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On the Reaction of Rice-husk Ash with Supersaturated $Ca(OH)_2$ Solution

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Introduction

The liquid phase of hydrating cement is saturated with Ca^{2+} and OH^- ions, so portlandite often exists in hardened cement, coherently its amount is increased as hydration continues. But the amount of portlandite in the pastes added with rice-husk ash (RHA), compared with that in control paste, is decreased with hydration time, for instance, in the paste with 30% RHA the peaks of portlandite become very weak after 28d (Fig. 1). This gives us a hint that RHA can react with the Ca^{2+} and OH^- ions released from hydrating cement, or with the portlandite formed in the hydrates. What material does the reaction form? In this study it has been observed that the SiO_2 in RHA can react with Ca^{2+} and OH^- ions to form $Ca_{1.5}SiO_{3.5}\cdot xH_2O$ which can also be found in the pastes blended with RHA.

Raw Materials and Experiments

Raw material

RHA, chemically pure $Ca(OH)_2$, normal portland cement and Toyoura standard sand were used. The RHA was burnt in a batch furnace and ground in a ball mill for 1 hr, with N_2 specific surface of 55.14 m^2/g. The silica in it, except for a small amount of crystalline SiO_2(α-cristobalite), is in amorphous form with high activity.

Experimental

At 40±3℃ C-S-H gel was obtained by continuously mixing RHA with saturated or supersaturated $Ca(OH)_2$ solution for some days (Table 1, Fig. 2 and Fig. 3). According to JIS R 5201 the strength of the mortars with or without the addition of the C-S-H gel was examined, the results are shown in Table 2.

Table 1 Mixture proportion and the products* of the reaction between RHA and $Ca(OH)_2$ solution

Sample	RHA (g)	$Ca(OH)_2$ (g)	w/s	Time	Observed phase in the product by XRD	Surface area
CS-2	5.00	Sat. solution**	—	12d	$Ca_{1.5}SiO_{3.5}\cdot xH_2O$, SiO_2	—
CS-5	50.00	50.00	10	6d	$Ca_{1.5}SiO_{3.5}\cdot xH_2O$, SiO_2 and $Ca(OH)_2$	66.84 (m^2/g)
CS-6	50.00	50.00	10	4d	$Ca_{1.5}SiO_{3.5}\cdot xH_2O$, SiO_2 and $Ca(OH)_2$	127.00 (m^2/g)
CS-7	50.00	30.00	12	4d	$Ca_{1.5}SiO_{3.5}\cdot xH_2O$, SiO_2	85.73 (m^2/g)
CS-18	70.00	42.00	9	4d	$Ca_{1.5}SiO_{3.5}\cdot xH_2O$, SiO_2	—

* dried at 65℃ for 24 hr in a drier with enough soda lime after filtrating residual solution, ** renewed every day

Table 2 The effect of the synthesized C-S-H gel on the properties of normal portland cement

Specimen	Flaw (mm)	Flexural strength (kg/cm^2)			Comp. strength (kg/cm^2)		
(w/c=0.65, s/c=2.00)		3 d	7 d	28 d	3 d	7 d	28 d
Normal portland cement	209	52 (563)*	62 (561)	67 (564)	220	334	485
97% cement+3% CS-5	203	48 (558)	65 (558)	67 (558)	203	332	498
97% cement+3% CS-6	199	57 (555)	62 (556)	68 (552)	226	339	463
97% cement+3% CS-7	205	45 (559)	64 (558)	70 (558)	200	335	502

*( )—average mass in gram of the 3 specimens of 40×40×160mm after demoulding

Results and discussions

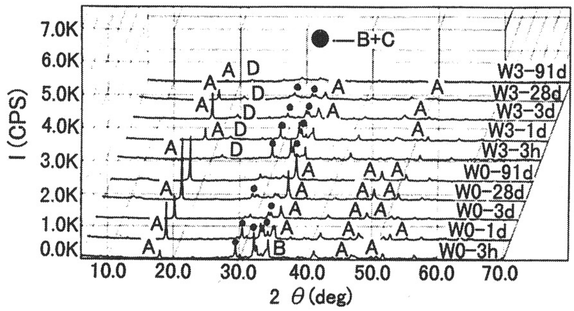
Fig.3 shows that the XRD patterns of the products are much different from those of the used RHA and $Ca(OH)_2$, which indicates the reaction between the amorphous silica in RHA and $Ca(OH)_2$ has occurred. The phases found in CS-2, CS-7 and CS-18 are only $Ca_{1.5}SiO_{3.5}\cdot xH_2O$ (PDF Card: 33-0306, one kind of C-S-H gel found in a fully reacted β-C_2S, at water : solid = 0.45, hydrated for 21 years at 25℃) and α-cristobalite. The existence of the latter in the products is because that at 40℃ the inert crystalline SiO_2 in the RHA can't react with $Ca(OH)_2$. When the proportion of $Ca(OH)_2$ was raised (CS-5 and CS-6) there was residual $Ca(OH)_2$ in the products.

Under SEM the above products appear as small granules (Fig. 4), the shape and size of which are varied with the condition under which they were synthesized. By laser diffraction method it was found the average particle size of the C-S-H gel is between 4.79 μm and 7.91 μm, less than that of the used RHA and $Ca(OH)_2$.

Tang,[1], W. Kurdowski[2] and P. P. Budnikov et al.[3] found that C-S-H gel can accelerate the hydration of cement and increase its strength due to the "crystalline nuclei effect". But the C-S-H gel we prepared has a variable influence on the strength of cement (Table 2), no great strengthening effect has been observed. The reasons for this may be: 1) the kind and microstructure of the C-S-H gel in this experiment is different from those they used, 2) the specific surface of this C-S-H gel is too large so that the compactedness of the specimens with the C-S-H gel is poorer than that of the control cement (Table 2) and 3) the residual $Ca(OH)_2$ in CS-5 and CS-6 may have a worsening effect on cement strength. Now innovation on the preparing method of C-S-H gel and its effect on cement strength as well is being undertaken. But the fact that C-S-H can be formed through the reaction of RHA with $Ca(OH)_2$ provides us with another useful evidence to explain why the strength of concrete can be considerably enhanced by adding RHA to it. This is the aim, maybe the most important aspect, of this study.

Conclusions

At the temperature of about 40℃ the silica in RHA can react with $Ca(OH)_2$ to form one kind of very fine C-S-H gel with a big specific surface. The shape and particle size of the C-S-H gel are varied with reaction condition. No considerable strengthening effect of this gel on cement strength has been observed. One of the main reasons for the increase of RHA blended concrete can be attributed to the reaction occurs between the amorphous silica in RHA and $Ca2^+$, OH^- ions, or/and the formed portlandite in hydrating cement.



A: $Ca(OH)_2$ – 4.913Å, 2.327Å and 1.795Å, B: Alite, C: Belite, D: α –Cristabolite

Fig. 1 XRD patterns of hydrated pastes at water solid ratio of 0.55 (W0-normal cement, W3-cement with 30% RHA addition)

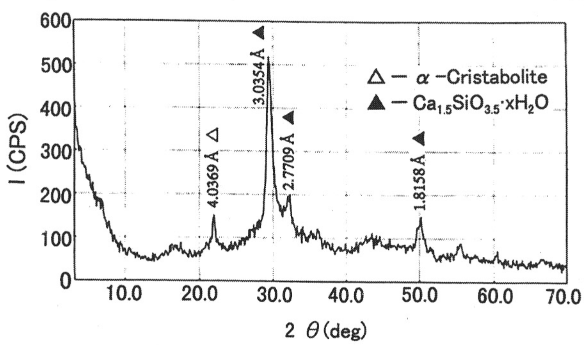
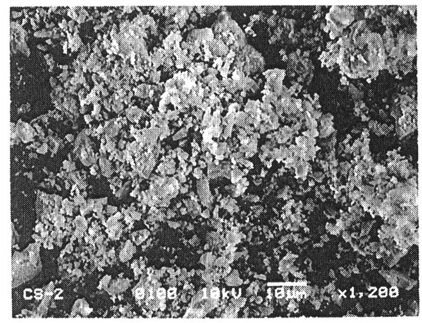
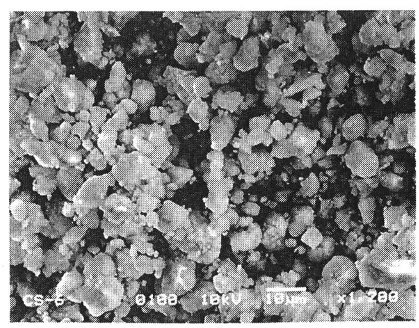


Fig. 2 XRD pattern of CS-2

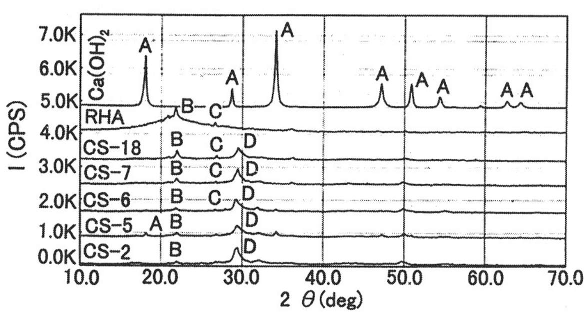


(a) CS-2



(b) CS-6

Fig. 4 SEM images of CS-2 and CS-6, 1200×



A: $Ca(OH)_2$, B: α –Cristabolite, C: β –Quartz, D: $Ca_{1.5}SiO_{3.5}{\cdot}xH_2O$ (C–S–H gel)

Fig. 3 Comparison of the XRD patterns of the RHA and $Ca(OH)_2$ with those of their reaction products

References

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