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Studies on delayed ettringite formation in heat-cured mortars II. Characteristics of cement that may be susceptible to DEF

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Abstract

Expansions of mortar bars, stored over (but not in) water after simulated steam curing to 85 °C, were related to certain cement compositional parameters. The relationship is expressed in the form of a "delayed ettringite formation (DEF) index." The DEF index is computed as the joint product of the SO_3/Al_2O_3 molar ratio of the cement, the sum of its SO_3 and Bogue C_3A percentages divided by 10 and the square root of the alkali content expressed as equivalent % Na_2O. The mortars studied were made with 18 different cements, prepared from a set of six representative clinkers by incorporating Terra Alba gypsum to total SO_3 contents that were 1% below optimum, at optimum and 1% above optimum (as defined in ASTM C 563). Measurements of expansion were recorded at intervals for up to 1400 days. Severe cracking and prominent DEF-induced expansions were observed in mortar bars derived from four of the six 'oversulfated' cements and lesser expansions from three of the six cements prepared at optimum SO_3 contents. No expansion was found for cements of DEF index below a threshold value; above this value expansions were approximately proportional to the difference between DEF index and its threshold value. The relationship confirms the significance of all three compositional parameters making up the index, e.g., the SO_3/Al_2O_3 molar ratio, the joint contents of SO_3 and C_3A, and the alkali content, in influencing the extent of DEF-induced expansion. In these measurements, the apparent pessimum effect for SO_3 content previously reported by others was not found, although SO_3 contents examined spanned the supposed pessimum value of 4%. Rather, expansion increased with increasing SO_3 content for mortars made with all clinkers exhibiting expansion.

Keywords: Delayed ettringite formation (DEF); Optimum sulfate content; Expansion; Cement composition; DEF index

1. Introduction

It has been generally believed in the past that various aspects of the composition of cement are major determining factors controlling the extent of delayed ettringite formation (DEF)-induced expansion observed in heat-cured laboratory mortars.

The molar ratio of SO_3 to Al_2O_3 in the cement has been considered to be of major importance. For example, in their pioneering work, Heinz and Ludwig [1] found that the DEF-induced expansions of laboratory mortars that had been exposed to a simulated steam-curing cycle progressively increased with increase in SO_3/Al_2O_3 molar ratio. However, later research carried out under different experimental conditions by Grabowski et al. [2] did not find this increasing tendency to progressively higher expansions with increased SO_3/Al_2O_3 molar ratios. Rather, they found that expansion was highest for specimens made from cements in which this ratio was close to 1.00, this constituting a pessimum value. Cements with molar ratios higher than this showed reduced expansion levels.

In addition to the SO_3/Al_2O_3 molar ratio, the contents of specific individual cement components were also found by other investigators to be important. For example, in a monumental study, Lawrence [3] summarized data for DEF-induced expansions for mortars made from 55 different cements cured at 100 °C. He found only limited correlation for any one compositional parameter by itself, but statistically significant correlations were shown in a multiple regression equation for SO_3 content, for the quant-

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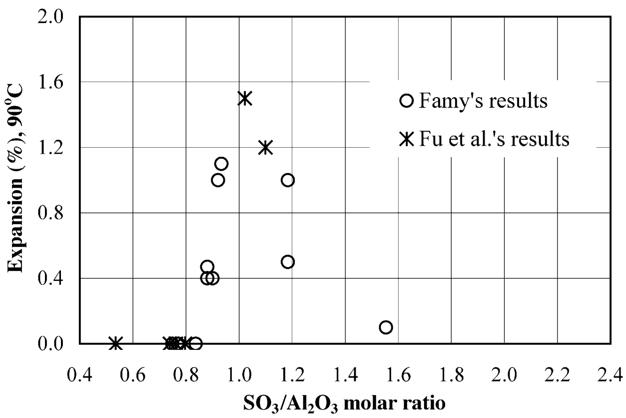

Fig. 1. Expansion vs. SO_3/Al_2O_3 molar ratio results of Famy [9] and Fu et al. [10].

itative XRD-determined content of C_3A and, surprisingly, for the MgO content.

Odler and Chen [4] found that significant expansions of heat-cured cement pastes took place only for cements with high contents of *both* SO_3 and C_3A. Kelham [5] reported similar findings, but he also found that, for the clinkers used in his study, there was a pessimum SO_3 content at about 4%. The existence of a similar pessimum SO_3 content at about the same level was also reported by Lewis [6].

Finally, the alkali content of the cement was linked to the magnitude of DEF-induced expansion by a number of investigators (e.g., Refs. [5,7,8]). These authors found that heat-treated laboratory specimens made with higher alkali cements typically showed higher DEF-induced expansions.

Recently, Famy [9] and Fu et al. [10] separately reported measurements of DEF-induced expansions for various 90 °C heat-treated mortars cured under water. The present writers have calculated SO_3 to Al_2O_3 molar ratios from their stated cement chemical compositions and scaled the highest value of expansion achieved for each mortar from their graphs. These highest expansion values are plotted vs. SO_3/Al_2O_3 molar ratios in Fig. 1.

It can be seen in the combined data sets plotted in Fig. 1 that no expansion at all took place in this combined data set for specimens made from cements with SO_3/Al_2O_3 molar ratios less than about 0.8. It is also shown in Fig. 1 that a pessimum SO_3/Al_2O_3 molar ratio was evidently present at about 1.0; maximum expansions are significantly less for cements with SO_3/Al_2O_3 molar ratios much beyond this value.

In the present paper, DEF-induced expansions from a large data set of specimens are presented and related to SO_3/Al_2O_3 molar ratio, and to various other cement compositional parameters. The specimens were suspended over, rather than immersed in water. Under these circumstances, initiation of expansion is slower and the period of active expansion is prolonged for years, more in accord with what takes place in field concrete experiencing DEF. Field concretes undergoing DEF are typically exposed to elevated temperatures during early hydration, but expansion often does not occur for some years. Accordingly, in our laboratory studies, comparisons are usually made for expansions measured at specific ages, in this case 800 and 1400 days. Thus, our expansion values do not represent maximum values, as expansion is continuing even after 1400 days.

In the present work, the measured expansions are related to the compositional parameters of an unusual suite of laboratory mixed cements. The cements studied were prepared from six different clinkers, but varied in total SO_3 contents in a specific manner. Relationships between DEF-induced expansions and various compositional parameters of these cements were explored, and an overall quantitative relationship linking these parameters to the measured DEF-induced expansions has been developed. This relationship may have general applicability with respect to selection of cements where DEF may be a potential field problem.

2. Experimental

As described previously [11], six ground clinkers were provided by CTL, for use in this research. The clinker SO_3 contents ranged from 0.07% to 2.48%. For each clinker, the optimum SO_3 content was determined according to ASTM C 563. Each clinker was then blended with the requisite amount of Terra Alba gypsum to prepare laboratory cements with varying total sulfate contents. For each clinker, cements were prepared at optimum SO_3 content (B level) as well as at SO_3 contents 1% below the optimum level (A level) and 1% above the optimum level (C level). The characteristics of the clinkers are given in Table 1.

Mortar bars (25 × 25 × 286 mm) were made from these cements using standard Ottawa sand. A blend of standard

Table 1
Analyses and characteristics of clinkers used

Clinker no.	1	2	3	4	5	6
% SiO_2	22.53	21.10	21.18	23.18	19.47	22.31
% Al_2O_3	5.66	5.15	5.89	2.66	6.37	4.80
% Fe_2O_3	2.84	3.86	2.56	4.21	2.21	3.26
% CaO	63.68	67.70	64.25	65.61	64.52	63.76
% MgO	3.28	1.23	1.97	2.63	2.74	1.00
% SO_3	0.38	0.07	2.27	0.74	1.86	2.48
% Na_2O	0.36	0.11	0.38	0.14	0.32	0.29
% K_2O	0.93	0.18	0.96	0.61	1.27	0.92
% TiO_2	0.30	0.31	0.30	0.14	0.26	0.15
% P_2O_5	0.09	0.30	0.14	0.04	0.34	0.19
% Mn_2O_3	0.06	0.02	0.22	0.06	0.07	0.13
% SrO	0.03	0.08	0.07	0.05	0.25	0.19
% Total	100.1	100.1	100.2	100.1	99.7	99.5
% Na_2O_{eq}	0.97	0.22	1.01	0.54	1.15	0.90
Optimum % SO_3	3.69	2.78	3.97	3.48	3.89	3.89
% C_3S	43.3	71.0	54.4	65.8	64.7	50.8
% C_2S	32.0	7.0	19.8	16.9	7.1	25.7
% C_3A	11.2	8.7	12.4	0.4	14.7	8.1
% C_4AF	8.6	11.8	7.8	12.8	6.7	9.9

ASTM C 778 graded sand (60%) and No. 20–30 sand (40%) were used to provide a relatively good distribution of particle sizes. The Ottawa standard sand was used in order to preclude the potential complication of ASR in this research, laboratory testing having previously indicated that this standard sand (unlike some others) is not ASR reactive. Duplicate mortar bars were exposed to a simulated steam curing cycle with a maximum temperature of 85 °C. The total length of the simulated steam curing cycle was 17 h; it included 5 h of precuring in a fog room, followed by 3 h of heating at 20 °C temperature increase per hour, 6 h of exposure at 85 °C and a 3-h cooling down period. The mortar bars were then exposed for long-term curing at room temperature suspended over, but not immersed in, water. Length changes were measured periodically using a standard length comparator meeting the requirements of ASTM C 490.

Additional details concerning the materials and test methods used in this investigation have been provided previously [11].

3. Results

The relation between expansions measured at 800 days and the SO_3/Al_2O_3 molar ratios of the cements used to produce mortar bars heat treated to a maximum temperature of 85 °C is shown in Fig. 2.

In this figure, it is seen that significant expansions were recorded for mortars made from cements with SO_3/Al_2O_3 molar ratios falling between about 0.85 and about 1.4, with the highest expansion occurring for specimens made from cements of molar ratios slightly above 1.00. Specimens made from cements of molar ratio less than about 0.8 did not expand. These results are generally analogous to those plotted in Fig. 1 for the results of Famy [9] and Fu et al. [10], and are in general accord with the earlier results of Grabowski et al. [2].

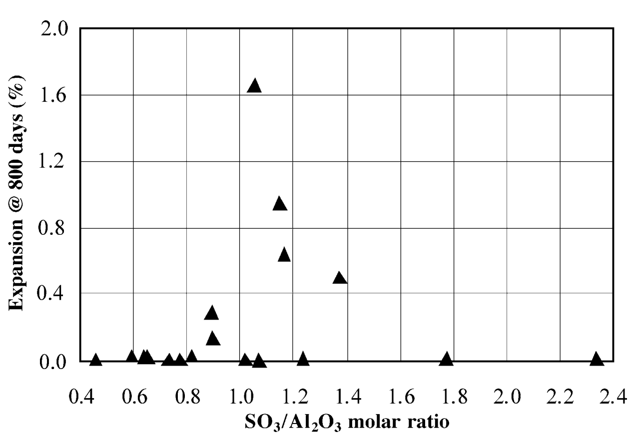

Fig. 2. Eight-hundred-day expansion of 85 °C treated mortar bars vs. SO_3/Al_2O_3 molar ratio of the cement used.

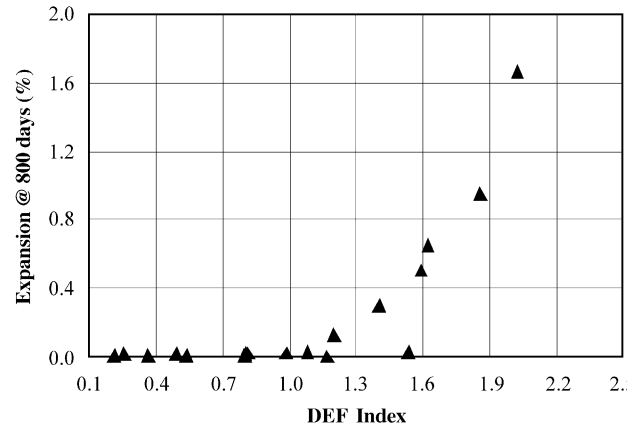

Fig. 3. DEF index of cement vs. expansion of mortar bars at 800 days.

However, it is seen in Fig. 2 that three points, representing specimens made from cements of molar ratios falling within the 0.85–1.4 "expansive" range of SO_3/Al_2O_3 ratio, nevertheless *did not* show expansion. Thus, it appears that, while SO_3/Al_2O_3 molar ratio is indeed an important compositional factor in predicting the extent of DEF-induced expansion, other compositional factors may intervene and limit or prevent expansion even if the SO_3/Al_2O_3 molar ratio is in the expansive range. Such compositional factors may include the actual SO_3 content, the C_3A content (a separate consideration from the Al_2O_3 content since in different cements, varying proportions of the Al_2O_3 are tied up as C_4AF) and especially the cement alkali content.

Through trial and error, a parameter was developed that was found to relate the compositions of the cements used in this study to the measured expansions of the mortar bar specimens.

This parameter, defined by us as the "DEF index," is a joint function of the SO_3/Al_2O_3 molar ratio and two other components that relate to expansive potential. One of these is the combined content of SO_3 and C_3A in the cement. Clearly, even if the *ratio* of SO_3 to Al_2O_3 is in the right range, if little SO_3 is in fact present, or if much of the Al_2O_3 is tied up as C_4AF, only little ettringite is likely to be formed.

Another important factor is the alkali content of the cement, as indicated by various authors [5,7,8].

The DEF index is defined by the following equation:

$$\text{DEF index} = (SO_3/Al_2O_3)_m \times [(SO_3 + C_3A)_w/10] \times \sqrt{Na_2O_{eq}} \quad (1)$$

where $(SO_3/Al_2O_3)_m$ is the molar ratio of SO_3 to Al_2O_3 of the cement; $(SO_3+C_3A)_w$ is the combined weight percentage of SO_3 and Bogue-calculated C_3A in the cement; and $\sqrt{Na_2O_{eq}}$ is the square root of the weight percentage of Na_2O_{eq} in the cement.

The use of a divisor of 10 in the term for the sum of the SO_3 and C_3A contents, and the use of the square root of the

Na_2O_{eq} term in the DEF index have no physical meaning even though the individual parameters themselves are known to be important in governing DEF-induced expansion. The index combines several cement compositional parameters in an arbitrary way that was found to be closely related to the measured expansions in the present data set.

The DEF indexes of the eighteen cements used in this research ranged from about 0.2 to about 2.0. Fig. 3 shows the close relationship between the DEF indexes of the 18 cements and the 800-day expansions of the mortar bar specimens originally exposed to an 85 °C maximum temperature.

It appears from Fig. 3 that, for the present specimens, there is a DEF index threshold value of about 1.1, below which no expansion occurs. For DEF index values higher than this, expansion at 800 days is approximately correlated with the difference between DEF index and its threshold value.

A single exception to the trend is present, in that one mortar with a DEF index value of about 1.6, which should have expanded, did not do so. This exceptional specimen was made from the optimum sulfate level (5B85) cement, as described previously [11]. It has high alkali and C_3A contents. Nevertheless, mortars made from it, like those made with other cements with optimum sulfate contents (as distinguished from oversulfated cements), appear to be slow to start expanding. As indicated earlier, no expansion was recorded at 800 days. This was in spite of the fact that small cracks were observed in the ends of the specimens. However, it appears that expansion for this mortar was only delayed, not prevented. The beginning of active expansion was noted at about 1100 days and expansion reached 0.2 % at 1400 days, and is continuing.

This prolonged expansion is characteristic for the present specimens, for which measurements up to, and in some cases beyond, 1400 days are available. These measurements indicate that the specimens that showed significant expansions at early ages continued to expand during subsequent storage, although at varying rates. The relationship between expansions of the mortar bar specimens recorded at 1400 days and their DEF index values is shown in Fig. 4. The data of Fig. 4 indicate that the overall trend shown for the 800-day measurements in Fig. 3 is maintained well at 1400 days, and indeed with the start of expansion for the 5B85 mortar, the single exception to the trend has started to approach its 'proper' expansion level. It is believed that this will continue at still later ages as the 5B85 mortars expand further.

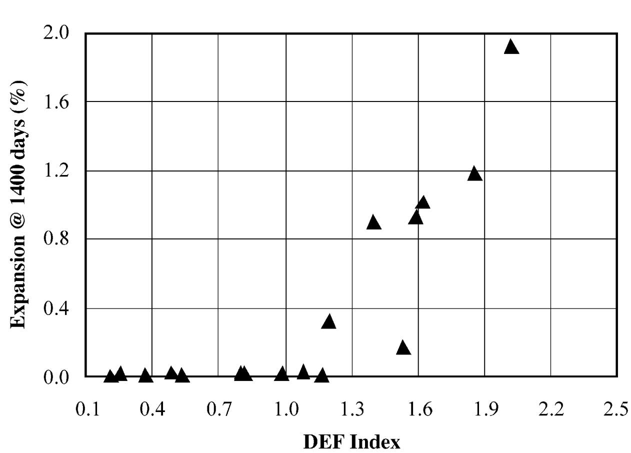

Fig. 4. DEF index of cement vs. expansion of mortar bars at 1400 days.

4. Discussion

The DEF index is proposed as a possible method to assess whether concrete made from a particular cement will suffer from DEF-induced expansion under certain circumstances, typically a combination of high temperature exposure at early ages and a prolonged exposure to moisture at later ages. It is hoped that this index, based entirely on cement composition, may provide some guidance for the industry in cement selection where DEF is a potential concern. It should be noted that fineness of the cement may also play a role, but the effect of fineness was specifically excluded in the present study, all of the clinkers being ground to the same fineness.

The DEF index is not meant to be an accurate predictor of the specific extent of expansion that may be found under various treatment and exposure regimes. For example, the maximum expansion data scaled from Famy [9] and Fu et al. [10] show a general trend of expansion vs. DEF index generally similar to that of Fig. 4, but different in detail. The maximum expansions, measured for underwater exposure, are linearly correlated with the DEF index, but the expansion values are different and the threshold DEF index for expansion is lower. For these immersed specimens, the limiting threshold for expansion was about 0.5, rather than about 1.1 as shown for the present specimens.

The proposed DEF Index is structured as the product of three terms. The first term, the SO_3/Al_2O_3, seems to be directly related to the stoichiometric condition that favors the formation of ettringite. Modern cements typically have supposedly 'balanced' proportions of sulfate and aluminate, but it is reasonable to believe that high SO_3 to Al_2O_3 molar ratios in cement favor the formation of ettringite instead of monosulfate. The second term, based on the combined percentage of SO_3 and Bogue-calculated C_3A in the cement, is clearly related to the amount of ettringite that can potentially be formed. With a cement in which SO_3/Al_2O_3 molar ratio favors ettringite formation, but in which only limited contents of SO_3 and C_3A are present, the volume of ettringite (or delayed ettringite) that could be formed is obviously limited and so will be the expansion. The Bogue calculated C_3A content, used in compiling the index, is admittedly less than perfectly accurate, but it has the virtue of being universally available for any cement. In contrast, the more accurate QXRD content of C_3A is rarely determined. The third term in the computation of the DEF index is based on the alkali content of cement. The alkali content is an extremely important element in predicting the extent of DEF-induced expansion, as indicated earlier. The field experiences of DEF surveyed by Hobbs [12] stress the importance of this factor. Indeed, Hobbs indicated that "all field cases of which the author is aware are associated with high-alkali cements."

The existence (or lack of it) of a pessimum value for SO_3 content requires some additional consideration. Kelham [5] and Lewis [6] both found that DEF-induced expansion values (for underwater exposure) peaked around 4% SO_3 and declined substantially for higher SO_3 contents, when other cement variables remained constant. Unfortunately, Kelham [5] did not provide complete details of cement compositions in his Fig. 3, in which this relationship was shown. However, it is apparent that the lines in the figure represent mixes of varying SO_3 content, each made from clinker, with different alkali content. Kelham [5] also indicated that the pessimum SO_3 content exhibited increased with increasing alkali content.

The cements used in the present experiments were specifically prepared to evaluate the effects of a range of SO_3 contents around the *optimum* SO_3 value for any given clinker. For the six clinkers used, the measured optimum SO_3 contents in ascending order were 2.8%, 3.5%, 3.7%, 3.9%, 3.9% and 4.0%. For each clinker cements were prepared at 1% below optimum, at optimum and at 1% above optimum. Thus, cements prepared from all but the lowest optimum SO_3 clinker covered the range over which the supposed 4% pessimum SO_3 should make its effects felt. No such effect was found in the present data (for exposure above water, but not underwater). Instead, in all series showing expansions, the expansions of the mortar bars increased with increasing SO_3 content.

5. Conclusions

1. A DEF index is proposed in this paper to relate certain cement compositional parameters to potential DEF-induced expansion of heat-cured cementitious systems. The index involves the SO_3/Al_2O_3 ratio, the sum of the SO_3 and Bogue C_3A contents, and the Na_2O equivalent alkali content, all factors well established as having major influence on the potential for DEF.

2. In the present experiments, mortars heat-cured to 85 °C then suspended over (but not immersed in) water underwent expansions that were closely related to the DEF index of the cement used. No expansions were found below a DEF index threshold value of about 1.1. For cements with DEF indexes above this threshold value, expansions were approximately linearly related to the difference between the DEF index and its threshold value. The threshold value may be different for different exposure conditions, as indicated by computing the DEF index for the cements used in the experiments reported by Famy [9] and Fu et al. [10].

3. The SO_3/Al_2O_3 molar ratio of the cement is an important factor in DEF. Our results suggest that DEF-induced expansions will most likely not take place when the cement SO_3/Al_2O_3 molar ratio is less than about 0.8. Maximum expansions were found near a pessimum SO_3/Al_2O_3 molar ratio of about 1.1. Nevertheless, some mortars in this pessimum range of SO_3/Al_2O_3 ratio did not expand at all, indicating the importance of additional cement parameters.

4. The actual contents of SO_3 and of C_3A were found to be critical for DEF-induced expansion to take place, for the obvious reason that they govern the amount of ettringite that can be produced.

5. The cement alkali content was found to have a significant effect on DEF-induced expansion, as is well established in the literature.

6. No pessimum SO_3 content for DEF-induced expansion was observed for any of the cements used in the current research.

Acknowledgements

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