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by

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Effect of Lime on Hydration of Pastes Containing Gypsum and Calcium Aluminates or Calcium Sulfoaluminate

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Chemical reactions responsible for ettringite formation in the commercial expansive cements are reviewed. X-ray diffraction analyses of the hydrated expansive compounds showed that in the presence of $Ca(OH)_2$ and $CaSO_4$ the tricalcium aluminate hydrated very slowly and the monocalcium aluminate quickly, whereas the calcium sulfoaluminate hydrated at a uniform rate during the early hydration period. Scanning micrographs are presented which show that ettringite formed in the presence of $Ca(OH)_2$ is colloidal. It is proposed that colloidal ettringite can adsorb large quantities of water, thereby causing slump loss in fresh concrete and expansion in hardened concrete.

I. Introduction

THEORETICALLY, chemical reactions that can cause expansion of hardened concrete under conditions of restraint can be exploited to make cements of varying degrees of expansivity, e.g. the shrinkage-compensating and self-stressing cements. Expansion in properly restrained shrinkage-compensating cement concretes produces a compressive stress of the order of 25 to 100 psi, which is regarded as adequate to compensate for tensile stresses induced later by drying shrinkage. Thus, the use of shrinkage-compensating expansive cements generally prevents drying-shrinkage cracking. In self-stressing expansive cements, restrained expansion in concrete must be high enough to stress the reinforcing steel and to produce compressive stress levels in the concrete approaching those attained in prestressed concrete made by conventional pre- or post-tensioning methods.

Chemical reactions that might produce controlled expansion of restrained concrete are (1) the formation of ettringite, $C_6A\bar{S}_3H_{32}$,* (2) hydration of MgO, and (3) hydration of CaO. Present commercial production of shrinkage-compensating and self-stressing expansive cements is based on ettringite formation, with the anhydrous calcium sulfoaluminate, $C_4A_3\bar{S}$, used as the source of aluminate ions. However, expansive cements based on C_3A and CA as the main sources of aluminate ions have also been introduced, and products based on CaO as an expansive agent are being investigated.

The expansive cements that contain $C_4A_3\bar{S}$ for ettringite formation are called type K cements, whereas those that contain CA or C_3A for this purpose are called type M and type S cements, respectively. The chemical compositions and physical properties of the expansive cements have been reported.[1-3] The major characteristics which distinguish the expansive cements from ordinary portland cement are (1) expansion under restraining conditions and (2) relatively higher water demand.

*Cement chemistry notation is used, i.e. C = CaO, A = Al_2O_3, S = SiO_2, $\bar{S}$ = SO_3, and H = H_2O.

Table I. Formation of Ettringite from Expansive Cements

Type K cement					
Reaction (1)	$C_4A_3\bar{S}$ +	$8C\bar{S}H_2$ +	6C +	80H →	$3C_6A\bar{S}_3H_{32}$
Weight (%)	16.2	36.6	8.9	38.3	100
Molar vol (cm³)	235	594	101	1440	2175
Type M cement					
Reaction (2)	CA +	$3C\bar{S}H_2$ +	2C +	26H →	$C_6A\bar{S}_3H_{32}$
Weight (%)	12.6	41.1	8.9	37.4	100
Molar vol (cm³)	53	223	34	468	725
Type S cement					
Reaction (3)	C_3A +	$3C\bar{S}H_2$		26H →	$C_6A\bar{S}_3H_{32}$
Weight (%)	21.5	41.1		37.4	100
Molar vol (cm³)	89	223		468	725

It is generally agreed that rapid ettringite formation in fresh concrete is responsible for high slump loss, whereas its formation in the hardened concrete can be accompanied by significant expansion. The question of why slump loss and expansion are associated with ettringite formation, however, has not been satisfactorily resolved. In the present work, the microstructure of hydrated expansive compositions was examined by X-ray diffraction and scanning electron microscopy with the objective of correlating the chemistry of hydration reactions with the physical properties.

The chemical reactions by which ettringite is formed from the expansive cements are given in Table I. Theoretically, the water required for hydration of portland cement constituents is ≈ 25 wt% of the total solids. It is not uncommon, therefore, for portland cement concretes with a water-cement (w/c) ratio of ≥ 0.5 to bleed. Assuming that an expansive cement contains $\approx 10\%$ expansive constituents (as represented by reactions (1), (2), and (3) in Table I), with the remainder made up of portland cement constituents, it can be computed that the water required for total hydration of expansive cements will be only 28.5%. Thus, excessive water demand, slump loss, and lack of bleeding in expansive cement concretes with w/c ratios of 0.6 to 0.7 remain unexplained.

Several hypotheses regarding the mechanism of expansion associated with ettringite formation have been reviewed by Mehta.[4] It has been proposed that the molecular volume of the reactants which form ettringite increases. However, the stoichiometry of the chemical reactions does not support this hypothesis, since in all cases, the reactants are reduced in total molar volume; in reaction (1) this reduction is $\approx 8\%$ and in reactions (2) and (3) $\approx 7\%$. The explanation for the expansion associated with ettringite formation, therefore, appears to lie elsewhere.

II. Materials and Procedure

For ease of microstructural identification, the number of phases involved should be minimized. Hence, in this investigation, laboratory mixtures of the compounds involved in reactions (1), (2), and (3) were used, rather than the expansive cements, which contain many compounds and impurities. Therefore, the conclusions drawn from this study
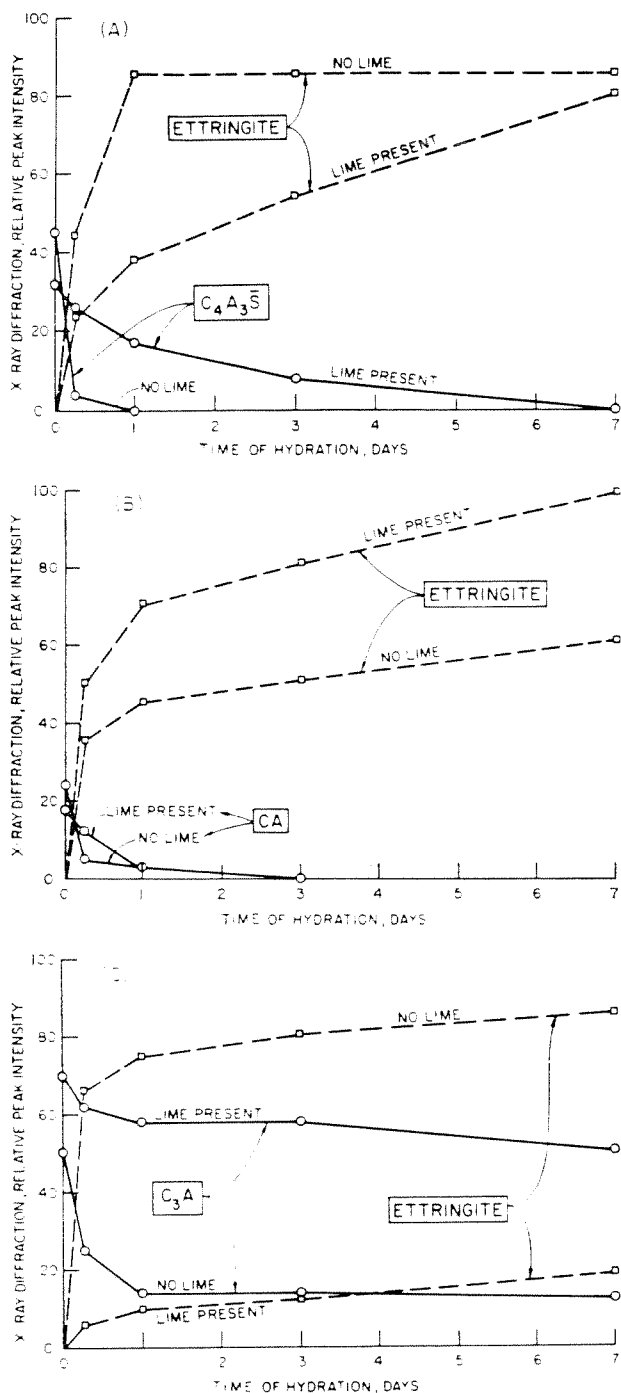
Fig. 1. Influence of lime on hydration characteristics of pastes containing gypsum and *(A)* $C_4A_3\bar{S}$, *(B)* CA, and *(C)* C_3A.

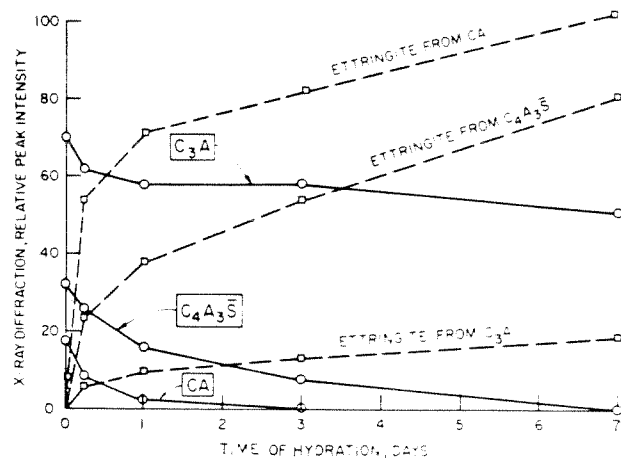
Fig. 2. Relative rates of ettringite formation and depletion of CA, $C_4A_3\bar{S}$, or C_6A in pastes containing both gypsum and lime.

are applicable to commercial expansive cements only in a general sense.

High-purity $C_4A_3\bar{S}$, CA, and C_3A clinkers made in the laboratory were ground to a Blaine fineness of ≈4000 cm² g. Readily hydratable* quicklime was made by calcining reagent-grade $CaCO_3$ at 2400°F, and reagent-grade gypsum, $C\bar{S}H_2$, was used to make up the synthetic compositions.

Reaction (3) shows that formation of ettringite from C_3A does not require lime. However, from a practical standpoint it is important to investigate hydration reactions in the pres-

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*Type K expansive clinker is made at 2300° to 2400°F; the free CaO present hydrates completely within 6 h.

ence of lime because some $Ca(OH)_2$ is always released in commercial cements because of rapid hydration of C_2S, which is the principal constituent of all portland and blended portland cements. Therefore, 5 wt% quicklime was added to one of the mixtures containing stoichiometric proportions of CA and $C\bar{S}H_2$. In reactions (1) and (2), lime is already present in the system. Therefore, to investigate the reaction in the absence of lime, corresponding mixtures were made in which quicklime was replaced by an equivalent weight of additional gypsum.

The mixtures were hydrated with distilled water, using a w c ratio of 0.5. The pastes were permitted to harden in plastic vials for 6 h and were then exposed to moist curing in a CO_2-free environment. Hydration and curing were conducted at room temperature. X-ray diffraction patterns of the hydrated pastes were obtained immediately after water was added and after 6 h, 24 h, 3 days, and 7 days. The hydration rates of $C_4A_3\bar{S}$, CA, and C_3A were determined by comparing the intensities of their strongest characteristic peaks directly and also by monitoring the relative intensity of the principal ettringite peak. Fractured specimens of selected samples were examined by scanning electron microscopy.

III. Results and Discussion

The results of the X-ray diffraction analyses are shown in Figs. 1 and 2. Although direct comparison of the intensities of the diffraction peaks provides at best semiquantitative estimates of the compounds, the following general conclusions can be drawn from the data:

(1) From Fig. 1(A), it appears that the presence of lime somewhat retarded the hydration of $C_4A_3\bar{S}$ during the first 6-h period; thereafter the hydration proceeded uniformly until no anhydrous $C_4A_3\bar{S}$ was detected after 7 days. Correspondingly, lime initially somewhat reduced the rate of ettringite formation; however, the 7-day samples contained similar quantities of ettringite in the presence and absence of lime.

Collepardi *et al.*[3] also reported that the hydration rate of $C_4A_3\bar{S}$ was reduced when $Ca(OH)_2$ and gypsum were added simultaneously to the system. These workers, however, observed that the lime liberated by C_3S hydration was not so effective a retarder of $C_4A_3\bar{S}$ hydration as lime added directly.

(2) From the data in Fig. 1(B), it appears that the effect of lime on the hydration of CA is similar to its effect on that of $C_4A_3\bar{S}$. In the presence of lime, there was more unhydrated CA at 6 h than in the absence of lime. Although more CA hydrated in the absence of lime, the corresponding quantity of ettringite formed was not increased. No other crystalline
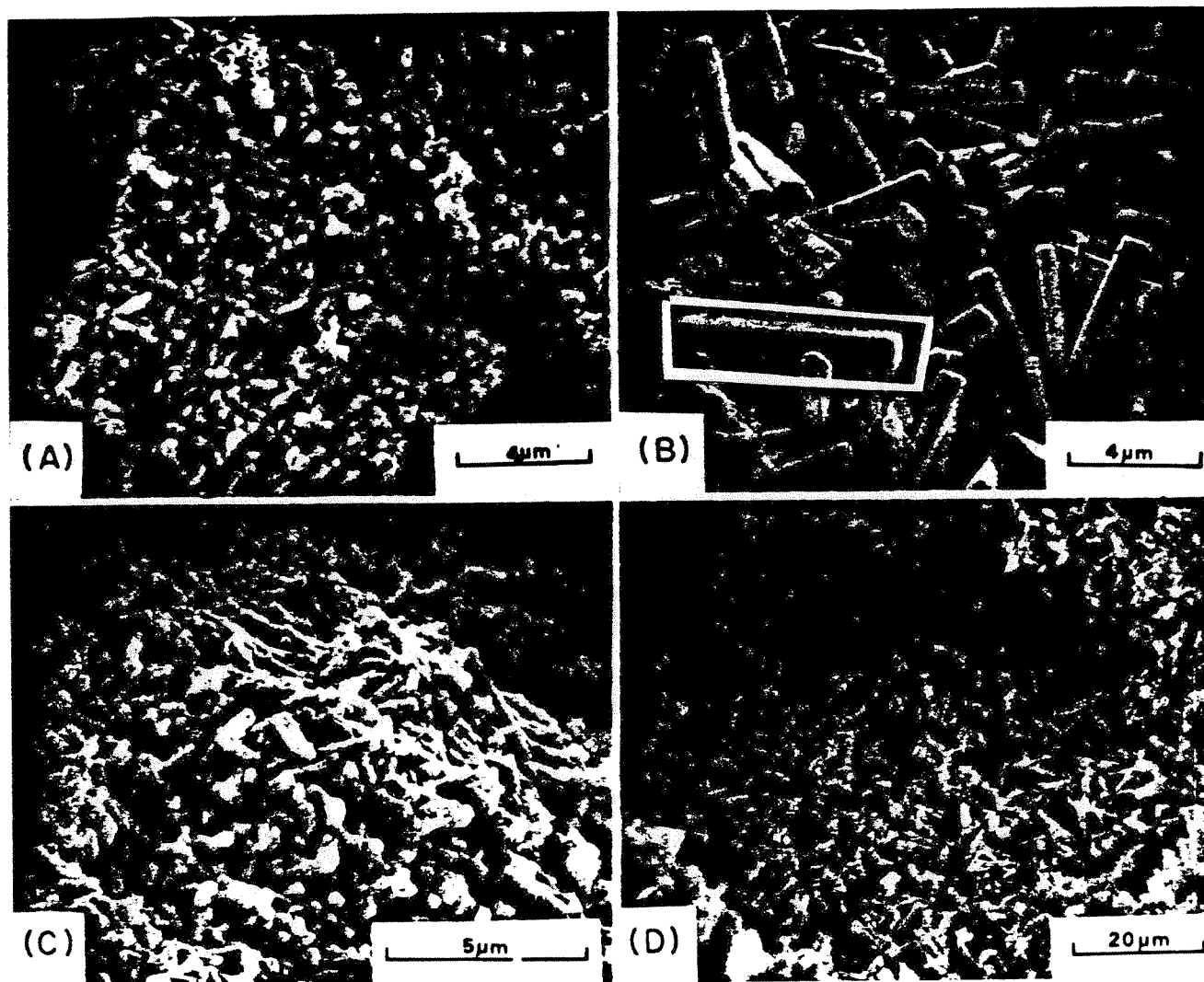
Fig. 3. Micrographs of C_4A_3S-CSH. paste hydrated *(A)* with lime, 24 h; *(B)* without lime, 24 h; *(C)* with lime, 72 h; and *(D)* without lime, 72 h.

hydrates were detected. The time lag between the hydration of the aluminate and the crystallization of ettringite probably indicates that the ettringite was formed by a through-solution reaction.

(3) From the data in Fig. 1(C), it appears that in the absence of lime the C_3A hydrated rapidly during the first 24 h; thereafter, the rate of C_3A hydration, and the rate of corresponding ettringite formation, became very slow. Unhydrated C_3A was still present in the 7-day sample. In the presence of lime, C_3A hydration was severely retarded after the initial 6-h period. Practically no hydration occurred during the period from 1 to 3 days, and thereafter the hydration was so slow that a large quantity of unhydrated C_3A was present in the 7-day sample. Thus, in the presence of lime the formation of ettringite in C_3A-gypsum pastes was severely retarded. The data agree with Forsen's results (quoted by Taylor'), in which hydration stopped after 15 min when C_3A was shaken with a saturated solution of $Ca(OH)_2$.

(4) The relative rates of hydration of C_4A_3S, CA, and C_3A and the rates of formation of ettringite from the pastes containing both lime and gypsum are summarized in Fig. 2. After the initial retardation by lime the pastes containing C_4A_3S hydrated more uniformly and produced more ettringite than those containing C_3A. During the first 6 h the ettringite formation from CA was relatively more rapid than that from C_4A_3S. The $C_4A_3\bar{S}$ hydrated at a more uniform rate than either CA or

C_3A during the period from 6 h to 7 days; this period is important for effective use of the expansion potential in expansive cements.

The results of the X-ray diffraction analyses clearly establish that the rates of hydration of the aluminates differ significantly in environments containing lime and gypsum. Although based on investigation of pastes containing expansive compounds, the results are applicable to the hydration characteristics and properties of the commercially produced expansive cements, as reported by Mehta and Lesnikoff.'

The scanning electron micrographs (Figs. 3–5) generally confirmed the results obtained by the X-ray diffraction analyses and provided additional useful information. Figure 3 shows the morphology of the hydrated pastes containing stoichiometric proportions (for ettringite formation) of C_4A_3S, CSH, and lime. In the absence of lime, the ettringite crystals had average lengths of 5 to 10 μm and average thicknesses of 0.5 to 2 μm. In the presence of lime, most ettringite crystals were $\approx$1 μm long and 0.25 μm thick. Comparing Fig. 3(C) with Fig. 3(D) also shows that the ettringite crystals formed in the absence of lime were about 6 times larger than those formed when lime was present. Micrographic results similar in regard to the size of the ettringite crystals were obtained when C_4A_3S was replaced by CA as the source of aluminate ions. It is concluded that ettringite formed in the presence of lime in solution is colloidal.
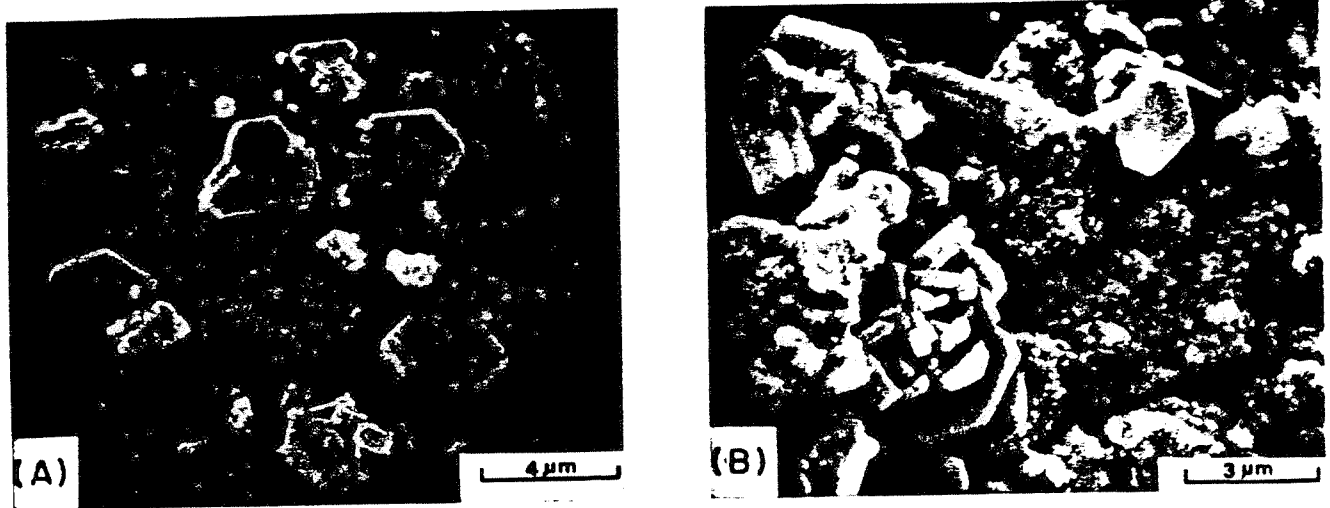
Fig. 4. Micrographs of $C_3A + 3C\bar{S}H_2$ paste containing lime. *(A)* Hexagonal plates of $Ca(OH)_2$ covering C_3A grain after 6 h and *(B)* poorly crystalline ettringite after 48 h.
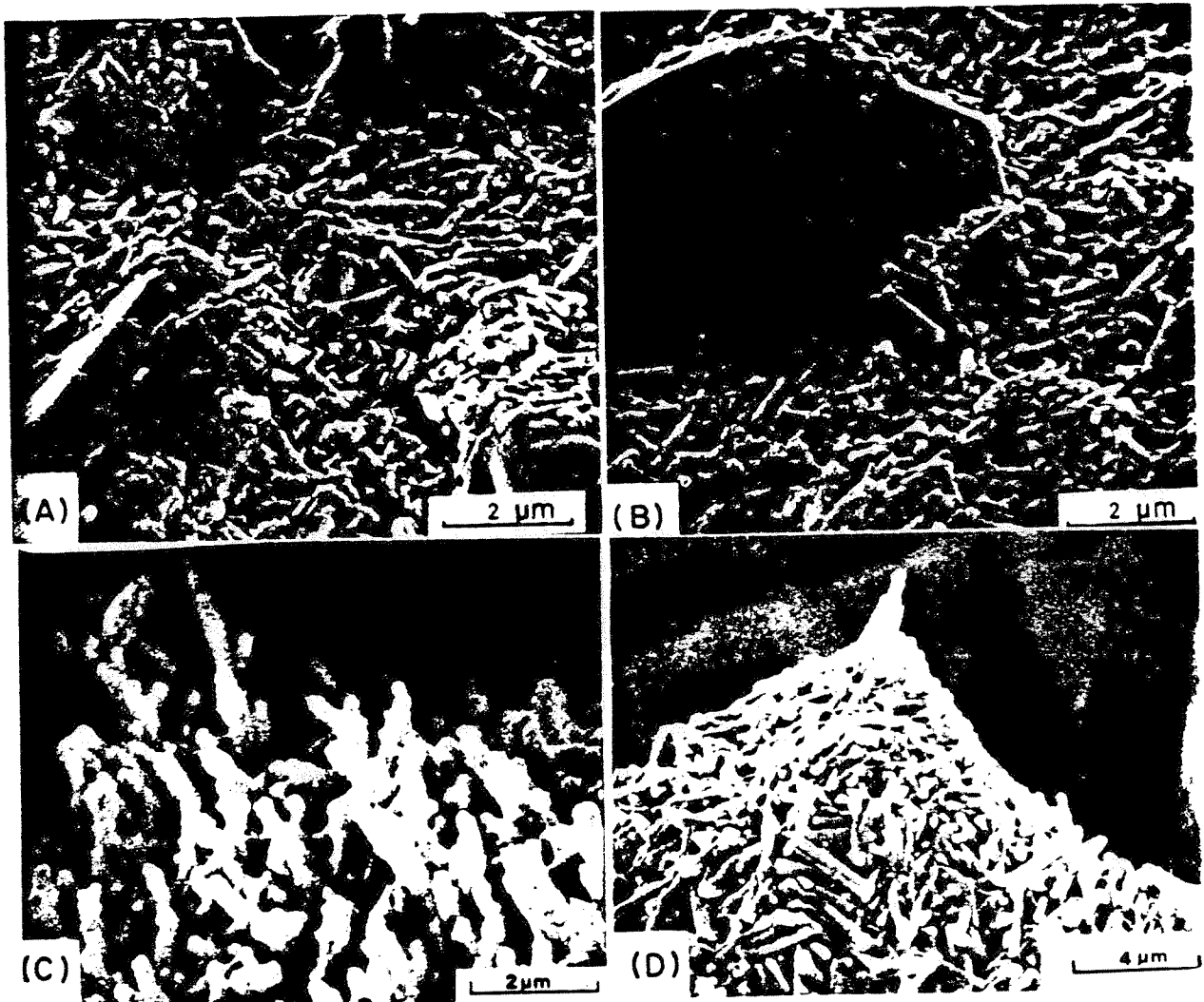

Fig. 5. Micrographs of $C_3A + 3C\bar{S}H_2$ paste hydrated for 24 h. *(A)* C_3A crystals surrounded by ettringite, *(B)* single C_3A crystal surrounded by ettringite, *(C)* ettringite crystals resembling short fibers of fiber-reinforced concretes, and *(D)* ettringite pile in a crack.

However, several investigators have identified long, fibrous or lath-like crystals of ettringite in hydrated cements. For example, Midgley and Pettifer[7] observed crystals of ettringite 120 μm long and 0.5 to 1 μm thick in scanning electron micrographs of hydrated supersulfated cements in which no $Ca(OH)_2$ was present at any time.

Since the hydrated supersulfated cements (which usually contain larger proportions of ettringite than the expansive cements) do not expand significantly on ettringite formation, Mehta[4] has proposed that the colloidal nature of the ettringite formed in solutions saturated with $Ca(OH)_2$ is important in the development of expansive pressures. Furthermore, he theorized that some colloidal substances, e.g. ettringite, because of their high specific surfaces and certain features of the internal crystal structure, can adsorb large quantities of water, thus producing swelling under unrestrained conditions and internal stresses when restrained. Thus, the mechanism of the expansion associated with ettringite formation in the expansive cements may be similar to the swelling observed in certain alkali silicate gels when they are exposed to water.

To test the hypothesis, Mehta[4] hydrated a very finely ground mixture of $C_4A_3\bar{S}$, $C\bar{S}H_2$, and lime (passing a No. 400 sieve) with 80 wt% water. The paste was cast in two Le Chatelier expansion rings. After hydration for 6 h, when ettringite formation was essentially complete, as confirmed by X-ray diffraction, the paste in one of the molds was sealed completely with paraffin, and the other mold was placed in a fog room. At 7 days, the dry-cured and wet-cured pastes were examined for expansion, which was large in the latter and insignificant in the former.

Scanning electron micrographs of hydrated $C_4A+3C\bar{S}H_2$ pastes without and with lime are shown in Figs. 4 and 5. It appears that for high-lime aluminates, such as C_4A, colloidal ettringite crystals were formed even when lime was not added to the anhydrous mixture. Also, all micrographs, including the one shown in Fig. 3, tend to show that the ettringite forms by a through-solution reaction. For instance, it can be seen from Fig. 5 that large quantities of ettringite have formed at random over and around the C_4A grains. This observation is consistent with the work of Chatterji and Jeffery,[8] who believe that early hydration products in portland cement pastes are formed by through-solution reactions.

Figure 4 shows hexagonal crystals of $Ca(OH)_2$ covering the C_4A grains when lime was present in the system. No ettringite was observed in the 6-h sample, but some very poorly crystalline ettringite is seen, along with $Ca(OH)_2$ plates, in the 48-h sample.

Comparing Fig. 4 with Fig. 3, it is obvious that lime retards ettringite formation from C_4A more severely than that from $C_4A_3\bar{S}$. It is theorized that, in the case of $C_4A_3\bar{S}$, the $Ca(OH)_2$ coating on the $C_4A_3\bar{S}$ grains is unstable because the stoichiom-

etry of the ettringite formation reaction requires removal of the $Ca(OH)_2$. The coating of lime remains on the C_4A grains, however, because C_4A does not require $Ca(OH)_2$ to form ettringite.

IV. Conclusions

X-ray diffraction analyses and scanning electron microscopy of hydrated pastes containing the expansive compounds typically present in the commercial expansive cements showed that the rates of hydration of the aluminates $C_4A_3\bar{S}$, CA, and C_4A were different. In the presence of lime, the hydration of C_4A-gypsum paste was severely retarded by a stable coating of $Ca(OH)_2$ on the C_4A crystals. During the early hydration reactions, lime accelerated the formation of ettringite from CA but somewhat retarded that from $C_4A_3\bar{S}$. For the period from 6 h to 7 days, $C_4A_3\bar{S}$ showed the most uniform rate of hydration in the presence of gypsum and lime.

Scanning micrographs showed that, instead of long lath-like crystals, colloidal ettringite of average dimensions 1 by 0.25 μm was formed from lime-saturated environments. The pastes containing colloidal ettringite swelled considerably in the presence of water. It is probable that the water adsorption characteristic of colloidal ettringite is responsible for slump loss in fresh expansive cement concrete and expansion in the hardened concrete.

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