

COMBINED EFFECT OF LIGNOSULFONATE AND CARBONATE ON PURE
PORTLAND CLINKER COMPOUNDS HYDRATION. III. HYDRATION OF
TRICALCIUM SILICATE ALONE AND IN THE PRESENCE OF
TRICALCIUM ALUMINATE

Saveria Monosi, Giacomo Moriconi and Mario Collepardi
Department of Materials Science
University of Ancona, Ancona, Italy

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ABSTRACT

The effect of carbonate and/or lignosulfonate on the hydration of C_3S alone and in the presence of C_3A has been examined by DTG and TG curves and by zeta potential measurements. The combined addition of sodium carbonate and lignosulfonate strongly retards C_3A hydration. However by mixing 20 % C_3A with C_3S the retarding effect is significantly lower. On the other hand the early C_3A hydration is completely blocked by sodium carbonate and lignosulfonate simultaneously added. It seems that the fluidifying effect of the combined addition of those admixtures could be ascribed to both the dispersing action and the completely blocking effect on the early C_3A hydration.

Mediante la DTG e TG ed attraverso misure di potenziale zeta è stata studiata l'effetto del carbonato e/o lignosolfonato sull'idratazione del C_3S da solo ed in presenza di C_3A . L'aggiunta combinata di carbonato di sodio e lignosolfonato ritarda fortemente l'idratazione del C_3S . Tutta via mescolando 20 % di C_3A con il C_3S l'effetto ritardante diminuisce sensibilmente. L'idratazione del C_3A risulta praticamente bloccata in presenza di carbonato e lignosolfonato. Sembra che l'effetto fluidificante degli additivi possa essere attribuito sia all'azione disperdente che all'arresto dell'idratazione iniziale del C_3A .

INTRODUCTION

In previous papers the influence of lignosulfonate-carbonate addition on the C₄AF (1) and the C₃A (2) hydration was examined. In the present paper the combined effect of lignosulfonate and carbonate on the hydration of C₃S alone or in the presence of C₃A is studied.

EXPERIMENTAL

Materials and Methods

Tricalcium silicate (C₃S) was synthesized from reagent grade CaCO₃ and silica by heating the mixture in the proper molar ratio at 1500°C. The C₃S, with a free lime content of 0.4 % was ground to a Blaine fineness of about 3000 cm²/g.

Tricalcium aluminate (C₃A) described in a previous paper (3) was used.

Reagent grade sodium carbonate (NC) and/or sodium lignosulfonate (lgs), said to be free of sugars or other carbohydrates, were dried mixed with C₃S or C₃S and C₃A as shown in Table 1.

Paste Hydration

Hydration at 20°C of pastes with water/C₃S or water/(C₃S+C₃A) ratio of 0.5 was examined.

After a certain time (30 min - 14 days) the hydration was stopped by grinding the pastes with methyl alcohol. The filtered solids were dried at 60°C for two hours and analyzed by a Netzsch apparatus in which DTA, DTG and TG curves are obtained simultaneously (weight of samples = 200 mg; heating rate = 10°C/min). Only DTG curves are shown in the present paper. From TG curves the percentage of CH by the weight of anhydrous sample were calculated. The weight

loss due to CaCO₃ at about 800°C was transformed into the equivalent CH weight and the total weight of CH is assumed to be proportional to the percentage of hydrated C₃S.

TABLE 1
Composition of Mixes

Mix	C ₃ S	C ₃ A	NC	lgs
A	100	-	-	-
B	100	-	0.300	-
C	100	-	-	0.300
D	100	-	0.300	0.300
A ₁	80	20	-	-
B ₁	80	20	0.300	-
C ₁	80	20	-	0.300
D ₁	80	20	0.300	0.300
A ₁ = A ₂	80	20	-	-
B ₂	80	20	0.900	-
C ₂	80	20	-	0.900
D ₂	80	20	0.900	0.900

Zeta Potential Measurements on Suspensions

Zeta potential measurements were performed using a Laser Zee Meter by Pen.Kem.Inc. as it was described in a previous paper (1).

For zeta potential measurements some suspensions were prepared by mixing 1 g of solid and 100 ml of CH saturated solution for 15 min. The composition of solid samples for the suspension experiments (water/solid = 100) was the same as that of Table 1 except for NC and lgs. The concentration of NC and lgs in the liquid phase of these suspensions have been changed from 0 to a maximum of 18 g/l. The 6 g/l or 18 g/l values in the suspension tests correspond to the concentration of the admixtures in the liquid phase of the paste experiments when 0.3 % or 0.9 % respectively have been used. The liquid phase was separated by vacuum filtration. A small portion of the solid samples was added to the filtered liquid phase and a suspension (10 mg/20 ml) was obtained with the same ionic strength of the original suspension and diluted enough to be observed to the microscope of the Laser Zee Meter.

RESULTS AND DISCUSSION

Influence of NC and lgs on C₃S Hydration

Fig. 1 shows the DTG curves of the hydration of C₃S with and without NC and/or lgs. When C₃S reacts with water without NC and lgs (Fig. 1A), C-S-H and CH are formed with a DTG peak at about 140°C and a sharper one at about 520°C respectively. A peak at about 800°C due to CaCO₃ is also observed.

The addition of NC (0.3 %) to C₃S (Fig. 1B) does not cause any significant change, except a retarded C₃S hydration.

In the presence of 0.3 % of lgs (Fig. 1C) the C₃S hydration is completely blocked for at least 14 days. Similar results have been obtained by Young who found that in the presence of lgs (0.8 %) the C₃S hydration is strongly retarded within 180 days (4). Ramachandran (5) found that by the addition of 0.8 % lgs the hydration of C₃S is stopped almost indefinitely.

The combined addition of NC (0.3 %) and lgs (0.3 %) blocks the C₃S hydration for at least 7 days (Fig. 1D). However, at 14 days C-S-H and CH peaks can be observed. So it seems that the C₃S hydration is less retarded in the presence of NC and lgs than in the presence of lgs alone.

In experiments with higher dosages of lgs or NC and lgs, which are not here reported, DTG curves showed that the above mentioned retarding effects were much more pronounced.

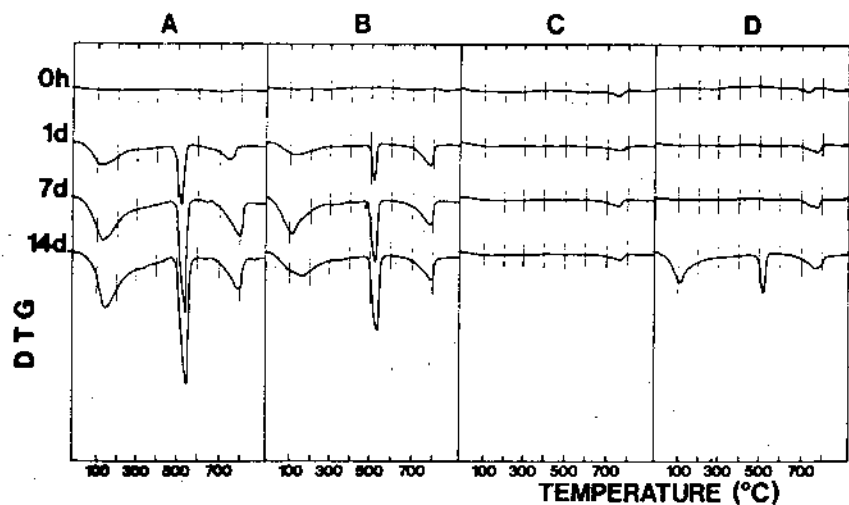


FIG. 1

DTG curves for C_3S pastes (See Table 1).

Fig. 2 shows the percentage of CH as a function of time for C_3S alone (control mix) and in the presence of 0.3% of additives.

When NC is added, no substantial change in the C_3S hydration rate is observed for times shorter than 8 hours. At longer ages the percentage of CH is remarkably lower in the presence of NC, thus indicating that NC retards the C_3S hydration.

In the presence of lignosulfonate the C_3S hydration does not occur even after 14 days, while the simultaneous addition of NC and lgs causes the blockage of C_3S hydration for 7 days only, thus confirming the DTG curves results.

In Fig. 3 the zeta potential as a function of NC and lgs concentration in the liquid phase is shown. The zeta potential value for C_3S without admixtures is about 0 mV. However, the scatter of the zeta potential of C_3S particles in the absence of admixtures was relatively large. Similar results have been obtained by Daimon and Roy (6) for cement particles in de-ionized water in the absence of admixtures.

The addition of either NC or lgs lowers zeta potential value. However, the latter is much more effective in the change of zeta

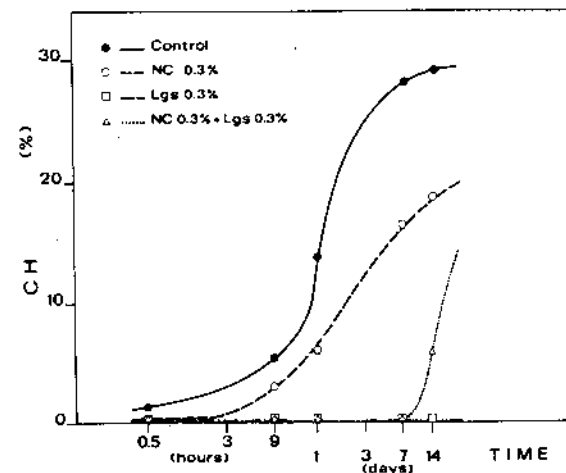


FIG. 2

Percentage of CH as a function of time for C_3S pastes.

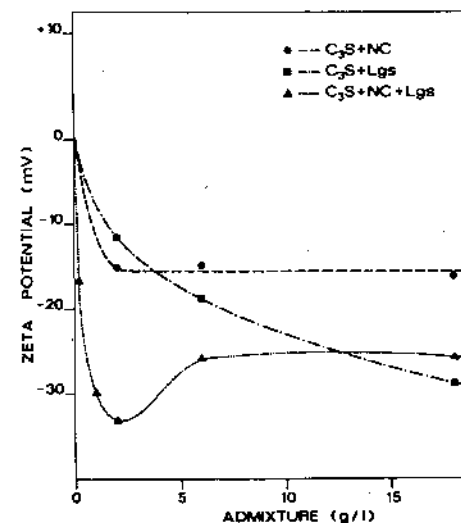


FIG. 3

Zeta potential of C_3S as a function of admixtures concentration in the liquid phase.

potential. For instance, with a concentration in the liquid phase of 18 g/l (corresponding to 0.9 % in the paste experiment) the zeta potential was about -17 mV or -29 mV when NC or lgs respectively were used.

When NC and lgs were simultaneously added, a minimum (-33 mV) in the zeta potential curve was observed. The concentration in the liquid phase of the admixtures corresponding to the minimum was about 2 g/l.

Influence of NC and lgs on C₃S hydration in the presence of C₃A

Fig. 4 and Fig. 5 show the DTG curves of C₃S-C₃A mixes hydrated for different periods of time.

In the sample not containing admixtures (Fig. 4A₁) three hydrated phases are observed : C-S-H (140°C), hexagonal hydroaluminat (200°C and 270°C) and CH (520°C). After 0.5 hours of hydration only the DTG peak of hexagonal hydroaluminat at about 200°C can be detected. Calcium hydroxide is observed after 9

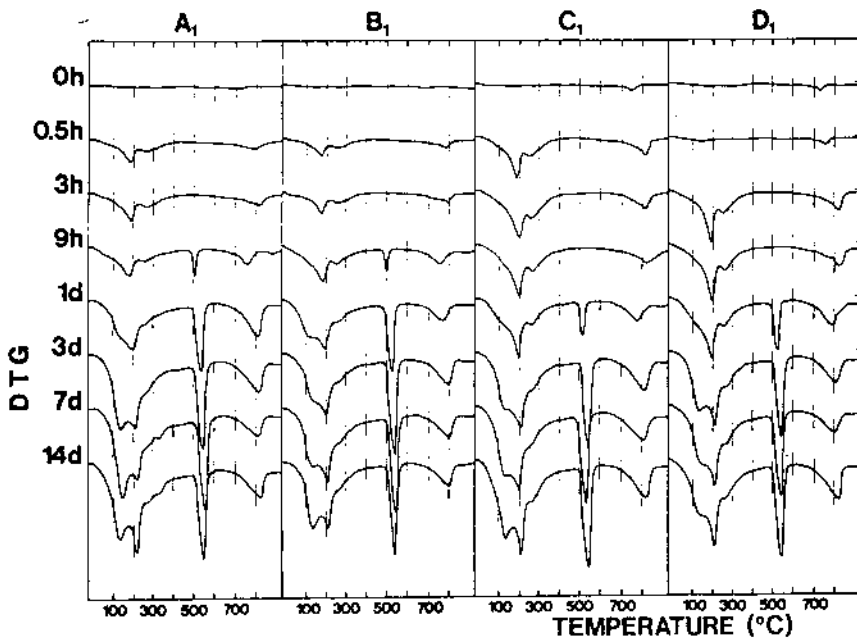


FIG. 4

DTG curves for C₃S-C₃A pastes with 0.3 % of admixtures (See Table 1).

hours, whereas a shoulder at 140°C due to C-S-H can be detected at 1 day only. Calcium hydroxide is always accompanied by calcium carbonate with a DTG peak at about 800°C. A very small peak at about 320°C due to C₃AH₆ is observed at 7-14 days.

The addition of NC at low concentration (0.3 %) to the C₃S-C₃A system does not cause any significant change (Fig. 4B₁), while at higher concentration (0.9 %) it seems that the total amount of the hydrated phase decreases (Fig. 5B₁), especially at longer ages.

In the anhydrous samples (0 hour) containing lgs (Fig. 4C₁ and Fig. 5C₁) or NC and lgs (Fig. 4D₁ and Fig. 5D₁) a DTG peak at about 720°C appears. This peak, in the presence of 0.9 % of lgs or NC and lgs (Fig. 5D₁) is preceded by a slight "positive" DTG peak at about 700°C, corresponding to an exothermal peak on DTA curves, not shown in the present paper. The phenomenon is attributed to the reaction between the carbon dioxide caused by the lgs thermal decomposition and the lime present in the starting mixture, thus forming CaCO₃ and increasing the weight of the sample. The same

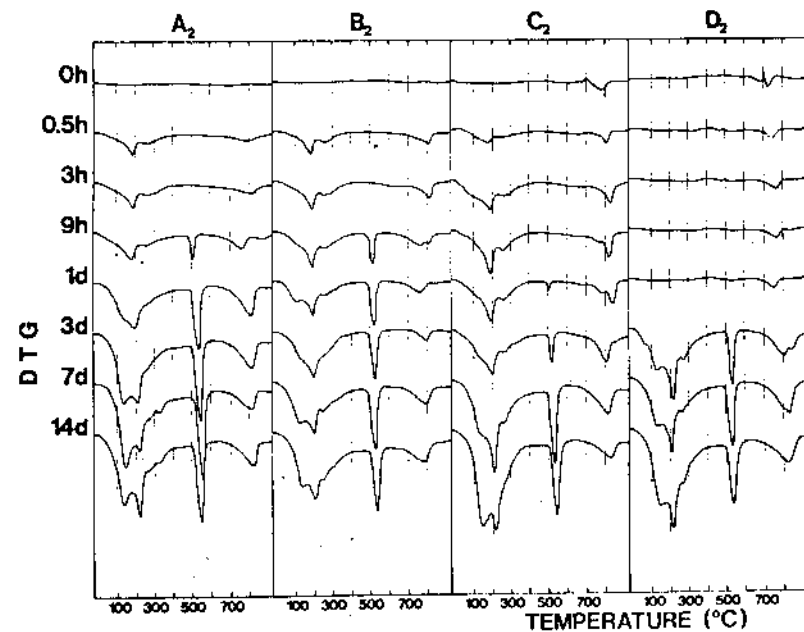


FIG. 5

DTG curves for C₃S-C₃A pastes with 0.9 % of admixtures (See Table 1).

effect was found in previous works (1,2) for the system C_4AF -CH-quartz and C_3A -CH-quartz in the presence of lgs or NC and lgs. In these systems, the "positive" DTG peak was found at about $570^\circ C$, and the difference in the temperatures ($700^\circ C$ and $570^\circ C$) is probably due to the presence of quartz. Indeed with additional DTA-DTG-TG tests on the system C_4AF -CH with lgs or NC and lgs, mixed in the same proportions used in the previous work (1) but excluding quartz, the "positive" DTG peak is shifted to the same temperature of about $700^\circ C$ as found in the present work. Moreover, the "positive" DTG peak disappears in all the hydrated samples containing lgs or NC and lgs (Fig. 4C, -4D, -5C, -5D₂) as they have been treated with methyl alcohol to stop hydration, thus causing the removal of lgs (1).

The influence of 0.3 % and 0.9 % lgs on the hydration of the C_3S - C_3A system is shown in Fig. 4C, and Fig. 5C, respectively. By the addition of 0.3 % lgs the C_3S hydration is stopped within the first 9 hours, while no substantial change appears in the products of C_3A hydration whose rate seems to be slightly accelerated. At longer ages the C-S-H and CH peaks may be observed and at 14 days the amount of the hydrated products becomes comparable to the one present at the same hydration time in the system without additives.

In the presence of a higher dosage (0.9 %), lgs remarkably retards the C_3S hydration till to 1 day. At 3 days the same degree of hydration of C_3S seems to be reached (Fig. 5C₂) as the one obtained after 1 day with a dosage of 0.3 % of lgs (Fig. 4C₁).

The C_3A hydration is not substantially changed by the addition of 0.9 % lgs except a slight retardation during the initial 30 min. The results concerning the influence of lgs addition on the hydration of C_3S alone (Fig. 1C) or in the presence of C_3A (Fig. 4C, -5C,) confirm the data obtained by Young (4) and Ramachandran (5) : in the presence of C_3A the lgs addition causes a remarkably lower retarding effect on the C_3S hydration. It seems that C_3A and/or its hydration products adsorb lgs by decreasing its concentration in the liquid phase so that the C_3S hydration is affected by the admixture to a significant lower extent.

The Fig. 4D, and 5D, show the DTG curves for the C_3S - C_3A system in the presence of both NC and lgs in percentages of 0.3 % and 0.9 % respectively.

The combined addition of NC and lgs completely stops both C_3S and C_3A hydration for a certain period of time. The C_3A hydration is blocked for 0.5 hours with 0.3 % NC and lgs (Fig. 4D₁) and at least for 1 day with 0.9 % of admixtures (Fig. 5D₂). This effect is specific for the combined addition of NC and lgs, since no substantial retardation in the C_3A hydration has been observed when NC (Fig. 4B₁ and 5B₂) or lgs (Fig. 4C₁ or 5C₂) were separately added.

Moreover, the combined addition of NC and lgs retard the C_3S hydration (Fig. 6 and 7) to a higher extent than lgs alone does particularly with a dosage of 0.9 % (Fig. 7).

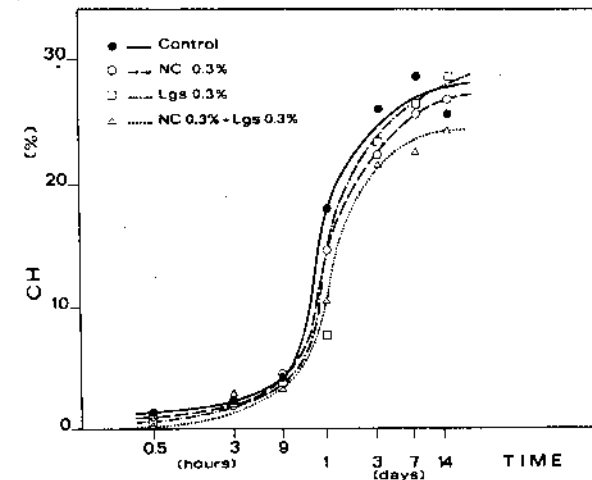


FIG. 6

Percentage of CH as a function of time for C_3S - C_3A pastes with 0.3 % of admixtures.

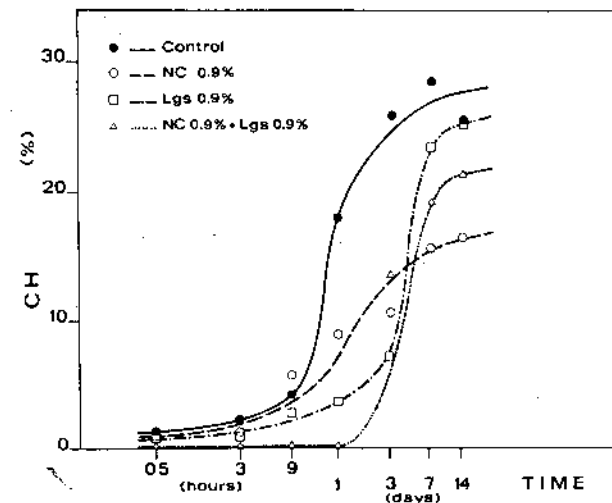


FIG. 7

Percentage of CH as a function of time for C_3S - C_3A pastes with 0.9 % of admixtures.

In Fig. 8 the influence of the admixtures on the zeta potential for the C_3S - C_3A is shown. The effect is very similar to that discussed for the addition of NC and/or lgs to C_3S alone (Fig. 3). In particular it seems that also in the C_3S - C_3A system there is a minimum in the zeta potential-concentration curve when NC and lgs are simultaneously added. Also in this case the lowest zeta potential value (-33 mV) occurs at a concentration of NC and lgs of about 2 g/l. Since no minimum has been observed for C_3A alone (2) in the presence of NC and lgs (2) it would seem that this minimum could be ascribed to the effect of NC and lgs on C_3S particles.

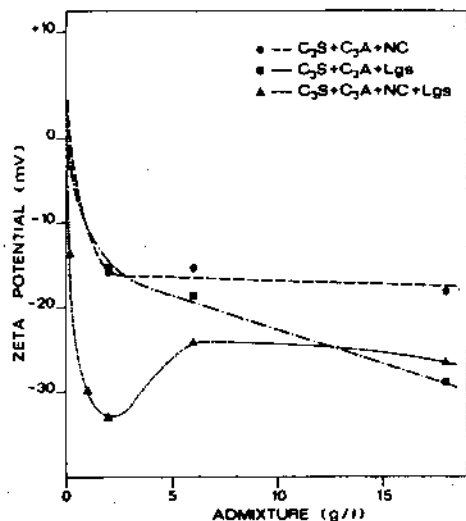


FIG. 8

Zeta potential of C_3S - C_3A as a function of admixtures concentration in the liquid phase.

CONCLUSIONS

1. In the presence of 0.3 % lgs the C_3S hydration is stopped for at least 14 days (Fig. 2), whereas by mixing 20 % C_3A with C_3S the hydration of C_3S is only slightly retarded (Fig. 6). These results confirm those obtained by Young (4) and Ramachandran (5). It seems that C_3A and/or its hydration products adsorb lgs by decreasing its concentration in the liquid phase so that the C_3A hydration is retarded by the admixture to a lower extent.

2. In a similar way the combined addition of NC and lgs (0.3 %) strongly retards the C_3S hydration (Fig. 2), whereas a much lower retarding effect is caused by the admixtures (0.3 %) when 20 % C_3A is mixed with C_3S (Fig. 6).
3. The combined addition of NC and lgs completely blocks the C_3A hydration for a certain period of time in the C_3S - C_3A system. Similar results have been obtained for C_4AF or C_3AF alone (1,2). The higher the percentage of NC and lgs the longer is the period of induction for C_3A hydration (Fig. 4D, and 5D). This effect is specific for the combined addition of NC and lgs, whereas lgs alone does not retard in a significant way the C_3A hydration (Fig. 4C, and 5C).
4. Sodium carbonate and lignosulfonate separately added reduce the zeta potential of C_3S (Fig. 3) or C_3S - C_3A system (Fig. 8). However the combined addition of NC and lgs causes a larger reduction in the zeta potential for both C_3S and C_3S - C_3A system. This could result in a better dispersion of C_3S and C_3A particles due to their mutual repulsion. Moreover a minimum in the zeta potential-concentration curve is found when NC and lgs are simultaneously added.
5. It would seem that the well known fluidifying effect of NC and lgs simultaneously added to a clinker Portland cement could be ascribed to both the dispersing action and the completely blocking effect on the early C_3A hydration.

REFERENCES

1. M. Collepardi, S. Monosi, G. Moriconi and M. Corradi, *Cem. Concr. Res.* **10**, 455 (1980).
2. M. Pauri, G. Baldini and M. Collepardi, *Cem. Concr. Res.* **12**, 271 (1982).
3. M. Collepardi, G. Baldini, M. Pauri and M. Corradi, *Cem. Concr. Res.* **8**, 571 (1978).
4. J.F. Young, *J. Am. Cer. Soc.* **52**, 44 (1969).
5. V.S. Ramachandran, *Cem. Concr. Res.* **2**, 179 (1972).
6. M. Daimon and D.M. Roy, *Cem. Concr. Res.* **8**, 753 (1978).