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Chemical Detection of Expansion Susceptibility of Concrete

by Ronald Lichtenwalner and Joseph T. Taylor

This experimental study evaluated the correlation between measured concrete expansion from a modified version of the miniature concrete prism test (MCPT) with the concentration of chemical markers leached from the prisms into an alkaline soak solution. Fifteen concrete mixture designs were tested for expansion and soak solution concentrations over time. The changes in expansion and soak solution concentrations were found to correlate well even with variations in alkali loading and substitution of cement with Class F fly ash. A model was developed to estimate the expansion potential of concrete based on an expansion reactivity index (ERI) that incorporated the concentrations of silicon, sulfate, calcium, and aluminum. The relationship between ERI and expansion was then used to identify potentially expansive concrete mixtures using the ERI of cores taken from a structure exhibiting potential alkali-silica reaction (ASR) expansion and concrete cylinders matching the mixture designs of the MCPT specimens.

Keywords: alkali-silica reaction; concrete expansion; delayed ettringite formation; miniature concrete prism test; Turner-Fairbank Alkali-Silica Reaction Aggregate Susceptibility Test (T-FAST).

INTRODUCTION

Deleterious concrete expansion is a significant source of premature deterioration of concrete infrastructure worldwide.[1] Expansion may be caused by a variety of factors, through physical mechanisms such as freezing-and-thawing, or through chemical mechanisms. Two notable chemical causes of expansion are alkali-silica reaction (ASR) and delayed ettringite formation (DEF).[1,2] ASR is a reaction between aggregates with reactive silica and alkali hydroxides that form a gel within concrete that swells in the presence of sufficient moisture, causing the concrete to expand.[1] For ASR to occur in concrete, three conditions must be met: sufficient moisture, an aggregate with a reactive form of silica, and sufficient alkali hydroxides to trigger the dissolution of the reactive silica from the aggregate.[1] The alkali hydroxide concentration within the concrete pore solution is largely determined by the alkali content of the cement. However, aggregates, supplementary cementitious materials (SCMs), and external alkalis from environmental sources can also contribute to the pore solution alkali concentration. DEF shares the requirement of sufficient moisture that ASR requires, but also requires sufficient sulfate (SO_4^{2-}) provided from external or internal sources.[2] The formation of delayed ettringite in localized voids and cracks can ultimately result in the expansion of the concrete.[2] Various mitigation strategies, primarily for the prevention of ASR, are employed throughout the industry, including substitution of cement with SCMs, inhibiting admixtures, restrictions on the alkali content of cement, restrictions on aggregate sources, and/or blending of aggregates.[1,3]

Current physical expansion testing and limitations

Most current laboratory tests for expansion focus on determining the ASR potential of a specific aggregate by measuring physical expansion and experience several limitations.[4] These tests of expansion include the miniature concrete prism test (MCPT, AASHTO T 380),[5] the accelerated mortar bar test (AMBT, ASTM C1260), and the concrete prism test (CPT, ASTM C1293).[6] The CPT is considered the most reliable of the expansion test methods; however, the test requires an extended time of at least a year to classify material as deleteriously reactive.[7] Additionally, CPT samples exhibit alkali leaching, which can yield results that diverge from concrete exposed to natural conditions.[8-10] The AMBT is the most accelerated of currently available tests, yielding results in 28 days, and has become the most widely used test method.[7] However, the AMBT suffers from poor accuracy, yielding both false negatives and false positives due to unrealistically aggressive conditions.[10,11] The MCPT lies between the two extremes of the CPT and AMBT tests. The MCPT is an accelerated version of the CPT that provides results within 84 days and has shown broad correlation with the CPT.[12,13] In one study, the MCPT was found to correlate better with exposure site block expansion compared to the CPT.[10] All of the expansion tests discussed thus far require significant preparation of the aggregates and are restricted to mixtures made using specific ingredients under highly controlled conditions not representative of the variety in field concrete mixture designs. To address these shortcomings, the accelerated concrete cylinder test (ACCT) has been developed.[14] The ACCT involves soaking a cylinder in alkaline solution at 60°C (140°F) within a volumetric change measuring device (VCMD) and recording length change measurements automatically. The ACCT has shown some promise in being used to test a wide array of mixtures that correlate well with the CPT.[14] However, the test is still new and there is little data on correlation with exposure site block expansion, which the CPT does not always agree with.[8-10]

Chemical testing of expansion susceptibility

Chemical tests for expansion of concrete are potentially capable of more explanatory power in revealing how and why concrete experiences expansion, however, chemical tests for expansion are much less common. One of these tests, ASTM C289, was withdrawn due to the method being

overly severe with poor reliability.[1] Recently, the Turner-Fairbank Alkali-Silica Reaction Aggregate Susceptibility Test (T-FAST, provisional standard AASHTO TP 144) has been developed. The T-FAST has provided rapid results in 21 days that have shown good correlation with standard expansion test methods, field cases, and long-term block farm expansion data.[15-17] The three elements used in T-FAST to assess expansion susceptibility are silicon (Si), calcium (Ca), and aluminum (Al). The Si measured is primarily present from the dissolution of silica from reactive aggregates. An increase in Al in the simulated pore solution corresponds with a mitigation of expansion potential and has shown mitigation in other studies.[18-20] The final component of the T-FAST results is the Ca concentration, which has generally exhibited more mixed data regarding its role in ASR expansion, but in the T-FAST model is shown to reduce the expansion potential.[3,15,16,21-24] Combined, these concentrations form a chemical reactivity index, shown in Eq. (1)

$$RI = \frac{[Si]}{[Al] + [Ca]} \tag{1}$$

where the concentrations are given in mol/m^3. The T-FAST test in the current state does share some of the drawbacks of expansion testing, such as requiring substantial preparation of coarse aggregates and testing only the isolated aggregate.

Ideal expansion test method

Each of the current standard test methods have some drawbacks and are unable to test concrete mixtures placed in the field or test complicated mixture designs representative of field concrete mixtures. Thomas et al.[7] proposed that the ideal test for expansion would be reliable, simple, rapid, and capable of assessing the susceptibility of an unmodified sample representing a concrete mixture proposed for a specific use. Such a test could be used for complex mixtures and potentially used to assess in-place structures for expansion potential.[7]

RESEARCH SIGNIFICANCE

Current expansion tests are not designed to predict the susceptibility and estimation of expansion in complex field concrete mixtures. This study describes a chemical model for concrete samples that can be used to determine the susceptibility of a concrete mixture to expansion using a modified MCPT. From the correlation of expansion and chemical reactivity markers in concrete soak solution, the potential expansion of laboratory-made concrete cylinders and field-obtained concrete cores are estimated. This correlation provides a potential approach to accurately and rapidly determine the expansion susceptibility of true job-specific concrete mixtures sampled from the field.

EXPERIMENTAL INVESTIGATION
Modified miniature concrete prism test

Concrete prisms were prepared with varying coarse aggregates, alkali loading, and replacement of cement with fly ash. A variety of aggregates were chosen to assess a broad spectrum of ASR reactivities. Several alkali loadings were used for two of the most reactive aggregates to determine if the expansion and chemical reactivity would correlate as the alkali content was adjusted. Concrete prisms of a specific mixture were placed in a polypropylene container with a soak solution that was adjusted with sodium hydroxide (NaOH) to match the estimated alkalinity of the concrete pore solution. The alkalinity of the soak solution in terms of NaOH concentration was estimated assuming all alkali from the cement was soluble using the weight and % Na$_2$O$_{Eq}$ of the cement in the mixture as demonstrated in Eq. (2)

$$[NaOH] = \frac{\frac{\% \ Na_2O_{Eq}}{100} \times W_{Cement} \times 32.2691}{V_{Water}} \tag{2}$$

where [NaOH] is the sodium hydroxide concentration in mol/m^3; %Na$_2$O$_{Eq}$ is the percent of sodium alkali equivalent of the cement; W_{Cement} is the weight of the cement in kg; 32.2691 is the conversion factor to convert from kg of Na$_2$O$_{Eq}$ to moles of NaOH; and V_{Water} is the volume of mixture water in m^3.

Concrete cylinders

To compare the feasibility of testing concrete cylinders with this method, concrete cylinders were cast for a subset of 10 out of the 15 MCPT mixtures and soaked in alkaline soak solutions calculated using Eq. (2).

Field concrete cores

To ascertain whether the test method in this study could potentially be used to assess in place structures, concrete cores from a North Carolina roadway exhibiting potential ASR were also soaked in alkaline solutions.

Materials

The chemical compositions of the cementitious materials used are listed in Table 1. Ten coarse aggregate sources were used, and the ASR reactivity of each source was estimated using a modified T-FAST with only conditions 2 and 4 performed. The reactivity classification of the aggregates and historical field record are summarized in Table 2. Moderately reactive aggregates are ordered based on the estimated reactivity from T-FAST testing, with the expected reactivity in decreasing order from MR-1 to MR-6. Graded Ottawa sand conforming to ASTM C778 was used as the fine aggregate in all the MCPT mixtures. A local fine aggregate was used in the concrete cylinder specimens and tested as nonreactive using a modified AASHTO TP 144 suitable for fine aggregates wherein the fine aggregate is dried, but no sieving is performed.[16]

Specimens

MCPT—Concrete prisms measuring 50 x 50 x 285 mm (2 x 2 x 11.25 in.) were cast and cured according to AASHTO T 380 specification with the following exceptions: prisms were made in duplicate instead of triplicate due to MCPT mold capacity and laboratory oven capacity; the alkali loading of the mixture water and the soak solution

Table 1—Composition of cementitious materials used in mixtures

Oxide, % wt	CEM-VHA	CEM-HA	CEM-LA	FA
SiO_2	20.62	19.99	20.28	44.60
Al_2O_3	3.76	4.85	4.91	21.90
CaO	62.09	63.58	63.96	4.21
Fe_2O_3	3.09	3.18	3.40	19.19
MgO	3.18	2.18	1.27	0.78
SO_3	3.42	2.63	2.80	1.44
LoI	2.20	2.60	2.78	2.16
Na_2O	0.31	0.14	0.12	1.53
K_2O	1.11	0.80	0.56	1.87
Na_2O_{Eq}	1.04	0.67	0.49	2.76

Note: LoI is loss on ignition.

Table 2—Aggregate reactivity classification

Aggregate ID	AASHTO TP 144 (T-FAST) ASR reactivity classification	Evidence of field ASR reactivity
HR-1	Highly reactive	Yes
HR-2	Highly reactive	No
MR-1	Moderately reactive	Yes
MR-2	Moderately reactive	No
MR-3	Moderately reactive	Yes
MR-4	Moderately reactive	No
MR-5	Moderately reactive	No
MR-6	Moderately reactive	No
NR-1	Nonreactive	No
NR-2	Nonreactive/slow reactive	No

Table 3—Concrete mixture designs used for MCPT and cylinder specimens

| Mixture design ID | Alkali loading, kg/m^3 | Cementitious materials | | Aggregate | | | |
		Cement used	Cement, kg/m^3	Class F fly ash, kg/m^3	Coarse, kg/m^3	Fine, kg/m^3	w/c
NR-1-1.55%	6.4	CEM-HA	415	0	804	982	0.48
NR-2-1.55%[*]	6.2	CEM-HA	402	0	778	951	0.49
HR-1-0.49%[†]	2.0	CEM-LA	410	0	794	970	0.47
HR-1-0.67%[†]	2.7	CEM-HA	405	0	784	958	0.50
HR-1-1.25%[†]	5.3	CEM-HA	427	0	1141	620	0.45
HR-2-0.67%	2.9	CEM-HA	431	0	1151	625	0.45
MR-1-1.55%[*]	6.5	CEM-HA	421	0	1125	611	0.45
MR-1-1.55%-FA[*]	6.5	CEM-HA	333	83	1114	605	0.45
MR-1-1.04%-A	4.4	CEM-VHA	421	0	1125	611	0.45
MR-1-1.04%-B[*]	4.4	CEM-HA	421	0	1125	611	0.45
MR-2-1.25%[†]	5.4	CEM-HA	429	0	1147	623	0.45
MR-3-1.55%[†]	6.6	CEM-HA	427	0	1141	620	0.45
MR-4-1.04%	4.4	CEM-VHA	426	0	1137	618	0.45
MR-5-1.55%[†]	6.6	CEM-HA	426	0	1139	619	0.45
MR-6-1.55%	6.5	CEM-HA	420	0	1121	609	0.45

[*]Matching cylinder made in duplicate.

[†]Matching cylinder made.

varied from the specified 1.25% Na_2O_{Eq} to determine the effectiveness of MCPT and the proposed test devised in this study at reflecting the variety of alkali levels seen in field concrete mixtures; the No. 78 aggregate was dried, but otherwise used as provided by the producer with no additional gradation or preparation to more realistically reflect concrete cast in the field; and the volume fraction for the coarse aggregate was 0.70 in most mixtures. The higher volume fraction of coarse aggregate matches the CPT test and was used to potentially induce more expansion from a larger reservoir of reactive silica being available. However, there is some evidence that the volume fraction of coarse aggregate has minimal influence on MCPT results, as Latifee[13] found "no clear relationship" between 0.65 and 0.70 volume fraction of coarse aggregate and the expansion of concrete prisms. The concrete mixture proportions as batched for the

MCPT and cylinder specimens are given in Table 3. The air content is not measured per AASHTO T 380, but was assumed to be 2.5% per the original MCPT research.[13] The mixture design ID schematic (XX-X-Y.YY%) indicates the aggregate identity (XX-X) and alkali in terms of Na_2O_{Eq} of cement (Y.YY%). The mixtures HR-0.49%, HR-0.67%, NR1-1.55%, and NR2-1.55% have designs notably different from the rest, as they were the first four mixtures batched as trials before a standardized mixture was decided upon. They were still included because the intent of this study was to correlate concrete expansion and the chemistry of the corresponding soak solution, rather than classify the reactivity of a standardized mixture. For MR-1-1.55%-FA, the estimated alkali content of the soak solution was made without considering the dilution effect and it was assumed to have the same alkali loading as the straight cement mixture. This was done

to isolate the mitigation effect due to the material properties of the fly ash from the dilutive effect of soluble alkalis that result from fly ash substitution.

Concrete cylinders—Cylinders measuring 76 x 152 mm (3 x 6 in.) were cast as noted in Table 3. Following the steps in ASTM C192, the cylinders were hand mixed and then rodding was used for consolidation; however, there was no preparation of the No. 78 sized aggregates beyond oven drying. The cylinders were demolded after 24 hours of curing at 21°C (70°F) and then placed into 100 x 200 mm (4 x 8 in.) concrete cylinder molds that had 800 mL of solution matching the estimated alkalinity of the cylinder pore solution from Eq. (2). One difference in the experimental setup for the cylinders from the MCPT is that a lower oven temperature of 55°C (131°F) was used, matching the temperature of the T-FAST. This change in temperature was done to assess whether the reactivity at similar ages would be significantly affected compared to the MCPT.

Concrete cores—Two 100 x 200 mm (4 x 8 in.) concrete cores from a North Carolina jointed plain concrete pavement constructed in 1984 that appeared to be exhibiting deleterious expansion were tested using a version of this test at 60°C (140°F). Companion cores to these were also sent out for petrography analysis and the results compared.

Items of investigation

Approximately every week, concrete prisms were measured for change in length expansion per AASHTO T 380. At the time of the expansion measurement, the temperature of each prism container's soak solution was also measured, and 20 mL of the soak solution was collected and filtered with a glass microfiber syringe filter. The filtered soak solution was then measured for Si, Ca, Al, sulfur (S), potassium (K), and sodium (Na) concentrations by wavelength-dispersive X-ray fluorescence (WDXRF). WDXRF is incapable of determining the exact form of elemental species, and in the case of sulfur, the sulfur was assumed to be present as SO_4^{2-}. To measure filtered solution concentrations by WDXRF, a nylon membrane was soaked in the solution for 1 minute, dried in an oven at 110°C (230°F), and then analyzed under vacuum on a 1.2kW WDXRF. The blank nylon membranes were also analyzed by WDXRF before being soaked to ensure there was no contamination present. Initial MCPT samples were tested for expansion and soak solution concentrations until 84 days. Later prisms were kept beyond 84 days to monitor the long-term expansion and corresponding concentrations of the soak solution. The concrete cylinder specimen and field-core soak solutions followed the same filtering and WDXRF procedure, except that analysis was only performed every 28 days.

ANALYTICAL INVESTIGATION
Development of a model correlating MCPT soak solution composition to expansion

The T-FAST reactivity index (RI) parameter was initially used to correlate the degree of reactivity of each concrete mixture with concrete specimen expansion. As more data from the study was collected, other parameters were trialed for inclusion in the equation to improve the correlation to the expansion measurements, as there exist other chemical mechanisms that also contribute to concrete expansion, such as DEF.[2,11,25] Therefore, dissolved sulfur, assumed to be present as SO_4^{2-}, was also added to the RI equation to determine if the correlation with expansion would improve. This new index, titled the expansion reactivity index (ERI), is given by Eq. (3)

$$ERI = \frac{[Si] + [SO_4^{2-}]}{[Al] + [Ca]} \qquad (3)$$

where the concentration is given in mol/m³ for each analyte. The ERI was then correlated with the expansion of the prisms produced from the concrete mixtures from 14 until 84 days. By the end of the testing period, an overall model was developed to estimate the level of concrete prism expansion based on the analyte concentrations leached into the soak solutions from the mixture. The developed ERI regression model was then used to determine a corresponding ERI threshold based on the generally agreed upon deleterious expansion threshold of 0.040%.[26]

Concrete cylinders

The ERI determined from soak solution concentrations was used to estimate the expansion for the concrete cylinders and results compared to the measured MCPT specimen expansion.

Field concrete cores

For the two cores received from the field and partitioned, one quarter was placed in a 1.25% Na₂OEq solution, one quarter was placed in a 0.80% Na₂OEq solution, and one was placed in distilled water only. Because the true mixture designs for these cores were unknown, the alkali solution concentrations using Eq. (2) were based on an estimated mixture that used 420 kg/m³ of cement with a 0.40 water-cement ratio (*w/c*). This could be considered typical of pavement mixtures approved for use in North Carolina. The ERI measured from the core soak solutions were used to estimate expansion and compared to petrography results.

EXPERIMENTAL RESULTS AND DISCUSSION
Expansion measurements

The results for the 56- and 84-day expansions or the closest day measured for each mixture design are shown in Fig. 1, including the range of the prism measurements of the two bars at 84 days. As expected, based on the behavior of the aggregates from their field history and testing with T-FAST, the expansion of most mixtures exceeded 0.040% by day 56. The mixtures that did not exceed 0.040% expansion were: the two mixtures containing assumed nonreactive aggregates (NR-1 and NR-2); the low alkali loading mixture of HR-1; the moderate alkali loading mixtures of HR-1 and HR-2; and the MR mixtures on the lower end of T-FAST reactivity, MR-5-1.55% and MR-6-1.55%. These results largely match the expected outcome, as HR-1-0.49% is considered a low-alkali mixture and included a lower coarse aggregate content than the other mixtures. HR-1-0.67% and HR-2-0.67% are mixtures with lower alkali loadings and
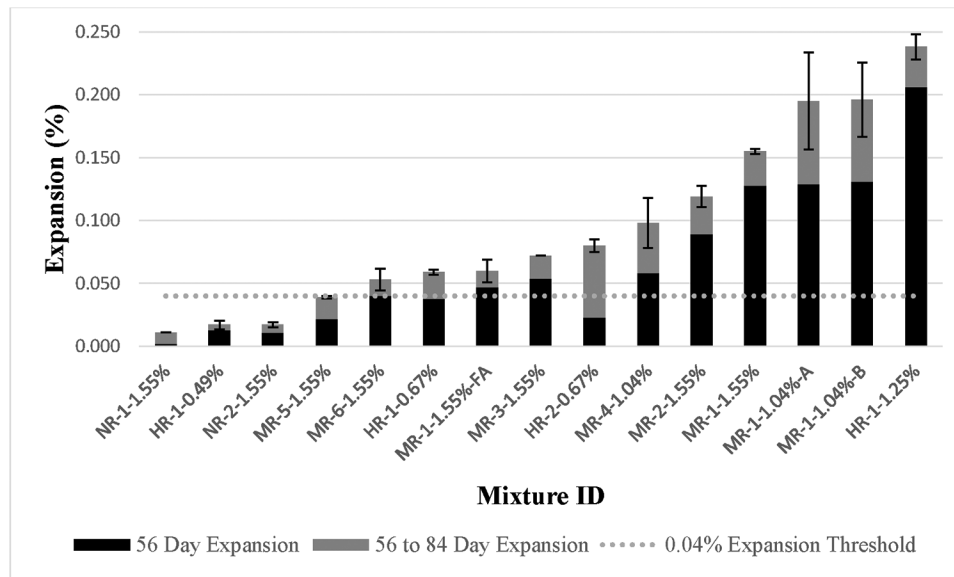
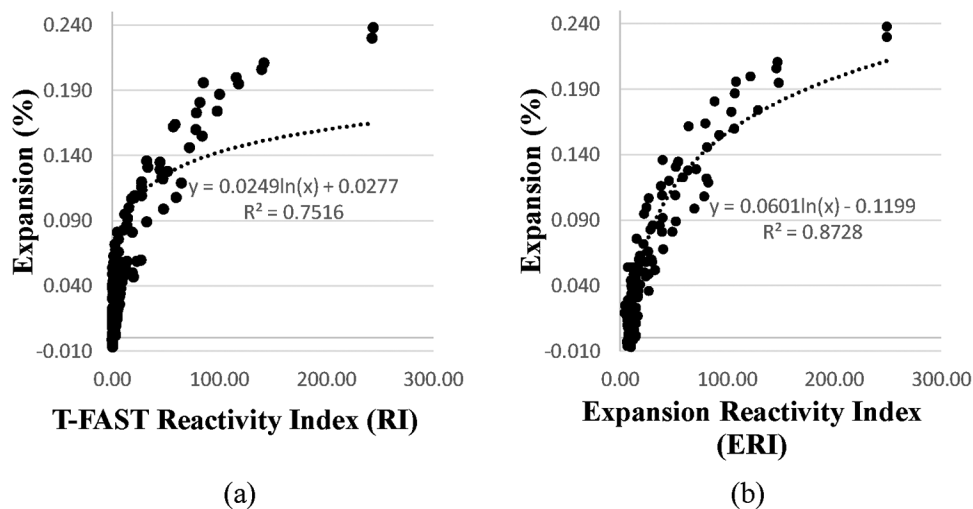Fig. 1—MCPT specimen expansion.

| (a) | (b) |

Fig. 2—Models of expansion: (a) T-FAST reactivity index equation; and (b) addition of sulfate to RI model equation.

would be expected to expand slower if deleterious expansion were to occur. Based on the T-FAST classification of the aggregates, MR-5-1.55% and MR-6-1.55% are the only mixtures that failed to reach the expected 0.04% threshold for deleterious expansion by 56 days. The trends from the 56-day readings were largely followed by the 84-day expansions and all mixtures surpassed 0.04% expansion, except for MR-5-1.55%, HR-1-0.49%, and the mixtures containing nonreactive aggregates (NR-1 and NR-2).

ERI results

Initially, the RI as used in T-FAST was used to correlate expansion to soak solution composition. As indicated by Fig. 2, when SO_4^{2-} was added to the equation as an indicator of deleterious expansion, the R^2 improved from 0.75 to 0.87. Subsequently, the ERI was then used to analyze and predict expansion susceptibility of samples. Figure 2(b) illustrates the overall strong relationship of expansion and the ERI across all days. The ERI from the prisms provides some illumination on the mechanism of the expansions measured.

On the extreme end, the lack of expansion of NR-1-1.55% and NR-2-1.55% can be attributed to the lack of available Si in solution for ASR gel to form. The initial classification of aggregates by the T-FAST indicated both aggregates had very little Si leaching into the alkaline solution that would be available to form ASR gel, which is reflected in the low ERI seen in this study. Similarly, the most reactive aggregates classified by the T-FAST (that is, HR-1, MR-1, and MR-2) show large expansions, owing to the abundant availability of Si to form ASR gel in highly alkaline solutions.

To test concrete mixtures obtained from the field, a determination of values of the ERI that correspond to deleterious expansion needs to be formulated. From the nonlinear relationship between ERI and expansion (Fig. 2), a logarithmic transformation of the ERI was performed, and a linear regression developed from this transformation. The results of the logarithmic transformation and subsequent linear regression performed on the data from Fig. 2(b) is shown in Fig. 3. The resulting linear regression equation is given by Eq. (4)
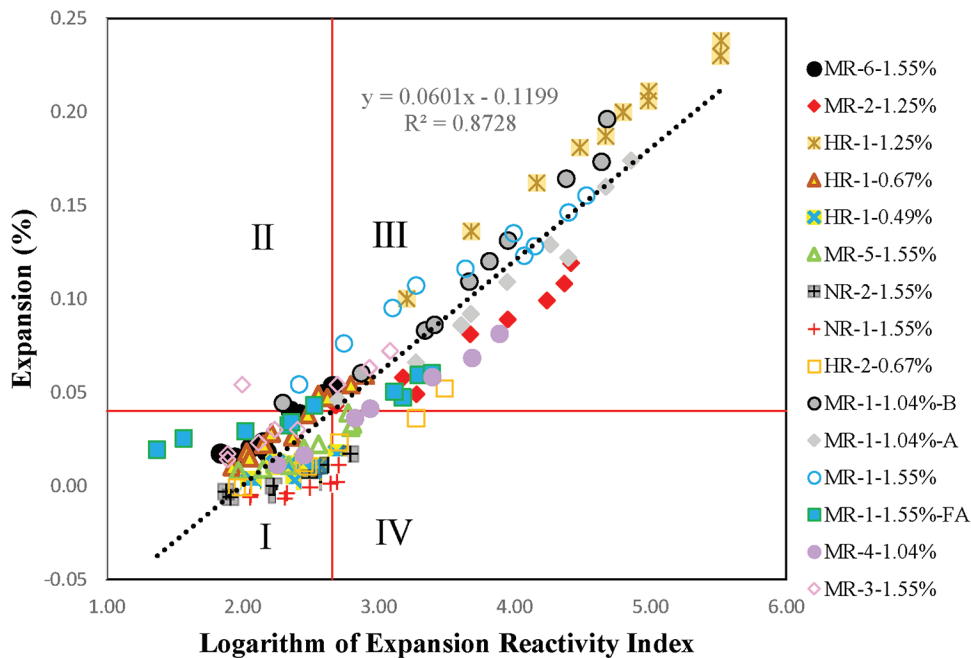
Fig. 3—Logarithmic transformation of MCPT results from 14 until 84 days.

$$Exp_{Pred} = 0.0601 \times \ln(ERI) - 0.1199 \qquad (4)$$

where Exp_{Pred} is the predicted percent expansion based on the natural logarithm of the ERI calculated from Eq. (3). Substituting 0.040% expansion into Eq. (4) results in a calculated ln(ERI) threshold level of 2.66. The horizontal and vertical lines in Fig. 3 indicate an ERI false negative or false positive when points lie in the second or fourth quadrant, respectively. There are a few false negative points in which the concrete had expanded beyond 0.040%, yet the ERI did not reach the equivalent threshold value. For the mixtures with large expansion at early measurement times, the probable cause is the lag between the concrete reaching chemical equilibrium with the soak solution. In these mixtures, the ASR gel formation is likely occurring rapidly within the concrete prisms and the concentrations, particularly Si, have not yet reached equilibrium with the soaking solution. This is particularly evident by the point in quadrant II of Fig. 3 for MR-1-1.55% and MR-1-1.04%-B, which occurred within the first 15 days of soaking.

Deviations in correlation for slowly and moderately reactive mixtures

Reaction equilibrium may also explain the deviation for MR-3-1.55% and MR-6-1.55%, as the ERI did not cross the threshold indicating deleterious expansion until later stages, well after expansion exceeded 0.040%. In these cases, a potential cause may be a masking of the Si dissolution in soak solution due to the presence of available Ca. As evidenced in Eq. (3), the ERI is highly dependent on the Si concentration. Prior to the exhaustion of Ca^{2+} in the solution, reactive silica that dissolves into solution from the aggregate is being readily consumed, forming calcium-silicate-hydrates and ASR products. Once the Ca^{2+} reserve has been exhausted, then the Si builds up in excess in the solution.[3,23,24] Figure 4 displays the relationship between the Si, Ca, and expansion from all the mixtures where Ca did not reach below 0.06 mol/m^3 until after 56 days in the soaking solution. As seen in Fig. 4, once the Ca content in solution is nearly exhausted, the Si content measured in solution increases rapidly. The overall rate of Si dissolution before this point may be greater than would be indicated by the Si detected in the soak solution due to the consumption of Si by available Ca in solution.[24] This suppression of excess Si in solution by Ca supports the lag seen between the ERI and expansion in the slow to moderate reactive mixtures. Once the Ca concentration in solution reaches low levels, approximately 0.06 mol/m^3, the apparent rate of Si dissolution increased and then remained largely constant after that time. For a specific example, MR-3-1.55% exceeded 0.040% expansion at 56 days, yet did not reach the ERI value corresponding to deleterious expansion until day 70 of testing, when the Ca concentration in solution reached below 0.06 mol/m^3. In another case, MR-6-1.55% solution tested beyond 84 days did not reach below 0.06 mol/m^3 of Ca until 109 days, at which point the ERI crossed the threshold indicating deleterious expansion as determined by Eq. (4).

Variation of ERI and expansion with changes in alkali loading for HR-1

The expansion and ERI results for the mixtures containing the reactive aggregate HR-1 with varied alkali loading were evaluated (Table 3). Figure 5 shows how the ERI and expansion varied under different alkali loadings, establishing that the ERI reflects the reduction in expansion measured under lower alkali loadings than typically used in standardized ASR expansion testing. The reduction in ERI at lower alkali loadings is primarily due to a large decrease in Si dissolution as the concentration of hydroxide in the soaking solution decreases.
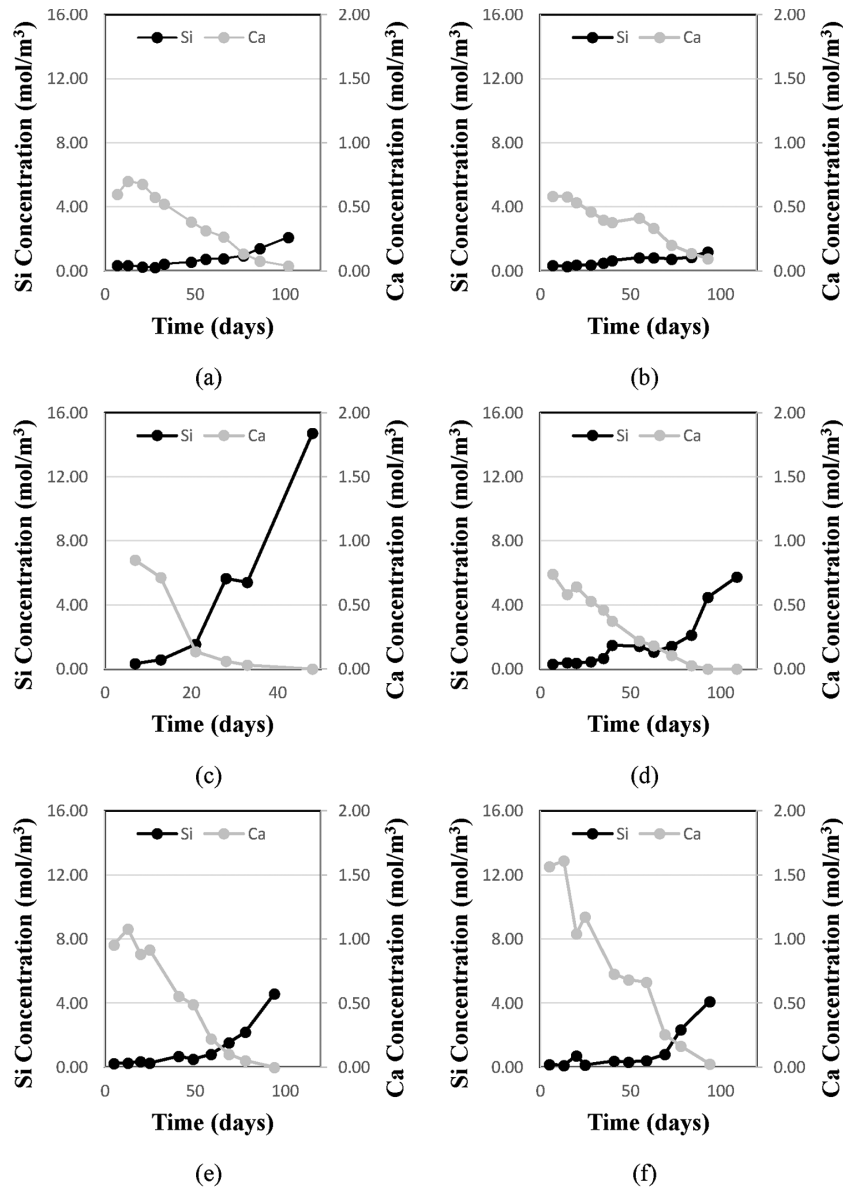
Fig. 4—Solution concentrations of calcium and silicon over time for: (a) MR-5-1.55%; (b) MR-6-1.55%; (c) MR-2-1.25%; (d) MR-3-1.55%; (e) MR-4-1.04%; and (f) HR-2-0.67%.

Variation of ERI and expansion with changes in alkali loading for MR-1

Three alkali loading variation mixtures were made for MR-1, two sets of prisms made with 1.04% Na_2O_{Eq} alkali content and one set of prisms at 1.55% Na_2O_{Eq}. The two sets of 1.04% Na_2O_{Eq} prisms differed in the source of cement, where MR-1.04%-A used a high-alkali cement that required no boosting of alkali content in the mixture water, while MR-1.04%-B used a 0.67% Na_2O_{Eq} cement and required NaOH to be added to the mixture water. This test was done to illuminate the assumption that the soak solution alkali content is more important than the small contribution the cement alkalis will provide. Latifee's[13] original research on the MCPT showed a 10% reduction in expansion when low-alkali cement boosted with NaOH in the mixture water was used versus a cement with $0.90 \pm 0.10\%$ Na_2O_{Eq} cement. However, this was done on only a single set of comparison specimens, and the standardized MCPT currently has no estimated precision.[5] The CPT, which is wholly reliant

on internal alkalis for expansion, has an estimated within-laboratory precision of 12% at expansion greater than 0.02% expansion; thus, it is possible that the MCPT variation seen with alkali boosting may be within the expected variation of the standardized test.[3,6]

The expansion and ERI data for the MR-1 alkali variation mixtures for up to 84 days of testing are displayed in Fig. 6. The two MR-1 mixtures containing 1.04% $Na2O_{Eq}$ displayed similar expansion, though slightly different ERI results, supporting the expectation that the alkali soak solution is likely the primary factor in expansion versus the internal alkalis. Interestingly, the ERI and the expansion both agree that this lower-alkali loading is more expansive than the MR-1-1.55% mixture. Thus, MR-1 may be an aggregate that displays a pessimum effect of higher reactivity at lower-alkali loadings that is seen in some reactive aggregates.[11] The increased ERI for MR-1-1.04% at 84 days is not due to an increase in the concentration of Si leaching into solution, which is nearly half the concentration leached from
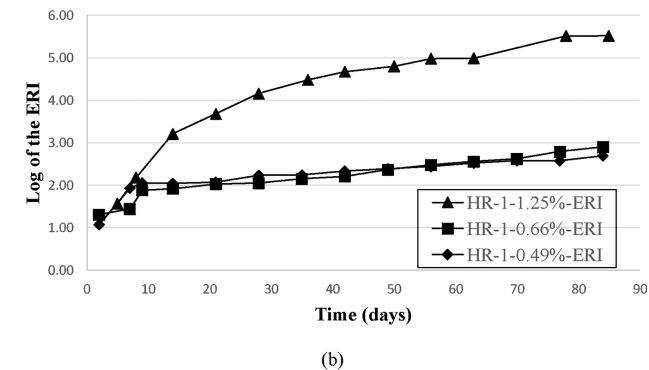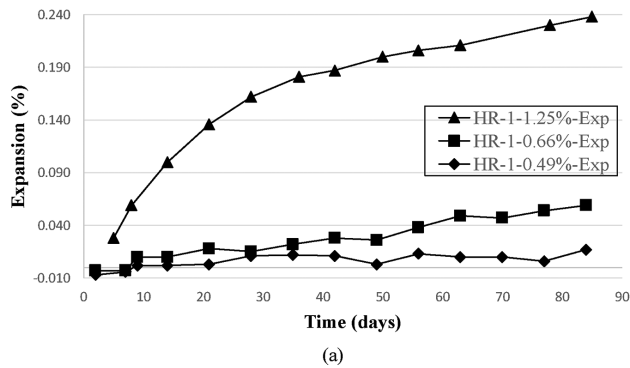
(a)

(b)

Fig. 5—Effect of alkali loading on HR-1 reactivity: (a) change in expansion; and (b) change in ln(ERI).

(a)

(b)
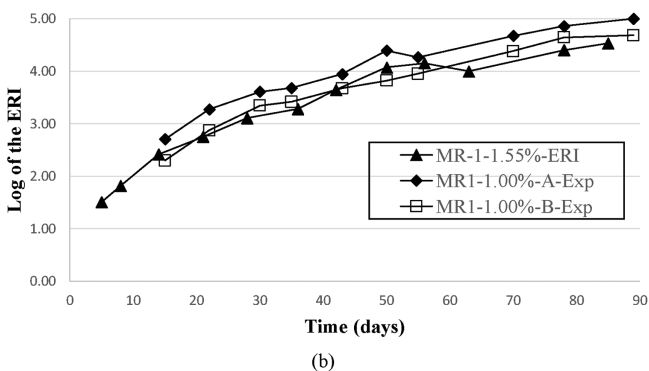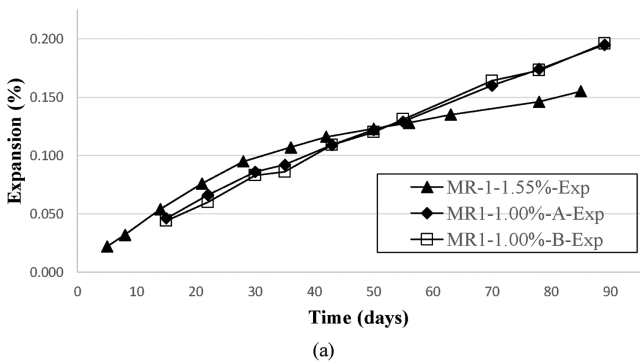
Fig. 6—Effect of alkali loading on MR-1 reactivity: (a) change in expansion; and (b) change in ln(ERI).

MR-1-1.55%. Rather, the increase is due to the decrease in the concentration of Al and an increase in the concentration of SO_4^{2-}. With the decrease in Al in solution, one effect that would be expected is less protection of Si dissolution; however, as measured here, the overall concentration of Si leached is less than the higher alkali mixture of MR-1. This
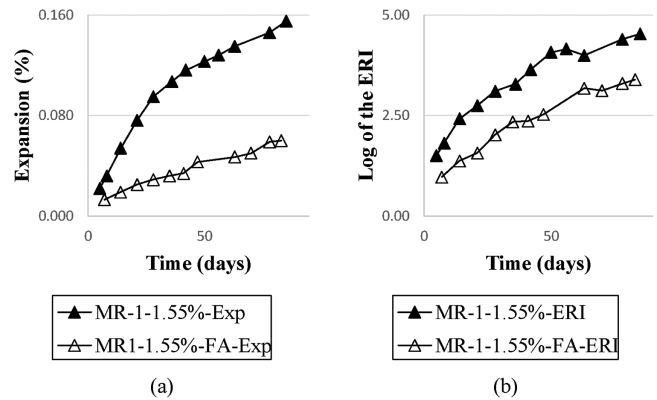

(a)

(b)

Fig. 7—Effect of 20% fly ash substitution on MR-1 reactivity: (a) change in expansion; and (b) change in ln(ERI).

Table 4—MR-1 reactivity results with mixture design variations at 84 days

Mixture design	Si, mol/ m³	Al, mol/ m³	SO_4^{2-}, mol/m³	ERI	Expansion, %
MR-1-1.04%-A	44.55	0.38	11.33	148.4	0.195
MR-1-1.04%-B	33.64	0.40	9.25	108.3	0.196
MR-1-1.55%	76.95	0.91	7.95	92.86	0.155
MR-1-1.55%-FA	40.79	1.53	1.54	27.0	0.060

implies there may be other factors causing optimum expansion, such as the ratio of alkali to Al in the pore solution.[18]

Mitigation of expansion and reduction in ERI with cement replacement by fly ash

Mixture MR1-1.55%-FA showed a marked drop in the expansion and the ERI compared to the straight cement mixture (Fig. 7). This indicates the solution chemistry and thus the ERI reflects some degree of expansion mitigation that occurs with the substitution of Class F fly ash. The expansion and ERI are still substantial, with an expansion greater than 0.040% at 56 days, indicating a likely lack of adequate substitution of Class F fly ash to completely mitigate the ASR reaction. Table 4 shows how the reduction in the ERI at day 84 compared to the straight cement mixture is a result of an increase in the Al and reduction of the Si and SO_4^{2-} concentrations. The decrease in Si available is likely due to the suppression of reactive silica by the additional Al in solution contributed by the fly ash.[18-20] Although the results show the mitigation of fly ash substitution in both the expansion and ERI, the ERI for MR-1-1.55%-FA is larger than would be expected based on Eq. (4). More research will need to be performed with mixtures containing fly ash to see if this is due to an interaction occurring in the mixture not modelled by the ERI, perhaps due to a pozzolanic reaction, or if it is indicative of latent expansion.

Comparison of concrete cylinders and MCPT ERI

Results comparing the ERI of the cylinders and MCPT specimens at equal ages of measurement are provided by Fig. 8. As the temperature and soak solution volume to concrete ratio differed between the two sets of specimens, the

comparison between cylinders and MCPT mixture reactivity merely provides a first step in the broader goal of classifying reactive concrete field mixtures. The expansion prediction equation from Eq. (4) was applied to the ERI of the cylinders to provide an estimate of the expansion. Note that MR-2-1.25%, MR-3-1.55%, and MR-5-1.55% were compared at 56 days and the remainder were at 84 days. This was due to scheduling conflicts where some measurements were missed for the cylinders.

The predicted cylinder expansion from Eq. (4) and the measured expansion in the MCPT mixture at the same ages are similar in most instances and duplicate cylinders agree well with each other. The largest deviation is by NR-2-1.55%, which indicates deleterious expansion from the cylinder ERI, but did not expand significantly in the MCPT test. NR-2 did exhibit borderline slow reactivity in the T-FAST test of the aggregate alone. HR-1-0.67% also shows some significant deviation, although both predicted and measured expansion indicate deleterious expansion. More testing is required to determine whether these discrepancies are due to test variations between cylinders and prisms, natural reactivity variation from the aggregate, or another factor.

Analysis of highway concrete cores suspected of ASR

Table 5 summarizes the soak solution measurements of field cores C-1 and C-5. The core portions soaked in 1.25% Na_2O_{Eq} solution were only tested until 32 days due to the early indication of a high degree of reactivity from the ERI. The estimated expansions given from the ERI and Eq. (4) for the core pieces soaked in alkaline solutions are well above 0.040% and would indicate the mixtures are susceptible to expansion with as little as 0.80% Na_2O_{Eq} and have similar reactivity to each other. The availability of reactive silica to dissolve from the aggregate even after decades in the field supports the possibility of identifying potentially expansive mixtures in field concrete. To support the findings from the soak solution testing, two cores taken near C-1 and C-5 were sent to an independent petrographer for assessment of ASR and general composition of the cores by ASTM C856. These cores submitted for petrography are referred to as C-1S and C-5S. Petrography noted the two cores had the same coarse and fine aggregate, were well graded, and had similar estimated w/c. Both cores exhibited microcracking, though C-5S was more extensive, extending to a depth of 61 mm, compared to 15 mm in core C-1S. Evidence of moderate ASR was observed in C-5S, including secondary deposits of ASR gel in reaction rims, subvertical microcracks, and air voids at various depths. In contrast, little evidence of ASR or deterioration was noted for core C-1S and only secondary deposits of ettringite were observed lining air voids and filling smaller air voids. The overall similarity in composition of cores C-1S and C-5S and the similarity in residual expansion of cores C-1 and C-5 determined by this study would suggest the most likely difference in the visible ASR in the cores is due to the environmental conditions at C-5S. The chemical identification of expansive potential corroborated by the petrography report shows promise for this method to be used on cores to identify the expansion potential of existing structures.
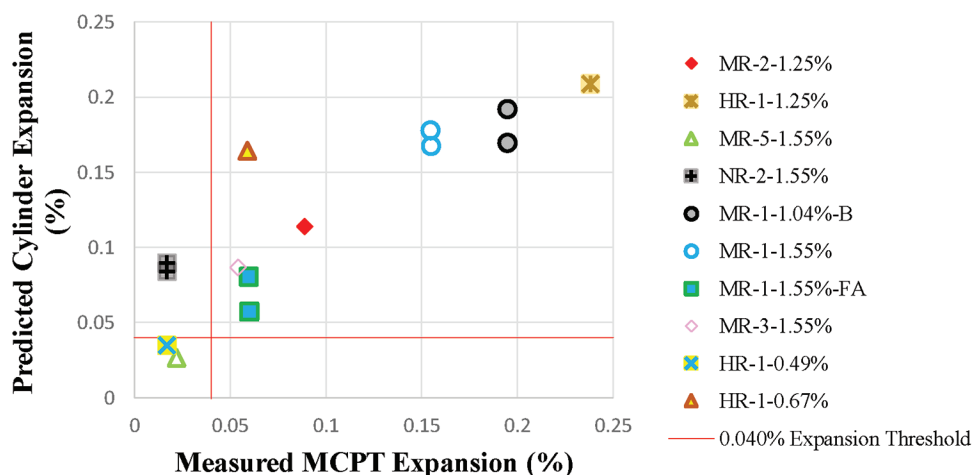

Fig. 8—Correlation of predicted cylinder mixture expansion with measured MCPT expansion.

Table 5—Field concrete core reactivity results

Core sample	Na_2O_{Eq} solution, %	Time, days	Si, mol/m³	Al, mol/m³	SO_4^{2-}, mol/m³	Ca, mol/m³	ln(ERI)	Estimated expansion, %
C-1	0	56	4.00	0.12	1.03	1.38	1.21	−0.047
C-1	0.80	61	31.55	0.58	7.43	0.00	4.21	0.133
C-1	1.25	32	14.00	0.89	5.75	0.00	3.10	0.066
C-5	0	56	1.85	0.11	1.36	1.00	1.06	−0.056
C-5	0.80	61	16.19	0.91	10.61	0.00	3.38	0.083
C-5	1.25	32	15.39	0.84	10.01	0.00	3.41	0.085

FURTHER RESEARCH

While these initial results are promising, more extensive testing will need to be performed to refine and validate the model relating ERI to expansion. Potential areas of further research include:

1. Optimizing testing conditions to provide a test that is as accelerated as possible while maintaining strong correlation with expansion.

2. Further validate the model linking ERI to expansion by matching mixture designs from long-term exposure site blocks and comparing the ERI of the replicated mixtures to the block expansion.

3. Testing of concrete specimens of varying sizes and mixture designs, including mixtures reflective of field concrete that contain concrete admixtures.

4. Verify that the reduction of ERI reflects the reduced expansion when other common ASR-mitigating materials are used, such as ground-granulated blast-furnace slag, Class C fly ash, silica fume, and lithium admixtures.

5. Testing of additional structures affected by expansion as well as control cores from structures unlikely to be experiencing expansion could be compared. Cores could be pinned, and residual expansion measured to further validate the ERI prediction model for existing structures.

CONCLUSIONS

The chemical model for expansion susceptibility developed in this study provides a potential pathway for the identification of expansive concrete mixtures and insights into the underlying mechanism of the expansion. The specific findings of this study that support this are:

1. Test results from this study showed a strong correlation between miniature concrete prism test (MCPT) expansion and the concentrations of Si, SO_4^{2-}, Al, and Ca leached into the MCPT alkaline soak solution. Concrete specimens that displayed deleterious expansion had elevated levels of Si and SO_4^{2-}, indicating the possible detection of the chemical triggers of alkali-silica reaction (ASR) and delayed ettringite formation (DEF) expansion. The increase in Al and Ca dissolved into solution from the concrete indicated lower expansion. In the case of Al, the likely cause is due to the reduction of reactive silica dissolution from aggregates.

2. The expansion reactivity index (ERI) correlated with expansion when the alkalinity of the mixture and soaking solution varied. For MR-1, a lower-alkali concentration resulted in an average 26% increase in expansion for two sets of MCPT specimens with an average increase of 38% ERI. For HR-1, the reduction of mixture alkalinity from 1.25% Na_2O_{Eq} to 0.67% Na_2O_{Eq} resulted in a 75% reduction in expansion and 93% reduction of the ERI. For the same highly reactive aggregate, the reduction of mixture alkalinity from 1.25% Na_2O_{Eq} to 0.49% Na_2O_{Eq} resulted in a 93% reduction in MCPT expansion and a 94% reduction in the ERI at 84 days.

3. The ERI indicated sensitivity to substitution with Class F fly ash. The partial substitution of cement with fly ash in a mixture with a moderately reactive aggregate showed a decrease in expansion of 61% at 84 days with a decrease of 71% in the ERI at the same alkali loading.

4. Nine out of 10 concrete cylinders matching MCPT mixtures were classified with the same broad reactivity when measured solely by ERI compared to MCPT expansion of the same mixtures.

5. The measured ERI of concrete cores from an ASR-affected structure were indicative of expansion susceptibility based on the model developed in this study. Petrographic analysis of cores from the same structure identified ASR as present in the concrete, agreeing with the assessment of the ERI model of an ASR susceptible mixture.

These findings relating the chemical ERI model to measured expansion provide the potential for a test method that would be accurate, fast, require minimal sample preparation, test job-specific concrete mixtures, and illuminate the underlying cause of expansion.

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