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Hydration and microstructure of ultra high performance concrete incorporating rice husk ash

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ABSTRACT

Rice husk ash (RHA) and silica fume (SF) have a similar chemical composition and a very high specific surface area, but RHA is not an ultra-fine material like SF. The high specific surface area of RHA originates from its internal porosity. For this reason RHA can be expected to behave differently from SF in terms of the hydration and the resulting microstructure of concrete. This still remains unclear in Ultra High Performance Concrete (UHPC). The objective of this research was to study the effect of RHA on the hydration and microstructure development of UHPC. The results are compared to those obtained with a control sample and a sample made with SF.

The results show that the addition of RHA can increase the degree of cement hydration in UHPC at later ages. RHA can also refine the pore structure of UHPC and reduce the $Ca(OH)_2$ content, but less significantly than SF. The thickness of the interface transition zone (ITZ) between sand particles and cement matrix of all samples is very small at the age of 28 days. The compressive strength of the sample made with RHA after 7 days was higher than that of the control sample and the sample made with SF. It is suggested that the porous structure of RHA and the uptake of water in this porous structure results in a kind of is attributable to the internal water curing of the RHA modified mixture.

1. Introduction

Ultra-high performance concrete (UHPC) is one of the latest advances in concrete technology. The advantages of this material include superior compressive and flexural strength, increased ductility due to the addition of fibres, and excellent durability. Depending on its composition and the curing temperature, its compressive strength ranges from 150 MPa to 800 MPa [1]. Owing to the use of very fine sand instead of ordinary aggregate, the content of cement in UHPC is as high as 900–1000 kg/m^3 [1,2]. In addition, silica fume (SF) is an essential ingredient in UHPC. It has an extreme fineness and a high amorphous silica content. The typical SF-to-cement ratio used is 0.25 regarding the filler effect and pozzolanic effect [1]. The high cement content with the SF-to-cement ratio of 0.25 leads to a high amount of SF in UHPC mixtures. However, this also causes some disadvantages in the modern construction industry, particularly in developing countries where there are limited resources and significant cost constraints. This provides the motivation for researching other materials with similar performances to be used instead of SF.

One possibility is using rice husk ash (RHA). This material is obtained after burning the rice husk, an agricultural waste. The RHA constitutes about 4% of the 690 million metric tons of rice paddy produced annually worldwide [3]. The ash obtained after complete combustion of the husk in controlled conditions contains 90–96% silica in an amorphous form. This ash was found to be highly pozzolanic and therefore an excellent supplementary cementing material [4]. The mean particle size of RHA generally ranges from 5 μm to 10 μm [5]. RHA has well-known porous structure. Therefore, although RHA is not an ultra-fine material like SF (with a mean particle size of 0.1–1 μm [6]), it has a very high specific surface area up to 100 m^2/g (determined by nitrogen adsorption) [4], whereas the surface area of SF ranges from 18 to 22 m^2/g [6]. With a similar chemical composition of RHA and SF, the RHA is still expected to behave differently from SF in the hydration and microstructure development of concrete because of the porous structure of the RHA.

Previous work by Nguyen et al. [7] showed that the effect of RHA on the hydration of cement paste determined by isothermal calorimetry is more pronounced than that of SF at a low water-to-binder (w/b) ratio, especially in the later stage. The author suggested that one of the main reasons is the porous structure of RHA. The water can be absorbed in the pores of RHA and is released from these pores to the surrounding paste matrix when the relative humidity in the paste decreases during cement

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hydration, and becomes available for further hydration in cement. Furthermore, Mehta [4] and Zhang et al. [8] found that the addition of RHA improves the development of the compressive strength of the low w/b ratio concretes at later ages. The compressive strength of the sample made with RHA is even similar to that of the sample made with SF at 90 and 180 days [8]. They also found that the percentage of unhydrated cement particles of the RHA modified sample as observed by image analysis is lower than that of both the control sample and the SF modified sample after 28 days of curing. This indicates a possible acceleration of cement hydration in the presence of RHA at the ages. In addition, the possibility to produce high performance concrete by using RHA instead of SF was analyzed by Chandrasekhar et al. [9]. RHA has been successfully used to replace SF in practice for achieving high strength/performance concrete [8,10]. It gives rise to the idea that RHA can be used to produce UHPC and improve the hydration and microstructure development of UHPC with a very low water-to-cement ratio, ranging from 0.10 to 0.25 [11,12].

The objective of the work is to study the effect of RHA on the hydration and the microstructure of UHPC. Also, the reduction of the calcium hydroxide content due to the pozzolanic reaction of RHA and compressive strength is evaluated. The results are compared with those obtained from the control sample and the SF modified sample.

2. Experiments

2.1. Materials

The materials used in this study were silica sand with a mean particle size of 225 µm; Portland cement (CEM I 52.5N) with a Blaine specific surface area of 4500 cm^2/g; condensed silica fume; rice husk ash; polycarboxylate-based superplasticizer with 30% solid content by weight. The SF contained an SiO_2 content of 97.2% and its mean particle size was about 0.1–0.15 µm. The specific surface area of SF determined by the nitrogen absorption method was 19.5 m^2/g.

The mean particle size of materials in this study was determined by laser diffraction.

Rice husk, an agricultural waste material from Vietnam, was burnt in a drum incinerator developed by Pakistan Council of Scientific & Industrial Research [13] under uncontrolled combustion conditions. Details of the oven and rice husk combustion process have been described elsewhere [14]. The ash obtained was ground in a vibrating ball mill for 90 min. The ash contained 88.0% SiO_2 (3.8% loss on ignition) and its mean particle size was 5.6 µm. The specific surface area of RHA determined by the nitrogen absorption method was 20.6 m^2/g.

X-Ray diffraction (XRD) patterns of RHA and SF are given in Fig. 1. The RHA sample contains a small amount of quartz, while the bulk of the ash is amorphous, similar with the SF sample.

Fig. 1 shows Scanning Electron Microscopic (SEM) images of typical particles of RHA and SF. It can be seen that the RHA is porous (Fig. 2a) and also contains very fine particles around the coarse particles.

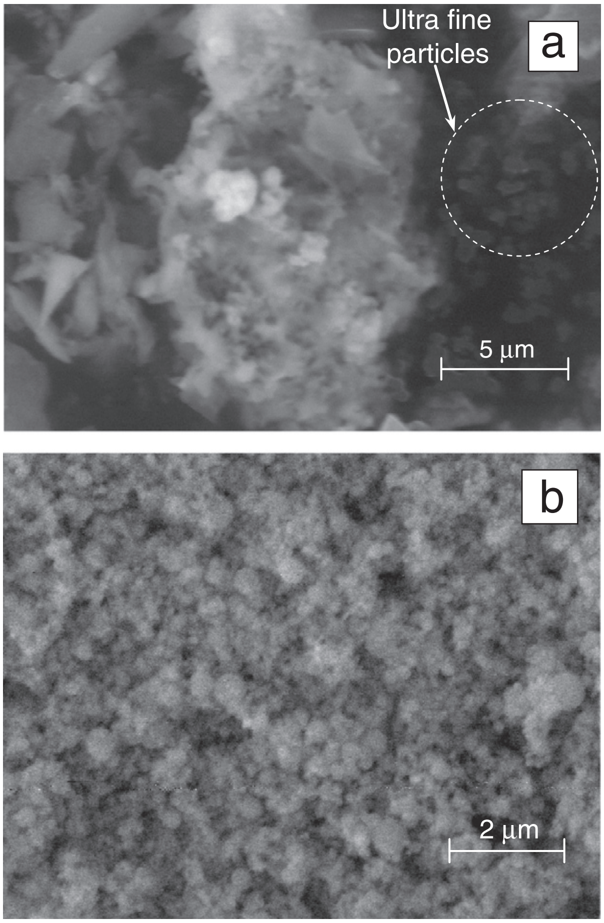

Fig. 2. SEM images of RHA (a) and SF (b).

2.2. Composition

The UHPC mix composition is shown in Table 1. The binder herein is the sum of cement and either SF or RHA. The quantities of superplasticizer were chosen so as to keep the workability of the UHPC mixtures between 210 and 230 mm, measured by means of the flow table test [15]. It can be seen that the cement replacement by SF has a positive effect on the workability of the mixture because the amount of superplasticizer used in the SF modified mixture is lower than that in the control sample. This can be attributed to spherical

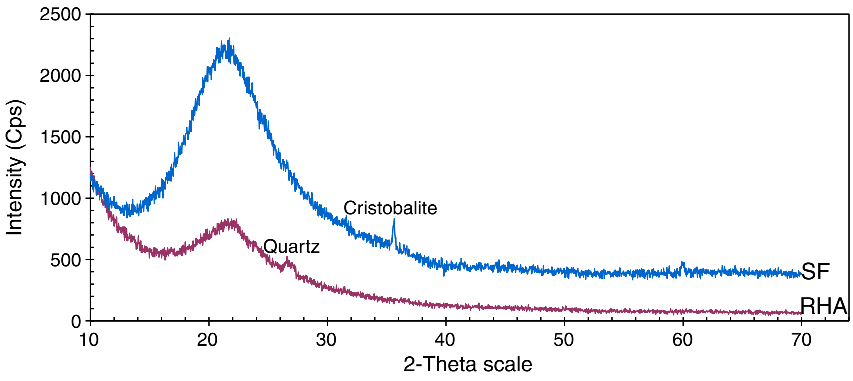

Fig. 1. XRD patterns of RHA and SF, showing a highly amorphous structure, only small amount of crystal phases.

Table 1
UHPC compositions used in this study.

Mix no.	Water to binder ratio (by weight)	Sand to binder ratio (by weight)	RHA (% by weight)	SF (% by weight)	Superplasticizer (solid % by weight of binder)
REF	0.18	1	0	0	0.90
SF20	0.18	1	0	20	0.76
RHA20	0.18	1	20	0	1.20

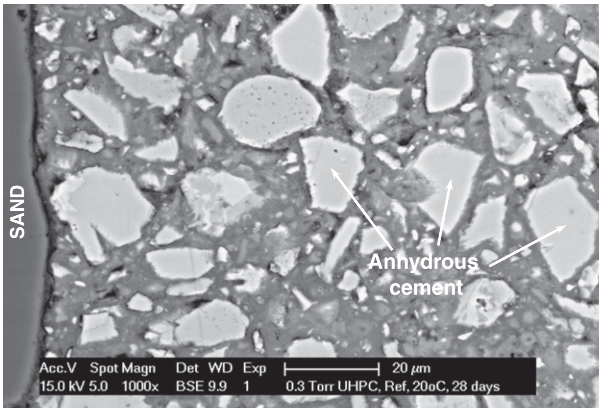

Fig. 4. BSE image of the paste (w/b ratio 0.18) in the control sample at 28 days.

shape of SF particles, which act as a lubricant. However, the addition of RHA, with its angular particle shape and porous structure, absorbs a certain amount of mixing water [14] and thus requires a high amount of superplasticizer (SP) to compensate for a given workability of all mixtures with a constant amount of water.

2.3. Experimental methods

All materials were prepared in a 20-liter Hobart mixer. The volume of each batch was 3.5 l. The mixing procedure is given in Fig. 3.

For compression testing, a set of mixtures were cast into $40\times40\times40$ mm^3 cubes. All mixtures were vibrated for 1 min, using a vibrating table with a frequency of 2500 cycles/min. After casting, the samples with moulds were cured in a fog room (20 ± 2 °C, RH > 95%) for one day. After demoulding, the samples continued to be stored in the fog room until the day of testing.

For microstructural studies, a set of mixtures were poured into 500 ml plastic bottles and then sealed with a plastic lid. The samples were cured at 20 °C until the age of testing; i.e. 0.25, 1, 3, 7, 28, and 91 days. At the end of each curing period, the cover of the plastic bottle was removed. Samples were cut into small pieces of about 1 cm^3. Cement hydration was terminated by immersing the samples into liquid nitrogen at a temperature of −195 °C. Finally, the samples were dried in a freeze drying chamber.

2.4. Microstructural investigation

Two techniques were used to examine the microstructure of the samples: Mercury Intrusion Porosimetry (MIP), and Environmental Scanning Electron Microscope (ESEM).

2.4.1. MIP

The total porosity and pore size distribution of the samples were measured by means of MIP. For each test, 2 or 3 samples with a total weight of approximately 4–6 g were used. Samples were tested at ages of 1, 3, 7, 28, and 91 days. Sample preparation and test procedure were referred to [16].

2.4.2. ESEM

Polished epoxy-impregnated specimens were examined in an ESEM, conducted on a Philips-XL30-ESEM in a gaseous (water vapor) environment. An acceleration voltage of 15–20 kV was used and the working distance was 10 mm. Details of the specimen preparation procedure can also be found elsewhere [16]. A magnification of 540× was chosen for analysis. The backscattered electron (BSE) image size was 1424 × 968 pixels with a resolution of 0.165 μm/pixel. For each sample, 12 images were captured in order to achieve an acceptable confidence in the results [16]. Samples were tested at ages of 1, 3, 7, 28, and 91 days.

According to stereology analysis [17], with sufficient sampling, the volume fraction of Portland cement can be assumed to be equal to its area fraction in BSE images. From the volume fraction of unhydrated Portland cement, the degree of cement hydration can be calculated.

2.5. Thermogravimetric analysis (TGA)

The quantity of calcium hydroxide (CH) in cement paste was determined by TGA. Analyses were conducted at heating rate of 10 °C/min from 35 °C to 1100 °C under flowing nitrogen. The CH content was determined from a measured weight-loss curve by a graphical technique [18,19]. Samples were tested at ages of 0.25, 1, 3, 7, 28, and 91 days.

3. Results and discussion

3.1. Microstructural investigations

Figs. 4 to 6 show the BSE images of the control sample (REF) and samples made with RHA and SF.

It is observed that the larger hollow-shell pores (Hadley grains) [20,21] were found in the SF modified sample only, and not in the control sample or the RHA modified sample. The cement grains formed hollow shells with remnant anhydrous cores, which are marked with arrows (Fig. 6).

In addition, it can be observed clearly that the thickness of the ITZ of the control sample without either RHA or SF is very narrow (Fig. 4) and the addition of RHA or SF does not influence this ITZ (Figs. 5–6). Normally, the microstructure of the ITZ is influenced by the “wall effect” in the vicinity of aggregate surfaces, and this region may extend some 50 μm from the grain surface into the cement paste [22]. However, in this study, sand with particle sizes ranging from only 100 to 300 μm was used as the main aggregate, which reduces the “wall effect” and the resulting thickness of the ITZ. Moreover, with such a small sand particle size and a very small thickness of the ITZ, the effect of mineral

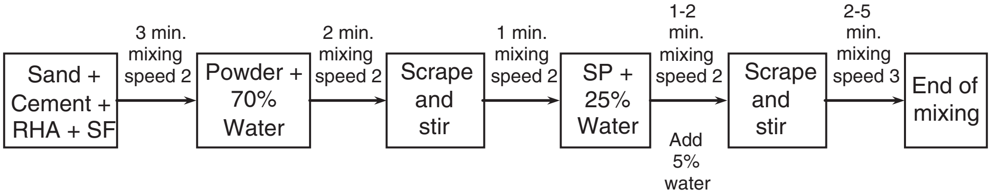

Fig. 3. Mixing procedure for UHPC.

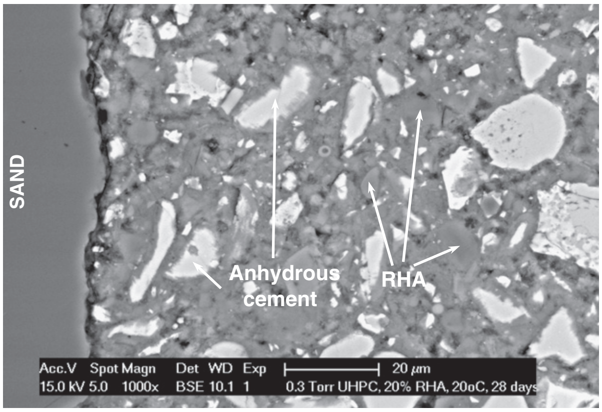

Fig. 5. BSE image of the paste (w/b ratio 0.18) in the RHA modified sample at 28 days.

admixtures such as SF or RHA in reducing the ITZ thickness will not be significant. For this reason, the thickness of the ITZ of all samples obtained in this study was similar and very small.

3.1.1. Degree of cement hydration in UHPC by image analysis

The percentage of unhydrated cement in paste of UHPC is shown in Fig. 7, and the corresponding degree of cement hydration is shown in Fig. 8. In general, the degree of cement hydration in UHPC samples was relative low, ranging from 0.30 to 0.40 after 91 days, which is in good agreement with earlier published studies [1,23,24]. It should be noted that the increase of the degree of cement hydration in the RHA modified sample was significant at later ages; i.e. after 7 days, even higher than that in the SF modified sample at 91 days.

It is suggested that the effect of RHA on cement hydration can be explained by water absorbed in the porous structure of its particles. RHA particles may absorb a certain amount of free water into their pores during mixing. On the one hand, this leads to less water available in the system for cement to react and thus the degree of hydration of cement is low at an early stage, especially in low w/b ratio mixtures. On the other hand, the pores in RHA particles act as water reservoirs. With the progress of cement hydration process, the relative humidity in the bulk cement paste drops and the absorbed water in RHA will be released from these reservoirs to promote the hydration of cement and thus the degree of cement hydration increases further at the later stages. The absorbed water can also increase the pozzolanic reaction of Ca^{2+} with silica ions from RHA inside its cellular spaces [25,26]. Furthermore, the lower concentration of Ca^{2+} caused by the pozzolanic reaction of RHA also leads to an enhancement of the hydration of cement.

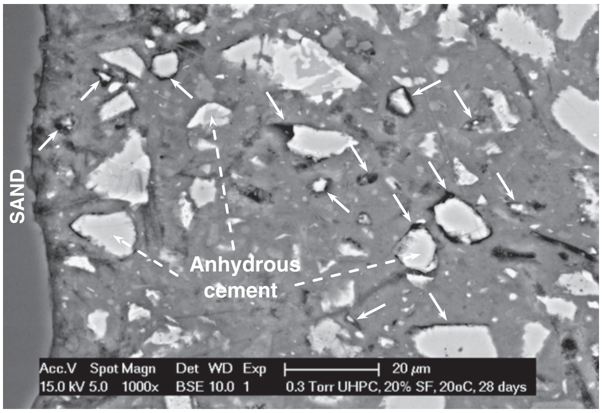

Fig. 6. BSE image of the paste (w/b ratio 0.18) in the SF modified sample at 28 days; white-solid arrows indicate the hollow-shell pores.

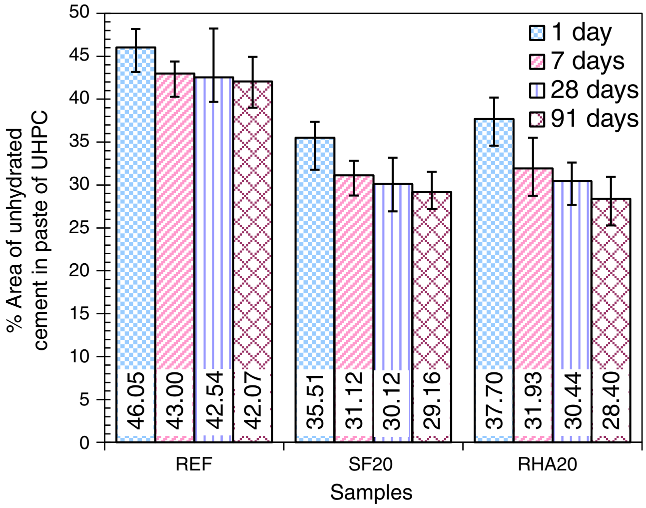

Fig. 7. The percentage of unhydrated cement in paste of UHPC at 1, 7, 28, and 91 days.

3.1.2. Pore structure in UHPC

The pore size distribution and total porosity of the UHPC samples that were measured by MIP at the ages of 1, 7, 28, and 91 days are provided in Fig. 9 and Table 2. It was found that the first peak of the differential curve, typically indicated as one of "critical pore diameters" [16], of the control sample was below 0.04 µm at all ages. The addition of RHA gave a pore refinement and a reduction of the total pore volume of UHPC due to the filler effect and high pozzolanic reaction of the very small RHA particles. The critical pore diameter of the RHA modified sample decreased from 0.04 µm at 1 day to 0.01 µm at 28 days and to less than 0.01 µm at 91 days.

It can be seen in Table 2 that the total porosity of both RHA- and SF-modified samples is lower than that of the control sample. Apparently, the total porosity of the RHA modified sample is higher than that of the SF modified sample because both filler effect and pozzolanic reaction of RHA are less significant than those of SF.

3.2. The calcium hydroxide content

Fig. 10 shows the calcium hydroxide content of UHPC samples over time. It can be seen that the calcium hydroxide content of the control sample increased with time. Both RHA and SF strongly reduced the calcium hydroxide content where the effect of SF is greater than that of RHA at later ages.

The calcium hydroxide content of the RHA modified sample was relatively low compared to that of the control sample and the SF

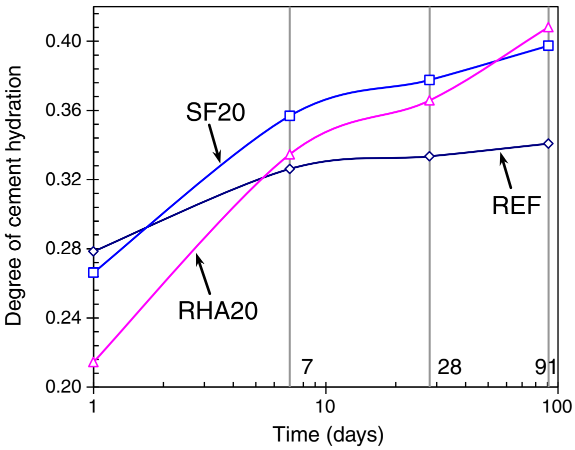

Fig. 8. The degree of cement hydration in UHPC over time.

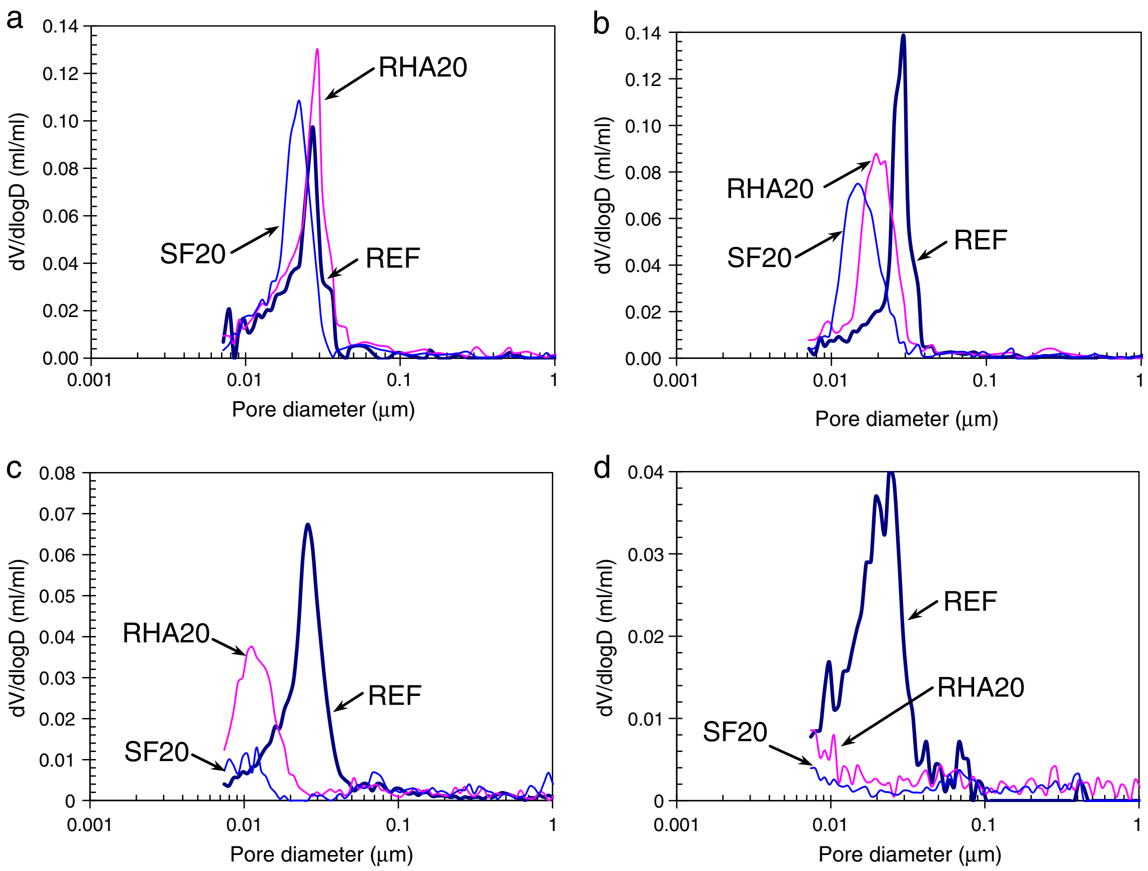

Fig. 9. Pore size distribution of UHPC samples at (a) 1 day, (b) 7 days, (c) 28 days, and (d) 91 days.

modified sample at an age up to 7 days. This may be caused by the low degree of cement hydration of the RHA modified sample (see Fig. 7) due to the fact that the RHA absorbed a certain amount of mixing water and thus less water is available in the system for the cement to react with. This leads to a small amount of $Ca(OH)_2$ generated from cement hydration and a resulting slow pozzolanic reaction of RHA. However, beyond 7 days the $Ca(OH)_2$ content of the RHA modified sample decreases significantly, but compared to the SF the reactivity of the RHA appears less strong. This can be attributed to the difference in their amorphous SiO_2 content and particle characteristics between RHA and SF, which was also suggested by Zhang et al. [8]. It is noticed that the addition of RHA gave 45% and 65% reduction of the calcium hydroxide content in UHPC at the ages of 28 and 91 days, respectively. The corresponding calcium hydroxide reduction values for the SF modified sample are 70% and 90%.

3.4. Compressive strength development

Fig. 11 shows the results for compressive strength of UHPC versus time. It is noticed that the compressive strength of the RHA modified sample is higher than that of the control sample at later ages, i.e. beyond 7 days. The compressive strength of the RHA modified sample is even higher than that of the SF modified sample after 3 days. The compressive strengths of the RHA modified sample are 175 and 185 MPa at the ages of 28 and 91 days respectively, whereas the corresponding values for the control sample are 163 and 173 MPa.

Table 2
Total porosity of UHPC samples at the different ages from 1 to 91 days.

	Total porosity of UHPC samples at the different ages, %			
	1 day	7 days	28 days	91 days
REF	11.15	8.13	7.5	6.95
RHA20	10.32	7.63	5.76	4.92
SF20	9.18	6.49	4.55	3.98

3.5. Discussions

3.5.1. Effect of RHA on the hydration and microstructure development of UHPC. The fact that addition of RHA increases the degree of cement hydration at later stages (Fig. 8) may be attributed to the release of water from the porous structure of RHA particles as discussed earlier. The mechanism is assumed to be similar to that suggested by Weber

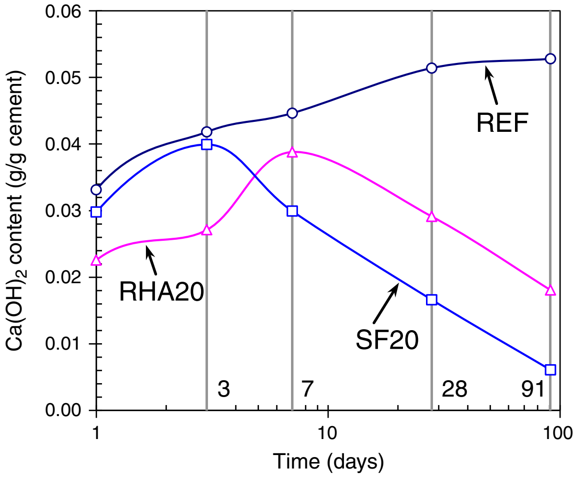

Fig. 10. The calcium hydroxide content of UHPC samples with time.

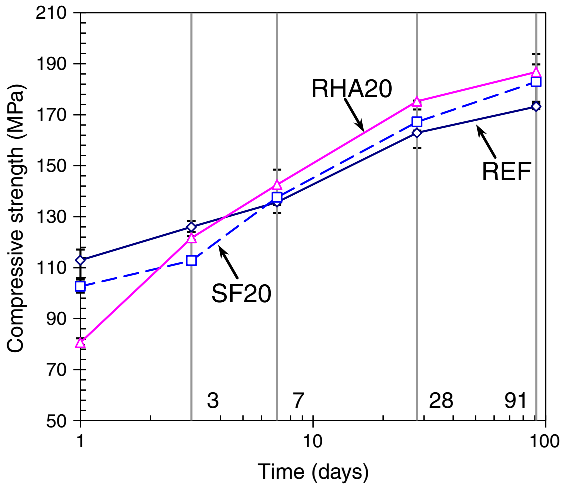

Fig. 11. Compressive strength development of UHPC over time.

and Reinhardt [27] and Breugel et al. [28] when using the water-saturated lightweight aggregates (LWA) and from Jensen and Hansen [29,30] when using superabsorbent polymer (SAP) particles for internal curing of concrete. The effect of RHA on the mitigation of autogenous shrinkage of cement paste [31] and UHPC [32] also supports this idea.

It is noticed that the size of pores in RHA particles (from 4 to 10 nm in diameter [33,34]) is much smaller than that of SAP particles (about 450 μm [35]) and that of LWAs (about 10–20 μm [36]). According to Kelvin's equation [37], this size range of pores in RHA particles corresponds to the change of relative humidity (RH) in the cement matrix from 74% to 88.7%. The effectiveness of water released from the pores of RHA particles to the surrounding cement matrix depends on the suction force, which in turn depends on the porosity and RH in the cement paste [38]. At early ages, i.e. before 7 days, the RH in cement paste with w/c ratio of 0.25 is still higher than 87% [39]. Thus, only water in big pores of the RHA particles will be released. A certain amount of water still remains in the smaller pores and is gradually released at later ages, up to more than 28 days, when the RH decreases to 78% as indicated in [39].

Furthermore, small pores, i.e. smaller than 4 nm in diameter, in the RHA particles remain water-filled for a longer period of time and in their saturated state may become filled with hydration products, which results in the absence of these empty pores surrounding the residual cement grains. This effect, in combination with the higher degree of cement hydration could contribute to the higher compressive strength achieved at later ages of the RHA modified sample. This phenomenon is also observed with high performance mortar using pre-wetted lightweight aggregates, as explained by Bentz and Stutzman [40].

In summary, the experimental results suggest the internal water curing of RHA in UHPC. However, more studies are needed to show this in more detail.

One of the other interesting features is that the hollow-shell pores, especially the larger hollow-shells, mainly appear in the SF modified sample, not in the control sample or the RHA modified sample. This can be explained in several ways. Normally, in the control paste without either RHA or SF, hollow shells are formed by the dissolution of cement grains at the early period and become filled with new hydration products at later period [20,41,42]. Kjellsen et al. [20] suggested that hollow shells are refilled by C–S–H in hollow-shell separations outside larger alite particles and by the other hydrates, mainly calcium hydroxide (CH), in smaller, completely hollow shells. However, in the systems containing SF, this is observed to a much lower extent and many hollow shells may remain also at later ages. Possibly, this is caused by the fact that there is a large number of ultra fine SF particles, i.e. approximately 100,000 [43], attached around each cement particle creating a dense SF layer to constrain both water to percolate inward to hydrate the cement cores and ions from the cement cores to migrate outward. It means that the refilling process of hydration products in previously formed hollow shells of larger alite particles in the SF system will be delayed and remain until later periods. In addition, the highly reactive SF particles available in the whole system will consume CH generated from cement hydration, which reduces the refilling ability of CH in smaller completely hollow shells formed earlier. This result is also in good agreement with that observed by Kjellsen and Atlassi [44].

In the RHA system, RHA particles with the mean size of 5.6 μm are approximately less than half the mean size of cement particles (about 13.7 μm), yet fifty times bigger than SF particles, and thus distribute randomly in the system rather than stay in contact with the surface of the cement particles (Fig. 5). Besides, it can be observed that the degree of cement hydration in the RHA system is relatively low compared to that of the control sample before 7 days (Fig. 8) and the pozzolanic reaction of RHA remains slow (Fig. 11). This leads to the assumption that the microstructure development of cement in the RHA modified sample is similar to that of the control sample. Although the pozzolanic reaction of RHA is significant after 7 days (Fig. 8), the degree of cement hydration is not much increased, especially from 14 days to 28 days (Fig. 11). Therefore, the larger hollow-shells in the RHA modified sample may be refilled up by CSH like in the control sample. The only one presumably different feature is that some smaller completely hollow-shells may not become entirely refilled because of the lack of CH due to the pozzolanic reaction of CH with RHA.

3.5.2. Effect of RHA on the development of compressive strength of UHPC. Regarding the compressive strength of the RHA modified sample, the experimental results (Fig. 12) show the positive effect of RHA on the compressive strength of UHPC at the later ages.

It should be noted that only normal curing conditions were applied in this study and the pozzolanic reaction is thus not enhanced strongly compared with the elevated temperature curing condition and that the hydration of cement at a very low w/b ratio is a slow process The improvement of compressive strength of UHPC by using RHA can be explained by the enhancement of the packing density of granular mixtures, the internal curing of RHA, and the lower effective w/b ratio of the RHA mixture. These situations can be considered as below:

One of the most important principles of making UHPC is the optimization of the particle packing of granular mixtures [1], especially since the degree of cement hydration in this concrete is relatively low (Fig. 8). The filler effect of mineral admixtures, such as SF, is primarily responsible for the strength improvement in low w/b ratio mixtures [45]. Therefore the addition of RHA with a smaller particle size than that of cement will increase the compressive strength of UHPC because of its filler effect. This should lead to a higher compressive strength of the RHA modified sample compared to that of the control sample at a same degree of cement hydration. However, the results here show a lower compressive strength of the RHA modified sample in early ages, i.e. before 7 days (Fig. 8). This is assumed to be caused by the lower amount of available water in the system for cement to hydrate, as RHA absorbs a certain amount of water during mixing. This absorbed water may promote the hydration of cement at later ages causing an increase of the compressive strength of UHPC, as discussed above. In addition, the higher compressive strength of the RHA modified sample can possibly be attributed to the reduction of effective w/b ratio in the RHA modified mixture, as a portion of free water is adsorbed by the added RHA and is retained in its small pores [34].

It is noticed that the development of the compressive strength of the RHA is even slightly higher than that of the SF modified sample at later ages, i.e. beyond 3 days. This is achieved in spite of the fact that the RHA particles are less suitable to obtain a very dense packing and these particles are less reactive than SF particles. Similar results were also obtained by Zhang et al. [8]. This seems consistent with the MIP (Fig. 10) and the TGA (Fig. 11) results, in which SF shows to yield a more significant pore refinement, respectively consumes more $Ca(OH)_2$, than RHA does. Therefore, this more pronounced improvement of the compressive strength of UHPC by adding RHA is supposed to be due to the internal water curing of RHA modified mixtures and the lower effective w/b ratio of the RHA modified mixture compared to that of the SF modified mixture. In addition, it should also be noted that SF has some disadvantages in the technical point of view which influences the positive effects of SF in concrete. For example, the ultra fine SF particles easily form agglomerates, even up to several hundreds of micrometers in diameter [46]. This reduces the positive effect of SF not only as regards the optimization of the packing density of granular mixtures, but also on the pozzolanic reaction of SF. Secondly, the addition of SF causes a high volume of hollow-shell pores in the system and these hollow shells cannot be recorded from the intrusion of mercury because of the "ink-bottle" effect [44]. Kjellsen and Atlassi [44] suggested that the porosity constituted by hollow shells may represent approximately 20% of the total porosity when the mixture contains 10% SF and a w/b ratio of 0.25. It means that SF still has some 'drawbacks', which influences its role in improving the properties of UHPC in comparison with RHA.

4. Conclusion

The effect of RHA on the hydration and microstructure development of UHPC has been studied experimentally in this work. The positive effects of RHA demonstrate that RHA is a promising material to substitute SF for making UHPC, with several technical, environmental, and economical benefits. The following conclusions can be drawn:

- BSE image analysis shows that the addition of RHA increases the degree of cement hydration in UHPC at the later ages, which may be caused by the porous structure of RHA and the uptake of water in this pore structure results in a kind of internal curing of RHA modified mixtures. The favorable effect of RHA on cement hydration was found to be stronger than that of SF.
- A significant pozzolanic reaction of RHA results in a reduction of the porosity of UHPC at 28 and 91 days.
- The compressive strength of UHPC containing RHA can reach at least 175 MPa and 185 MPa at 28 days, respectively 91 days. The development of the compressive strength of the RHA modified sample is higher than those of both the control sample and the SF modified sample after 7 days. This is possibly due to the optimal packing density of granular mixtures, the internal water curing of RHA modified pastes and the lower effective w/b ratio of the RHA modified mixtures.
- RHA is suitable for use as a supplementary material to make UHPC.

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