

Acceleration of Early Hydration in Belite-Rich Cement by Remelting Reaction

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再融反応によるビーライトセメントの初期水和の促進

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Hydration activity of belite-rich cement, based on the heat evolution for up to ~10 d, was effectively improved by a remelting reaction of the constituent belite. The modified cement, termed "remelted belite cement," is mainly composed of belite in which the remelting reaction occurred for a large extent, and thus distinct from the conventional belite-rich cement. The liquid, exsolved by the reaction, contained a much higher concentration of alkalis than the host belite. The alkalis accelerated the hydration and the main heat evolution peak began ~7 h earlier during the initial stage up to ~30 h. The subsequent heat evolution between ~30 h and ~10 d was mainly increased by the presence of twin boundaries in the host β -phase belite; the boundaries on the crystal surface behaved like active centers for the reaction with water. The grindability was also improved by the remelting reaction, in agreement with a previous study.

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1. Introduction

Belite-rich cement has been the subject of extensive study because it has more advantages than the normal Portland cement, the main component of which is alite, for saving energy and reducing CO₂ gas emission in the production process.¹⁾ In view of the recycling of cement mortar, it seems profitable to use it as the raw material for the belite-rich cement, because the Ca/Si molar ratio of the cement mortar, including the fine aggregate, is small and normally less than unity. However, the main disadvantage of the conventional belite-rich cement for practical use is the lack of hydration activity as well as grindability.

The hydration activity and grindability of the belite-rich cement have been markedly improved by the remelting reaction²⁾⁻⁶⁾ of the constituent belite.^{7),8)} The modified cement, termed "remelted belite cement," was mainly composed of the belite in which the remelting reaction had sufficiently occurred, and thus distinct from the conventional belite-rich cement.⁸⁾ The activity was increased by the higher specific surface area of the former cement. The weaker resistance to fracture for the remelted belite compared to the quenched material caused the better grindability.

The remelting reaction is accompanied by an exsolution of the liquid, which is rich in impurity components (e.g., Na₂O, K₂O, Al₂O₃ and Fe₂O₃) of the parent α -phase belite.²⁾ The rate of the reaction depends not only on the temperature but also on the Al/Fe ratio of the exsolved liquid.⁴⁾ When the Al/Fe molar ratio, which is originally determined by the relative concentration of Al with respect to Fe in the parent belite, is greater than unity, the exsolved liquid readily spreads onto the lamellae, leading to the high reaction rate.

The α'_L -to- β martensitic transformation of belite has been reported to be athermal.⁹⁾⁻¹¹⁾ Thus, the transformed fraction at any temperature (T) is dependent on the starting temperature (M_s) and finishing temperature (M_f) of the transformation. The belite with $M_f < T < M_s$, for example, is composed of both the α'_L - and β -phases at T . The decrease in crystal symmetry from orthorhombic to monoclinic fre-

quently leads to the formation of polysynthetic twinning on (100) _{β} but rarely on (001) _{β} .¹²⁾

The hydration behavior has been compared between the α'_L - and twinned β -phases with identical chemical compositions.¹³⁾ With pulverized crystals, the intersections of the twin boundaries and the crystal surface behaved like active centers of the reaction with water. The β -phase, therefore, showed a much higher hydration activity than the α'_L -phase during the early stage of the hydration process. In general, the rate of early hydration can also be accelerated by the presence of alkalis in the water in contact with the hydrating cement.¹⁴⁾

The present study deals with the acceleration mechanism of the early hydration of the remelted belite cement. The remelted belite exclusively consisted of the twinned β -phase, together with the exsolved liquid in high alkali concentration. The conventional belite-rich cement, used as the control, was mainly composed of the quenched belite, which contained the alkalis in solid solution to stabilize the α'_L -phase.

2. Experimental

2.1 Materials

The raw mixture with the composition of a belite-rich cement clinker was prepared from limestone, chemical reagents (Al₂O₃, Fe₂O₃, MgO and CaSO₄·2H₂O) and laboratory cement mortar (Ca/Si=0.15). The cement mortar contained a small amount of P₂O₅ and a relatively high concentration of alkalis (1.3 mass% Na₂O and 2.3 mass% K₂O) that originated from the fine aggregate. The bulk chemical composition of the clinker to be obtained after firing is given in Table 1. The estimated mineral composition using the procedure of Bogue¹⁵⁾ was 77.5% belite, 4.6% alite and 14.6% interstitial material (5.5% calcium aluminate and 9.1% calcium aluminoferrite).

The raw mixture was finely ground and pressed into pellets (5.0 g each, 20 mm ϕ × 7 mm). A part of the pellets was heated at 1400°C for 30 min, rapidly removed from the electric furnace and then quenched by blowing air. The sample thus prepared was termed S-A. The α -phase was stable

Table 1. Chemical Composition of Belite-Rich Clinker

Substance	Composition (mass%)
CaO	62.11
SiO ₂	28.35
Al ₂ O ₃	4.02
Fe ₂ O ₃	3.01
MgO	0.70
Na ₂ O	0.48
K ₂ O	0.83
SO ₃	0.50
Al ₂ O ₃ /Fe ₂ O ₃	1.34

for the belite at 1400°C, together with the alite and interstitial liquid. The other pressed pellets were heated at 1400°C for 30 min, cooled at 2°C/min to 1250°C and then quenched by blowing air (sample S-B). During the slow cooling, the remelting reaction occurred after the α -to- α'_H transition. Upon quenching the interstitial liquid crystallized and separated into calcium aluminate and calcium aluminoferrite.

2.2 Characterization

Polished sections were prepared for both samples and their microtextures were observed using the optical microscope. The phase composition of the belite was examined using an X-ray powder diffractometer (XRD; Model XD-D1, Shimadzu Corp., Kyoto, Japan). The profile data were collected using Ni-filtered Cu K α radiation (30 kV, 30 mA) and a step-scan technique (step width=0.04° and fixed time=4 s).

The chemical composition of the belite in S-A was determined using an electron probe microanalyzer (EPMA; Model JSM-840, JEOL, Ltd., Tokyo, Japan). The accelerating voltage was 15 kV and the probe current was 0.012 μ A. The average composition was obtained by measuring one point for each of the thirty crystals used. The corrections were made by the ZAF routines.

Concentration distribution maps for Na₂O, K₂O, Al₂O₃ and Fe₂O₃ were obtained using the EPMA. The area of analysis in S-B was 86 μ m \times 86 μ m with 500 \times 500 pixels and the dwell time was 20 ms (accelerating voltage, 15 kV; probe current, 0.05 μ A). The quantitative spot analysis was also made within the same area.

The powder specimens with particle size distributions between 0.18 and 0.30 mm were prepared for both samples. Each sample (7.0 g) was put into an agate container (45 ml volume) of a planetary micromill (Model P-7, Fritsch, Idar-Oberstein, Germany) together with seven agate balls (10 mm ϕ) and then ground for fixed times in the range from 100 to 600 s. The particle size fractions were measured using a laser granulometer for every grinding time (Model LA500, Horiba Co., Kyoto, Japan). The absolute size constant (D_e) and the distribution constant (n) of the Rosin-Rammler distributions were then determined.

Each powder specimen less than 125 μ m in size was mixed with the reagent gypsum, and ground using the micromill for 30 min to obtain the belite-rich cement. The

SO₃ concentrations of both cements were 2.0 mass%. The specific surface area was measured by the BET three-point method (Model Nova1000, Yuasa Ionics Co., Osaka, Japan). Each cement (20.0 g) was mixed with distilled water (water/cement=0.5 in weight) in a conduction calorimeter (Model TCC-23, Tokyo Rikou Co., Tokyo, Japan). The rate of heat evolution at 20°C was measured for 28 d. The accuracy of the cumulative heat was estimated to be within 3 J/g based on the calibration made by electric heating.

3. Results and discussion

3.1 Microtextures and phase constitution

The optical microscopy showed that the mineral compositions of both samples, S-A and S-B, were nearly the same and consistent with the Bogue calculation result. The belite in S-A showed the intracrystalline lamella structure formed by the α -to- α'_H polymorphic transition upon quenching (Fig. 1(A)).¹⁶⁾⁻¹⁸⁾ From the XRD (Fig. 2) the crystals were composed mostly of the α'_L -phase with a small amount of β -phase. This indicated that the successive phase transitions of $\alpha \rightarrow \alpha'_H \rightarrow \alpha'_L$ were complete, while the $\alpha'_L \rightarrow \beta$ transition was incomplete at ambient temperature (20°C). As the latter transformation is athermal, the M_s and M_f temperatures satisfied the relationship $M_f < 20^\circ\text{C} < M_s$.

The belite crystals in S-B showed the typical microtexture during the final stage of the remelting reaction (Fig. 1(B)).³⁾ The parent α -phase belite was completely remelted during slow cooling and decomposed into the liquid and the new α'_H -phase belite. The resulting belite must have contained a lower concentration of impurities than the parent α -phase, which raised the M_f temperature above 20°C.

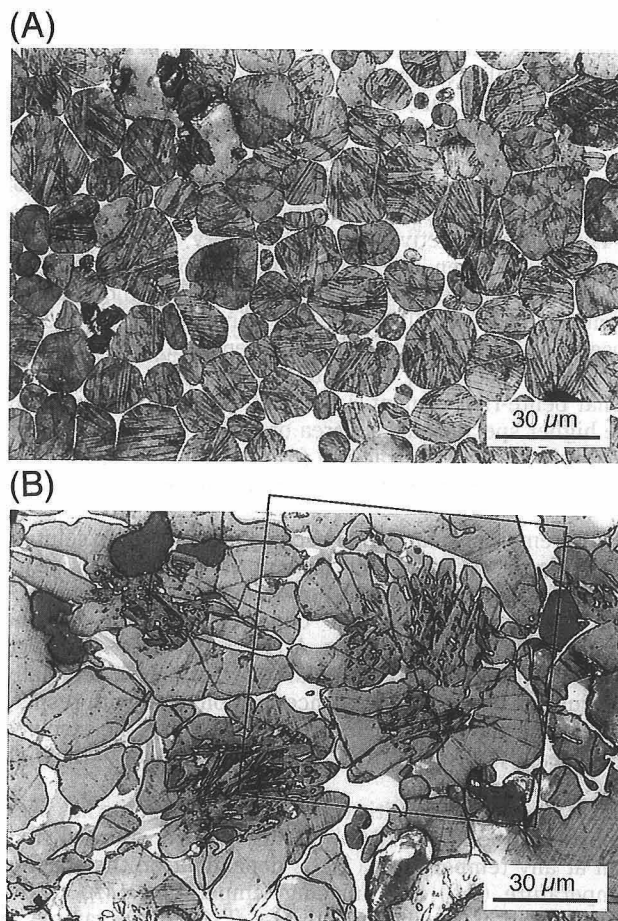


Fig. 1. Optical micrographs of (A) S-A and (B) S-B. Polished sections etched with nital. Reflected light.

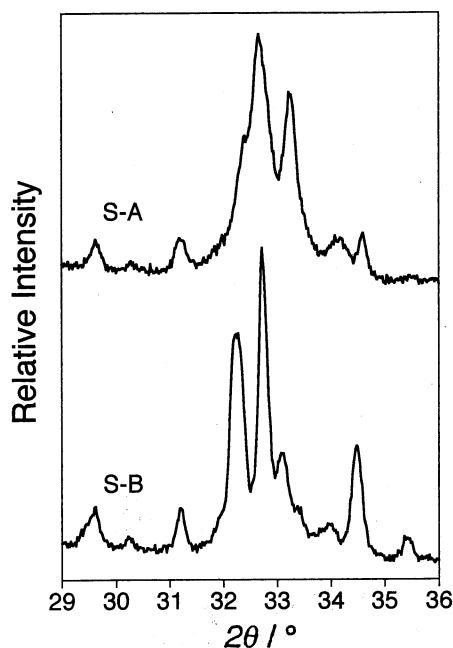


Fig. 2. Powder XRD patterns of S-A and S-B. The belite crystals in the former are composed mainly of the α'_L -phase with a small amount of β -phase, and those in the latter are exclusively composed of the β -phase.

Thus, the successive phase transitions of $\alpha'_H \rightarrow \alpha'_L \rightarrow \beta$ completely occurred upon quenching and the phase constitution at 20°C was exclusively β (Fig. 2).

3.2 Chemical compositions of parent β -phase belite and exsolved liquid

Based on the oxide compositions of the belite in S-A (Table 2), the chemical formula has been derived on the

Table 2. Chemical Composition of Belite

Substance	Composition (mass%)
	Average $\pm 1\sigma$
CaO	62.72 \pm 0.69
SiO ₂	32.46 \pm 0.97
Al ₂ O ₃	0.87 \pm 0.45
Fe ₂ O ₃	0.97 \pm 0.36
MgO	0.32 \pm 0.08
Na ₂ O	0.35 \pm 0.11
K ₂ O	0.32 \pm 0.06
SO ₃	0.21 \pm 0.08
P ₂ O ₅	1.47 \pm 0.17
TiO ₂	0.08 \pm 0.05
Total	99.78 \pm 0.90

Table 3. Numbers of Atoms in Belite on the Basis of 4 Oxygens

Substance	Number
Ca	1.927(9)
Mg	0.013(3)
Na	0.019(6)
K	0.012(2)
Al	0.015(8)
Fe	0.011(4)
Ti	0.002(1)
Σ	2
Si	0.93(2)
Al	0.014(7)
Fe	0.010(4)
P	0.036(4)
S	0.005(2)
Σ	1.00(2)
O	4
Al/Fe	1.3(2)

Figures in parentheses indicate standard deviations.

basis of 4 oxygen atoms in one formula unit (Table 3). The amphoteric atoms, Al and Fe, occupy the Ca- and Si-sites based on the assumption that the distribution is ideal, which is expressed by

$$N_{Al}^{Si} \cdot N_{Fe}^{Ca} = N_{Al}^{Ca} \cdot N_{Fe}^{Si}$$

where N_p^q represents the number of p atoms in a q site. As the Al/Fe molar ratio (=1.3) was greater than unity, the remelting reaction should proceed to its final stage with prolonged heat treatment.⁴⁾ This is consistent with the microtexture of the remelted belite in S-B.

The concentration distribution maps in S-B (Fig. 3) clearly indicated that the exsolved liquid had a large abundance of alkalis compared to the host belite. The exsolved liquid is now crystallized and probably separated into calcium aluminate and calcium aluminoferrite, analogous to the interstitial liquid. Under reflected light, the two phases, crystallized out of the interstitial liquid, were easily distinguishable; the calcium aluminate is darker in contrast than the calcium aluminoferrite (Fig. 1). When the alkali content was compared, it was much richer in the former than in the latter (Fig. 3).

3.3 Grindability

As the grinding proceeded the median sizes and the D_e -values of both samples steadily decreased (Fig. 4). When compared within 300 s at the same grinding time, sample S-B always showed a smaller median size and D_e -value than sample S-A. Accordingly, the grindability was effectively increased by the remelting reaction in accord with the previous studies.^{7,8)} The better grindability for S-B was

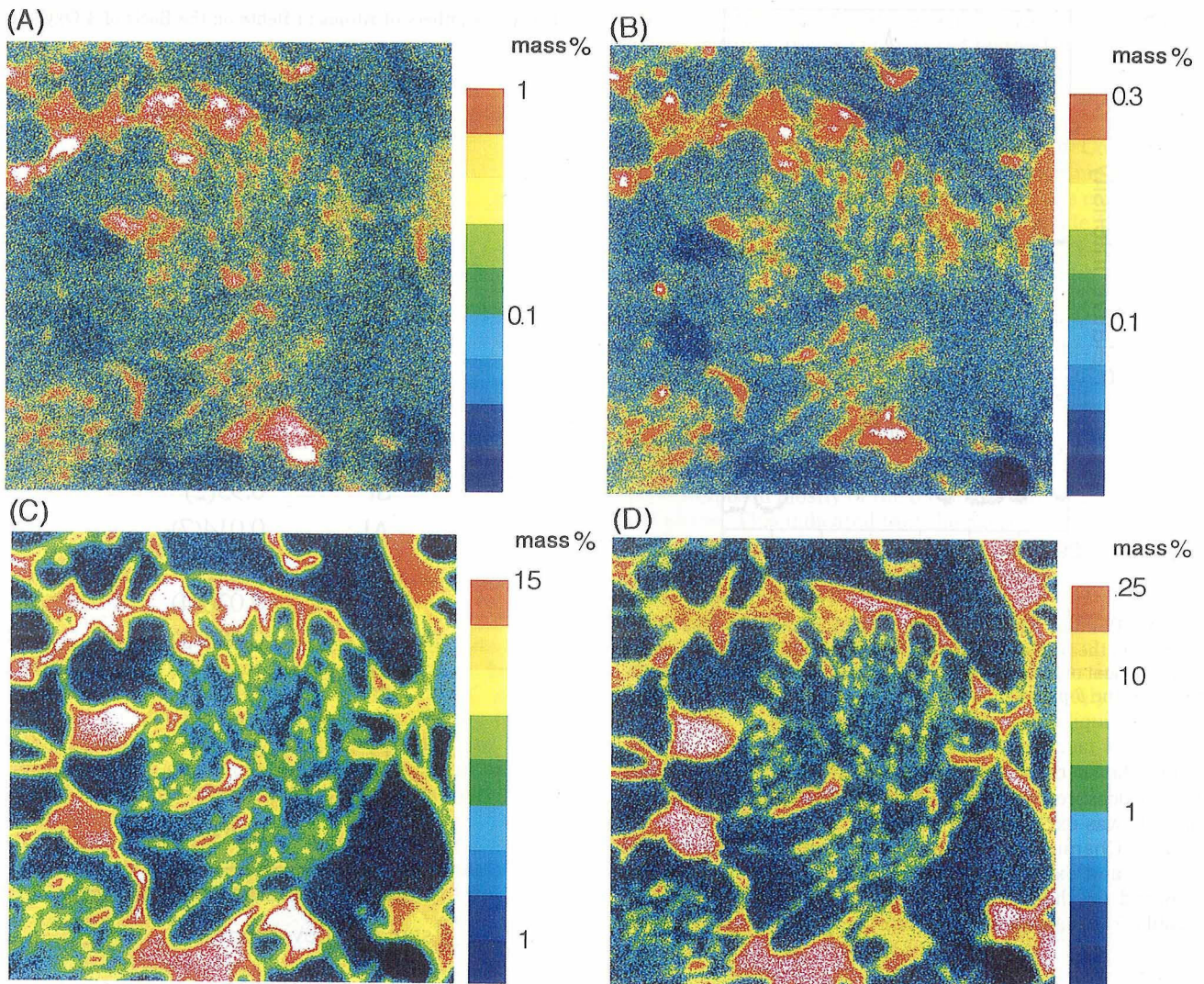


Fig. 3. Concentration distribution maps for (A) Na_2O , (B) K_2O , (C) Al_2O_3 and (D) Fe_2O_3 in the area depicted by the open square in Fig. 1(B). Sample S-B. The concentrations of these oxides are much higher for the exsolved liquid (now crystallized) than for the host belite. The figures beside the color columns represent the weight percentage of the relevant oxides.

probably derived from the weaker resistance to fracture for the remelted belite than for the quenched material. After 300 s, both samples had nearly the same median sizes and D_e -values of, for example at 600 s, ~ 15 and ~ 16 μm , respectively. The n -values of all samples at any grinding time were between 1.3 and 1.7.

3.4 Hydration behavior

One of the present cement samples consisting of S-B and gypsum is termed the “remelted belite cement” using the nomenclature followed in the previous study.⁸⁾ The other belite-rich cement sample, of which the constituent belite was rapidly quenched to depress the occurrence of the remelting reaction, was used as the control. Both cements showed nearly the same specific surface areas of $0.8 \text{ m}^2/\text{g}$ as well as very similar particle size fractions (Fig. 5). Accordingly, the differences in hydration behavior between the two cements, as will be mentioned later, would be independent of their powder properties.

The main heat evolution peak of the remelted belite cement began earlier and rose more steeply than that of the control up to ~ 30 h; the former maximum was reached ~ 7 h earlier than that of the latter (Fig. 6(A)). During the early stage of the 5 d hydration, the cumulative heat evolution of the remelted belite cement ($\sim 196 \text{ J/g}$) was ~ 1.3 times

that of the control ($\sim 151 \text{ J/g}$) (Fig. 6(B)). Accordingly, we concluded that the early hydration activity, evaluated from the heat evolution, was higher for the remelted belite cement than for the control.

During the hydration up to ~ 10 d, the cumulative heat of the remelted belite cement was always higher than that of the control, however, after ~ 11 d, both cements showed nearly the same cumulative heat of $\sim 230 \text{ J/g}$ (Fig. 6(B)). During the subsequent curing, the remelted belite cement, on the contrary, showed a lower cumulative heat than the control. The hydration heat of both samples was steadily liberated up to 28 d and the eventual cumulative heat of the former ($\sim 243 \text{ J/g}$) was ~ 0.8 times that of the latter ($\sim 298 \text{ J/g}$). Such cements with a low heat liberation would be the most suitable for large construction (e.g., dams).

3.5 Exsolved liquid and twin boundaries as hydration accelerators

Taking into consideration both the weight percentage and alkali concentration of the quenched belite in the clinker (Tables 1 and 2), the belite, as a whole, contained $\sim 55\%$ of the total amount of Na_2O and $\sim 30\%$ of the total amount of K_2O . As the belite after the remelting reaction contained a minute amount of alkalis in solid solution, most of these alkalis were concentrated in the exsolved li-

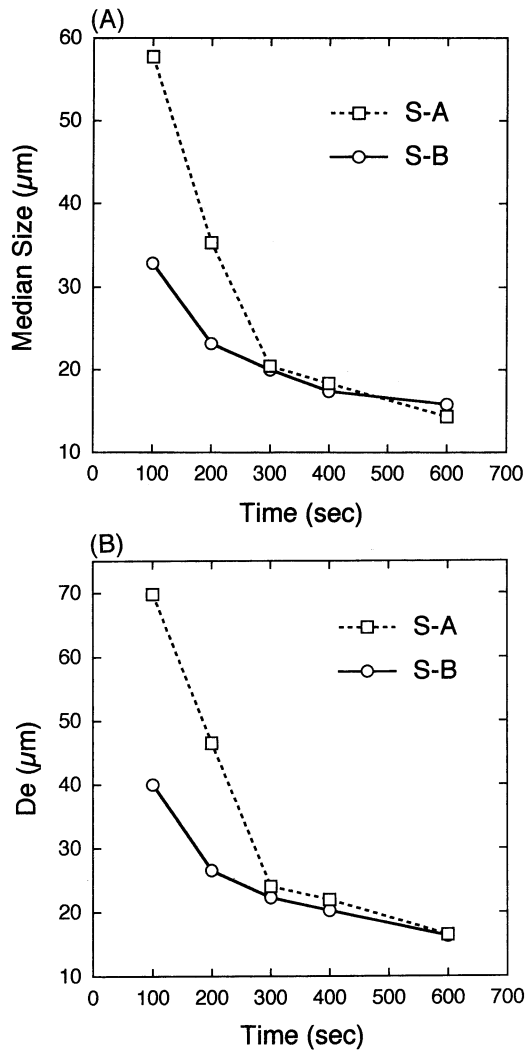


Fig. 4. Change in (A) median size and (B) D_e of Rosin-Rammlar distribution with grinding time.

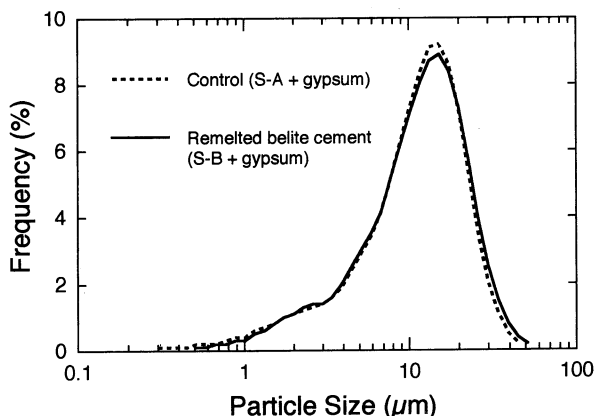


Fig. 5. Particle size distributions of the remelted belite cement and the control. The median sizes (M), the constants of the Rosin-Rammlar distributions (D_e and n) are $M=11.2\ \mu\text{m}$, $D_e=13.6\ \mu\text{m}$ and $n=1.6$ for the former and $M=10.9\ \mu\text{m}$, $D_e=13.8\ \mu\text{m}$ and $n=1.5$ for the latter.

quid, as demonstrated by the distribution maps (Fig. 3).

In general, the rate of cement hydration is significantly increased by the dissolved alkalis in the water in contact with hydrating cement.¹⁴ When the remelted belite

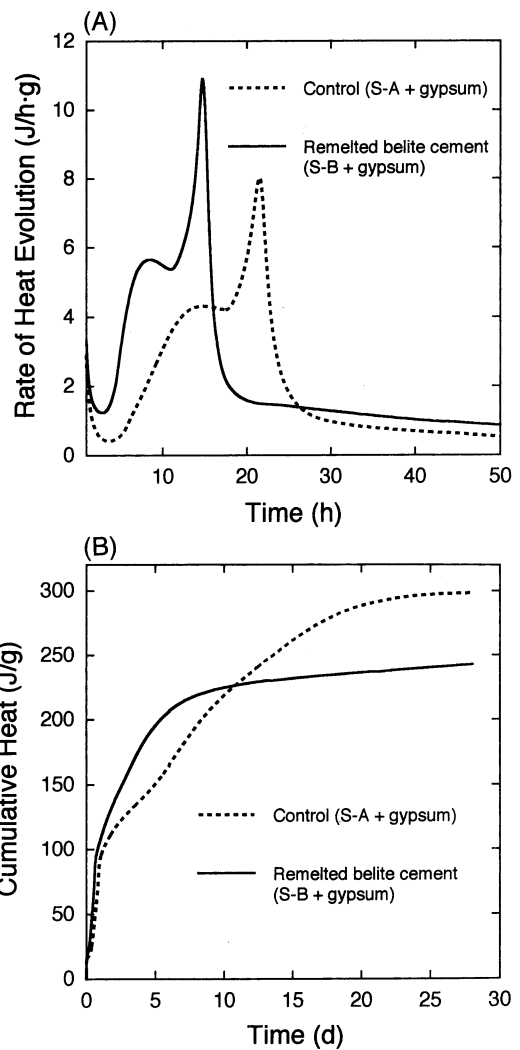


Fig. 6. Heat evolution at 20°C and water/cement=0.5 by weight. (A) Rate of heat liberation for 50 h. (B) Cumulative heat for 28 d.

crystals, together with the exsolved liquid (now crystallized), were finely pulverized and mixed with water, the exsolved alkalis would readily dissolve into the water. This probably causes the high reactivity during the initial stage (up to ~ 30 h) of the cement hydration.

The higher hydration activity for the remelted belite cement between ~ 30 h and ~ 10 d (Fig. 6(B)) was mainly ascribed to the presence of the twin boundaries of the β -phase belite. The twin boundaries would act like active centers on the crystal surface to increase the reactivity during the early stage of the hydration process.¹³ As a result, we have proposed two accelerators for early hydration of the remelted belite cement. One was the exsolved liquid rich in alkalis, contributing primarily to the hydration up to ~ 30 h, and the other was the twin boundaries of the β -phase, mainly contributing to the subsequent hydration up to ~ 10 d. The specific surface area, which played an important role in the previous studies,^{7,8} was independent of the distinction in hydration behavior between the two cements.

4. Conclusions

(1) The remelted belite contained a lower impurity concentration than the quenched belite. The phase constitution was, therefore, exclusively β for the former and mainly α'_L for the latter.

(2) The liquid formed by the remelting reaction contain-

ed a much higher concentration of alkalis than the host belite. The exsolved alkalis behaved as a hydration accelerator and the main heat evolution peak began ~7 h earlier during the initial stage up to ~30 h.

(3) The hydration activity between ~30 h and ~10 d was higher for the remelted belite cement than for the control. This is mainly induced by the twin boundaries of the β -phase, which behaved on the crystal surface like active centers for the reaction with water.

(4) The grindability of the belite-rich cement was significantly increased by the remelting reaction, in accord with a previous study.

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