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On the C-S-H Gel Formed from the Reaction of Rice-husk Ash with $Ca(OH)_2$ and Its Effect on the Properties of Concrete

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Introduction

Studies on rice-husk ash (RHA) blended concrete show that the strength and durability of concrete can be improved considerably by adding RHA to it [(1)]. Sugita and Yu et al. attributed the main reasons for this to: 1) the decrease of the average pore size of concrete, 2) the decrement of the practical water cement ratio in RHA blended concrete due to the water adsorption characteristics of RHA, and 3) the promotion of cement hydration [(2)]. Besides these reasons are there any other factors which also contribute to the improvement? It was found that the amount of portlandite in the paste added with 30% RHA was decreased with hydration time instead of the increase of the amount of C-S-H gel [(3)]. This phenomenon does give us a hint that the active SiO_2 in RHA may react with the Ca^{2+} and OH^- ions released from hydrating cement, or with the portlandite in hydrates to form C-S-H gel. In this study it has been observed that the SiO_2 in RHA can react with Ca^{2+} and OH^- ions to form one kind of calcium silicate hydrate—$Ca_{1.5}SiO_{3.5}\cdot xH_2O$.

Raw Materials and Experiments

Raw material

Chemically pure $Ca(OH)_2$ was used in this experiment. RHA was burnt in a batch furnace and ground in a ball mill for 1 hr, with an average diameter of 15.4 μm. Its chemical compositions are shown in Table 1. The silica in it, except for a small amount of crystalline α-cristobalite, is almost in amorphous form and with a high chemical activity.

Table 1 Chemical composition(%) and N_2 specific surface of the RHA used in the experiment

Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	C	Total	Surface area
2.93	91.90	0.25	0.41	0.38	0.21	0.05	2.78	0.01	0.36	0.16	0.41	99.85	55.1 (m^2/g)

Experimental

$Ca_{1.5}SiO_{3.5}\cdot xH_2O$ was obtained by continuously mixing RHA with saturated or supersaturated $Ca(OH)_2$ solution at 40 ±3°C for some days. The experimental conditions and the reaction products are shown in Table 2.

Table 2 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 phases in the product by powder XRD	Av. size (μm)	N_2 surface area (m^2/g)
CS-2	5.00	Sat. solution**	—	12d	$Ca_{1.5}SiO_{3.5}\cdot xH_2O$, α-cristobalite	4.79	—
CS-5	50.00	50.00	10	6d	$Ca_{1.5}SiO_{3.5}\cdot xH_2O$, α-cristobalite, $Ca(OH)_2$	7.91	66.8
CS-6	50.00	50.00	10	4d	$Ca_{1.5}SiO_{3.5}\cdot xH_2O$, α-cristobalite, $Ca(OH)_2$	7.72	127.0
CS-7	50.00	30.00	12	4d	$Ca_{1.5}SiO_{3.5}\cdot xH_2O$, α-cristobalite	7.62	85.7
CS-18	70.00	42.00	9	4d	$Ca_{1.5}SiO_{3.5}\cdot xH_2O$, α-cristobalite	6.95	—

*dried at 65°C for 24 hr in an oven with enough soda lime after filtering out residual solution, ** renewed every day

Results and discussions

The pH value and electrical conductivity of $Ca(OH)_2$ solution at 40°C are 12.16 and 8.59 mS/cm respectively. After adding RHA to the solution both of them are gradually decreased with time (Fig. 1), which indicates that the Ca^{2+} and OH^- concentration of the solution is reduced with mixing time as pH value is directly related to the amount of free OH^- ions in the solution and the electrical conductivity is mainly dependent on the Ca^{2+} and OH^- concentration of the solution. On another hand, Fig. 2 shows that the XRD patterns of the products are much different from those of the used RHA and $Ca(OH)_2$. The above phenomena reveal that the reaction between RHA and $Ca(OH)_2$ solution has occurred. By comparison to PDF-33-306 the new material formed in the mixture was identified as $Ca_{1.5}SiO_{3.5}\cdot xH_2O$ (one kind of C-S-H gel almost with an amorphous structure, it was found by Mohan and Taylor in a β-C_2S paste hydrated for 21 years at 25°C and at a water solid ratio of 0.45). Because the α-cristobalite contained in RHA is inert at normal temperatures, it will retain in all of the products. When the proportion of $Ca(OH)_2$ to RHA in the mixture is raised to 1 : 1, there will be residual $Ca(OH)_2$ in the final products (Table 2). The shape and size of the products are varied with the condition under which they were synthesized. By laser diffraction analysis it was found that the average size of them is between 4.79 μm and 7.91 μm (Table 2), less than that of the used RHA and $Ca(OH)_2$, which means that the products maybe formed

Key words: C-S-H gel, $Ca(OH)_2$, rice-husk ash, concrete, strength

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by a dissolution-precipitation process. Under SEM the C-S-H gel appears as small round grains (Fig. 3-a), but at higher magnification it can be found that they practically have a flocculent structure with a great number of fine pores (Fig. 3-b), which directly explains why they have a so large N_2 adsorption specific surface.

The liquid phase of hydrating cement is also saturated with Ca^{2+} and OH^-ions, therefore compared with the concrete without RHA addition there may be more C-S-H gel and less portlandite in the concrete with RHA addition due to the reaction occurring between RHA and the Ca^{2+} and OH^-ions in hydrating cement. This has been confirmed by the following fact. In the paste with 30% RHA addition and hydrated for 28d, there exists much of this kind of C-S-H gel which fills in pores and plays a bridging role between hydrates and unhydrated cement particles (Fig. 3-c), and no portlandite has been observed by XRD and SEM. The formation of more C-S-H gel and less portlandite is certainly advantageous to the improvement of the strength and other properties of the concrete blended with RHA.

Conclusions

At temperatures around 40°C the silica in RHA can react with $Ca(OH)_2$ to form one kind of fine C-S-H gel with a very big specific surface, its shape and size are varied with reaction condition. One of the main reasons for the improvement on the properties of the concrete blended with RHA, such as strength and resistance to acid attack, carbonation and penetration, can be attributed to the formation of more C-S-H gel and less portlandite in it due to the reaction occurring between the amorphous silica in RHA and the Ca^{2+}, OH^-ions in hydrating cement.

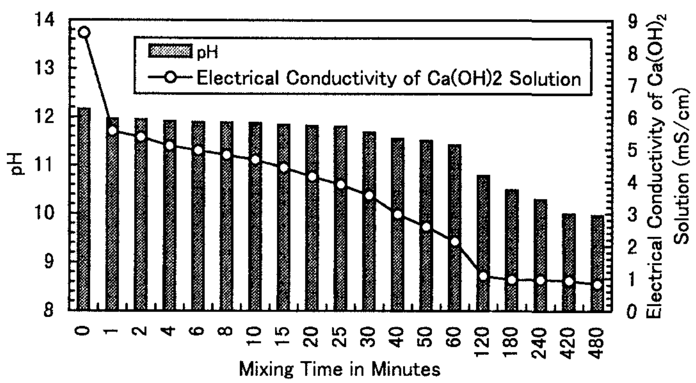
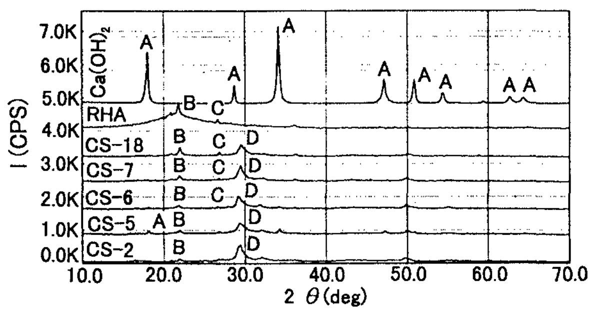
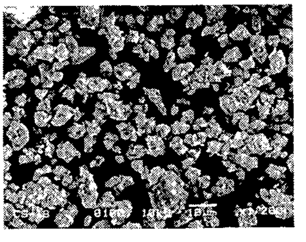


Fig. 1 Variation of pH and electrical conductivity of 200ml saturated $Ca(OH)_2$ solution with mixing time in the presence of 5.000g RHA

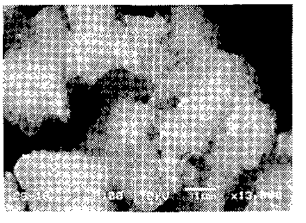


A: $Ca(OH)_2$, B: α — Cristobalite, C: β — Quartz, D: $Ca_{1.5}SiO_{3.5}\cdot xH_2O$

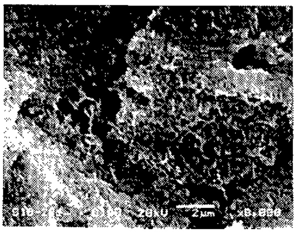
Fig.2 XRD patterns of $Ca(OH)_2$, RHA and their reaction products



(a) CS-18, 1200×



(b) CS-18, 13000×



(C) C-S-H gel in the paste for 28d, 8000×

Fig.3 SEM images of the synthesized C-S-H gel and the C-S-H gel existing in the cement paste with RHA addition

References

1. S. Sugita et al., "Preparation of highly active rice husk ash and its effect on the properties of concrete", The Concrete Way to Development, FIP Symposium 1997, Johannesburg, South Africa, Vol. 2, Mar., 1997, pp. 621-30.
2. S. Sugita et al., "The resistance of rice-husk ash concrete to carbonation, acid attack, and chloride-ion penetration", in preparation, to be presented to 1997 International Conference-High Performance Concrete: Design and Materials and Recent Advances in Concrete Technology, Malaysia.
3. Q. Yu et al. "On the reaction of rice husk ash with supersaturated $Ca(OH)_2$ solution", 平成八年度土木学会東北支部技術研究発表会講演概要, 平成九年三月十四日, pp.492-93.