Pergamon

Cement and Concrete Research, Vol. 27, No. 3, pp. 473-474, 1997
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0008-8846/97 $17.00 + .00

PII S0008-8846(97)00037-9

LETTER TO THE EDITOR
ETTRINGITE NOMENCLATURE

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Several forms of the ettringite phase may form in the hydration of Portland cement and this process may, or may not cause expansion and cracking of concrete. Mather [1] suggested to classify different ettringite forms as "primary", "secondary", "early" and "late". Fu and Beaudoin [2] differentiated between "delayed" and "secondary" ettringite formation. In our view one must distinguish between the following ettringite formation mechanisms and forms of ettringite:

First, significant amounts of ettringite are formed in the initial stage of cement hydration in a reaction between tricalcium aluminate (and in a lesser amount calcium aluminate ferrite) and calcium sulfate. This reaction comes to its end within a few hours, due to the consumption of calcium sulfate and is typically followed by a conversion of the ettringite to monosulfate. As most of the ettringite forms at a stage when the paste is still of plastic consistency, the process is not associated with an expansion. At water/cement ratios commonly used in concrete technology the formed ettringite is microcrystalline; it may be detected by x-ray diffraction or DTA, but not by SEM or optical microscopy. We suggest to refer it as "early primary ettringite".

If excessive amount of calcium sulfate is ground with the clinker, the above reaction may continue for days or even weeks, causing an expansion of the paste/concrete. We suggest referring to this type of ettringite as "late primary ettringite".

Additional amounts of ettringite may also be formed, if the excessive SO_3 migrates into the concrete from an outside source, rather than being present in the original cement. In such case it will react either with C_3A not consumed in the formation of "early primary ettringite" or with the monosulfate present in the paste. The reaction is also associated with an expansion and the process is generally known as "sulfate attack". We suggest calling this form of ettringite "external ettringite".

A separate form of ettringite is formed in concrete mixes that were heat cured at temperatures above the range of thermodynamic stability for this phase, i.e. above about 70°C. The precursor of this form of ettringite is the monosulfate that forms in the hydration of C_3A at high temperatures instead of ettringite, even in the presence of free calcium sulfate; it may also be formed by high temperature conversion of primary ettringite that had been produced before the temperature of the paste attained 70°C. This (microcrystalline) form of ettringite usually forms very slowly and its delayed formation may cause expansion and cracking of the hardened paste and concrete. In our view, it should be referred to as "delayed ettringite"..

The last form of ettringite to be mentioned is the one found in macrocracks of concrete that underwent repeated wetting and drying, after being heat cured at high temperatures. Such cracks are preferentially located at the macroaggregate/paste interface and develop due to the formation of "delayed" ettringite. Similar cracks may be also created in response to

TABLE 1

Forms of Ettringite

Designation	Time of formation	Conditions of formation	Al2O3 source	Texture/ expansivity
early primary	first hours of hydration	normal conditions of hydration	C3A	microcryst./ no
late primary	first days/weeks of hydration	excessive amounts of gypsum in cement	C3A	microcryst./ yes
external	any time	migration of SO3 from outside	monosulfate	microcryst./ yes
delayed	months after heat curing	after heat curing at T > 70°C	monosulfate	micricryst./ yes
secondary	months after heat curing	recrystallization of ettringite in formed cracks upon wetting and drying	ettringite	macrocryst./ no(?)

the formation of "late primary" ettringite, severe drying, or other factors. This form of ettringite is usually well detectable by SEM, optical microscopy, or even visually. It is produced by recrystallization of "primary" or "delayed" ettringite into preexisting cracks and, in our view, should most appropriately be designated "secondary ettringite".

The main characteristics of the different forms of ettringite are summarized in the enclosed table.

References

1. B. Mather, Cem. Concr. Res. 26, 1745 (1996).
2. Y. Fu and J.J. Beaudoin, Cem. Concr. Res. 26, 979 (1966).