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Extension of the chemical index model for estimating Alkali-Silica reaction mitigation efficiency to slags and natural pozzolans

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HIGHLIGHTS

- Relation between oxides in cements and SCMs and expansion of mortars is investigated.
- The chemical index model is extended to use with natural pozzolans and slags.
- An improved optimization strategy is proposed.
- Minimum cement replacement needed to mitigate ASR can be better estimated.

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ABSTRACT

Supplementary cementitious materials (SCMs) can mitigate alkali silica reaction (ASR) but the level of cement replacement required is difficult to estimate for a particular SCM. The Chemical Index Model was recently proposed to estimate the relation between mortar expansion and the chemical compositions of cement and fly ash but has not been tested extensively for use with other SCMs. This study uses natural pozzolans and blast furnace slags, in addition to fly ashes, with two portland cements and a reactive aggregate to evaluate the effectiveness of the model to estimate 14-day ASTM C 1567 expansion. The reactivities of different oxides are discussed. Model parameters are calibrated for use with mortars containing slags or natural pozzolans. Improvements are suggested to the optimization strategy in the model. Errors in the estimated minimum cement replacement to limit expansion to 0.1% are significantly lowered when the calibrated model is used with these improvements.

1. Introduction

Alkali-silica reaction (ASR) is a durability problem in portland cement concrete structures that can lead to shortened service lives or the need for expensive repairs. It occurs as a reaction between alkalis (and hydroxyl ions) in the pore solution, coming from the cement or other sources, and certain reactive siliceous aggregates to form a gel which leads to deleterious expansion upon absorption of water. The expansion can lead to cracking, which can initiate or exacerbate other durability issues such as corrosion and sulfate attack. Although many researchers have studied this reaction and the expansion mechanisms [1–5], it is still poorly understood. Nevertheless, various methods of mitigating this problem exist [6–12], some being more effective and/or economical than others. One of the more economical and better understood methods is the use of supplementary cementitious materials (SCMs) to partially replace the portland cement in the mixture [13]. SCMs can mitigate ASR by reducing the alkalis from the cement, by reacting with cement hydration products to reduce permeability, by binding alkalis, etc. Their effectiveness is generally known to depend on their chemical or mineral composition, their fineness, and their dosages (levels of cement replacement). Many test have been proposed to evaluate the ASR risk of cementitious mixtures [14–19]. Some of these use concrete while others use mortar specimens, and the test duration can vary greatly between them. As such, for practical reasons, the short-duration ASTM C 1567 [20] "accelerated mortar bar test" (AMBT) is perhaps the most commonly employed ASR test (considered together with ASTM C1260 [21]), despite some concerns about the high temperature and bath concentration used. Although this test allows the assessment of the effectiveness of a chosen SCM in reducing the expansion of a reactive aggregate-cement pair at hand, the test needs to be performed several times for each new SCM, at different cement replacement levels to determine the minimum SCM content needed to "pass"

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the test i.e. achieve a 14-day expansion of 0.1% or less. Hence, several researchers have attempted to relate the physical and chemical composition of SCMs, mostly fly ashes, to expansion [13,22–27]. For example, it has been stated that the CaO and SiO_2 contents of a fly ash have the greatest effect on its efficiency of mitigating ASR [22,28]. Chemical composition is often evaluated as oxide composition, rather than mineralogy, since the former is more easily quantified. Fineness also influences the effectiveness of a fly ash [29] but Venkatanarayanan and Rangaraju [25] found that chemical composition dominates in the typical size range for fly ash, fineness becoming significant for sizes below ~ 10 μm.

Based on such observations, Malvar and Lenke [24] proposed a model for estimating the ASTM C 1567 14-day expansion of fly ash-cement-aggregate mortars, using only the oxide compositions of the fly ash and cement, and the 14-day expansion of the cement-aggregate control. This "chemical index model" was developed for fly ash only, using data from five separate studies that investigated ASTM C 1567 expansion of mortars with 29 different fly ashes, with CaO contents of ~3 to 30%. Each study used different aggregates and cements. The cement-only (control) mortar 14-d expansions were as high as 0.8%. For a given ash, cement, and aggregate reactivity, the model was able to estimate the minimum cement replacement needed to ensure, with a chosen reliability, that the 14-day expansion would remain below a chosen level (0.08% in their study rather than 0.1% given in the standard)/However, they did not provide any discussion of the difference (error) between estimated and measured (or interpolated from measurements) cement replacement levels for individual ashes. Schumacher and Ideker [26] applied the model to mortars made with high-lime and/or high-alkali fly ashes and showed the index to "work well for low-CaO and low-alkali ashes" but stated "adjustments are necessary to use this methodology to predict replacement levels of moderate and high-alkali fly ashes". They also compared the estimated and measured minimum replacement levels for the five fly ashes and two different reactive aggregates they used and found that not only was the error greater for the higher-lime ashes, but also that the estimated minimum required replacement percentage exceeded 100% (so all the cement would need to be replaced) for fly ashes with greater than 30–35% CaO. A need for modification of the chemical index was suggested for high-lime ashes. Wright et al. [30] also used the model on mortars made with recycled glass sand and six fly ashes. They reported the model being conservative with the average cement replacement required to control ASR expansion up to ~70% higher than the experimentally-determined minimum for the low-lime ashes and up to ~145% higher (e.g. 54% estimated, 22% experimental) for the higher-lime ashes.

Even though this method was developed for fly ash, many other SCMs are commonly used to replace cement. Ground, granulated blast furnace slags are known to be effective in controlling ASR [31], albeit at higher replacement levels. Natural pozzolans, although not a waste or by-product, are increasingly being used due to the higher uniformity of their chemical compositions [32]. It is expected that the large differences in the oxide compositions and reactivities of fly ashes and other SCMs can influence the ability of the chemical index to relate to expansion. This study attempted to extend the "chemical index model" to slags and natural pozzolans, and to determine whether the model could be modified to yield improved estimates.

2. Background on the chemical index model

The Chemical Index Model [24] divides the oxides in fly ash and cement into two groups: Those that increase expansion (CaO, Na_2O, K_2O, MgO, and SO_3) and those that decrease expansion (SiO_2, Al_2O_3, and Fe_2O_3), in the AMBT. Other minor oxides are not considered. Building on previous studies that related CaO/SiO_2 to measured expansion, they define a chemical index, C_b, for the "blend" of cement and fly ash in which the numerator is a CaO equivalent and the denominator is an SiO_2 equivalent defined as:

$$CaO_{eq\alpha b} = CaO + \alpha(0.905Na_2O + 0.595K_2O + 1.391MgO + 0.700SO_3) \quad (1)$$

$$SiO_{2_{eq\beta b}} = SiO_2 + \beta(0.589Al_2O_3 + 0.376Fe_2O_3) \quad (2)$$

where α and β are weighting factors to account for the differences in reactivity of the grouped oxides with those of the CaO and SiO_2. $CaO_{eq\alpha b}$ represents a combination of the CaO molar equivalents of the expansion-increasing constituents, and $SiO_{2_{eq\beta b}}$ represents a combination of the SiO_2 molar equivalents of the expansion-decreasing constituents. Then;

$$C_b = \frac{CaO_{eq\alpha b}}{SiO_{2_{eq\alpha b}}} = \frac{CaO + \alpha(0.905Na_2O + 0.595K_2O + 1.391MgO + 0.700SO_3)}{Si_2O + \beta(0.589Al_2O_3 + 0.376Fe_2O_3)} \quad (3)$$

can be obtained. It can understood that a higher α value indicates a greater expansion-increasing contribution of the oxides Na_2O, K_2O, MgO, and SO_3, while a higher β value indicates a greater expansion-decreasing contribution of the oxides Al_2O_3 and Fe_2O_3. The same index could also be used for the cement-only case (C_c), if the oxide contents for the cement are used, or for the fly ash-only case (Cfa), if the oxide contents for the ash are used.

Malvar and Lenke [24] normalized the 14-day AMBT expansions, E_{14b}, of each mortar using the expansion of the control (no fly ash) mortar, E_{14c}, and plotted them against C_b/C_c, the chemical index for the blend normalized by the chemical index for the cement, calculated for the cement/fly ash blend in each mortar. The best fit to the data was obtained using a nonlinear hyperbolic tangent model:

$$\frac{E_{14b}}{E_{14c}} = \frac{a_1}{2}\left(1 - tanh\left(\frac{(C_b/C_{c)-a_3}}{a_4}\right)\right) + \frac{a_2}{2}\left((1 + tanh\left(\frac{(C_b/C_{c)-a_3}}{a_4}\right)\right) \quad (4)$$

where a_1, a_2, a_3, and $a_4$are the parameters of the hyperbolic tangent curve fit to E_{14b}/E_{14c} vs. C_b/C_c. Through an optimization process with the objective of minimizing the sum of the squares of the difference between measured and estimated $\frac{E_{14b}}{E_{14c}}$ for all ash/cement blends, they found the parameters that gave the best fit to their data (for a reliability of 50%) and adopted the following values for their subsequent work: α = 6, β = 1, a_1 = 0, a_2 = 1.0530, a_3 = 0.7386, a_4 = 0.1778. Using this fit curve, Malvar and Lenke [24] were able to determine the amount of fly ash needed to keep 14-day expansion below a chosen limit (0.08% in their study). If $E_{14c}$is the expansion with cement only, then the maximum normalized expansion sought is $0.08/E_{14c}$. Entering $0.08/E_{14c}$ on the y-axis of E_{14b}/E_{14c} vs. C_b/C_c gives a maximum value of C_b/C_c needed to limit expansion. Defining the inverse of the hyperbolic tangent function of E_{14b}/E_{14c} vs. C_b/C_c as function g yields the following:

$$\frac{C_b}{C_c} = g\left(\frac{0.08}{E_{14c}}\right) = a_4 tanh^{-1}\left[\frac{2\left(\frac{0.08}{E_{14c}}\right) - (a_1 + a_2)}{a_2 - a_1}\right] + a_3 \quad (5)$$

However, from Eq. (3)

$$C_b = \frac{CaO_{eq\alpha b}}{SiO_{2eq\beta b}} = \frac{WCaO_{eq\alpha fa} + (1 - W)CaO_{eq\alpha c}}{WSiO_{2eq\beta fa} + (1 - W)SiO_{2eq\beta c}} \quad (6)$$

where W is the percent fly ash substitution by weight (expressed as a decimal), $CaO_{eq\alpha fa}$ and $SiO_{2_{eq\beta fa}}$ represent the combination of the