A kinetic model for prediction of cement susceptibility to delayed ettringite formation in concrete, Part 2: Model validation and application

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Abstract

This work is a continuation of the process of developing a model for predicting the potential of Portland cements to exhibit expansion due to delayed ettringite formation, as presented in part 1 [1]. The model was derived basing on the kinetics theory applied to cement chemistry and evaluates two primary conditions of, the presence of sufficient active alumina in cement and the requirements for sulphate to alumina ratio applied against the countering microstructural effects, to determine the underlying kinetic characteristics for DEF in the system. The primary purpose of the model is determination of the intrinsic presence of the potential for DEF in cements.

In the second part of this work herein presented, the model is validated and tested for robustness by its application to a wide range of existing experimental data for DEF studies, taken from various global sources available in the literature. Over 164 data sets taken from various independent works, were used in the validation. It was found that the model was in strong agreement with experiment data for both expansive and non-expansive cements. However, some few outputs showed disagreements between model predictions and experimental observations. Most of the important disparities appear to occur with cements of high Fe_2O_3/Al_2O_3 ratios and may be related to inadequacy of the Bogue formula used in the model. These revealed aspects where future refinement of the model will be required. The model at this stage is applicable to plain Portland cements with a future possibility of improvements to examine more complex systems containing pozzolanic materials.

Introduction

In the first part **[1]** of the present work, a kinetic model consisting of a set of two equations was derived for predicting susceptibility of cementitious systems to DEF-induced expansive damage. The model given in equations **(1)** and **(2)**, basically suggests that for damage to occur as a result of delayed ettringite formation, the cement should have enough calcium aluminate beyond a threshold value, and that its sulphate to aluminate ratio should be greater than a certain minimum threshold. In the subsequent sections, the fundamental model parameters are established and applied in the model validation.

$$A_c > \frac{3.745 f\Phi}{m} \quad \textbf{(1)}$$

$$\frac{S_c}{A_c} > \frac{7.491 f\phi}{nA_c} + \frac{m}{n} \quad \textbf{(2)}$$

Here, $\boldsymbol{A_c}$ stands for aluminate content of cement used in the mix, $\boldsymbol{S_c}$ is the sulphate content of the cement, while ***f*** is the shift factor that accounts for the proportion of the capillary pores that are available to accommodate the expansive delayed ettringite formed, and $\boldsymbol{\Phi}$ is the capillary porosity of the material; **m** represents the proportion of the reactive alumina still left in the system after heat curing relative to the total alumina content in the cement; and ***n*** is the proportion of available sulphate to the initial sulphate in the cement used.

To validate the model, it is necessary to first determine the parameters ***f, Φ, m,*** *and* ***n,*** for use in the computations. These parameters will be primarily fitted using a number of case studies where cements with specific compositions have been used to make mortar prisms for DEF-related expansion measurements. The formula will then be tested on another set of experimental data for DEF expansion studies, to check whether the prediction of DEF expansiveness based on the model formulae are positively confirmed by existing experimental results. While the model estimates the quantities of the main reactants and their products responsible for expansion, these considered are only valid in relative terms, and are therefore not the main focus of the model output. Also, the model at this stage is applicable to plain Portland cements while more complex cementitious systems containing cement extenders such as fly ash, slag, silica fume etc. will require modification of the model based on scientific understanding of their mechanisms and effects.

Determination of Parameters *m, n, and Φ*

It has already been established in many instances that there is a pessimum value of alumina that lead to the maximum expansion for a specific sulphate content **[2]**. From Taylor *et al*'s work **[3]**, it is shown that a vast majority of Portland cements lie in the range of high alumina, low sulphate side of the expansion - alumina content curve, which means that any binding of alumina will increase expansion, while increases in the alumina content will result in less expansion. Factors that affect the amount of alumina available for delayed ettringite formation are, among others, the ferrite content, magnesia, silica, alkalis, curing temperature and duration.

The content of Fe_2O_3 in the cement used, and more importantly the Fe_2O_3/Al_2O_3 ratio determines the amount of alumina in cement that will be left available for ettringite formation. This arises from the known fact that initial alumina first combines with ferrite and calcium oxide to form the tetra-calcium aluminoferrite. It is after this reaction has taken place that the remaining alumina will then be available for ettringite formation. This is possibly why sulphate-resisting Portland

cements, which typically have high Fe_2O_3/Al_2O_3 ratios, show insignificant or no expansions due to DEF [ ]. Furthermore, it is on this basis that the Bogue formula for the calculation of tricalcium aluminate uses the molar difference between the total alumina and the ferrite in the cement.

As for MgO, it can combine with alumina and form periclase (an $MgO\text{-}Al_2O_3$ hydrate phase), thus reducing the alumina content available for ettringite formation. Variation of magnesia content is inversely proportional to the parameter ***m***. SiO_2 hydrates and forms CSH which binds aluminium ions, reducing the amount of Al_2O_3 available for the formation of ettringite. Therefore increasing silica content of cement reduces ***m***. Alkalis make ettringite unstable, thus reducing the amount of alumina bound as early ettringite formed, and in turn increasing the amount of alumina available for delayed ettringite formation. Increasing the alkali content results in increase of ***m***. As for factors affecting the amount of sulphate available in the system for ettringite formation, the alkali and silica contents in cement feature prominently. As discussed above, high content of alkalis will lead to less quantities of early ettringite formed, thus resulting in higher sulphate contents being available for reaction later to form delayed ettringite. Accordingly, increase in content of alkalis increases ***n***.

The capillary porosity of the system is affected by, among other factors, the pore tortuosity of the specimen. Finer cements results in less porous specimens, which would offer less space to accommodate ettringite formed, thus resulting in greater DEF-related expansions. Based on above considerations, the following expressions [ ] given in equations (3) to (4), were used to determine the parameters m, n, and Φ.

$$m = C_m (Na_2O_{eq})^{Pm1} \left(\frac{C_{m1}}{SiO_2}\right)^{Pm2} \left(\frac{C_{m2}}{MgO}\right)^{Pm3} \quad \textbf{(3)}$$

$$n = C_n (Na_2O_{eq})^{Pn1} \left(\frac{C_{n1}}{SiO_2}\right)^{Pn2} \quad \textbf{(4)}$$

$$\Phi = C_\Phi \left(\frac{C_{\Phi 1}}{Fineness}\right)^{P\Phi 1} \quad \textbf{(5)}$$

Where P_{m1}, P_{m2}, P_{m3}, P_{n1}, P_{n2}, $P_{\phi 1}$ are power contants,
And C_m, C_{m1}, C_{m2}, C_{n1}, C_{n2}, C_ϕ are empirical constants or coefficients.

Application of the Test Formula on Cements used in some DEF-Related Expansion Studies

The model formulae were applied on cement clinkers used in DEF expansion tests in the literature. Constants C_m, C_{m1}, C_{m2}, C_n, C_{n1}, C_Φ, $C_{\Phi 1}$, P_{m1}, P_{m2}, P_{m3}, P_{n1}, P_{n2}, $P_{\Phi 1}$, were determined through fitting using some expansion data in the literature. In all instances, the shift factor ***f*** has been taken at 5%, meaning that only 5% of capillary pores volume are available to accommodate ettringite formed before the system start expanding. Tixier **[4]**, in his model validation, used variable values of ***f*** in the range of 5% to 45%. Preference has been given to take the least value of this range (0.05) so as to base the test on the worst case scenario possible, thus ensuring conservative results. That is, cements that would be in the borderline are declared by the model as potentially expansive.

Table 1 Fitting of values for formulae constants

C_m	C_{m1}	C_{m2}	P_{m1}	P_{m2}	P_{m3}	C_n	C_{n1}	P_{n1}	P_{n2}	C_Φ	$C_{\Phi 1}$	$P_{\Phi 1}$
0.2	21	5	0.55	3.5	0.4	0.71	20	0.55	0.45	0.15	380	0.6

From this stage, the formulae are then tested against other sets of DEF expansion data from literature sources. The tables 2 to 4 present DEF susceptibility prediction results compared against expansion data taken from different works available in the literature references **[5-17]**. The model uses the value **1** to denote expansion, and **0** to indicate absence of expansion.

As can be seen in the tables of results, expansion predictions by model are generally consistent with the expansion results observed in many cases. It has to be noted that in some instances, the test predicts expansion potential while the experiments did not show any expansion. This could be explained by two possible reasons, the first being that the expansion data recorded might not be definitive in terms of period of occurrence. It has been shown **[16]** that some specimens that were not showing any sign of expansion up to a soaking period of around 800 days started expanding later and by 1400 days had reached quite noticeable levels of expansion. The second reason could be due to other factor such as the size and shape of the specimen, which impact on how fast alkalis are leached out of the specimen, knowing that this is very decisive on DEF related expansion.

Table 2 Comparison of model predictions against experimental results from Lawrence [5]

Cement ID Or Type	Soaking period of specimen (days)	S_c	S_c/A_c	Fe_2O_3 /Al_2O_3	Model output	Experimental results
3970					1	1
3971					1	1
3973					1	1
3974					0	1
3975					1	1
4023					1	1
4024					1	1
4025					1	1
4026					0	0
3982					1	1
3984					1	1
4037					1	1
3986					1	1
3988					1	1
3990					1	1
3992					1	1
3994					1	1
3996					1	1
4031					1	1
4036					1	1
4044					1	1
D58					1	1
3572					1	1
3579					1	1
3580					1	1
3577					1	0

Table 2 cont'd

Cement ID or Type	Soaking period of specimen (days)	S_c	S_c/A_c	Fe_2O_3/Al_2O_3	Model output	Experimental results
3595					1	1
3594					1	1
3597					0	1
3730					1	1
3747					1	0
3748					1	1
3749					1	1
3750					1	1
3751					0	0
3752					0	1
3740					1	1
3753					1	1
3576					1	1
3721					0	0
3722					0	0
3723					0	0
3724					1	0
3725					1	0
3999					1	1
4000					1	1
4144					1	1
4019					0	0
4077					1	1
4078					0	1
4167					1	1
4174					0	0
4811					0	1

1 = expansive, 0 = non-expansive

Table 3 Comparison of model predictions against experimental results from various sources [6-15]

Data source / Specimen	Cement ID or Type	Soaking period of specimen (days)	S_c	S_c/A_c	Fe_2O_3 /Al_2O_3	Model output	Experimental results
Fu et al. [6] ……. specimen						0	0
						1	0
						0	0
						1	1
						1	1
						0	0
Grattan-Bellew et al. [2] ……. specimen						1	1
Ramlochan et al. [7] 25x25x285 mm mortars						1	1
						1	1
Barbarulo et al. [8] ……. specimen						1	1
						0	0
						1	1
Ramlochan et al. [9] 25x25x285 mm mortars						1	1
Fu and Beaudoin [10] ……. specimen						0	0
						0	1
						1	1
Pavoine et al. [11] ……. specimen						1	1
Yang et al. [12] ……. specimen						1	1
Famy et al. [13] ……. specimen						1	1
Tosun [14] ……. Specimen						1	1
						1	1
						1	1
						1	1
						1	1
						1	1
						1	1
						1	1
						1	1
Odler and Chen [15] ……. Specimen						1	1
						1	1
						1	1
						1	1

1 = expansive, 0 = non-expansive

Table 4 Comparison of model predictions against experimental results from Zhang et al. [16] and others

Data source / Specimen	Cement ID or Type	Soaking period of specimen (days)	S_c	S_c/A_c	Fe_2O_3 /Al_2O_3	Model output	Experimental results
Zhang et al. [16] ……. Specimen	1A					1	0
	2A					0	0
	3A					1	0
	4A					0	0
	5A					1	0
	6A					1	0
	1B					1	1
	2B					0	0
	3B					1	1
	4B					0	0
	5B					1	0
	6B					1	0
	1C					1	1
	2C					0	0
	3C					1	1
	4C					0	0
	5C					1	1
	6C					1	1
Ekolu et al. [17] 25x25x285 mm mortar							

1 = expansive, 0 = non-expansive

It should be emphasized that the model test formulae, assess the likelihood of a cementitious specimen to exhibit DEF expansive behaviour given all the necessary conditions i.e. high temperature treatment during early ages, moist environment storage, and also ease of alkalis leaching out from the specimen. The analysis in the model is based on intrinsic kinetic characteristics of the cement. As to whether the specimen will actually show DEF expansion in the lab or field will depend on other factors which may be beyond the capabilities of this present model. However, results of the model are expected to be conservative and generally in line with actual expansive behaviour of concrete and other cementitious systems.

Also, attention should be directed to cases highlighted in the tables 2 to 4, where the model predicts no expansion whilst experimental proved the opposite to be true. This disparity, we think, might be related to inadequacy of the Bogue method (applied in the model) to accurately determine the active alumina in the cement. It can be noted that these test failures mainly or only occur in cement composition with high ferrite to alumina ratios. These relate mainly to the case of sulphate-resisting cements, where the available alumina in the cement is supposed to have mainly combined as tetracalcium alumino-ferrite, with only a small portion of it remaining for DEF formation reactions. Improving this aspect of the model formula might possibly require the use of XRD quantitative data, instead of the Bogue formula, for determination of tricalcium alumina in the cement used.

CONCLUSIONS

Model test formulae aimed at predicting the susceptibility of a specific Portland cement to DEF expansion have been devised, validated and tested for robustness using over 164 experimental data sets obtained from a wide range of literature sources.

Expansion is understood to stem from the formation of ettringite in hardened concrete. Before expansion can effectively start occurring, it is necessary that the amount of ettringite formed should to a certain extent exceed a threshold corresponding to the portion of the capillary pores that can accommodate it. The model formulae consists of two conditions:- that the cement used should contain sufficient active alumina beyond some minimal value, and that the sulphate to aluminate ratio be greater than a threshold value. Threshold values of aluminate content and sulphate to aluminate ratio are dependent upon both the chemical composition of the cement and the specimen microstructure, the latter being related to cement fineness. Verification of the model against expansive results obtained from a number of studies in the literature shows that the model is in good agreement with experimental results.

However, a few failures recorded on some cements with high ferrite to alumina ratios appears to suggest that the model test formulae which are based on the Bogue formula for calculation of active alumina, might be inadequate and may require more accurate quantitative methods for estimating the tricalcium aluminate content of cement such as the QXRD.

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