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Discussion

Reply to the discussion by W. Hime of the "Reply to the discussion by S. Chatterji of the paper: Delayed ettringite formation in heat-cured Portland cement mortars"

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Hime raises the interesting and controversial question as to whether delayed ettringite formation (DEF) may occur in cementitious products stored continuously at ambient temperatures. He states that in our reply [1] to the discussion by Chatterji [2] of our paper concerned with DEF in heat-cured Portland cement mortars [3] that we showed that DEF may occur at ambient temperatures. This is not what was intended. What we reported is the "late formation" [1] or "regrowth" [4] of ettringite in mortars cured at ca. 20 °C.

To make this fine distinction between DEF and late formation of ettringite may, at first sight, seem to be pedantic, but it is important, in view of the lively controversy that has arisen about the mechanism of DEF (see, e.g., Diamond [5] and Taylor et al. [6]), to distinguish clearly between ettringite formation that results in expansive damage and that that does not. In Ref. [1], we deliberately avoided use of the term DEF when describing our observations at room temperature because they differed from those made in heat-treated mortars [3,7] and pastes [8] in at least one important respect. In heat-treated products that display DEF significant expansion is observed, the cement product displays cracks and the ettringite is observed microscopically in the form of bands, (e.g., 3, 5–8). In contrast, the microstructure of the Portland cement mortars that contained the late-formed ettringite after continuous curing at room temperature did not contain any bands of ettringite crystals, nor did the mortars expand. We would not, therefore, describe this phenomenon as DEF.

We have, in fact, investigated three Portland cement mortars in some detail, and have observed regrowth of ettringite in all of them, without any accompanying expansion [4]. Typically, on curing at 20 °C, ettringite was formed within 24 h and reached a maximum amount at a time that varied between 1 and 28 days. The sulfate phases, gypsum, hemihydrate and anhydrite, had completely reacted after 28 days. The ettringite content then decreased until it reached a minimum value. Meanwhile, the development of monosulfate was essentially the opposite to that of ettringite. The time of formation of its maximum amount correlated reasonably well with that to reach the minimum amount of ettringite. Subsequently, the ettringite content increased continuously for up to 2 years of hydration, accompanied by a decrease in the amount of monosulfate observed. Although there are unavoidable errors associated with each individual determination, there is no doubt whatsoever about the overall trend. Similar observations have been made by Odler and Chen [9] and Lewis [10].

We could not find any evidence that the direct source of the sulfate ions was the cement clinker. Hime suggested that DEF at ambient temperature might be due to the slow release of sulfate ions from belite. Although we monitored variations of the degree of hydration of belite with aging at room temperature for more than 1 year, we found no correlation between them and the regrowth of ettringite [4,11]. Instead, we believe that it is more likely to be the C–S–H gel that initially sorbs sulfate ions and subsequently releases them gradually, hence, facilitating the conversion of monosulfate to ettringite. Evidence in favour of this hypothesis has been obtained from X-ray microanalysis [12,13]. We note that the sulfate contents of our three cements are only just above 3% (Table 1), and the sulfate levels in the clinkers based on these cements, determined by QXDA, all fall below the critical level for DEF (3%) suggested by Hime. It would be interesting to see the results from further investigations into the hydration of cements with high sulfate clinker contents.

Hime also comments that two-tone relics can occur at room temperature. We observed that the two-tone structures in the inner products faded with decrease in curing temper-

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Table 1
Chemical and mineralogical composition of the Portland cements used [4,11]

Oxides	A*	B*	C*	Minerals**	A	B	C
CaO	64.5	64.8	64.4	Alite	57.6	59.6	48.3
SiO_2	20.3	20.5	21.6	Belite	20.4	13.1	26.1
Al_2O_3	6.0	5.0	4.9	C_3A (cubic)	4.7	0.0	4.7
Fe_2O_3	2.4	2.9	2.2	C_3A (orth)	3.4	2.3	2.6
MgO	1.2	2.3	1.0	Ferrite	8.8	13.1	8.3
SO_3	3.2	3.3	3.1	Gypsum	0.7	0.0	0.0
K_2O	0.6	0.7	0.5	Hemihyrite	0.0	0.8	1.2
Na_2O	0.2	0.1	0.1	Anhydrite	1.8	1.7	2.5
Free CaO	(1.8)	(0.5)	(2.4)	MgO	1.7	2.6	1.1
Total	98.4	99.6	97.8	Quartz	0.4	1.0	0.4
				Total	99.5	94.2	95.2
				RF	0.0024	0.0043	0.0034

RF = reliability factor.

* As supplied by the cement manufacturers.

** Mineralogical composition was determined by QXDA.

ature and had disappeared completely at room temperature [11]. In conjunction with the report by Diamond et al. [14], it seems to us that the two-tone structures can be readily observed in cement products cured at elevated temperatures, but only in some such products that are continuously cured at ambient temperature.

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