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The reaction between rice husk ash and $Ca(OH)_2$ solution and the nature of its product

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Abstract

In this study it was confirmed that, at temperatures around 40°C and in the presence of water, the amorphous silica contained in rice husk ash (RHA) can react with $Ca(OH)_2$ to form one kind of C-S-H gel ($Ca_{1.5}SiO_{3.5}\cdot xH_2O$). The C-S-H gel looks like flocs in morphology, with a porous structure and large specific surface. The average particle diameter of the reaction product, ranging from 4.8 to 7.9 μm, varies slightly with the condition under which the reaction occurs. When the product is heated, it gradually loses the water that exists in it, but it maintains an amorphous form up to 750°C. Above 780°C it begins to transform to crystalline $CaSiO_3$. One of the main reasons for the improvement of concrete properties upon addition of RHA possibly may be attributed to the formation of more C-S-H gel and less portlandite in concrete due to the reaction occurring between RHA and the Ca^{2+}, OH^- ions, or $Ca(OH)_2$ in hydrating cement. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Rice husk ash; $Ca(OH)_2$; Reaction; Calcium silicate hydrate; Pozzolan

Similar to silica fume, rice husk ash (RHA) also contains about 90% silica by mass. A well-burnt and well-ground RHA, with most of its silica in an amorphous form and with N_2-specific surface varying between 40 and 60 m^2/g, is very active and can considerably improve the strength and durability of concrete [1–3]. Regarding the strengthening mechanism of RHA-blended concrete, Sugita et al. [2,4] suggested that (1) the average pore size of RHA concrete, compared with that of control concrete, is decreased; (2) the practical water-to-cement (w/c) ratio of RHA concrete is less than the used one because a portion of free water has been adsorbed in the great number of mesopores existing in RHA particles and having an average pore diameter of about 80Å; (3) cement hydration is improved; and (4) more C-S-H gel may be formed in RHA concrete due to the reaction that probably occurs between the silica in RHA and the Ca^{2+}, OH^- ions, or $Ca(OH)_2$ in hydrating cement. However, until now, no direct evidence for such a reaction has been observed.

It is known that silica fume can react with $Ca(OH)_2$ to produce C-S-H gel, and the CaO to SiO_2 ratio of the C-S-H gel formed in a paste with silica fume addition decreases markedly as the addition of silica fume increases [5]. Lately, Jiang et al. [6] reported that C-S-H gel also could be formed in slag pastes activated with 5M NaOH at a w/c ratio of 0.4. In this study it was observed that, at ordinary temperatures and in the presence of water, RHA also can react with $Ca(OH)_2$, forming $Ca_{1.5}SiO_{3.5}\cdot xH_2O$.

1. Raw materials and experiments

1.1. Raw materials

Chemically pure $Ca(OH)_2$, distilled water, and Portland cement were used. RHA used in this experiment was burnt in a batch furnace at about 600°C and ground in a ball mill for 1 h. The RHA had an average particle diameter of 15.4 μm and N_2-specific surface of 55.1 m^2/g. The chemical compositions are shown in Table 1. Except for a small amount of crystalline α-cristobalite, the silica in it is almost in amorphous form. Using the method proposed by Luxan et al. [7], it was observed that the change in electrical conductivity of saturated $Ca(OH)_2$ solution at 40 ± 1°C after the addition of the RHA was 3.22 mS/cm, which shows the RHA has a very good pozzolanic activity.

1.2. Experiments

A glass beaker containing 200 mL of saturated $Ca(OH)_2$ solution at 40 ± 1°C was placed in a water bath at the same temperature, then 5.000 g of RHA was added with the solu-

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Table 1
Chemical compositions (%) of RHA used in the experiment

LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	C	Total
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

LOI, loss on ignition.

tion under continuous stirring. A digital pH meter and an electrical conductivity meter were used to record the variations in pH value and electrical conductivity of the solution with time. The results are shown in Fig. 1.

According to Table 2, suspensions with different addition of RHA and $Ca(OH)_2$ were prepared at water-to-solid ratios between 9 and 12. The solutions were sealed in beakers and then placed in water baths at 40 ± 3°C and kept under constant stirring. For preparation of sample CS-2, 5.00 g of RHA was added to 0.4 dm^3 of saturated $Ca(OH)_2$ solution; the solution was filtered every 24 h and replaced with fresh saturated $Ca(OH)_2$ solution of the same temperature. Finally, the filter residue of every suspension was dried at 65 ± 2°C for 24 h in an oven in which there was sufficient soda lime. X-ray diffraction (XRD) analysis, thermogravimetric differential thermal analysis (TG-DTA), N_2 isothermal adsorption test, and scanning electron microscopy (SEM) were conducted.

In addition, sample CS-11 was heated at 100°C, 300°C, 400°C, 700°C, 750°C, 780°C, and 820°C for 2 h in a Muffle furnace to investigate the variation of its property and composition with heating temperature.

2. Results and discussion

2.1. Reaction between RHA and $Ca(OH)_2$ solution

The pH value and electrical conductivity of saturated $Ca(OH)_2$ solution at 40 ± 1°C were 12.16 and 8.59 mS/cm, respectively. After adding RHA to the solution, these values both gradually decreased with time (Fig. 1), which indicated that both Ca^{2+} and OH^- concentration of the solution were reduced with time, because: (1) pH value was directly related to the amount of free OH^- anions in the solution; and (2) electrical conductivity was mainly dependent on the effective concentration of Ca^{2+} and OH^- ions in the solution. The reason for the decrease in the concentration of Ca^{2+} and OH^- ions probably can be attributed to the interaction between them and the RHA that was added. In addition, XRD shows that: (1) the products produce much different XRD patterns from those of their starting materials: $Ca(OH)_2$ and RHA (Fig. 2); and (2) a new phase has been formed in the product (Fig. 3). In comparison to PDF-33-306, the new phase was proved to be $Ca_{1.5}SiO_{3.5}\cdot xH_2O$. $Ca_{1.5}SiO_{3.5}\cdot xH_2O$, also called C-S-H gel, was found for the first time by Mohan and Taylor [8] in a β-C_2S paste at a water-to-solid ratio of 0.45 and hydrated for 21 years at 25°C.

These results reveal that the reaction between the SiO_2 in RHA and $Ca(OH)_2$ solution can take place and yields C-S-H gel.

2.2. Product of the reaction and its properties

The crystalline α-cristobalite contained in RHA was inert at normal temperatures; therefore, it remained in all the products (Table 2). When the molar ratio of $Ca(OH)_2$ to RHA was raised to 0.88 (CS-5 and CS-6), unreacted $Ca(OH)_2$ existed in the products even though the reaction time of CS-5 had been prolonged for 2 days compared with that of the

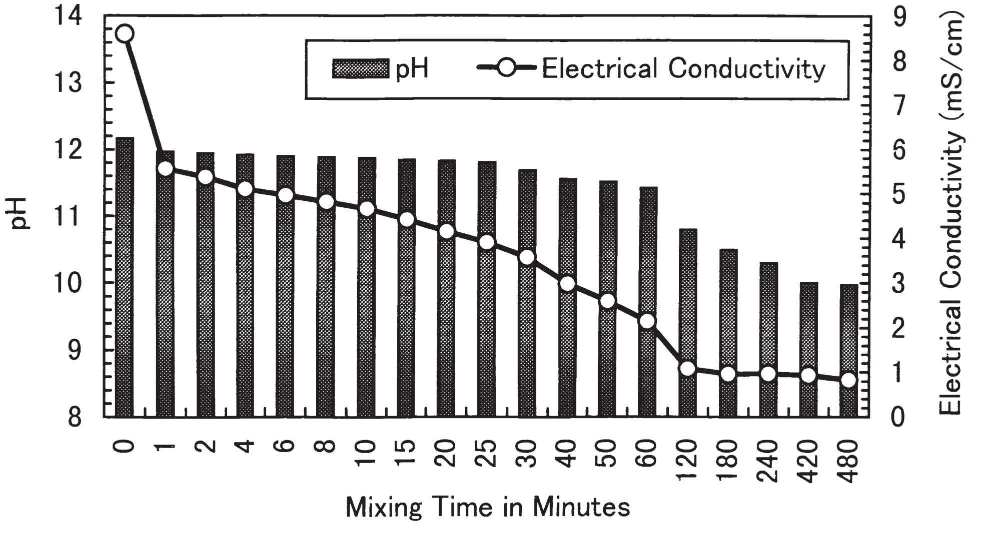

Fig. 1. Variation of pH value and electrical conductivity of saturated $Ca(OH)_2$ solution with time in the presence of RHA.

Table 2
Reaction products of RHA with $Ca(OH)_2$ in the presence of water

Sample	RHA (g)	$Ca(OH)_2$ (g)	w/s*	Age (days)	Observed phases in the product by XRD	Average size (μm)	N_2-specific surface (m^2/g)
CS-2	5.00	Saturated solution	0.4 (dm^3)	12	C-S-H[†] α-cristobalite	4.8	—
CS-5	50.0	50.0	10.0	6	C-S-H, α-cristobalite, $Ca(OH)_2$	7.9	66.8
CS-6	50.0	50.0	10.0	4	C-S-H, α-cristobalite, $Ca(OH)_2$	7.7	127.0
CS-7	50.0	30.0	12.0	4	C-S-H, α-cristobalite	7.6	85.7
CS-11	65.0	39.0	10.0	4	C-S-H, α-cristobalite	—	—
CS-18	70.0	42.0	9.0	4	C-S-H, α-cristobalite	7.0	—

* Water-to-solid ratio, in the case of CS-2 0.4 dm^3 of saturated $Ca(OH)_2$ solution was used.

[†] $Ca_{1.5}SiO_{3.5}\cdot xH_2O$.

suspensions with less $Ca(OH)_2$ to RHA ratios. In this case, that $Ca(OH)_2$ could not completely combine with the silica in RHA may be because the reaction temperature, being only 40°C, was lower than that adopted by others [9,10]. Because the molar ratio of $Ca(OH)_2$ to SiO_2 of all the suspensions was less than 1.5, there certainly existed residual RHA in the final products. Therefore, the reaction product, except CS-5 and CS-6, was practically a mixture of $Ca_{1.5}SiO_{3.5}\cdot xH_2O$, α-cristobalite, and residual RHA.

The size of the products varied slightly with the condition under which the reaction occurred (Fig. 4). By laser diffraction it was observed that most of the resulting particles were less than 10 μm in diameter (Fig. 5). Their average diameter, which varied between 4.8 and 7.9 μm (Table 2) and was smaller than those of the RHA and $Ca(OH)_2$ used, is larger than that of the C-S-H particles in hardened cement paste [5]. The reason for this seems to be the difference that exists between their growing conditions. In cement paste, the available water and space for the growth of C-S-H gel is more limited.

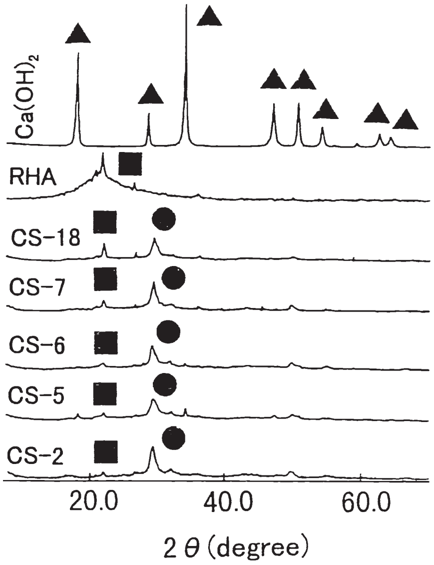

Fig. 2. XRD patterns of $Ca(OH)_2$, RHA, and their reaction products in the presence of water (CuK$_{\alpha1}$ radiation). Symbols: ▲, $Ca(OH)_2$; ■, α-cristobalite; ●, $Ca_{1.5}SiO_{3.5}\cdot xH_2O$ (C-S-H gel, 3.040 Å, 2.790 Å, 1.820 Å).

By N_2 isothermal adsorption it was observed that samples CS-5, CS-6, and CS-7 had a specific surface between 60 and 130 m^2/g (Table 2), which was larger than that of the RHA used. Under SEM the products appeared to be small round grains at a magnification of 1200× (Fig. 4). At higher magnifications, however, it was observed that they had a flocculent and porous structure (Fig. 6). The pores were mainly between 10 and 100Å, with an average radius of about 20Å (Fig. 7).

Being porous in structure and large in specific surface, the products contained much adsorbed water. Therefore, CS-2, for instance, had marked weight loss before 141°C because of evaporation of adsorbed water that was in it (Fig. 8). Above this temperature its structural water was gradually released, but it kept an amorphous form up to 750°C (Fig. 9). From 780°C it began to crystallize to $CaSiO_3$ (PDF-27-88, wollastonite-2M). The exothermal peak in the DTA curve at about 827°C (Fig. 8) was due to this effect. Mi et al. [11] also observed that the afwillite obtained by a mechanochemical method decomposed at about 835°C to form wollastonite.

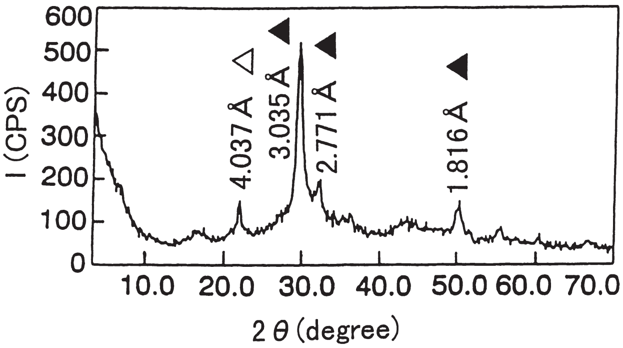

Fig. 3. XRD patterns of the reaction product of RHA with saturated $Ca(OH)_2$ solution at 40 ± 3°C (CuK$_{\alpha1}$ radiation). Symbols: ▲, $Ca_{1.5}SiO_{3.5}\cdot xH_2O$; ▼, $CaSiO_3$ (wollastonite); △, α-cristobalite; ▽, β-quartz. (1) room temperature; (2) 100°C, 2 hr; (3) 300°C, 2 hr; (4) 400°C, 2 hr; (5) 700°C, 2 hr; (6) 750°C, 2 hr; (7) 780°C, 2 hr; (8) 820°C, 2 hr.

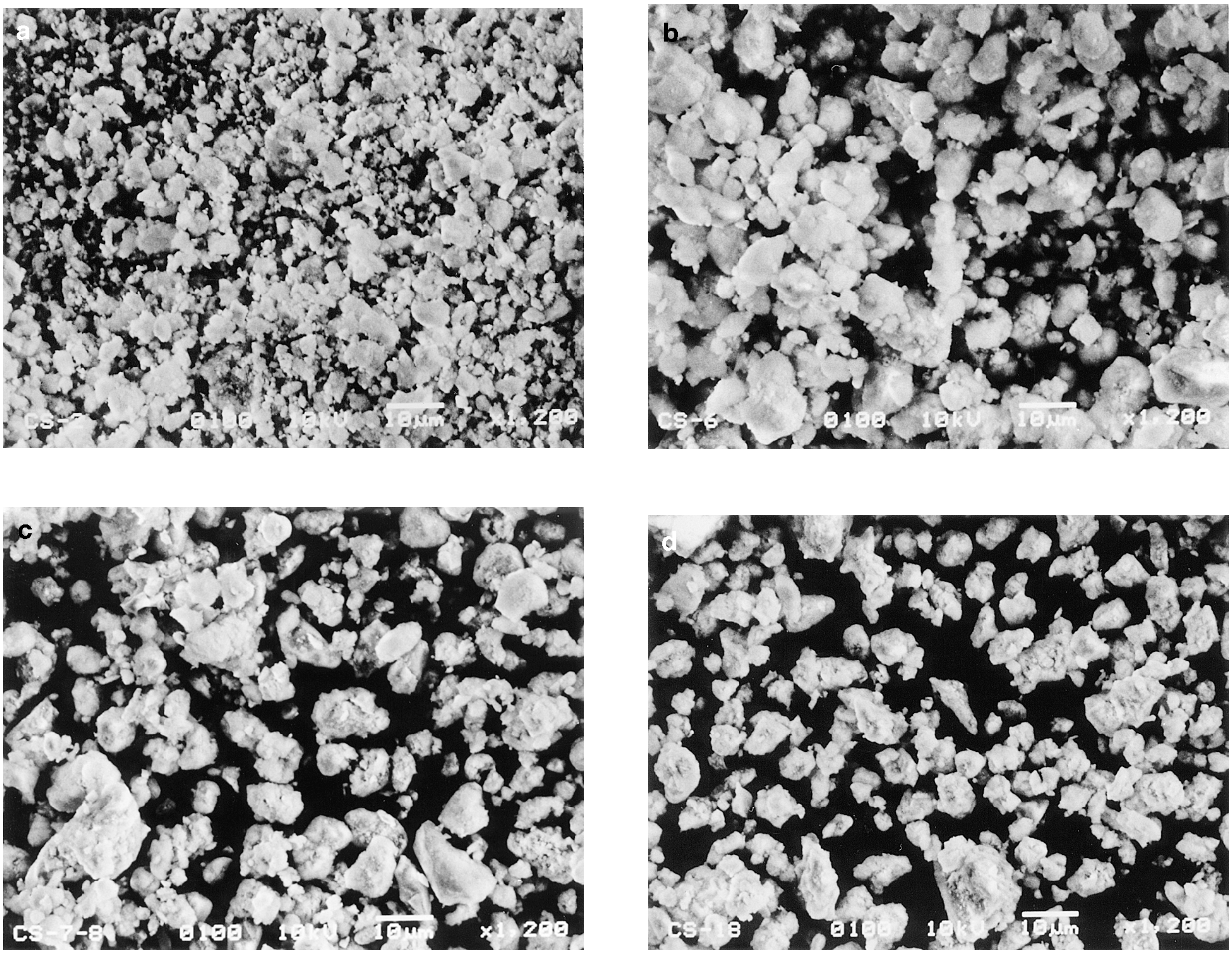

Fig. 4. (a–d) SEM images of the reaction products of RHA with $Ca(OH)_2$ in the presence of water at 40 ± 3°C. (a) CS-2, 1,200×; (b) CS-6, 1,200×; (c) CS-7, 1,200×; (d) CS-18, 1,200×.

2.3. Formation mechanism of the product

Inoue and Hara [1] observed that, by stimulation with 1N NaOH solution, the silica in a well-burnt RHA was almost dissolved into solution in only 1 h. Like NaOH solution, $Ca(OH)_2$ solution, with its pH value larger than 12, also has a damaging effect on the Si-O bond of amorphous silica [5]. Therefore, the formation mechanism of C-S-H gel under this condition may be as follows: the silica in RHA, stimulated by the $Ca(OH)_2$ solution, is quickly dissolved into solution forming SiO_4^{4-}; then, under continuous stirring, the SiO_4^{4-} ions react with Ca^{2+} and OH^- ions in the solution to form $Ca_{1.5}SiO_{3.5}\cdot xH_2O$. That is to say, the $Ca_{1.5}SiO_{3.5}\cdot xH_2O$ is formed by a dissolution-precipitation process. That the average particle diameters of the products (Table 2) were

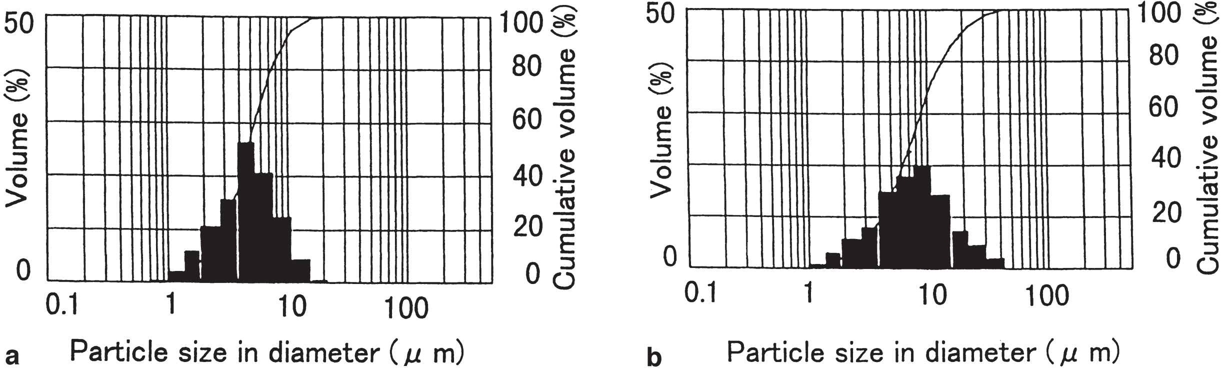

Fig. 5. Particle size distribution of samples (a) CS-2 and (b) CS-7 determined by laser diffraction.

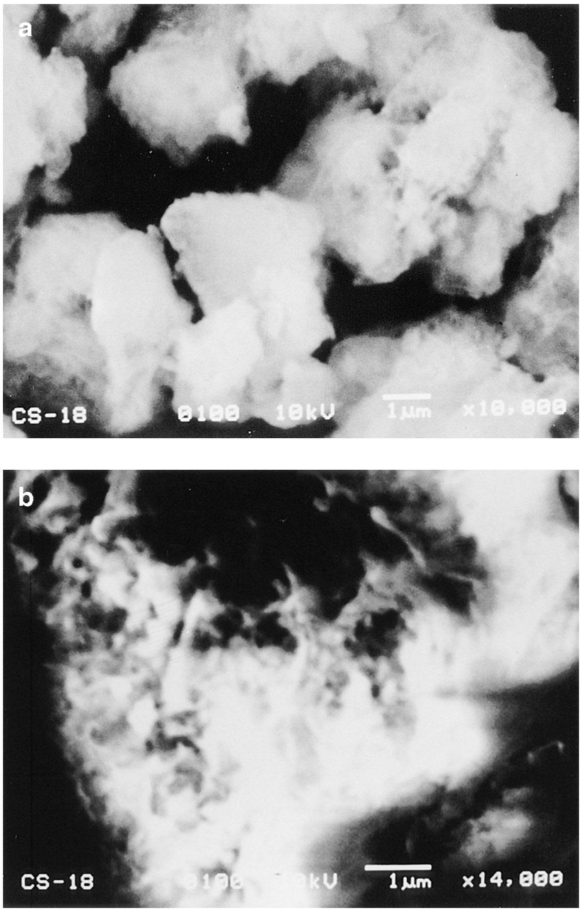

Fig. 6. SEM images of sample CS-18. (a) CS-18, 10,000×; (b) CS-18, 14,000×.

less than that of the raw material RHA used ($D_{av.}$ = 15.4 μm) gives a direct evidence for this.

2.4. Mechanism of the strengthening effect of RHA addition on concrete

The liquid phase of hydrating Portland cement is saturated with Ca^{2+} and OH^- ions; therefore, portlandite often exists in hardened cement. From Figure 10 it can be seen that the amount of $Ca(OH)_2$ in the paste with 30% RHA (W_3) added begins to decrease after 3 days, and by 91 days it reaches nearly zero, whereas in the control paste (W_0) it is adversely increased with hydration time. Figure 11 shows that in the paste with 30% RHA added there exists $Ca_{1.5}SiO_{3.5}\cdot xH_2O$. Under SEM it can be observed that the C-S-H gel, with its CaO to SiO_2 molar ratio of about 1.43 (close to that of $Ca_{1.5}SiO_{3.5}\cdot xH_2O$), fills in pores and plays a bridging role between hydrates and unhydrated cement particles (Fig. 12). This phenomenon reveals the reaction between RHA and Ca^{2+} and OH^- ions, or $Ca(OH)_2$ also can

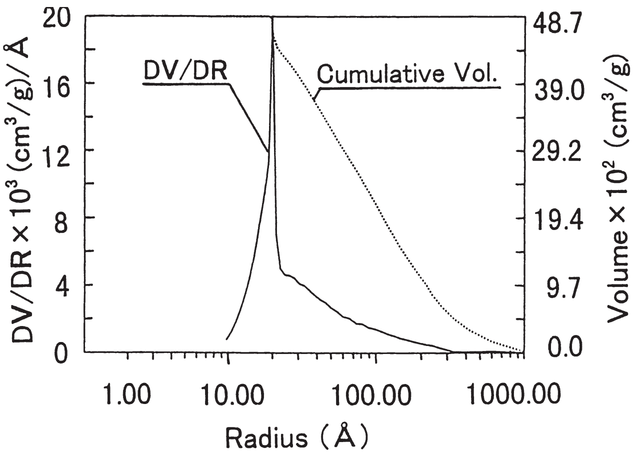

Fig. 7. Pore distribution of sample CS-7 determined by N_2 isothermal adsorption and desorption.

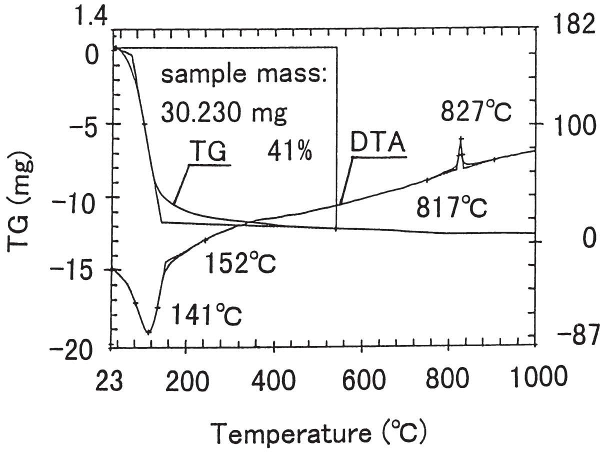

Fig. 8. TG-DTA curves of sample CS-2.

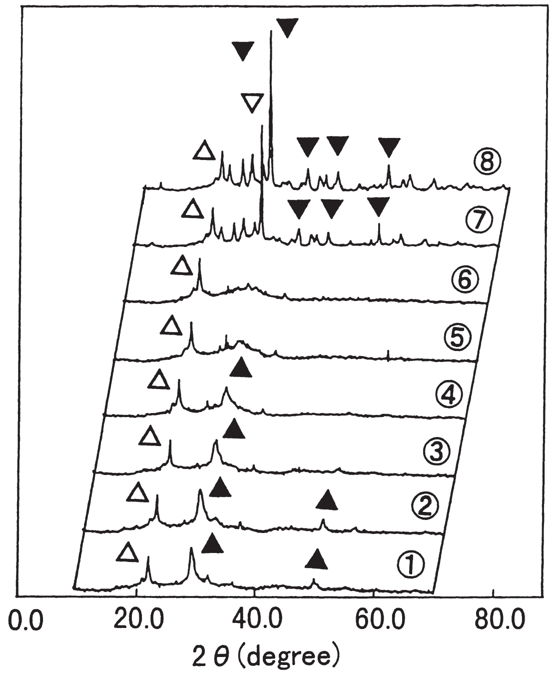

Fig. 9. XRD patterns of CS-11 after heating for 2 hours at various temperatures (CuK$_{\alpha 1}$ radiation). ▲, $Ca_{1.5}SiO_{3.5}\cdot xH_2O$; ▼, $CaSiO_3$ (wollastonite); △, α-cristobalite; ▽, β-quartz. (1) room temperature; (2) 100°C, 2 hr; (3) 300°C, 2 hr; (4) 400°C, 2 hr; (5) 700°C, 2 hr; (6) 750°C, 2 hr; (7) 780°C, 2 hr; (8) 820°C, 2 hr.

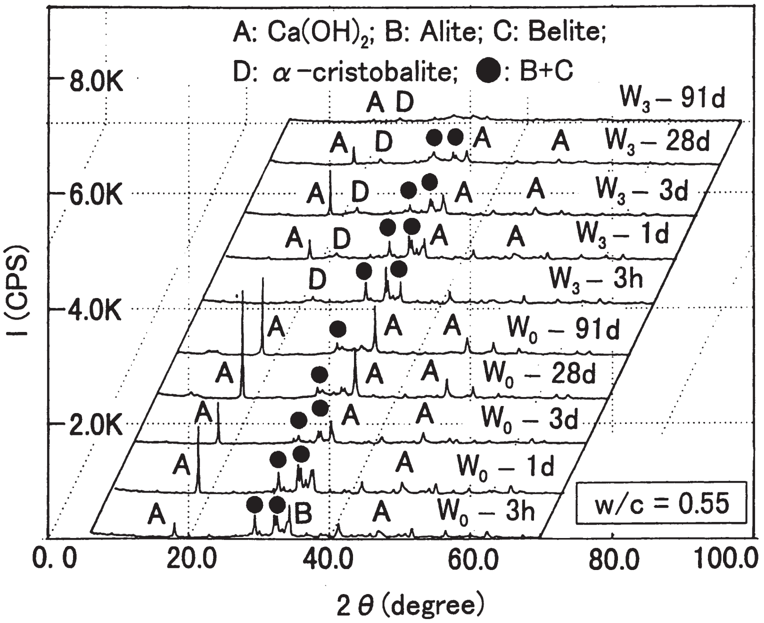

Fig. 10. XRD patterns (CuK$_{\alpha 1}$ radiation) of pastes at a w/c ratio of 0.55 and hydrated at 20 ± 1°C for different ages. W_0, Portland cement paste; W_3, paste with 30% RHA addition.

occur in a paste blended with RHA. Therefore, in comparison to the concrete without RHA addition, there will be more C-S-H gel and less portlandite in the concrete with RHA addition. This will contribute to improvement in the strength of the concrete and its resistance to acid attack, carbonation, and penetration [2,4].

3. Conclusions

1. At temperatures around 40°C and in the presence of water, RHA can react with $Ca(OH)_2$ to form one kind of fine C-S-H gel ($Ca_{1.5}SiO_{3.5}\cdot xH_2O$). The particle size of the reaction product, with an average diameter between 4.8 and 7.9 μm, varied slightly with the condition under which the reaction occurs.
2. The C-S-H gel appears to be flocs in morphology, with a porous structure and large N_2-specific surface. The pores in the gel are mainly between 10 and 100Å with an average radius of about 20Å.
3. When the product is heated, it gradually loses the water it contains, but it will keep an amorphous form up to 750°C. Above 780°C it will be transformed to crystalline $CaSiO_3$ (wollastonite).
4. One of the main reasons for the improvement in properties of concrete, such as strength and resistance to acid attack, carbonation, and penetration, by adding RHA to concrete possibly may be attributed to the

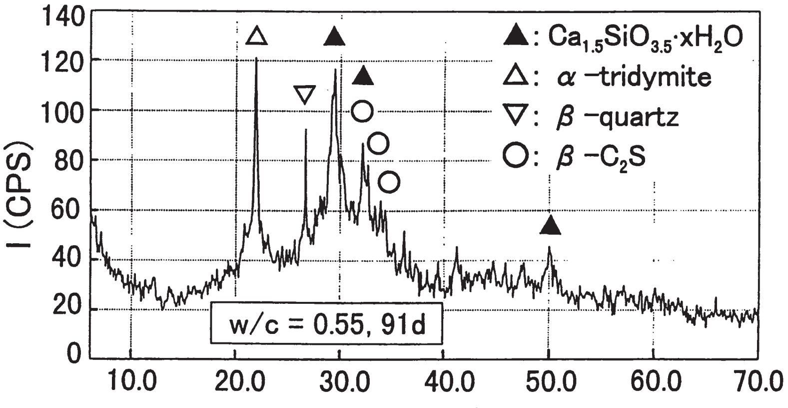

Fig. 11. XRD pattern (CuK$_{\alpha 1}$ radiation) of paste at a w/c ratio of 0.55 with 30% RHA addition and hydrated at 20 ± 1°C for 91 days.

formation of more C-S-H gel and less portlandite in it due to the reaction occurring between RHA and the Ca^{2+} and OH^- ions, or $Ca(OH)_2$ in hydrating cement.

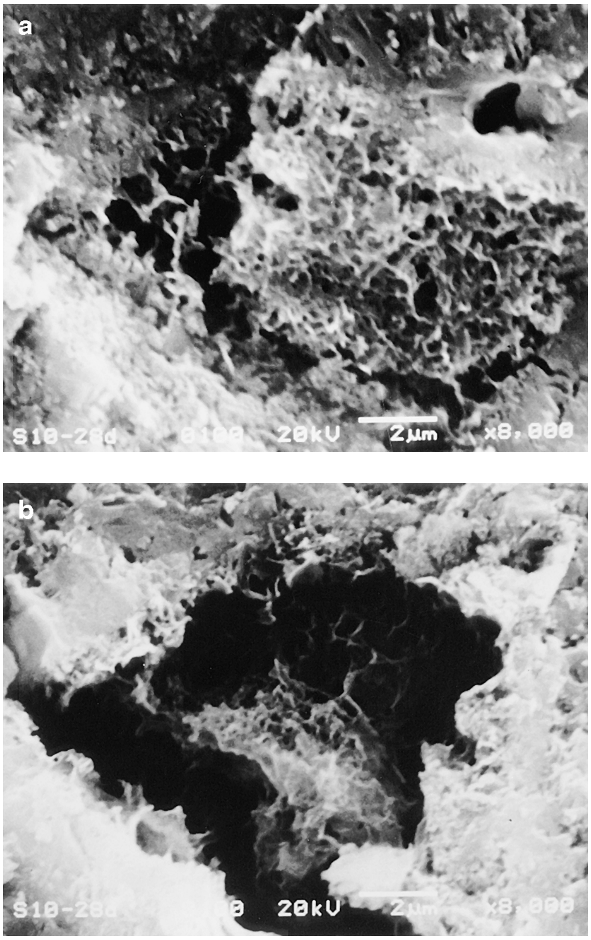

Fig. 12. SEM images of C-S-H gel in the paste with 10% RHA added and hydrated at 20 ± 1°C for 28 days, with CaO to SiO_2 molar ratio of about 1.43 determined by X-ray microanalysis. (a) C-S-H gel observed in paste, 8,000×; (b) C-S-H gel formed in pores, 8,000×.

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