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Self-Compacting Paste Systems Containing Secondary Raw Materials

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Abstract

Self-compacting paste (SCP) systems are the vehicles for the transport of aggregates within self-compacting mortar and concrete systems. SCP systems incorporating different types of cements and secondary raw materials (SRM's) were studied for SRM particle characteristics and powder parameters including water demand (WD), setting times and flow. Strength, early volume stability and microstructure of SCP systems are also reported. The results showed that SRM particle characteristics have a significant bearing on the system's WD, super-plasticizer demand (SPD), strength and microstructure. Inclusion of pozzolanic SRM's in SCP systems as ten per cent cement replacements increased the strength and durability due to three parallel operative mechanisms of filler (physical), hydration and pozzolanic actions (chemical).

Keywords

Self-compacting pastes, Particle morphology, Flow, Strength, Microstructure and early volume stability

1. Introduction

Self-compacting concrete is a new "technology of the decade" in construction. It is likely to replace the conventional concrete used in construction in near future at least in the developed world. SCP systems are the vehicles for the transport of aggregates present in the self-compacting mortar (SCM) systems and self-compacting concrete (SCC) systems. SCP systems are immensely important but have rarely been studied. SRM's are added to cementitious systems to modify and to improve the desired properties of modern cement based systems in both fresh and hardened states. The properties of modern high performance concrete (HPC) and SCC depend very significantly on the properties of SCP systems (ACI 209R-92, Almudaiheem and Hansen 1989, Ferraris and Gaidis 1992, Guo 1994, Uno 1998). A typical study program on SCP systems may start with the SRM particle characterization by using various methods including laser technique, scanning electron microscopy (SEM) and vapor sorption. Once SRM surface morphology, internal porosity and particle texture are known and understood, it becomes easy to explain the results regarding water demand (WD), flow, strength, microstructure and early volume stability of self-compacting cementitious systems (SCCS). Both amorphous rice hush ash (RHA) and crystalline rice husk ash (RHAP) and as produced powdered SF were selected as SRM's for the comparison purposes of the resultant properties of the SCP systems. Simultaneous use of RHAP and RHA in similar mix proportions of SCP systems would highlight the response differences of the amorphous and crystalline rice-husk ashes. Usually such SRM/(s) should be used which optimize WD and flow and also increase the strength due to pore refinement effect realized by simultaneously operating filler action, hydration and pozzolanic mechanisms attributable to physical and chemical processes.

2. Research Significance

The technology of SCC is the most recent, innovative and has been termed as the "technology of the decade" wherein paste phase is the vehicle for the transport of aggregate phase during flow of SCCS. The properties of hardened mortars or concretes depend on paste component to a great extent. Performance of concrete structures also depends on properties of paste phase as all reinforced concrete deterioration processes attack and operate through the paste phase. Surprisingly there is not enough reported research on SCP systems using various SRM's. In agricultural developing countries, suitable amorphous rice-husk ash can be used as SRM in place of SF in SCCS (Rizwan, 2006). During manufacturing process, it is possible that the resultant ash may become crystalline instead, particularly in the absence of a sophisticated and controlled incineration process like fluidized bed technology. The response of SCCS containing rice husk ashes depends largely on the type and properties of ash used. This paper compares the properties of SCP systems containing various secondary raw materials including SF, amorphous rice-husk ash (RHA) and crystalline rice-husk ash (RHAP).

3. Materials

The materials used in this investigation consisted of German cements CEM I 42.5R, CEM II –B/S 32.5R (30 % blast-furnace slag) and CEM III/B 32.5 N NW/HS/NA (70 % blast-furnace slag). SRM's consisted of amorphous and crystalline rice-husk ashes (RHA and RHAP respectively) and as produced silica fume (SF) of Germany. Melflux by BASF construction chemicals Germany, a third generation poly-carboxylate ester (PCE) type powder super plasticizer (SP), has been used for producing flow target of around 30 cm measured by Hagerman's' mini slump cone of 6x7x10 cm dimensions.4x4x16 cm prisms were cast, cured and tested for various parameters as per DIN EN 196 standard. BET surface areas of powders were measured by Beckmann Coulter LS 230 Laser granulometer. Table 1 gives the physical and chemical properties of powders used.

Table 1: Physical and Chemical Properties of Powders used in the Study

Parameters	**CEM I**	**CEM II**	**CEM III**	**RHA**	**RHAP**	**SF**
Specific gravity	3.15	2.99	2.97	2.26	2.45	2.36
Particle size (d50), µm	18.42	21.13	14.38	6.80	6.17	12.16
BET surface areas, m^2/g	1.098	1.229	3.230	28.920	2.520	20.450
Chemical Analysis						
Loss on ignition	2.75	5.45	0.75	4-6	0.28	1.60
Silicon Dioxide	19.17	22.17	28.13	90.0+%	88.0	95%
Aluminum Oxide	5.21	7.08	10.02	<0.01	3.73	0.20
Ferric Oxide	2.39	1.66	0.94	0.032	1.67	0.05
Calcium Oxide	61.12	52.44	42.38	0.60	1.49	0.25
Magnesium Oxide	2.78	4.39	8.36	0.37	0.90	0.40
Sulfur Trioxide	3.30	4.04	5.98	0.14	0.21	-
Sodium Oxide	1.25	1.00	0.94	0.14	0.78	0.10
Potassium Oxide	1.01	0.99	0.78	2.30	1.26	1.20

4. SRM Shapes

SEM technique used FEI XL 30 environmental scanning electron microscope with field emission gun (ESEM FEG). Figure 1 shows the SEM pictures of SF, RHA and RHAP which have been used as SRM's. The shape, size, surface texture and internal porosity of SRM's effect properties of SCCS in fluid and hardened state. They also affect WD and adsorption of super-plasticizer (SP) on cement/SRM particles. SRM particle characterization details can be seen elsewhere (Rizwan, 2006, Rizwan and Bier, 2006b, Rizwan and Bier, 2009).

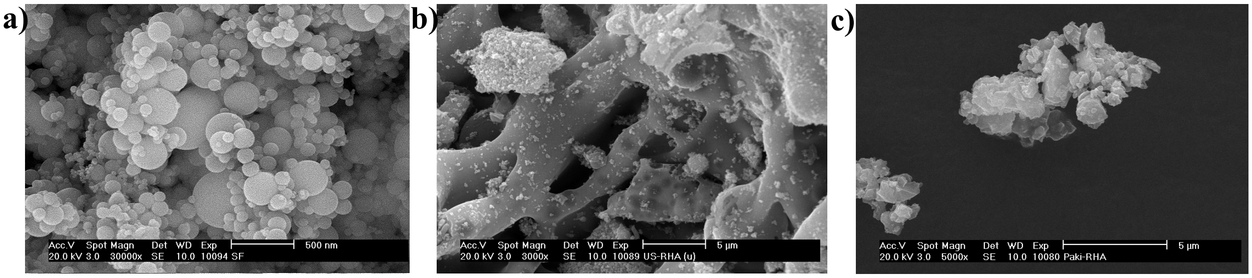

Figure 1: (a) SF (b) RHA-Amorphous (c) RHAP - Crystalline

5. Mixing and Curing Regimes

The mixing was done using Hobart Toni Technik mixer. The dry constituents of pastes along with powder type SP were manually mixed first and were then fed into the bowl of mixer containing the required mixing water content. Slow mixing (145 rpm) was done for 30 seconds and then interior of the bowl was cleaned. Thereafter, the formulations received 150 seconds of fast mixing (285 rpm). The RHA formulations needed slightly more mixing time and looked very viscous due to irregular, abrasive and internally porous particles of RHA. Flow was measured and 4x4x16 cm prisms were cast for flexural and compressive testing at various ages as per DIN EN196 and linear initial shrinkage measurements were also made. Curing, casting and testing were done in accordance with DIN EN 196. Thereafter samples were marked, weighed and put in water at 20°C after first 24 hours of moist air curing (r.h > 90 %) and were then subsequently tested in saturated surface dry (SSD) condition.

6. Results

6.1 Water Demand

The WD of SCC consists of WD of powders and aggregates. WD of powders is about 95% of the WD of SCC formulation (Rizwan, 2006). Therefore an approximate idea about the WD of SCC mix can be obtained even from the WD of the powders. Tables 2 and 3 give the WD and Vicat setting- times of various cements incorporating the three SRM's used in this study.

For 5% RHA in CEM I, the initial and final setting times were four hours and fourteen minutes and five hours and four minutes respectively. For 10 % RHA, these times were six hours and seventeen minutes and more than seven hours respectively. For 5% RHAP in CEM I, the water demand was 31.5% and setting times were 2.6 and 2.86 hours respectively. While at 10% RHAP in CEM I, the water demand was 34% and setting times were 2.74 and 3.51 hours respectively. SRM's had a mass of 10% of the mass of cement were added to cements as replacements.

Table 2: Water Demands and Setting Times of Cements with SF

No.	SF, %	CEM I			CEM II			CEM III		
		WD^a, %	IST	FST	WD^a, %	IST	FST	WD^a, %	IST	FST
1	0	29.5	3-10	3-40	27.0	3-24	3-47	29.5	4-07	4-47
2	5	32.5	3-06	3-32	28.5	3-22	4-02	32.0	4-28	5-12
3	10	37.0	3-15	3-34	32.0	3-33	4-00	36.5	5-42	6-07
4	15	41.5	3-30	3-42	37.0	4-29	4-46	41.5	5-57	6-17
5	20	47.5	4-01	4-10	44.0	4-45	4-57	47.5	-	-

[a] WD is in per cent of cement mass. Vicat initial setting time **(IST)** and final setting time **(FST)** are in hours and minutes.

Table 3: Water Demands of Cement Systems with RHA

Water Demand, %	CEM I with RHA, %			CEM II with RHA, %			CEM III with RHA, %		
	0	5	10	0	5	10	0	5	10
	29.5	32.5	35	27	28.5	31	29.5	33	36

6.2 MIP of SRM's

In MIP measurements, Autoscan 33 Porosimeter was used and the contact angle was taken as 140^o and the specimens were oven dried at 110^{o}C for 24 hours in order to stop hydration. Figure 2 gives the MIP results of SRM's used and a magnified image of SEM picture of SF particles.

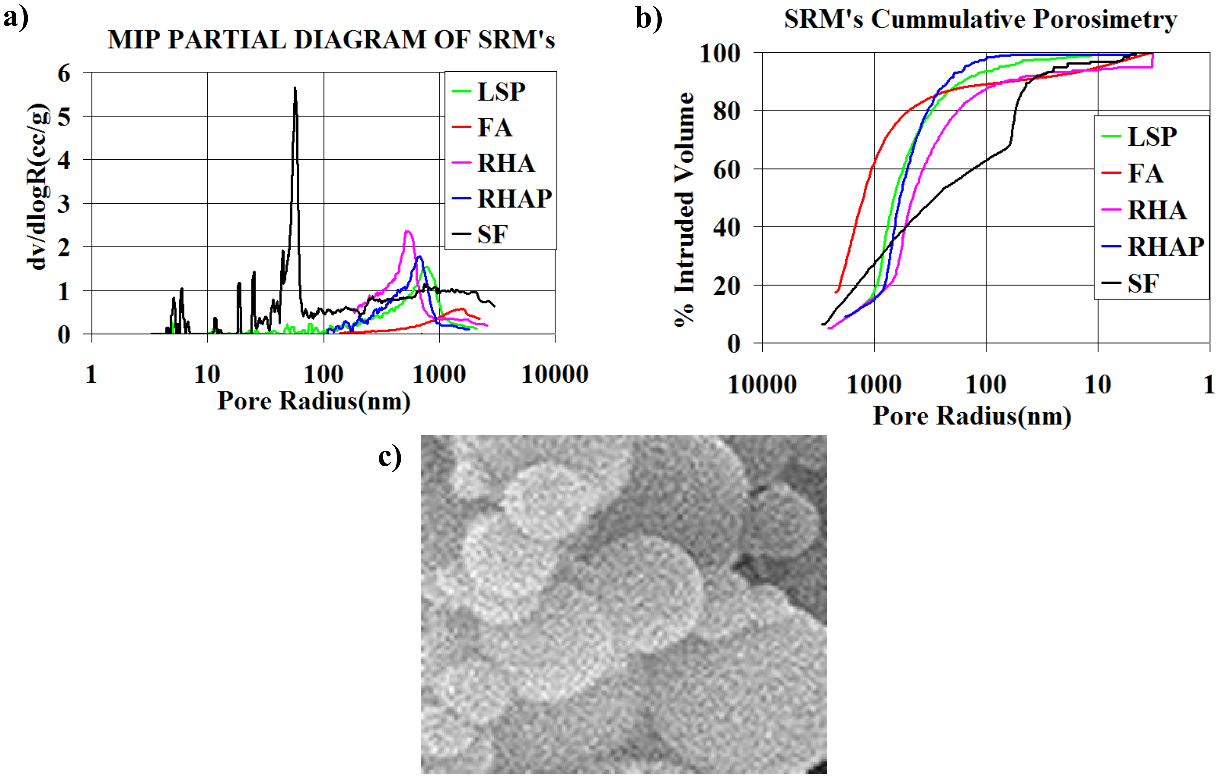

Figure 2: (a) Partial MIP Curve of SRM's (b) Cumulative MIP Curve of SRM's (c) Magnified SEM Picture of SF-x 100000

6.3 Flow

The flow was measured by using Hagerman's mini-slump cone of 6x7x10 cm dimensions. The target average flow spread diameter of 30 ± 1 cm was obtained by using varying amounts of SP for different formulations. It is a common perception amongst scientists and engineers that SP gets grafted only on cement phases which is not true as some of the SP is adsorbed /entrapped by the SRM's particles also (Rizwan *et al.*,2007). The rate and quantity of adsorbed SP depends upon the SRM particle characteristics including size, surface area, internal porosity and morphology. Figure 2 shows the measurement of flow of SCP systems. It was proposed by the author (Rizwan, 2006) to measure T25 cm time (sec) to have an idea about the viscosity of the system while total spread represented its yield. Figures 3 and 4 show the flow measurement process, effect of water-cement ratio on SP demand for the target flow and flow-SP relation of powders used in SCP systems respectively.

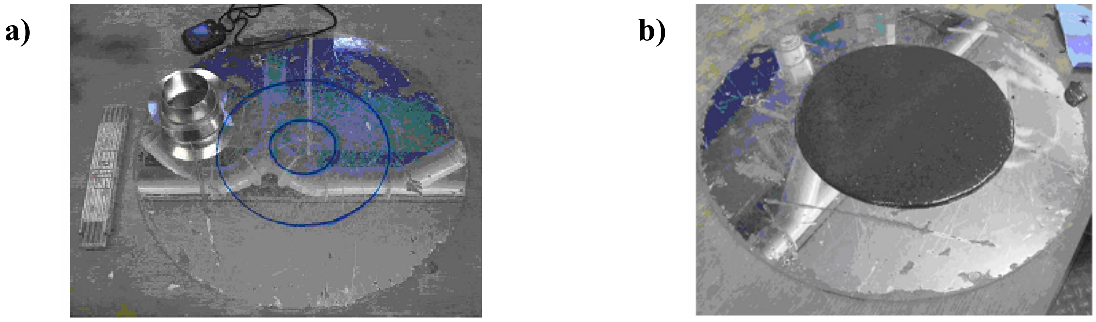

Figure 3: a) Hagermann's Mini-Cone Flow Apparatus b) Flow Spread After Removal of Cone

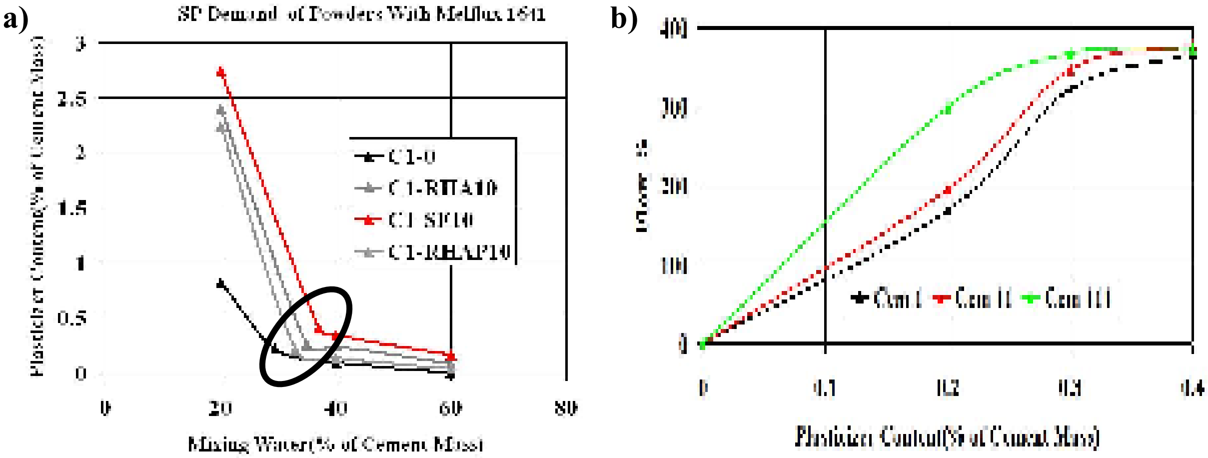

Figure 4: a) SP Demand of SCP Systems at Various Mixing Water Contents b) Flow of Cement Pastes at Respective Water Demands with 10% SF.

Note: The encircled points on the four lines in figure 4(a) indicate the SP requirement at their respective water demands. For high performance concrete constructions, a mixing water content equal to the demand of the system should be added for the reasons of economy and durability.

6.4 Strength

Compressive and flexural strengths of the paste systems were determined as per EN 196-1: 1994 at the age of 1, 3, 7 and 28 days. The flexural strength at any age was the average of three specimens while compressive strength was the average of six specimens. The strengths shown in Figure 5 were within statistical acceptance limits. In total 252 prisms were cast for paste systems with CEM I and CEM III in laboratory at a temperature of 20±2°C and relative humidity of 35±5% as per EN 196-1:1994.

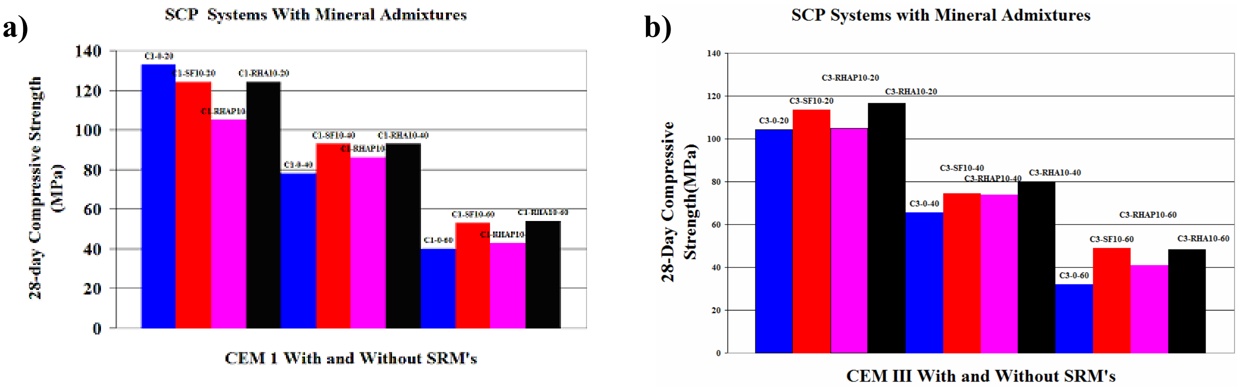

Figure 5: a) 28 Day Age-Strength Relationship of SCP System at Three Mixing water Contents With CEM I b) 28-Days Age-Strength Relationship of SCP System at three Mixing Water Contents With CEM III

6.5 Microstructure

It was studied by SEM and MIP techniques. FEI XL 30 environmental scanning electron microscope with field emission gun (ESEM FEG) was used to study the microstructure by scanning electron microscopy Figure 6 shows hydration products of pure cement paste and those containing RHA,RHAP and SF at 10% replacement level with 40% mixing water(w/c = 0.40) at the age of seven days. Nomenclature of paste systems, for example, for C1-RHA10-40-7 would mean that it was a paste system with CEM I wherein RHA was taken as 10% mass of cement and the mixing water was 40% of the cement mass. The last digit (7) indicates the age of the sample in days.

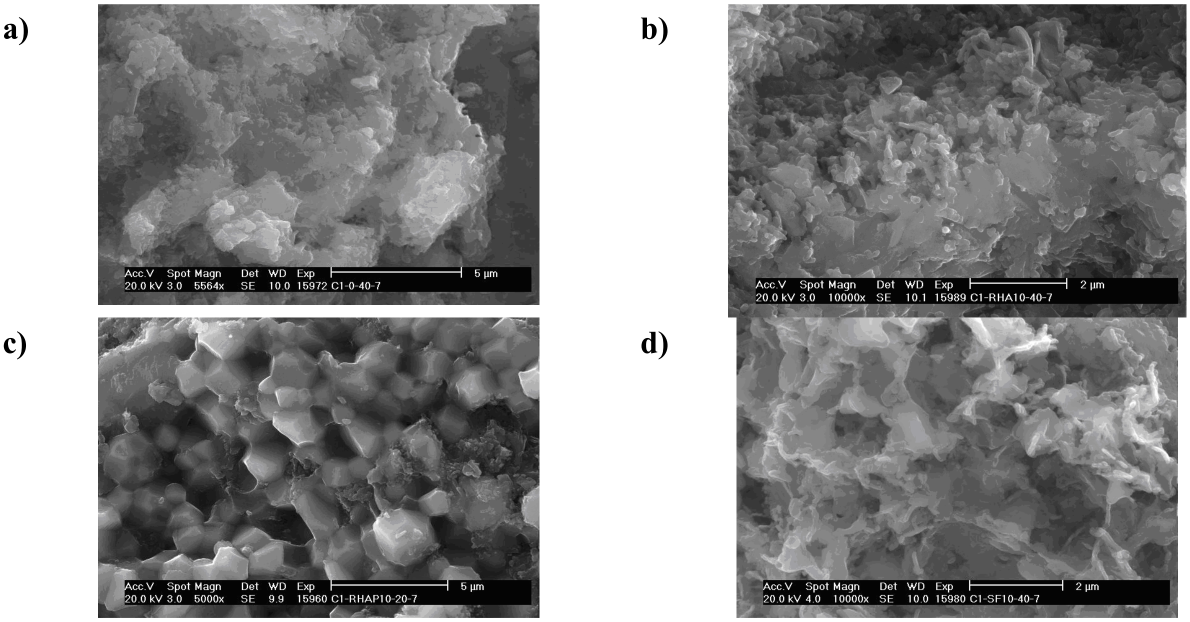

Figure 6: a) C1-0-40-7 Self-Compacting Paste System b) C1-RHA10-40-7 Self-Compacting Paste System c) C1-RHAP10-40-7 Self-Compacting Paste System d) C1-SF10-40-7 Self-Compacting Paste System

Figure 7 shows the maximum pore sizes in nanometers (taken from partial MIP curves) versus age (in days) relation for the SCP systems studied. MIP was done with the help of Autoscan 33 Porosimeter.

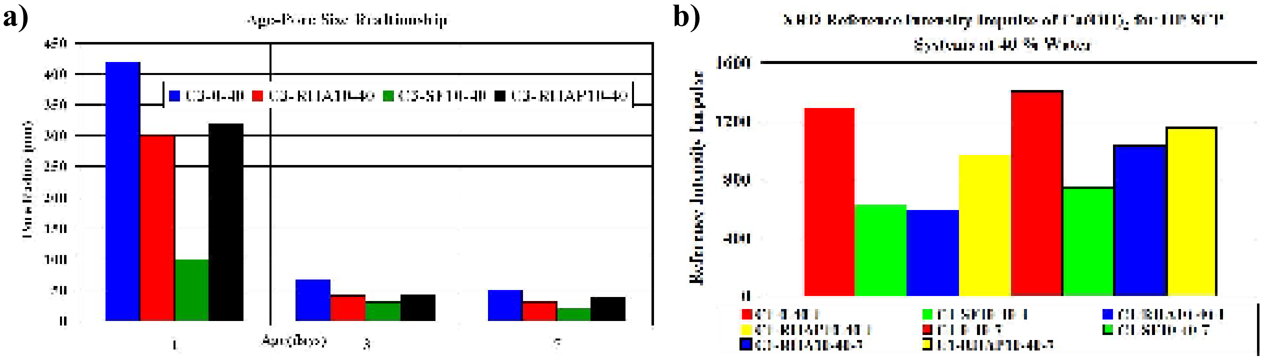

Figure 7: a) Maximum Pore Size and W/C Relation of Pastes With and Without SRM's b) XRD Results of HP SCP Systems for $Ca(OH)_2$ Contents at the Age of 1 and 7 Days

6.6 Early Shrinkage

Early shrinkage of modern cement based systems is another durability consideration. In this study a modified version of German classical "Schwindrinne" meaning shrinkage channel apparatus measuring 4x6x25.4 cm was used at 20±1°C and RH of 31±5% with specimen uncovered and covered with plastic sheet. It was interfaced with computer and had a sensitivity of 1.2 microns/m. The results are shown in Figure 8.

Self-compacting paste samples with and without SRM's/SP were tested and measurements lasted for initial 24 hours. The average of two statistically acceptable measurements is reported. It can be seen that covering the samples immediately after placement considerably reduces the total shrinkage. The detailed treatment can be seen elsewhere (Rizwan and Bier 2006 a, Rizwan and Bier 2006 b, Rizwan and Bier 2005a, Rizwan and Bier 2005b).

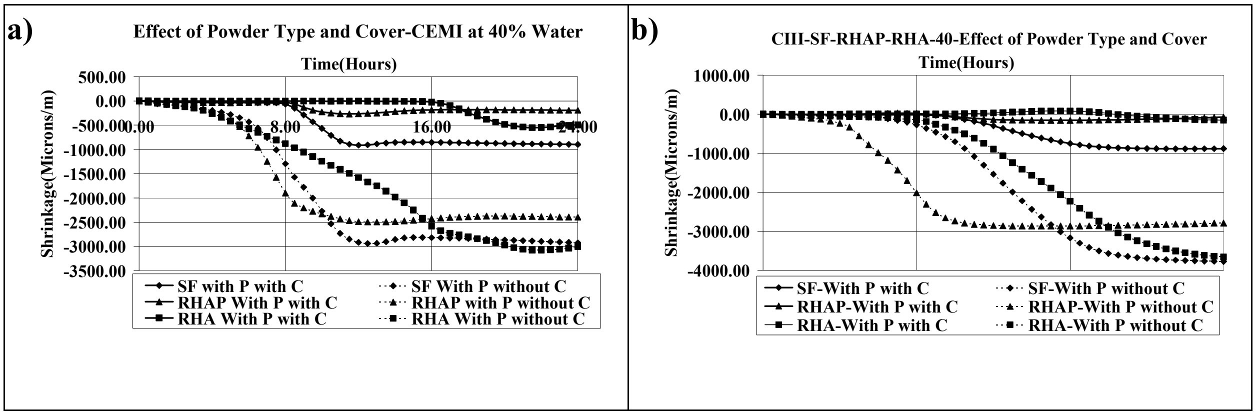

Figure 8 a) Early Shrinkage of Pastes With and Without SRM's With CEM I b) Early Shrinkage of Pastes With and Without SRM's With CEM III

7. Discussion

The particle size of SF as measured by Laser technique (Table 1) is not that of a single particle but instead it is the size of particles forming primary group due to inter-particle cohesion. Therefore the particle size of SF can best be seen in SEM technique [Figure 1 (a)] wherein it is clearly a sub-micron sized particle. Both SF has higher internal MIP porosity than RHA (Rizwan and Bier, 2006 b) as indicated by SEM pictures and MIP results on SRM's. Figure 4 (a) shows that for mixing water contents less than WD of the system, the SP content required for the desired flow (around 30 cm spread) is very high which further increases for the formulations containing both RHA and SF because of the water/SP uptake by these SRM's. SP content needed for target flow does not reduce drastically if mixing water is higher than the WD of the system. It establishes that high performance cementitious systems should contain mixing water closer to WD of the system for the reasons of economy and durability. With reference to Figure 5 (a), RHA formulation gave higher strength than formulation containing SF with CEM III than with CEM I, which may translate into saying that reaction products and processes of RHA in CEM III are denser and these powders are more compatible than those with CEM I. Both RHA and SF gave almost equal 28 days strength at equal cement replacement level of 10% for both cements. Their incorporation improves the strength and microstructure of neat self-compacting cement pastes. This is due to their pore refinement effect which can be seen in terms of maximum MIP pore radius of paste systems at equal flow level (30 cm spread) shown in Figure 7 (a) at three water contents at the age of seven days. Figure 6 (a) shows calcium hydroxide (CH) crystals in neat SCP which is due to the absence of a pozzolanic reaction. Figure 6 (b) and 6 (d) show the microstructure of SCP containing RHA and SF. Both figures show different crystal shapes, sizes and morphology but distinctly visible CH is not seen which indicates significant pozzolanic reaction. It was earlier shown (Rizwan, 2006) that principal XRD intensity impulse can be used to indicate CH content in a formulation. It was also evident in XRD results [Figure 7 (b)] that neat cement paste gives higher CH content than formulations containing SRM's. It is due to dilution effect. Moreover it was observed that CH content at 7 days was higher than that at 1 day. Beyond 7 days CH content starts reducing and may pick up again afterwards. It is due to the fact that at 1 day, the hydration did not progress significantly coupled with some retardation effects due to SP. However at different sample sites and at different w/c ratios, the nature and morphology of reaction products of SCP systems containing SF and RHA can show some resemblance also. With regard to early volume stability in terms of linear adiabatic shrinkage measured in laboratory under controlled temperature and humidity, it is shown in Figure 8(a) that addition of RHA and SF in cement paste as 10% replacement SRM's increases the shrinkage which is again attributed mainly to the water uptake by the particles of these SRM's in addition to other simultaneous operative mechanisms. A typical legend item in Figure 8, for example **"with P with C"** would mean a SCP system having super-plasticizer (P) for the target flow and covered(C) with plastic sheet. Similarly other legends can also be understood. RHAP quickens up the setting time and shows lower shrinkage while RHA does just the reverse. RHA incorporating SCP gives much delayed setting and shrinkage almost equal to that brought about by SF containing SCP. Covering the systems immediately after placements, results in significant reduction of early shrinkage. RHAP shows strength improvement of SCP systems mainly due to filler effect as it possesses little pozzolanic activity. Uncovered formulations allow evaporation requiring consumption of heat resulting into a cooler system and increased shrinkage. Similar SCP formulations show higher early shrinkage with CEM III(Figure 8b) due to finer pore structure, lesser heat of hydration (and hence lesser thermal expansion) and reduced generation of $Ca(OH)_2$ crystals which are expansive in nature.

8. Concluding Remarks

RHA can be readily locally available in almost all countries of the world and seems to give a response similar to SF in SCP formulations. Based on this study it can be stated that the mixing water content for high performance and self-compacting cementitious systems should be closer to the WD of the systems for the reasons of economy, efficiency, durability and better service life performance. The SRM particle shape, size and morphology (particle characterization) is very important for modern cement based systems as it affects almost all the resulting properties of cement based systems. Both RHA and SF produce almost similar improvements in strength and microstructure of the cement based formulations. However their flow response is different. Similar SCP formulations in CEM III gave higher early shrinkages than those in CEM I. The rate of strength development with CEM III is slightly lower up to 28 days but beyond that usually there is no significant difference in strength compared with those in CEM I. CEM III formulations are generally considered better in terms of microstructure and are more durable especially for water retaining and training structures. RHAP gives the maximum pore size from MIP partial curve results (and hence lowest strength in pastes with SRM's) and it can be verified from the open structure of hydration products as seen in SEM picture.

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