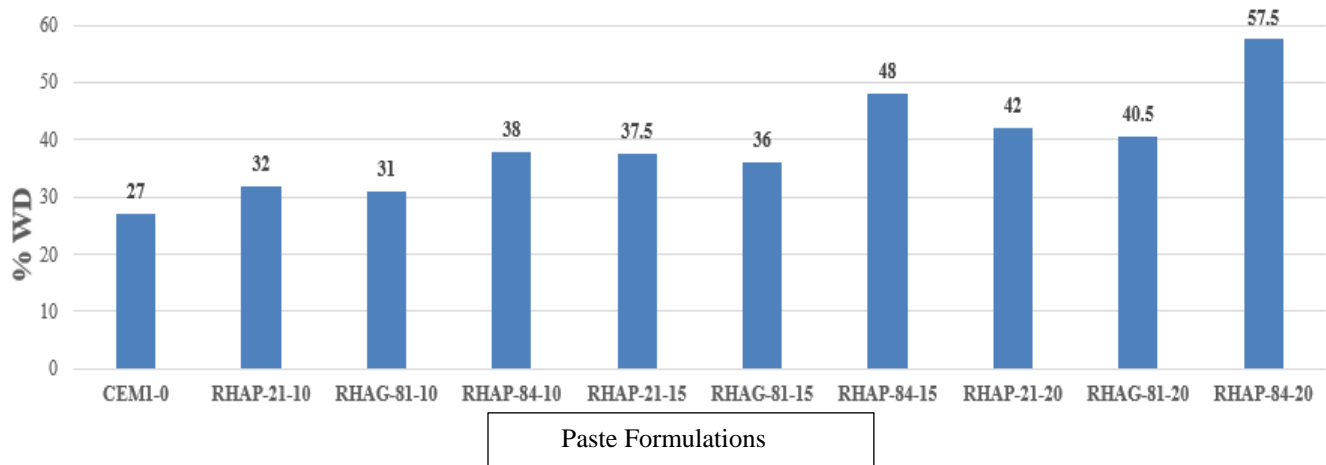


Figure 14: Water Demand of Paste systems containing RHAP-21, RHAP-84 and RHAG-81

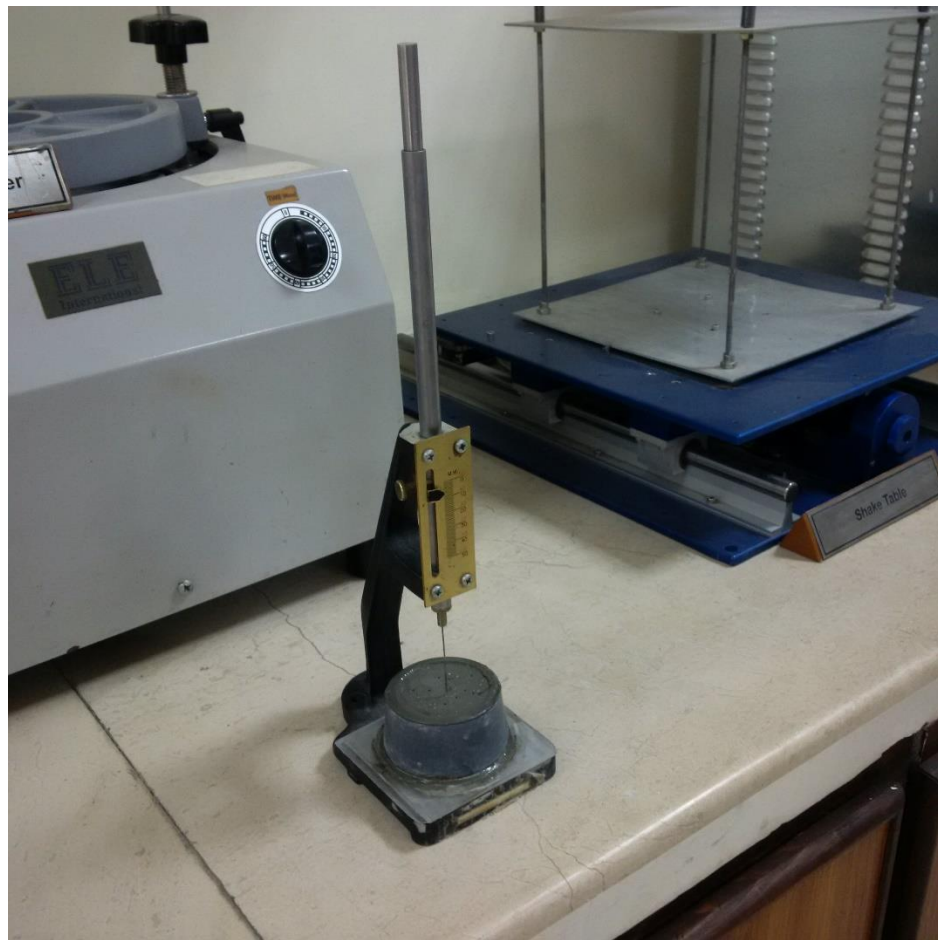


Figure 15: Vicat apparatus used for calculating water demands of paste systems

5.4 Setting Times

Setting times were calculated using Vicat apparatus at water demands of the systems. The tests were conducted on control mix and 15% replacement levels with respect to cement to find the trend of setting times. Following figure give account of the setting times

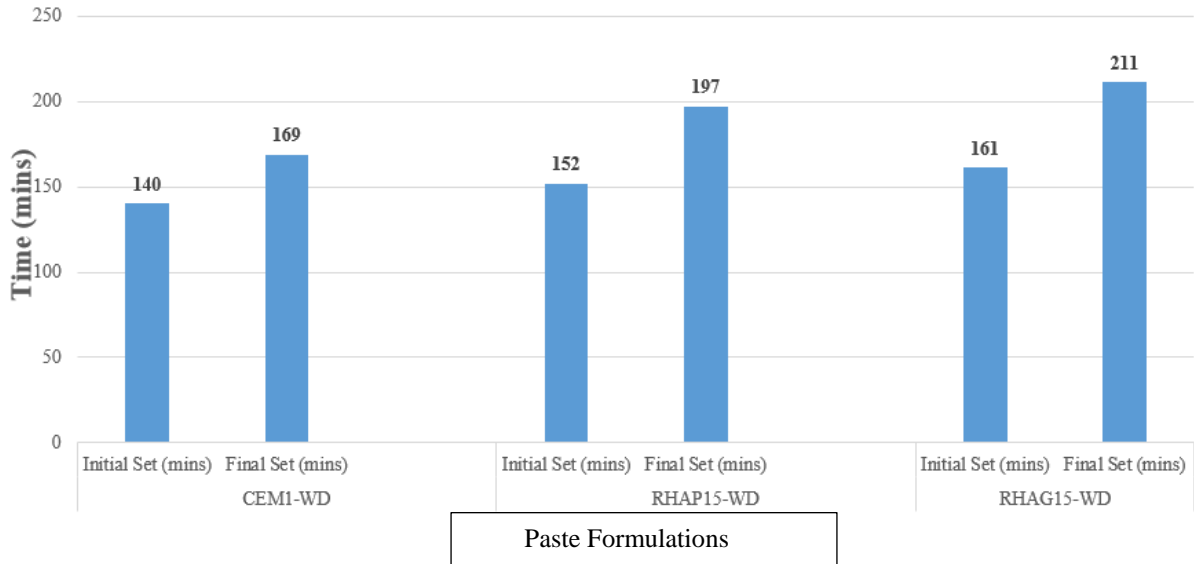


Figure 16: Setting times of paste formulations containing RHAP-21, RHAP-84 and RHAG-81

5.5 Air Content

German made Luftporengehalt apparatus was used to calculate the air content in the formulations that showed increased strengths as compared to control mix. Hence the formulations with 15% replacements were tested for air content. The capacity of the apparatus was 1 litre. It was seen the addition of RHAs tend to increase the air content which is more prominent in lower w/b ratios as in 0.4 in this case. Following figure gives the results of air content.

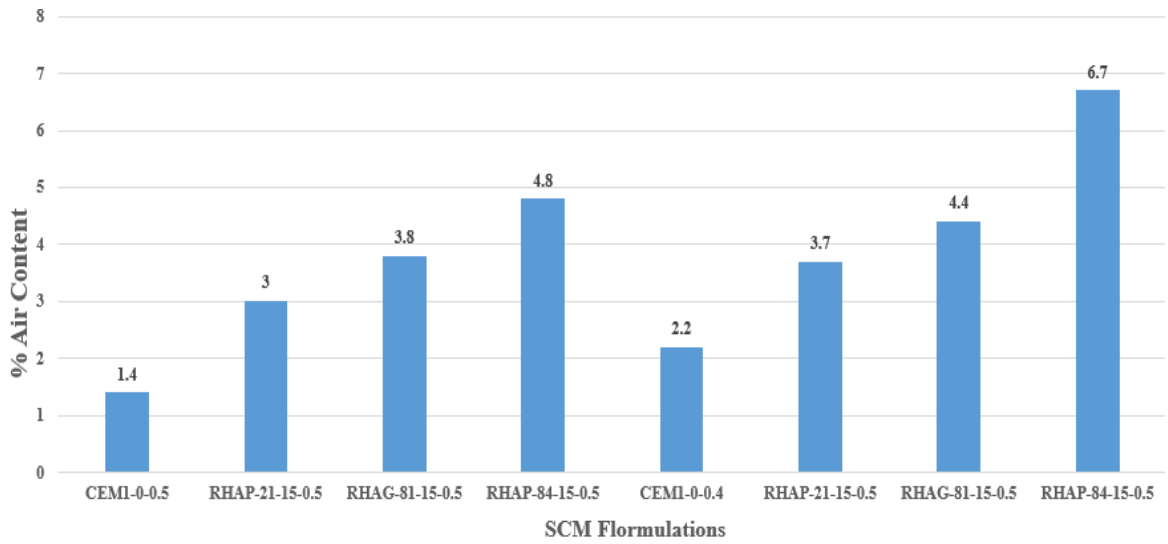


Figure 17: Air content of SCM formulations containing RHAP and RHAG



Figure 18: Luftporengehalt apparatus used to calculate air content of SCM formulations containing RHAP and RHAG

5.6 Super Plasticizer Demand of SCM Formulations for Target Flow

The super plasticizer was used for a target flow of 30 ± 1 cm which was measured by Hagerman's cone ($6 \times 7 \times 10$ cm³). Mixing regime reported earlier was followed and all the systems were designed for the same target flow and SP demand were noted. The mixing water-binder ratios were 0.4 and 0.5. Figures 4.7 and 4.8 illustrate the SP demands for the SCM systems.

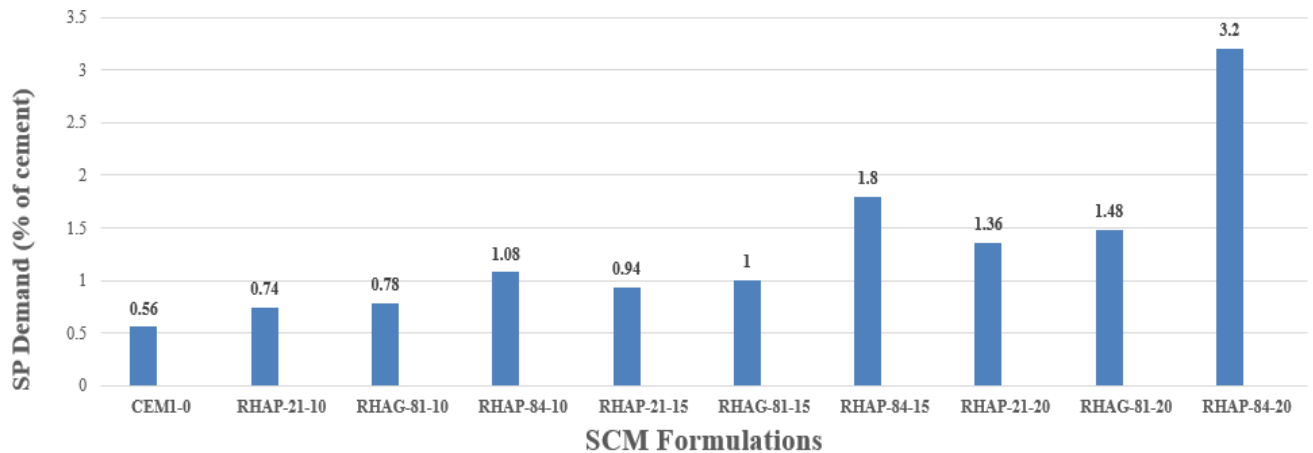


Figure 19: SP Dosage of w/b ratio 0.4 for SCM formulations

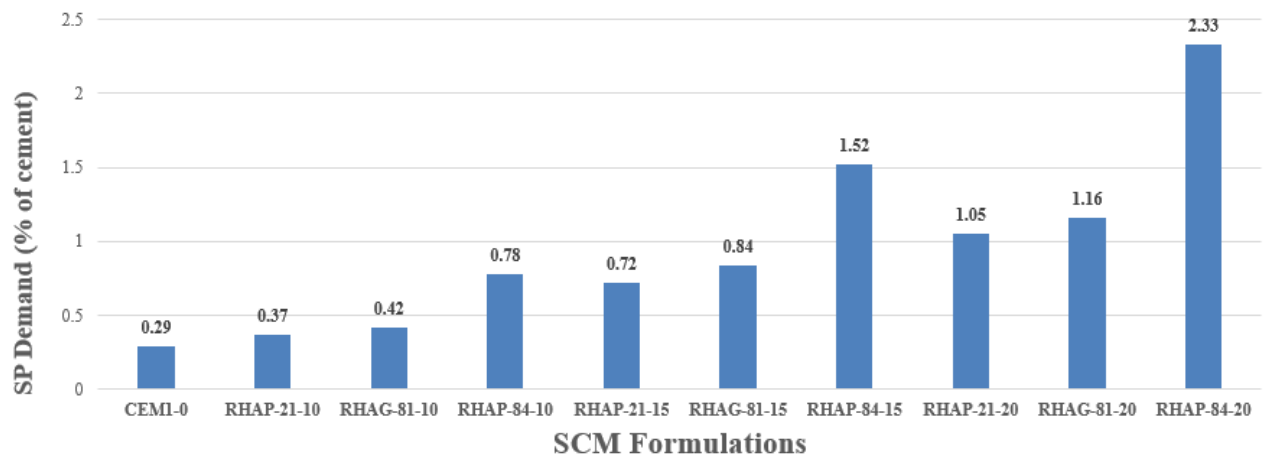


Figure 20: SP Dosage of w/b ratio 0.5 for SCM formulations

5.7 Flow Values

Flow was measured by Hagerman's cone ($6 \times 7 \times 10$ cm³) and times were recorded for T₂₅ and T₃₀ (cm) flow. Following figure shows the time corresponding to flow.

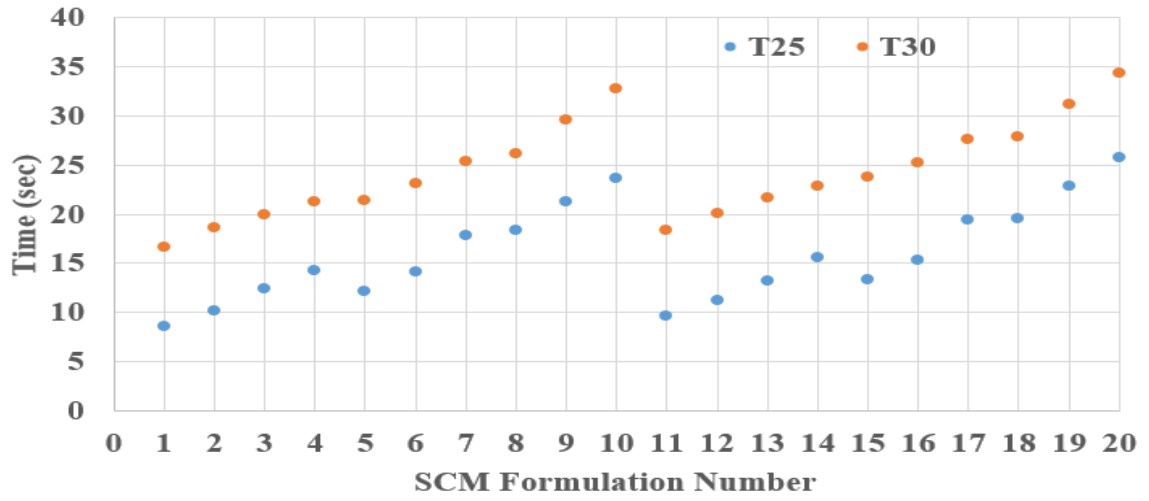


Figure 21: Flow times of SCM formulations



Figure 22: Haggerman's cone for measure the spread of SCM formulations

5.8 Strength Data

The samples of 4x4x16 cm³ were cast and were tested for flexure and compression values at the age of 2, 7 and 28 days in SSD condition as per DIN 196. Average strength of the samples are reported in Table 8 below. For flexure average of three samples were taken while for compression average of 6 samples has been reported. Subsequently after demoulding at 24 hours, SCM Samples were cured in water.

SCM Formulations	w/b 0.5 Flexure (Mpa)			w/b 0.5 Compression (Mpa)		
	2 Day	7 Day	28 Day	2 Day	7 Day	28 Day
CEM1-0-0.5	0.875	1.93	3.18	15.5	27.81	43.7
RHAP-21-10-0.5	0.75	1.67	2.937	8.87	21.93	43.11
RHAP-21-15-0.5	0.68	1.56	2.81	9.93	26.87	45.88
RHAP-21-20-0.5	0.562	1.375	2.56	9.59	25.62	44.93
RHAG-81-10-0.5	1	1.53	2.75	9.62	24.75	43.81
RHAG-81-15-0.5	0.625	1.437	2.56	10.18	26.31	46.93
RHAG-81-20-0.5	0.437	1.12	2.43	10.12	24.65	45.68
RHAP-84-10-0.5	0.34	1.09	1.56	5.92	14.6	26.11
RHAP-84-15-0.5	0.28	0.93	1.11	5.10	11.5	21.41
RHAP-84-20-0.5	0.21	0.68	0.98	4.25	9.67	16.22
SCM Formulations	w/b 0.4 Flexure (Mpa)			w/b 0.4 Compression (Mpa)		
	2 Day	7 Day	28 Day	2 Day	7 Day	28 Day
CEM1-0-0.4	1.125	2.437	4.23	23.12	38.81	54.38
RHAP-21-10-0.4	1.06	1.53	2.73	18.79	35.47	54.07
RHAP-21-15-0.4	0.875	1.47	2.5	19.32	37.88	56.92
RHAP-21-20-0.4	0.68	1.21	2.31	19.01	36.97	55.31
RHAG-81-10-0.4	0.937	1.44	2.62	19.11	35.19	54.44
RHAG-81-15-0.4	0.812	1.32	2.47	19.78	35.4	58.1
RHAG-81-20-0.4	0.681	1.03	2.13	19.32	35.75	52.88
RHAP-84-10-0.5	0.46	1.24	1.77	6.73	18.57	31.24
RHAP-84-15-0.5	0.38	1.07	1.35	5.91	13.38	25.77
RHAP-84-20-0.5	0.29	0.76	1.13	4.78	10.67	20.43

Table 8: Strength data of SCM formulations

5.9 Viscosity Measurements of SCP Formulations

Viscosity measurements were taken on Brookfield DV-III Ultra Programmable Rheometer coupled with SC4-27 spindle. The SCP systems used to test the effect of RHAs

content on viscosity at constant w/b of 0.5 and SP content of 0.8% was used. Tests were done on four shear rates which are 17 s^{-1} , 24.7 s^{-1} , 27.2 s^{-1} and 34 s^{-1} for 25 seconds. These shear rates are usually experience in hauling, pumping and handling concrete on site[45]. 10, 15 and 20 grams cement was replaced by both the RHAs to see the effect of RHA on viscosity as opposed to 10, 15 and 20% replacement. Fig 4.11 and 4.12 gives the result of viscosity measurements.

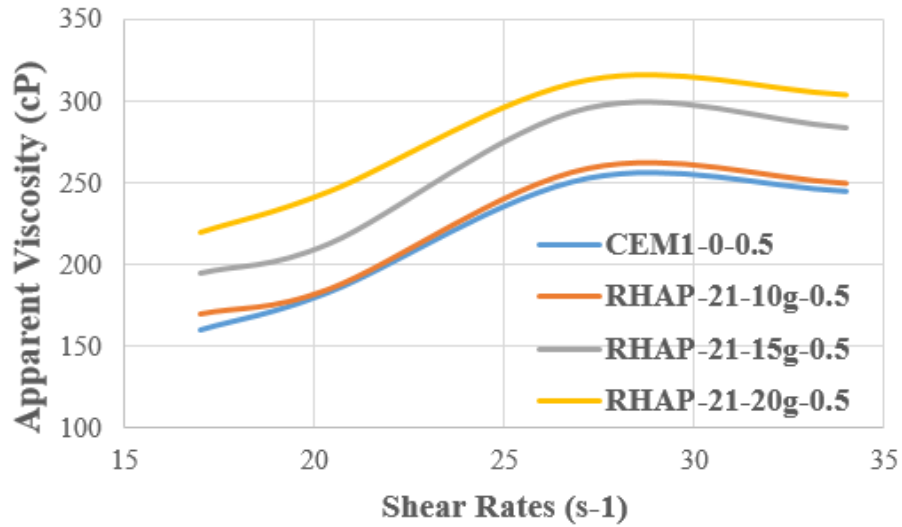


Figure 23: Apparent viscosity of SCP systems containing RHAP-21

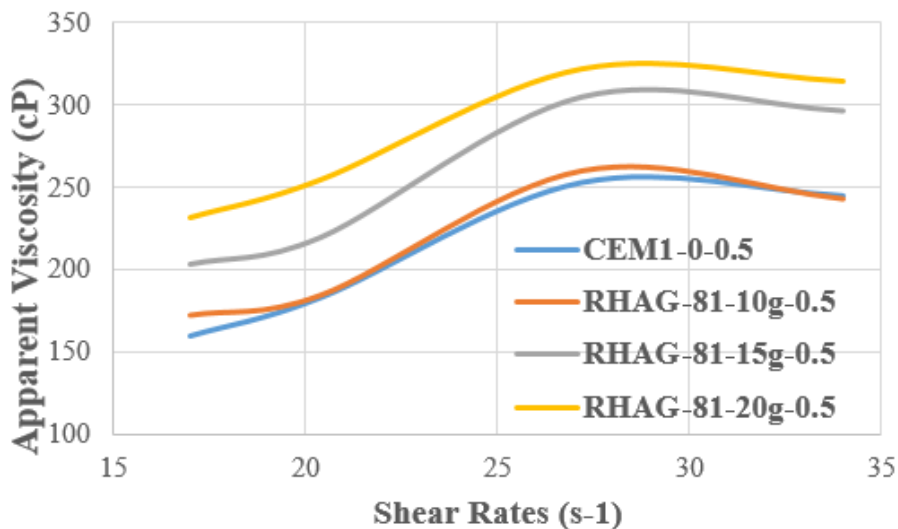


Figure 24: Apparent viscosity of SCP systems containing RHAG-81

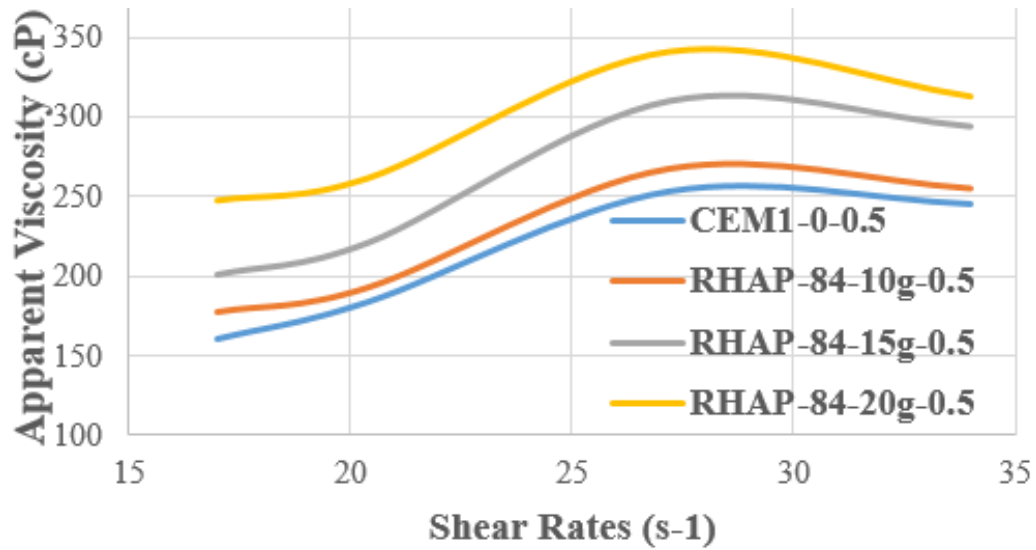


Figure 25: Apparent viscosity of SCP systems containing RHAP-84

5.10 Calorimetry of SCM Formulations

F-Cal 8000 field calorimeter was used to study the hydration kinetics and the extent of exothermic reaction. 700 g of sample was poured in polythene bag which were then placed in the containers of F-Cal 8000 field calorimeter. The results of the hydration kinetics are given in Figure 4.13 to 4.16 as follows.

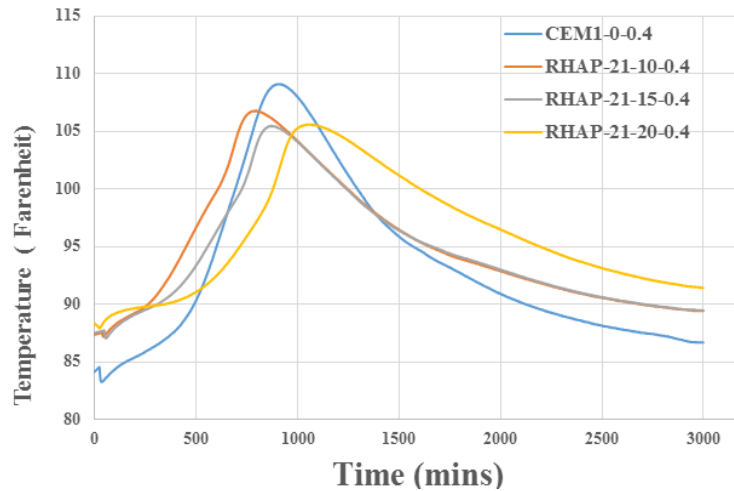


Figure 26: Calorimetry response of SCM systems containing RHAP-0.4 w/b

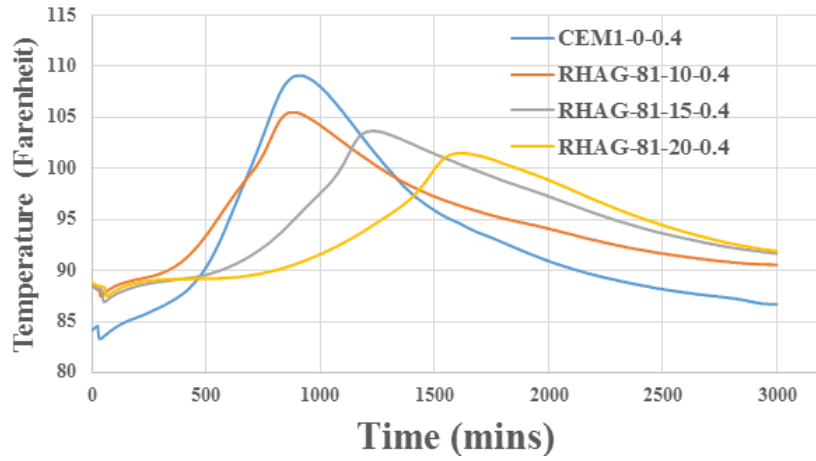


Figure 27: Calorimetry response of SCM systems containing RHAG-0.4 w/b

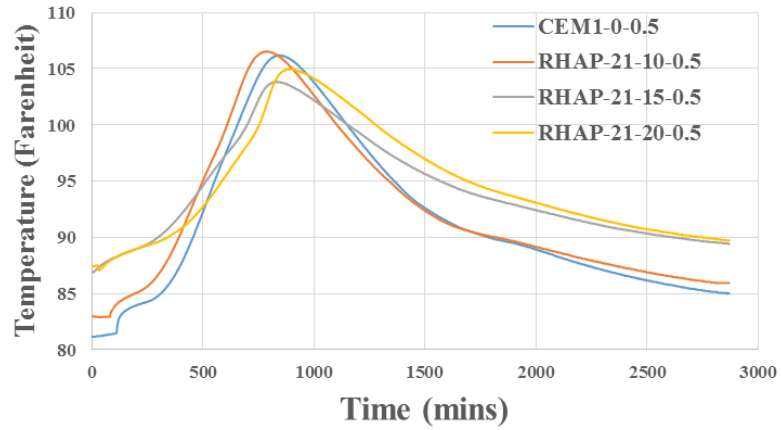


Figure 28: Calorimetry response of SCM systems containing RHAP-0.5 w/b

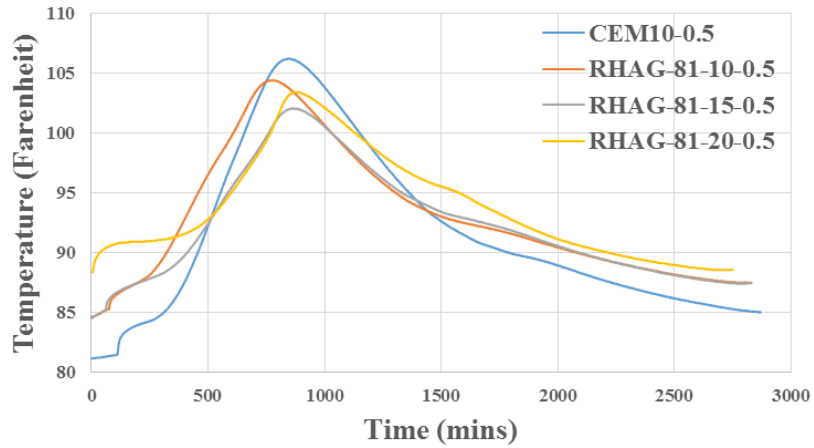


Figure 29: Calorimetry response of SCM systems containing RHAG-0.5 w/b

5.11 Shrinkage Measurements of SCM Formulations

Volumetric stability of the mortar systems was studied using German Schwindrine apparatus. The apparatus measures linear shrinkage. Mortar was poured into the channels of the apparatus and then covered with polythene sheet to avoid the moisture from the system to escape.

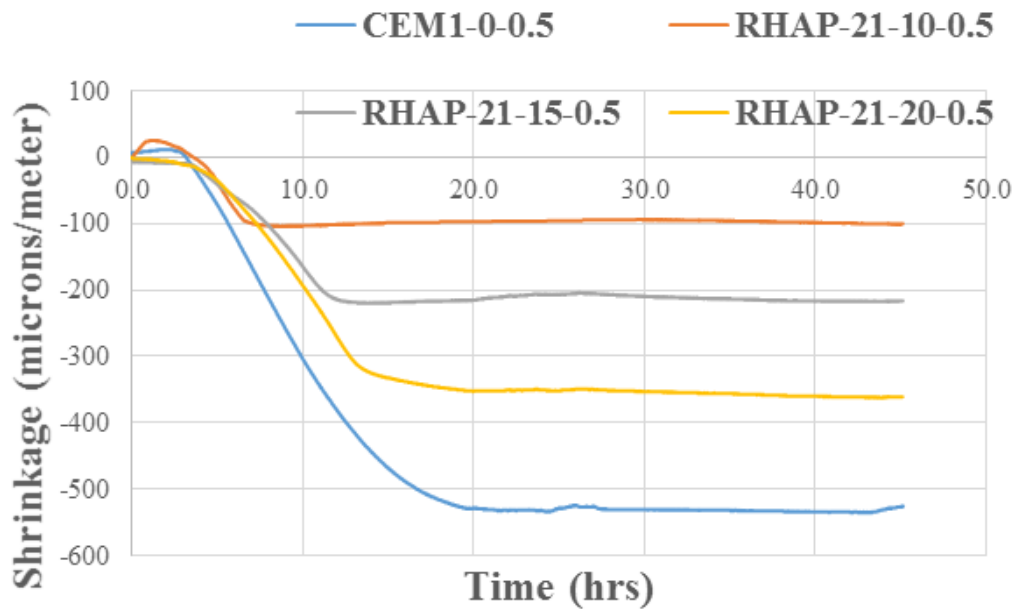


Figure 29: Shrinkage response of SCM systems containing RHAP-21-0.5 w/b

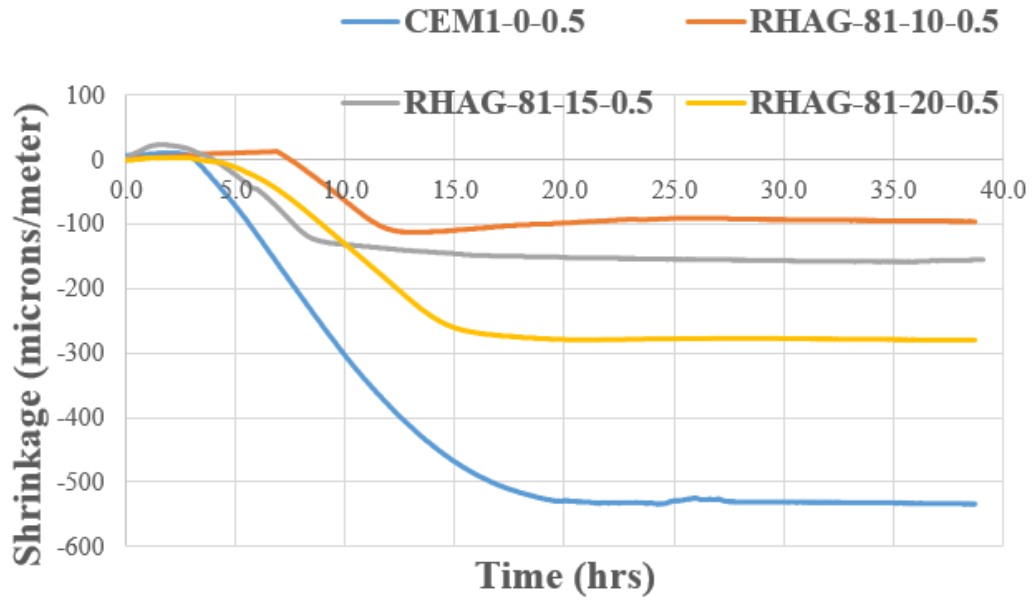


Figure 30: Shrinkage response of SCM systems containing RHAG-81-0.5 w/b

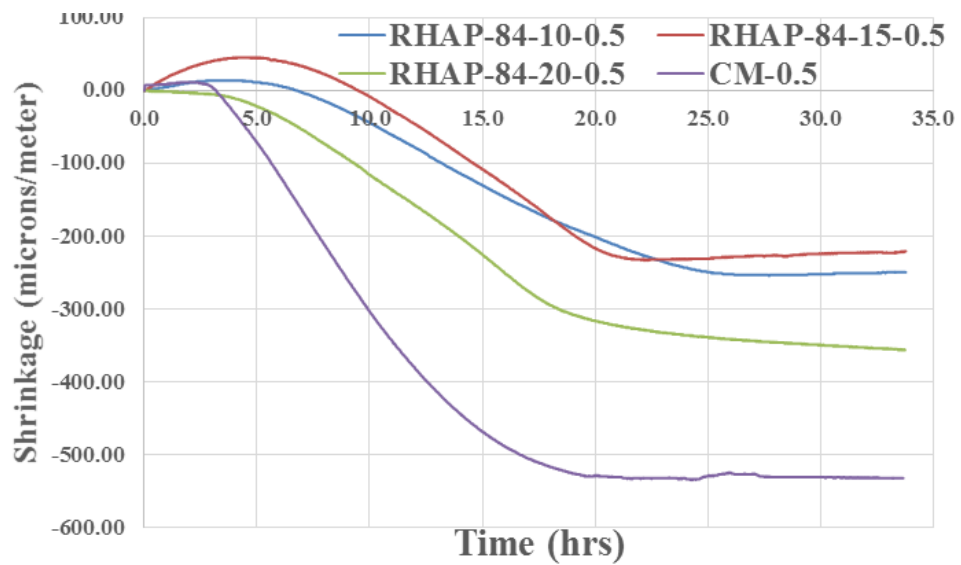


Figure 31: Shrinkage response of SCM systems containing RHAP-84-0.5 w/b

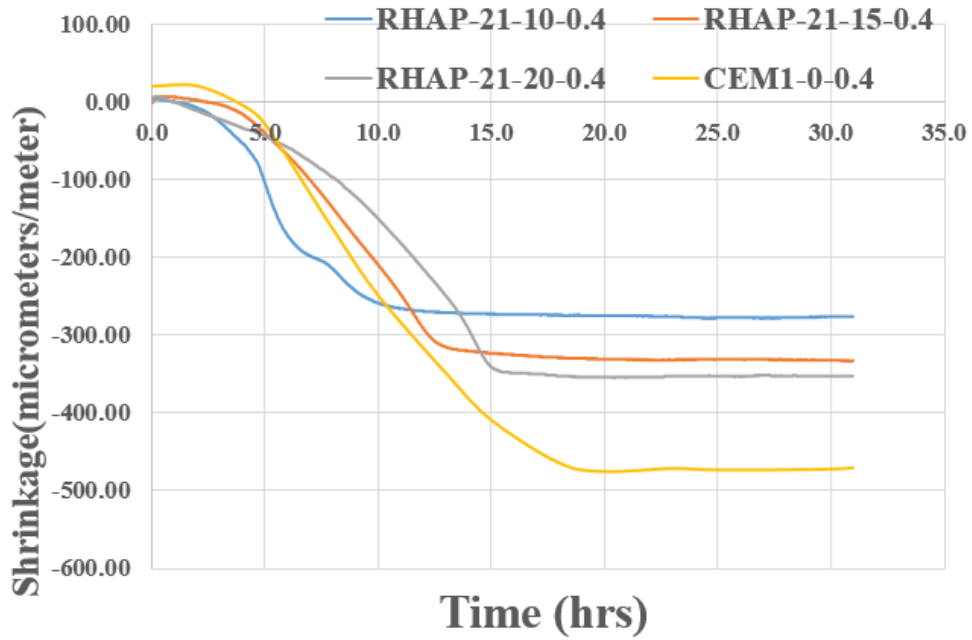


Figure 32: Shrinkage response of SCM systems containing RHAP-21-0.4 w/b

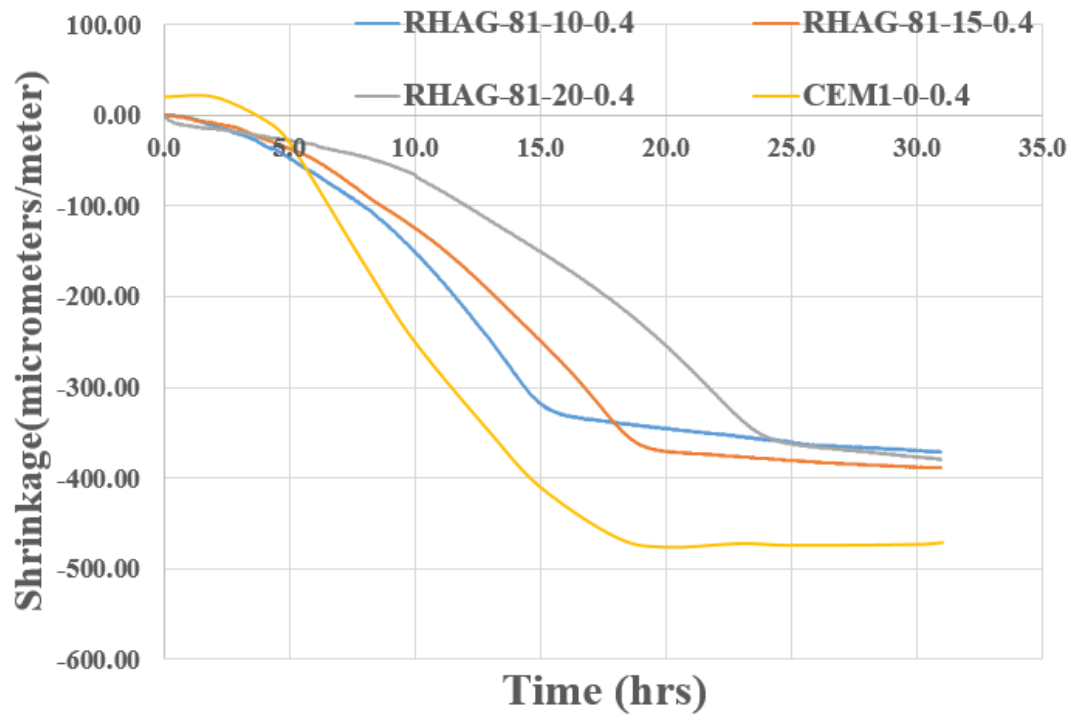


Figure 33: Shrinkage response of SCM systems containing RHAG-81-0.4 w/b

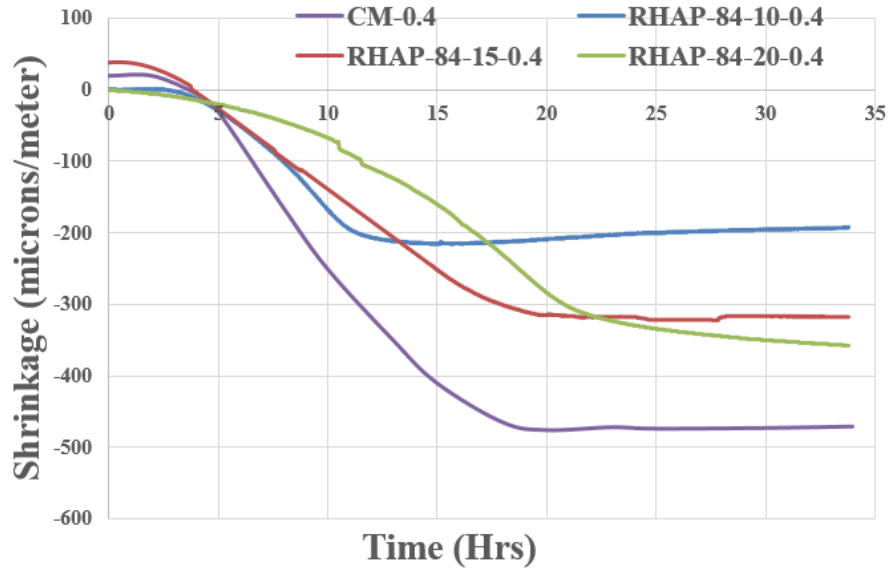


Figure 34: Shrinkage response of SCM systems containing RHAP-84-0.4 w/b

5.12 Electrical Conductivity of Saturated $\text{Ca}(\text{OH})_2$ Solution with RHAs

Variation in electrical conductivity of a saturated $\text{Ca}(\text{OH})_2$ solution give account of pozzolanic activity[16, 42, 46]. A glass beaker with 200 mL of saturated $\text{Ca}(\text{OH})_2$ solution was prepared at $40 \pm 1^\circ\text{C}$ prepared using distilled water. The beaker was placed on a hot plate to control the temperature while a magnetic mixer constantly stirred the solution gently. A digital pH meter EU Tech pH700 and electrical conductivity meter of make OAKTON, CON-II series was placed in the beaker with solution to measure the drop in electrical conductivity. 5 grams of RHAP and RHAG were added in separate tests. Table 9 tabulates the results.

System	Drop in Electrical Conductivity ($\Delta\text{mS/cm}$)
RHAP-21	3.79
RHAG-81	3.97
RHAP-84	1.93

Table 9: Variation in electrical conductivity

5.13 XRD for drop in $\text{Ca}(\text{OH})_2$ Content

XRD test were carried out on hardened samples at the age of 2, 7 and 28 days to indirectly check the pozzolanic activity of RHAs. It was seen that the intensity corresponding to peaks of 2theta angle 18.035° and 34.085° increased at 7 day while decreased with further age at 28 day. The drop in absolute intensity can be taken as a count of diffracted x-rays implying

a decrease in Ca(OH)_2 after 7 days. Higher CH peaks values usually occur at 34.085° for SCP systems however because of contamination due to aggregate in mortar systems and presence of quartz and feldspar most of the SCM systems give peaks at 18.035° [47].

SCP Formulation	Age (Days)	Absolute Intensity (18.035°)	Drop in Absolute Intensity
RHAP-21	2	331	
RHAP-21	7	484	177
RHAP-21	28	307	
RHAG-81	2	334	
RHAG-81	7	600	285
RHAG-81	28	315	
RHAP-84	2	381	
RHAP-84	7	379	13
RHAP-84	28	366	

Table 10: Absolute intensities corresponding to 2theta angle of 18.35 and 34 degrees

5.14 Electrical Conductivity of Hardened SCM Formulations containing RHA

Measure of electrical conductivity of hardened SCM samples gives us an insight on the capacity of such systems to transfer ions when a potential difference is provided at the ends of the sample. This flow is made possible by presence of ions in pore solution in the system. A lower concentration of such ions would imply that the silica present in RHA has reacted with the constituents of the matrix leaving behind lesser effective ion concentrations for a good electrical flow. Hence, a lower conductivity or its inverse, high resistivity, would imply a more reactive RHA. The tests were therefore conducted to indirectly check the effect of SiO_2 . Following table tabulates the results.

Sample Name	Electrical Conductivity (micro Siemens per meter)
CM	0.134
RHA1	0.155
RHA2	0.069
RHA3	0.135

Table 11: Electrical conductivity of hardened SCM samples containing RHAs

5.15 Thermal Conductivity of Hardened SCM Samples containing RHA

Thermal conductivity of the samples were conducted to indirectly study the porosity of the systems as thermal conductivity mostly depends on internal porosity and connectivity of these pores. A more porous system would show less conductivity and since the packing effect of SRMs is main contributor in effectively controlling total porosity, this test would give us an insight on the effect of particle size in SCMs containing RHAs. Table 7 gives results of thermal behavior of the samples containing RHA.

Sample Name	Thermal Conductivity (W/k.m)
CM	1.765
RHA1	1.438
RHA2	1.510
RHA3	1.379

Table 12: Thermal conductivity of Hardened SCM samples containing RHAs

CHAPTER 6: DISCUSSION

6.1 General

This chapter will elaborate and discuss the results shown in previous chapter.

6.2 Characterization

From the XRD results it is evident that both the RHAs are amorphous in state. The peak corresponding to 2theta angle 24° is α -Cristobalite while the second peak at 2theta angle of 27° is of crystalline form of SiO_2 , sylvite, which probably originates from use of fertilizers[27]. The XRD result of RHAP is humped shaped and is similar in shape reported by other researchers [16, 27, 48] while the shape of RHAG has relative sharper peaks which indicates lesser amorphous state level however it does not resemble the XRD patterns of crystalline RHA as shown in literature[25, 49].

The chemical analysis reveals that RHAG-81 has a higher SiO_2 content than RHAP-21 and RHAP-84. This is probably the reason that even with a higher mean particle size (MPS), D_{50} , RHAG-81 exhibits comparable strength to that of RHAP-21 and control mix. Active pozzolans are more reactive in finely divided particles however in current case the effect is being balanced out by higher silica content in RHAG-81. It can be said that if the particle size of RHAG-81 was comparable to that of RHAP-21, the overall performance of RHAG-81 would have been better than RHAP-21. Another important thing to notice here is the BET surface area value of RHAP-21. Having more surface area explains the higher water demand that RHAP-21 exhibits as compared to RHAG-81.

6.3 Water Demand

Addition of RHA tends to increase the water demand of the system[50]. RHAP-84 shows the most water demand probably due to its high surface areas. RHAP-21 has higher water demand than RHAG-84 which is attributed to higher surface area value of $21.20 \text{ m}^2/\text{g}$ of RHAP-21 and finer particle size of 20.33 microns. Decrease in particle size results in decrease in total pore volume but increases specific surface area (SSA) resulting from collapse of macro-pore RHA structure. Since the total SSA of RHA is sum of internal pore

surface area and external RHA particle area, a smaller D_{50} would mean lesser internal pore surface area and more external RHA particle area[51]. RHAG-81 has MPS of 81.83 microns, as compared to 20.33 microns of RHAP-21, with total surface area of $15.98 \text{ m}^2/\text{g}$, as opposed to $21.20 \text{ m}^2/\text{g}$ of RHAG-81, implying more water for RHAP-21 to coat the surface of the particles hence the increased water demand.

. It can be seen that water demand increases with an increase of surface area of RHA regardless of particle size. The silica in RHA reacts with lime to form calcium silicate hydrate (CSH) gel however the level of reactivity is surface assisted (depends on surface area) and is a function of temperature at which the RHA is burned[36]. A study shows change in the surface area of RHA with change in burning temperature[37] which could be another reasons other than partial burning that RHAG-84 has lowest surface put under different burning regime. Also, RHA produced after burning is usually grey in color while black color may indicate partial burning[35], RHAP-21 and RHAP-84 are grey in color while RHAG-81 is black. This partial burning of RHAG-81 could be a reason for lower surface area even at higher particle size when compared to RHAP-84 as cellulose lignin matrix is not properly burnt leaving behind a lesser porous silica skeleton. SEM images of the ashes show that all ashes have porous structure.

6.4 Setting Times

For this research a considerable change in setting times was not noticed rather a small delay in setting times is reported. Here the particle size or SiO_2 content does not play significant role as to bring about change in setting times. RHAP-84 however shows delay in setting times due to its higher surface area which leaves behind lesser effective w/b ratio for proper hydration and creates a dilution effect.

6.5 Air Content

It can be seen from the above result that SCMs containing RHAP-21 show lowest air content as opposed to RHAP-84 and RHAG-81. The lower air content of RHAP-21 can be attributed to its finer size or lower mean particle size (MPS). The smaller particles fill the gaps between the bigger particles thus lowering the overall air content and eventually the total porosity of the system in hardened state. Total porosity of the system plays a vital

role in strength of the system. RHAP-84 and RHAG-81 have bigger particle size hence higher air content. . SiO₂ does not play any role in controlling the air content. This increase in air content for RHAP-84 could be the reason for lesser strength shown by SCM formulations containing RHAP-84.

6.7 Super Plasticizer Demand of SCM Formulations for target Flow

RHAP-84 showed increase in SP dosage for the same workability level as compared to RHAP-21 and RHAG-81. RHA, in general, has high surface area due to its honeycomb structure[48] and particle type is usually angular. Larger particles would hinder smooth flow thus requiring higher dosage. RHAG has higher MPS thus the increase in SP dosage to overcome internal friction. SiO₂ content has little or no role to play in effecting SP demand.

6.8 Flow Values

Bigger particle size shows higher flow times as compared to smaller particle size. Larger particle size of RHAP-84 seems to be responsible as SCM systems containing larger particle sizes become more viscous, hinders flow and offer more internal friction. This manifests in elongated flow times which are reported in this research and corroborates the said explanation. However the use of high dosage of SP seems to increase the flow time for large particle.

6.9 Strength Test

Strength data shows rather interesting results as both ashes (RHAP-21 and RHAG-84), although with different physical and chemical properties, yield comparable results confirming indirectly the smaller particle size with lower SiO₂ may be considered equivalent in performance to bigger size and higher SiO₂ content of RHA in self-compacting mortar systems. RHAP-84 however shows poor performance in terms of strength. Strength is govern by dense microstructure and lower total porosity. RHA addresses this by two actions namely filler/packing effect and chemical pozzolanic reaction. RHA offers nucleation sites thus promoting chemical reaction. MPS also dictates filling of small macro and micro spaces thus increasing strength. RHAG-81 has high silica content and contributes

by chemical action. RHAP-21 has small MPS and good quantity of amorphous silica thus giving strengths comparable to that of control mix with even 20% replacements.

6.10 Viscosity Measurements of SCP Formulations

Increase in viscosity can be attributed to multiple reasons however adsorption and association [52] may be the primary cause in increase. At higher shear rate the viscosity decrease and it may be attributed to breakage and alignment of polysaccharides in the direction of flow. Systems incorporating bigger particle sizes tend to be more viscous and RHAG exhibits slightly higher values as compared to RHAP. Increase flow times also supplement and confirm that systems containing RHAG are more viscous. Size and shape play vital role in controlling viscosity as irregular and bigger particles offer more internal friction.

6.11 Calorimetry of SCM Formulations

Exothermic reaction is primarily a paste property and with addition of RHAP and RHAG as partial replacement the total quantity of ordinary portland cement is reduces thus delay is seen along with slight drops in peaks. RHAP-21 and RHAG-81 also participate in hydration however due to difference in rate and intensity of hydration of OPC and RHAs a delay can be noticed. Here larger particle size higher silica content seems to be delaying the hydration kinetics compared to RHAP-21.

6.12 Shrinkage of SCM Formulations

For w/b ratio of 0.5 a substantial decrease in shrinkage can be noticed. Larger particle size of RHAG-81 and RHAP-84 shows better shrinkage response due to internal restraint offered by larger particles. For w/b ratio of 0.4 the reduction in shrinkage is relatively less. This could be because of more water readily available for hydration in 0.5 w/b ration which would promote hydration as compared 0.4 w/b ratio. It is reported by other researchers that incorporating fine sized particle shows more shrinkage due to the effect of micro fine particles[53]. RHAP-21 shows more shrinkage due to its finer particle size.

6.13 Electrical Conductivity Drop of Saturated Ca(OH)₂ Solution

Containing RHAs

Saturated solution of Ca(OH)₂ is rich in Ca⁺² and OH⁻ ions and this is the primary reason for the electrical conductivity. RHA reacts in the presence of Ca(OH)₂ to reduce the concentration of the ions hence the drop in the conductivity. The values obtained from this test show a relatively good drop indicating that both the ashes are pozzolanic in nature. RHAG offers higher silica content while RHAP having smaller particle size would be more reactive even at lower silica content this is the reason that both ashes shows comparable drops.

6.14 XRD for drop in Ca(OH)₂ Content

From the XRD results it can be seen that there is a drop in concentration of calcium hydroxide after 7 days of age indicating consumption of Ca(OH)₂ by silica in the ashes to precipitate hydration products. Absolute intensity can be taken as a count of quantity of calcium hydroxide present in the system. The results support the drop in electrical conductivity test conducted on saturated solutions of Ca(OH)₂ as RHAP-21 and RHAG-81 show good electrical conductivity drops and drops in absolute intensity counts while RHAG-84 shows poor results in both tests. The Silica content of RHAG-81 seems to take lead over the particle size and produce better results.

6.15 Electrical Conductivity of Hardened SCM Formulations containing RHA

Flow of electric charge is mainly attributed to the presence of ions in the system. For a non-hindered electrical flow the ions in micro and macro pores of the system align themselves in an orderly manner to direct non opposed electric flow[54]. RHA2 shows lower flow as opposed to the other two implying that the higher silica content consumes ions in presence of moisture and makes hydration products. This could be the primary reason for good strength of samples containing RHA2 even with larger particle size as opposed to samples containing RHA1 whose finer size/filler effect seems to counter the lack of higher silica content.

6.16 Thermal Conductivity of Hardened SCM Samples containing RHA

Thermal conductivity of air is 0.026 W/km where as it is 1-3 W/km for concrete stone but thermal conductivity depend greatly on amount of pores and their inter connectivity[55]. A porous sample would therefore show lower conductivity values and imply a sample with more air content. This test gives an insight in to the micro structure of the samples and the results show that RHA3 shows the lowest values of thermal conductivity. Air content test performed on fresh state of SCM system containing RHA3 also shows the most air content for samples with RHA3. RHA2 shows more conductivity which could mean that over time the silica content hydration results in good products which fill the pores with age and gain strength.

CHAPTER 7: CONCLUSION

- 1 20% addition of RHA3 (largest particle size) approximately doubles the water demand attributed to its higher surface area and requires approximately 2.35 times higher SP dosage compared to control mix, to overcome internal friction. Larger particle size shows more viscosity, extended flow times and entrains more air.
- 2 Larger particle size shows better volumetric stability, RHA3 shows 32.3% reduction in early age linear shrinkage as opposed to finer particle size for lower w/b ratio.
- 3 RHA with higher silica content and bigger particle size (RHA2) is more reactive with RHA having finer particle size and lower silica content (RHA1).
- 4 Reactivity of RHA depends more on silica content than surface area as RHA with higher silica content and lower surface area showed better results with RHA having low silica content but higher surface area. Silica content in RHA can be termed more important in strength development than particle size.
- 5 Electrical and thermal conductivity indicate that RHA2, due more silica content, seems to decrease the porosity in hardened state as opposed to fresh state possibly by precipitation of hydration products of reaction between silica content with calcium hydroxide.

References

- [01] Md Safiuddin, "Development of self-compacting high performance concrete incorporating rice husk ash", Ph.D Thesis, University of Waterloo, 2008.
- [02] P.K.Mehta, "Rice Hush Ash-A unique supplementary cementing material", Proceedings of CAMNET/ACI Internaional Symposium on Advances in Concrete Technology" V.M. Malhotra, ed., Athens, Greece, 1992: p. 407-430.
- [03] Okamura H. and Ouchi M., "Self-Compacting High Performance Concrete." Proceedings of Structural Engineering and Materials, 1998. Vol. 1 Issue No. 4, pp. 378-383.
- [04] The European Guidelines for Self-Compacting Concrete, Specification, Production and Use.
- [05] R.J Detwiler, "The Microstructure of Durable Concrete. Proceedings" 6th International Colloquium on Concrete in Developing Countries, Lahore Pakistan (Ed's S. A. Sheikh and S. A. Rizwan), January 4-6, 1997: p. 459-468.
- [06] D.D.Bui, "Rice husk ash as a mineral admixture for high performance concrete", Ph.D Thesis, Delft University, 2001.
- [07] S.A. Rizwan, "High performance mortars and concretes using secondary raw materials", Ph.D Thesis, TU Freiberg Germany, 2006.
- [08] Post, W., <https://www.washingtonpost.com/news/work/wp/2015/03/24/how-china-used-more-cement-in-3-years-than-the-u-s-did-in-the-entire-20th-century/>.
- [09] Okamura H. and Ouchi M., "Self-Compacting Concrete", Journal of Advanced Concrete Technology, April 2003. Vol. 01, Issue No. 1, pp. 5-15.
- [10] V.M.Malhotra, "Fly Ash, Slag, Silica Fume and Rice Husk Ash in Concrete: A Review". Concrete International, 1993. Vol. 15: p. 23-28.
- [11] P. Dale, "Effect of Cement Particle Size Distribution on Performance Properties of Portland Cement Based Materials". Cement and Concrete Research Vol. 29 1999, pp 1663-1671.
- [12] Detwiller and P.K. Mehta, "Chemical and Physical Effects of Silica Fume on the Mechanical Behaviour of Concrete". ACI Materials Journal 1989, Vol. 86, Issue No. 06, pp. 609-614.
- [13] S.A. Rizwan, T.A. Bier, "Self-consolidating mortars using various secondary raw materials", ACI Materials Journal, 106-M04, 2009, pp25-33.
- [14] S.A. Rizwan, T.A. Bier, "Self-consolidating mortars using various secondary raw materials", ACI Materials Journal, 106-M04, 2009, pp25-33.

- [15] P.K. Mehta, "Natural Pozzolans, Supplementart Cementing Materials for Concrete" Canadian Government Publishing Center, CANMET-SP-86-8E, Ottawa., 1987.
- [16] J.Qujin, "The reaction between rice husk ash and $\text{Ca}(\text{OH})_2$ solution and the nature of its products", Cement and Concrete Research 1999, Vol. 29, pp. 37-43.
- [17] ACI-363R-92, "State of the Art Report on High Strength Concrete". ACI Detroit, USA., Reapproved 1997.
- [18] T.Sasatani, K. Torri, and M. Kawamura, "Five Year Exposure Test on Long-Term Properties of Concretes Containing Fly Ash, Blast Furnance Slag and Silica Fume". Proceedings of Fifth International Conference on Fly Ash, Slag and Natural Pozzolans in Concrete, Milwaukee, USA, SP-153, V.M Malhotra, ed., American Concrete Institute, Farmington Hills, Mich., 1995: p. 238-296.
- [19] A. Bilodeau and V.M. Malhotra, "Concrete Incorporating High Volumes of ASTM Class F Fly Ashes: Mechanical Properties and Resistance to Deicing Salt Scaling and to Chloride-Ion Penetration". Proceedings of Fourth International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Istanbul, Turkey, SP-132, V.M Malhotra ed., American Concrete Institute, Farmington Hills, Mich., 1992: p. pp 319-349.
- [20] V. Ramasamy, "Compressive strength and durability properties of rice husk ash concrete", KSCE Journal of Civil Engineering 2011, Vol.16, Issue 01, pp. 93-102.
- [21] N.Maeda, et al., "Chloride Diffusivity of Concrete Incorporating Rice Husk Ash". Fifth CANMET/ACI International Conference on Recent Advances in Concrete Technology, 2001: p. pp 291-308.
- [22] Zhang and Malhotra, "High-Performance Concrete Incorporating Rice Husk Ash as a Supplementary Cementing Material". ACI Materials Journal, Title No. 93-M72.
- [23] Safiuddin, S. West, and A. Soudki, "Properties of Freshly Mixed Self-Consolidating Concretes Incorporating Rice Husk Ash as a Supplementary Cementing Material". Construction and Building Materials 2012, Vol. 30, pp. 833-842.
- [24] G.R. Sansale, "Effect of rice husk ash on durability of cementitious materials", Cement and Concrete Composites 2010, Vol. 32 Issue 09, pp. 718-725.
- [25] D.G. Nair, A. Fraaij, A.K.Klaassen, P.M. Kentgens, "A structural investigation relating to the pozzolanic activity of rice husk ashes", Cement and Concrete Research 2008, Vol. 38, pp. 861-869.

- [26] S. Yoshida, Y. Onishi, and K. Kitagishi, "The Chemical Nature of Silica in Rice Plant". *Journal of Soil, Plant and Food*, 1959 Issue No. 5, pp 23-27.
- [27] Zhang and Malhotra, "Rice Husk Ash Paste and Concrete: Some Aspects of Hydration and the Microstructure of the Interfacial Zone Between the Aggregate and Paste". *Cement and Concrete Research* 1996, Vol. 26, pp. 936-977.
- [28] M.H. Govindarao, "Utilization of Rice Husk, A Preliminary Analysis". *Journal of Science and Industrial Research* 1980. Vol. 39, pp 495-515.
- [29] D.F Houston, "Rice Hulls ". *Rice Chemistry and Technology* (Ed. D.F Houston), American Association of Cereal Chemists, St. Paul, Minnesota, 1972, pp 301-352.
- [30] A. Kaupp, "Gasification of Rice Hulls". Vieweg, Braunschweig, 1984.
- [31] M.A. Concotto, V. Agopyan, and V.M. John, "Optimization of Rice Husk Ash Production". *Vegetable Plants and Their Fibres as Building Materials*, Proceedings Second International RILEM Symposium, Salvador, Bahia , Brazil (Ed. S.M Sobral) Chapman and Hall, London, Sep 17-21 1990: p. pp 334-341.
- [32] M. Nehdi, J. Duquette, and A.E. Damatty "Performance of rice husk ash produced using a new technology as an admixture in concrete", *Cement and Concrete Research* 2003, Vol.33, pp. 1203-1210.
- [33] J. James, and M.S. Rao, "Reactivity of Rice Husk Ash". *Cement and Concrete Research* 1986. Vol. 16, pp 329-336.
- [34] M.A. Hammad, I.A.Khattab, "Effect of the combustion process on the structure of rice husk silica", *Thermochimica Acta*, 1981, pp. 343-349.
- [35] M.S. Ismail, and A.M. Walliuddin, "Effect of Rice Husk Ash on High Strength Concrete". *Construction and Building Materials* 1996. Vol. 10 Issue No. 07, pp 521-526.
- [36] J. James, and M.S. Rao, "Reactivity of Rice Husk Ash". *Cement and Concrete Research* 1986. Vol. 16, pp 329-336.
- [37] J. James, and M.S. Rao, "Characterization of Silica in Rice Husk Ash". *The American Ceramics Society Bulletin*, 1986. Vol. 65 Issue No. 8, pp. 1177-1180.
- [38] T.H Liou, and F.W. Chang, "The Nitridation Kinetics of Pyrolyzed Rice Husk Ash". *Industrial Engineering and Chemical Research* 1996. Vol. 35 Issue No. 10, pp 3375-3383.
- [39] D.M. Ibrahim, and M. Helmy, "Crystallite Growth of Rice Husk Silica". *Thermochimica Acta*, 1981, Vol. 45, pp 79-85.

- [40] S. Hanafi, et al., "Surface Properties of Silica Produced by Thermal Treatment of Rice Husk Ash". *Thermochimica Acta*, 1980. Vol. 37, pp 137-143.
- [41] D.M. Ibrahim, et al., "Thermal Treatment of Rice Husk Ash:Effect of Firing on Pore Structure and Crystallite Size". *Thermochimica Acta*, 1980. Vol. 37, pp 347-351.
- [42] D.D.Bui, "Rice Husk Ash a Mineral Admixture for High Performance Concrete" [PhD] Thesis, Delft University 2001.
- [43] Arum, C., "Effects of Packing Densities of Aggregates on Workability and Strength of Concrete". *Proceedings 4th West Africa Built Environment Research (WABER) Conference, Abuja, Nigeria, 299-312., 24-26 July 2012.*
- [44] G. Sua, and N. Mukul, "The Use of Residual Rice Husk Ash from Thermal Power Plant as Cement Replacement in Producing Self-Compacting Concrete". *Advanced Materials Research Vols 415-417*, pp 1490-1495. Trans Tech Publications, Switzerland.
- [45] Le, H.T., Nguyen, S.T. & Ludwig, HM, "A study on high performance fine-grained concrete containing rice husk ash", *Concrete Structure Materials 2014*, Vol. 8, Issue 04, pp. 301-307.
- [46] M.P.Luxan, F.Madruga, J.Saavedra, "Rapid evaluation of pozzolanic activity of natural products by conductivity measurements", *Cement and Concrete Research* 1989, Vol. 19, pp. 63-68.
- [47] S.A. Rizwan, T.A. Bier, "Applications of XRD, Calorimetry, Thermal Analysis Techniques in the Study of Hydration Kinetics of High Performing Self-Compacting Cement Based Systems", *ACTA*, September 30, 2014, Islamabad, pp-84-102.
- [48] Zhang, and V.M. Malhotra, "High Performance Concrete Incorporating Rice Husk Ash as a Supplementary Cementing Material". *ACI Materials Journal*, 1996. Title No. 93-M72: p. 629-636.
- [49] Nair, D.G., Jagadish. K.S, and A. Faraji, "Reactive Pozzolanas From Rice Husk Ash: An Alternative to Cement For Rural Housing". *Cement and Concrete Research* 2006, Vol 36, pp 1062-1071.
- [50] Le, H.T., Nguyen, S.T. & Ludwig, HM, "A study on high performance fine-grained concrete containing rice husk ash", *Concrete Structure Materials 2014*, Vol. 8, Issue 04, pp. 301-307.
- [51] L.Thanh, M. Kraus, K.Siewert, M. Ludwig, "Effect of Macro-Mesoporous Rice Husk Ash on Rheological Properties of Mortar Formulated from Self-

- Compacting High Performance Concrete”, *Construction and Building Materials* 2015, Vol. 80, pp. 225-235.
- [52] K.H.Khayat, "Viscosity Enhancing Cement-Based Systems", *Cement and Concrete Composites* 1998, Vol. 20, pp 367-376.
- [53] G.A. Habeeb, M.M Fayyadh, “Rice Husk Ash Concrete: The Effect of RHA Average Particle Size on Mechanical Properties and Drying Shrinkage”. *Australian Journal of Basic and Applied Sciences* 2009, Vol. 03: p. 1616-1622.
- [54] Madhavi and Annamalai, "Electrical Conductivity of Concrete". *ARNP Journal of Engineering and Applied Sciences*, 2016. Vol. 11(Issue No. 09): p. pp 5979-5982.
- [54] Mnahoncakova, Milena, Pavlik, Lukas and Pavla, Effect of Moisture on Thermal Conductivity of Cementitious Composite" *European Conference on Thermo-physical Properties*, 2005, Slovak Republic.

1. Safiuddin, "Development of Self-Consolidating High Performance Concrete Incorporating Rice Husk Ash". [Ph.D] Thesis, University of Waterloo 2008.
2. Mehta, P.K., *Rice Husk Ash- A Unique Supplementary Cementing Material*. Proceeding of "CAMNET/ACI International Symposium on Advances in Concrete Technology" V.M. Malhotra, ed., Athens, Greece, 1992: p. 407-430.
3. Okamura H and Ouchi M, *Self-Compacting High Performance Concrete*. Proceedings of Structural Engineering and Materials, 1998. **1 (4)**: p. 378-383.
4. The European Guidelines for Self-Compacting Concrete, Specification, Production and Use.
5. Detwiler and R.J, *The Microstructure of Durable Concrete*. Proceedings "6th International Colloquium on Concrete in Developing Countries, Lahore Pakistan (Ed's S. A. Sheikh and S. A. Rizwan), January 4-6, 1997: p. 459-468.
6. Bui, D., *Rice Husk Ash as a Mineral Admixture for High Performance Concrete*. [Ph.D thesis] Delft University, 2001.
7. Ali, R.S., *High Performance Mortars and Concretes Using Secondary Raw Materials*. [Ph.D thesis] TU Frieberg Germany, 2006.
8. Post, W., <https://www.washingtonpost.com/news/wonk/wp/2015/03/24/how-china-used-more-cement-in-3-years-than-the-u-s-did-in-the-entire-20th-century/>.
9. Okamura H, O.M., *Self-compacting Concrete*. Journal of Advanced Concrete Technology, April 2003. **01**, (No. 1): p. 5-15.
10. Malhotra, V.M., "Fly Ash, Slag, Silica Fume and Rice Husk Ash in Concrete: A Review". Concrete International, 1993. **Vol. 15**: p. 23-28.
11. Dale, P., "Effect of Cement Particle Size Distribution on Performance Properties of Portland Cement Based Materials". Cement and Concrete Research 29 (1999) 1663-1671, 1999.
12. Detwiler, R.J. and P.K. Mehta, "Chemical and Physical Effects of Silica Fume on the Mechanical Behaviour of Concrete". ACI Materials Journal, 1989. **86(06)**: p. 609-614.
13. Rizwan, S.A. and T.A. Bier, "Self-Compacting Mortars Using Various Secondary Raw Materials". ACI Materials Journal, 2009. **01**.
14. Rizwan, S.A. and T.A. Bier, "Self-Consolidation Mortars Using Various Secondary Raw Materials". ACI Materials Journal, 2009. **106-M04**: p. 25-32.
15. Mehta, P.K., "Natural Pozzolans, Supplementary Cementing Materials for Concrete" Canadian Government Publishing Center, CANMET-SP-86-8E, Ottawa., 1987.
16. Qijun, *The Reaction Between Rice Husk Ash and Ca(OH)₂ Solution and The Nature of its Products*. Cement and Concrete Research 29 (1999) 37-43.
17. ACI-363R-92, "State of the Art Report on High Strength Concrete". ACI Detroit, USA., Reapproved 1997.
18. T.Sasatani, K. Torri, and M. Kawamura, "Five Year Exposure Test on Long-Term Properties of Concretes Containing Fly Ash, Blast Furnance Slag and Silica Fume". Proceedings of Fifth International Conference on Fly Ash, Slag and Natural Pozzolans in Concrete, Milwaukee, USA, SP-153, V.M Malhotra, ed., American Concrete Institute, Farmington Hills, Mich., 1995: p. 238-296.
19. Bilodeau, A. and V.M. Malhotra, "Concrete Incorporating High Volumes of ASTM Class F Fly Ashes: Mechanical Properties and Resistance to Deicing Salt Scaling and to Chloride-Ion Penetration". Proceedings of Fourth International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Istanbul, Turkey, SP-132, V.M Malhotra ed., American Concrete Institute, Farmington Hills, Mich., 1992: p. pp 319-349.

20. V.Ramasamy, *Compressive Strength and Durability Properties of Rice Husk Ash Concrete*. KSCE Journal of Civil Engineering January 2011. **16**(01): p. 93-102.
21. N.Maeda, et al., "*Chloride Diffusivity of Concrete Incorporating Rice Husk Ash*". Fifth CANMET/ACI International Conference on Recent Advances in Concrete Technology, 2001: p. pp 291-308.
22. Zhang and Malhotra, "*High-Performance Concrete Incorporating Rice Husk Ash as a Supplementary Cementing Material*". ACI Materials Journal, Title No. 93-M72.
23. Safiuddin, S. West, and A. Soudki, "*Properties of Freshly Mixed Self-Consolidating Concretes Incorporating Rice Husk Ash as a Supplementary Cementing Material*". Construction and Building Materials 30, 833-842, 2012.
24. Sansale, G.R.d., *Effect of Rice Husk Ash on Durability of Cementitious Materials Cement and Concrete Composites* 2010. **32**(09): p. 718-725.
25. Nair, D.G., et al., "*A Structural Investigation Relating to the Pozzolanic Activity of Rice Husk Ashes*". Cement and Concrete Research 38 pp 861-869, 2008.
26. Yoshida, S., Y. Onishi, and K. Kitagishi, "*The Chemical Nature of Silica in Rice Plant*". Journal of Soil, Plant and Food, 1959(Issue No. 5): p. pp 23-27.
27. Zhang and Malhotra, "*Rice Husk Ash Paste and Concrete: Some Aspects of Hydration and the Microstructure of the Interfacial Zone Between the Aggregate and Paste*". cement and Concrete Research 26 (1996) 936-977, 1996.
28. Govindarao, M.H., "*Utilization of Rice Husk, A Preliminary Analysis*". Journal of Science and Industrial Research, 1980. **Vol. 39**: p. pp 495-515.
29. Houston, D.F., "*Rice Hulls*". Rice Chemistry and Technology (Ed. D.F Houston), American Association of Cereal Chemists, St. Paul, Minnesota, 1972: p. pp 301-352.
30. Kaupp, A., "*Gasification of Rice Hulls*". Vieweg, Braunschweig, 1984.
31. Concotto, M.A., V. Agopyan, and V.M. John, "*Optimization of Rice Husk Ash Production*". Vegetable Plants and Their Fibres as Building Materials, Proceedings Second International RILEM Symposium, Salvador, Bahia , Brazil (Ed. S.M Sobral) Chapman and Hall, London, Sep 17-21 1990: p. pp 334-341.
32. Nehdi, M., J. Duquette, and A.E. Damatty, "*Performance of Rice Husk Ash produces using a new technology as an admixture in concrete*". Cement and Concrete Research 33, pp 1203-1210, 2003.
33. James and Rao, "*Silica From Rice Husk Through Thermal Decomposition*". Thermochemica Acta 1986: p. 329-336.
34. Hammad and Khattab, "*Effet of the Combustion Process on the Structure of Rice Husk Silica*". Thermochemica Acta, 1981: p. 343-349.
35. Ismail, M.S. and A.M. Walliuddin, "*Effect of Rice Husk Ash on High Strength Concrete*". Construction and Building Materials 1996. **Vol. 10**(No. 07): p. pp 521-526.
36. James, J. and M.S. Rao, "*Reactivity of Rice Husk Ash*". Cement and Concrete Research 1986. **Vol. 16**: p. pp 329-336.
37. James, J. and M.S. Rao, "*Characterization of Silica in Rice Husk Ash*". The American Ceramics Society Bulletin, 1986. **Vol. 65**(No. 8): p. 1177-1180.
38. Liou, T.H. and F.W. Chang, "*The Nitridation Kinetics of Pyrolyzed Rice Husk Ash*". Industrial Engineering and Chemical Research 1996. **Vol. 35**(No. 10): p. pp 3375-3383.
39. Ibrahim, D.M. and M. Helmy, "*Crystallite Growth of Rice Husk Silica*". Thermochemica Acta, 1981. **Vol. 45**: p. pp 79-85.
40. Hanafi, S., et al., "*Surface Properties of Silica Produced by Thermal Treatment of Rice Husk Ash*". Thermochemica Acta, 1980. **Vol. 37**: p. pp 137-143.

41. Ibrahim, D.M., et al., "*Thermal Treatment of Rice Husk Ash:Effect of Firing on Pore Structure and Crystallite Size*". *Thermochimica Acta*, 1980. **Vol. 37**: p. pp 347-351.
42. D.D.Bui, "*Rice Husk Ash a Mineral Admixture for High Performance Concrete*" [PhD] Thesis, Delft University 2001.
43. Arum, C., "*Effects of Packing Densities of Aggregates on Workability and Strength of Concrete*". *Proceedings 4th West Africa Built Environment Research (WABER) Conference, Abuja, Nigeria, 299-312.*, 24-26 July 2012.
44. Sua, G. and N. Mukul, "*The Use of Residual Rice Husk Ash from Thermal Power Plant as Cement Replacement in Producing Self-Compacting Concrete*". *Advanced Materials Research Vols 415-417*, pp 1490-1495. Trans Tech Publications, Switzerland.
45. AW, S., J. HM, and S. SP, "*New Methodology For Designing Self-Compacting Concrete*". *ACI Materials Journal*, 2001. **Vol. 98, No. 6**.
46. Luxan, M.P., F.Madruga, and J. Saavedra, "*Rapid Evaluation of Pozzolanic Activity of Natural Products by Conductivity Measurements*". *cement and Concrete Research* 19 63-68, 1989.
47. Rizwan, S.A. and T.A. Bier, "*Applications of XRD, Calorimetry, Thermal Analysis Techniques in the Study of Hydration Kinetics of High Performing Self-Compacting Cement Based Systems*". *ACTA* 2014, September 30, 2014: p. pp84-102.
48. Zhang, M.-H. and V.M. Malhotra, "*High Performance Concrete Incorporating Rice Husk Ash as a Supplementary Cementing Material*". *ACI Materials Journal*, 1996. **Title No. 93-M72**: p. 629-636.
49. Nair, D.G., J. K.S, and A. Faraji, "*Reactive Pozzolanas From Rice Husk Ash: An Alternative to Cement For Rural Housing*". *cement and Concrete Research* 36 (2006) 1062-1071, 2006.
50. HT, L., N. ST, and L. HM, "*A Study on High Performance Fine-Grained Concrete Containing Rice Husk Ash*". *Concrete Structure Materials* 2014. **8(4)**: p. 301-307.
51. Thanh, I., et al., "*Effect of Macro-Mesoporous Rice Husk Ash on Rheological Properties of Mortar Formulated from Self-Compacting High Performance Concrete*". *Construction and Building Materials* 80, 225-235, 2015.
52. K.H.Khayat, "*Viscosity Enhancing Cement-Based Systems*". *Cement and Concrete Composites*, 1998. **Vol. 20**.
53. G.A.Habeeb and M.M.Fayyadh, "*Rice Husk Ash Concrete:The Effect of RHA Average Particle Size on Mechanical Properties and Drying Shrinkage*". *Australian Journal of Basic and Applied Sciences*, 2009. **03**: p. 1616-1622.
54. Madhavi and Annamalai, "*Electrical Conductivity of Concrete*". *ARPN Journal of Engineering and Applied Sciences*, 2016. **Vol. 11**(Issue No. 09): p. pp 5979-5982.
55. Mnahoncakova, et al., "*Effect of Mixture on Thermal Conductivity of Cementitious Composite*".