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Assessment of binary and ternary blends of metakaolin and Class C fly ash for alkali-silica reaction mitigation in concrete

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ABSTRACT

The potential for binary and ternary blends of metakaolin, with two differing particle size distributions, and Class C fly ash to mitigate alkali-silica reactions (ASR) with a highly reactive fine aggregate were evaluated using accelerated mortar bar test (AMBT) and concrete prism test (CPT) methods. Binary blends of metakaolin or Class C fly ash reduced expansion by 55–90% and 25–37% compared to the control, respectively. When incorporating metakaolin with a lower mean particle size, binary blends showed a greater reduction in expansion compared with Class C fly ash. Ternary blends of metakaolin and Class C fly ash resulted in a marginally higher expansion than binary blends incorporating the same amount of metakaolin. Correlation between AMBT and CPT results was good at high levels of expansion but poor for those compositions producing expansions near the acceptable limits corresponding to increased addition rates of metakaolin and/or Class C fly ash.

1. Introduction

Deterioration of concrete structures by the alkali-silica reaction (ASR) has become a concern in modern construction with the increasing use of marginal aggregates, high alkali cements and supplementary cementitious materials (SCMs), higher cement contents in concrete, and exposure to external alkalis supplied by deicing chemicals [1,2]. While ongoing research continues to better understand the underlying mechanisms and nature of the reaction products formed by ASR, it is generally accepted that reactions between alkali anions (K^+, Na^+) and hydroxyl groups (OH^-) present in the pore solution and poorly crystallized siliceous minerals found in some aggregates results in the formation of an ASR gel product [1,3,4]. In the presence of sufficient moisture, swelling of this gel results in expansion and cracking of the affected concrete element [1].

The use of SCMs, such as fly ash, slag, silica fume, and metakaolin has shown marked suppression of ASR-induced expansion in accelerated mortar bar (AMBT, as in ASTM C 1260 and C 1567), concrete prism (CPT, as in ASTM C 1293), and field exposure tests [3,5]. The four possible mechanisms by which ASR is controlled when utilizing SCMs as replacement for cement are:

(1) Formation of supplementary calcium silicate hydrates [6,7] and in the case of metakaolin, calcium aluminate and calcium aluminosilicate hydrates through reaction with the $Ca(OH)_2$ (CH) produced during Portland cement hydration [6,8,9]. This results in lower permeability, thus limiting the ingress of external alkalis and moisture by densification of the paste fraction and interfacial transition zone [1,2,8,9].
(2) Formation of supplementary hydrates provides additional adsorption sites for the binding of alkalis, contributed by the materials used to produce the concrete or that may ingress from the environment, thus limiting ASR gel production [8,10,11].
(3) Replacement of cement with SCMs that have lower alkali contents results in a "dilution" effect — reducing the alkali loading (kg/m^3) in the concrete [3,4].
(4) Excess Ca^{2+} contributed by CH present in the pore solution may replace Na^+ and K^+ bound in the alkali-silica gel, initiating a complex interaction between "mature" and "immature" gel (i.e., gel which has or has not reacted with Ca^{2+}) which results in microstructural damage [12,13]. The consumption of CH by pozzolanic reactions may limit ASR damage by reducing the amount of free calcium present in the pore solution and thus limiting gel swelling.

Earlier research performed on binary blends of SCMs with cement has shown low-calcium, ASTM C 618 Class F (CSA A23.5 Type F) fly ash, metakaolin, and silica fume to be most effective at mitigating ASR [14]. High-calcium ASTM C 618 Class C (CSA A23.5 Type CH) fly ash and slag have shown decreased ability to mitigate ASR, requiring higher levels, upwards of 40% to 50% cement replacement for moderate to highly ASR reactive aggregates [3,14,15]. Considering

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the overall desired properties of a concrete mixture, the use of two types of SCMs as a ternary blend has the potential to synergistically optimize the contributions of each, considering factors such as early and late-age strength, workability, durability (ASR in the case of the present study), and economy [2,16].

Here, the use of two metakaolins (with differing particle size distributions) and Class C fly ash, to mitigate expansion caused by ASR, was examined in binary and ternary blends. Expansion measurements using AMBT and CPT methods were performed using a highly reactive natural aggregate source. The principal objectives of this study were: (1) to investigate the effectiveness of metakaolin and Class C fly ash binary and ternary blends in suppressing ASR-induced expansion, (2) to study the effect of metakaolin surface area and particle size distribution on the mechanisms of ASR mitigation, and (3) to examine the applicability of both the AMBT and CPT methods in evaluating ASR susceptibility in concrete incorporating SCMs as a replacement for cement.

2. Experiment

Binary blends of metakaolin and Class C fly ash and ternary blends of metakaolin with Class C fly ash were evaluated using standard expansion test methods. Two types of high purity metakaolin were used for mortar and concrete mixes: MK_a (Kaorock) and MK_b (Kaorock F) with surface areas of 11.2 and 25.4 m^2/g, respectively. Class C fly ash was chosen primarily for its relatively higher early strength contributions compared to Class F fly ash, increased workability, and its lower cost when compared to other SCMs, such as slag [17]. Metakaolin was chosen for its high pozzolanic reactivity and high alumina content, which reduces expansion from ASR through microstructural densification, binding of alkalis, and consumption of CH while also contributing to early age strength [1,10].

Twelve mortar mixes, consisting of a control, binary blends of 8% and 15% metakaolin, and 25% Class C fly ash, and ternary blends of 3%, 5%, and 8% metakaolin with 25% Class C fly ash, were prepared and evaluated using the AMBT method. Eight concrete mixes, consisting of a control, binary blends of 8% and 15% metakaolin, and 25% Class C fly ash, and ternary blends of 8% metakaolin with 25% Class C fly ash were evaluated using the CPT method. Following the 2-year duration CPT, samples were sectioned and examined by scanning electron microscopy and thermogravimetric analysis.

2.1. Materials

Commercially available ASTM C 150 Type I/II cement [18] (Holcim Inc.) was used for all mortar and concrete specimens. MK_a and MK_b used in mortar and concrete mixes had approximately the same composition and were provided by Thiele Kaolin Company of Sandersville, GA. MK_a was produced from Cretaceous kaolin, while MK_b was produced from Tertiary kaolin. Both metakaolins were processed using the same procedure: vertical hearth fluid bed calciners, into which the clay was fed at the top and the product collected from the bottom. The metakaolins were not ground further after processing and maintained their natural particle sizes. Surface areas of MK_a and MK_b were measured by a sedimentation process commonly used to measure the surface area of clays. Fig. 1 shows the particle size distributions for MK_a, MK_b, and Class C fly ash determined by laser particle size analysis, using slurries of the SCMs suspended in ethanol. While the mean particle size of MK_b was found to be larger than MK_a, the higher proportion of particles below 1 μm present in MK_b contributes to its higher surface area. The fly ash used met the requirements of ASTM C 618 Class C [19] (Holcim Inc.). Oxide analyses for the Type I/II cement (including Bogue potential compositions), MK_a and MK_b, and Class C fly ash used for mortar and concrete mixes are shown in Table 1.

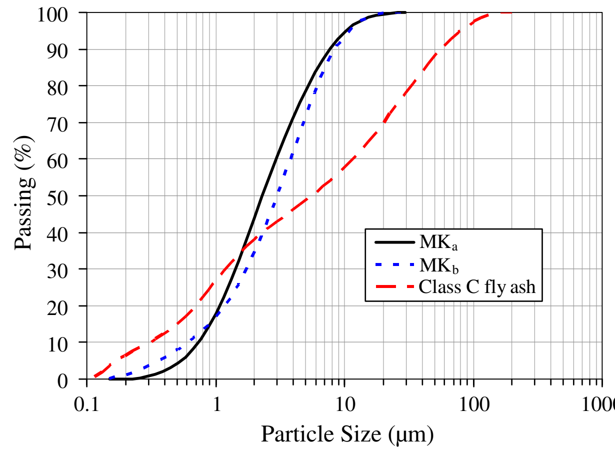

Fig. 1. Particle size distribution for metakaolins MK_a and MK_b.

Mortar and concrete mixes were made with a highly ASR reactive quartz/chert/feldspar sand from Texas. The sand was sieved and graded to produce a fineness modulus of 3.05 for mortar and 2.70 for concrete testing. Coarse aggregates used for concrete mixes were a historically non-ASR reactive crushed granitic gneiss graded according to the provisions of ASTM C 1293 [20]. Potable tap water was used for the preparation of mortar and concrete specimens. Detailed mixture proportions for mortar and concrete specimens used in the present study are provided in Tables 2 and 3, respectively. For sample identification, the first letter describes if the mixtures is a mortar (M) or a concrete (C), followed by the % cement replacement of MK_a, MK_b, and/or Class C fly ash (herein referred to as FA). For example, a ternary blended mortar of 5% MK_a with 25% Class C fly ash would read M/MK_a5/FA25.

2.2. Sample preparation

Mortars were prepared with a planetary mixer per ASTM C 305 [21], with mixing carried out for ~5 min after addition of water. Concretes were mixed with a 71 L capacity counter current batch mixer in accordance with ASTM C 192 [22]. First, aggregates were added to the mixer, followed by addition of cement and SCMs and then water. Workability was low in binary blends of 15% MK_b. A superplasticizer conforming to ASTM C 494 Type F designation [23] was used for mortars, as needed. Since these were mortar samples

Table 1
Composition of Type I/II cement, MK, and FA.

Characteristic	Composition (%)			
	Type I/II cement	MK_a	MK_b	FA
SiO_2	20.66	51.37	52.10	36.89
Al_2O_3	5.22	44.60	44.03	18.11
Fe_2O_3	3.64	0.46	0.92	6.08
CaO	62.80	0.23	0.47	24.82
MgO	1.56	0.03	0.13	5.85
Na_2O	0.13	0.39	0.02	1.88
K_2O	0.45	0.07	0.14	0.51
TiO_2	0.26	1.99	1.42	1.35
MnO_2	0.02	0.01	0.01	0.05
P_2O_5	0.25	0.19	0.17	1.24
SrO	0.08	0.01	0.01	0.38
BaO	0.04	0.01	0.02	0.71
SO_3	2.88	0.014	0.00	1.69
LOI	2.01	0.51	0.56	0.10
Moisture	N/A	0.19	0.34	0.43
C_3S	50.12	–	–	–
C_2S	21.43	–	–	–
C_3A	7.66	–	–	–
C_4AF	11.09	–	–	–

Table 2
Mixture proportions with $^{w}/_{cm}=0.47$ for AMBT.

Mix	MK type	MK (%)	FA (%)	Cement (kg/m^3)	Water (kg/m^3)	Fine aggr. (kg/m^3)	MK (kg/m^3)	FA (kg/m^3)
M	–	0	0	902.1	↑	↑	0	0
M/MK$_a$8	MK$_a$	8	0	829.9			72.7	0
M/MK$_a$15	MK$_a$	15	0	766.8			135.3	0
M/MK$_b$8	MK$_b$	8	0	829.9			72.7	0
M/MK$_b$15	MK$_b$	15	0	766.8	423.8	2030.8	135.3	0
M/FA25	–	0	25	676.9			0	225.2
M/MK$_a$3/FA25	MK$_a$	3	25	650.3			26.6	225.2
M/MK$_a$5/FA25	MK$_a$	5	25	632.2			44.8	225.2
M/MK$_a$8/FA25	MK$_a$	8	25	604.2	↓	↓	72.7	225.2
M/MK$_b$3/FA25	MK$_b$	3	25	650.3			26.6	225.2
M/MK$_b$5/FA25	MK$_b$	5	25	632.2			44.8	225.2
M/MK$_b$8/FA25	MK$_b$	8	25	604.2			72.7	225.2

produced in limited quantities (according to the ASTM C 1260 specifications), slump measurements were not possible. No superplasticizer was used in concrete specimens. Mortar and concrete specimens were cured for 24 h in a 23 °C fog room before demolding and prior to making the initial expansion measurements.

2.3. Accelerated mortar bar test (AMBT)

Expansion measurements were performed on mixes listed in Table 2 according to the accelerated mortar bar test (AMBT) ASTM C 1260 [24] procedure, which follows the same procedures as the more recent standard for mortars containing SCMs, ASTM C 1567 [25]. Four 25×25×286 mm mortar bars of each mortar mix were cast with embedded stainless steel gage studs used for expansion measurements. After the initial curing period following mixing, specimens were demolded and stored in water at 80 °C for 24 h. The specimens were then immersed in a 1 N NaOH solution at 80 °C to accelerate ASR and expansion. Expansion measurements were made using a length comparator accurate to 1 µm at approximately two day intervals up to 28 days, which is twice as long as the standard AMBT duration. According to the AMBT test, expansion measured at 14 days of 0.2% or greater indicates an aggregate that is prone to ASR, while expansion less than 0.1% at 14 days indicates an aggregate that is relatively innocuous (i.e., nonreactive). Intermediate 14-day expansions of 0.1% to 0.2% indicate an aggregate that may be prone to ASR damage but requires further study by the CPT [24,25].

2.4. Concrete prism test (CPT)

The concrete prism test (CPT) method ASTM C 1293 [20] was used to measure expansion in concretes listed in Table 3. Concrete mixtures were selected for the long-term concrete prism test based on AMBT results; generally selecting mortars which showed either acceptable or marginally acceptable 14 day expansion (i.e., less than 0.2%) during the AMBT. In conformance with the guidelines of ASTM C 1293, NaOH was added to mix water to increase the Na_2O_{eq} ($Na_2O_{eq}=Na_2O+0.658{\cdot}K_2O$) to 1.25% by mass of cement. It is noted that the Na_2O_{eq} for the cement itself is required to be greater than 0.90% according to ASTM C 1293. This is higher than that of the cement used in this study (0.43%, see Table 1), as the same Type I/II cement has been used in a broader study on binary and ternary blends [26,27].

Three 75×75×286 mm concrete prisms of each concrete mix design were cast with embedded stainless steel gage studs used for expansion measurements. Following curing, samples were demolded, initial readings taken, and stored in a 38 °C and 100% relative humidity environment. Expansion measurements were made using a length comparator accurate to 1 µm at 1, 7, 28 days and subsequently at 3, 6, 9, 12, 18, and 24 months of age. Prior to each expansion measurement, specimens were conditioned for 16 h in a fog room maintained at 23 °C. When expansion of concrete prisms with addition of SCMs exceeds 0.04% at 2 years, ASTM C 1293 classifies the aggregate as potentially deleteriously reactive [20].

2.5. Microscopy

Following the 2-year CPT expansion measurement, concrete prisms were sectioned using a water cooled diamond saw to obtain samples for examination by scanning electron microscopy (SEM) using backscattered imaging. Concrete sections were further reduced in size using a low-speed saw with ethanol lubricant to produce approximately 1×1×0.5 cm specimens. Specimens were impregnated with low-viscosity epoxy using multiple vacuum/atmospheric pressure cycles followed by curing in a 55 °C oven. Epoxy-impregnated specimens were then polished, sputter-coated with gold, and examined using a LEO 1530 thermally-assisted field emission scanning electron microscope (FE-SEM) equipped with a backscattered electron and energy dispersive X-ray spectroscopy detector.

2.6. Thermogravimetric analysis

At the end of the 2-year CPT expansion measurement, 1×1×1 cm specimens were sectioned from the center of concrete prisms using a water-cooled diamond saw to obtain samples for thermogravimetric analysis (TGA). After sectioning, specimens were crushed into powder

Table 3
Mixture proportions with $^{w}/_{cm}=0.45$ for CPT.

Mix	MK type	MK (%)	FA (%)	Cement (kg/m^3)	Water (kg/m^3)	Fine aggr. (kg/m^3)	Coarse aggr. (kg/m^3)	MK (kg/m^3)	FA (kg/m^3)	NaOH (kg/m^3)
C	–	0	0	427.2	↑	670.4	↑	0.0	0.0	1.9
C/MK$_a$8	MK$_a$	8	0	393.0		661.5		34.2	0.0	1.8
C/MK$_a$15	MK$_a$	15	0	363.1		653.8		64.1	0.0	1.6
C/MK$_b$8	MK$_b$	8	0	393.0	192.2	661.5	1121.3	34.2	0.0	1.8
C/MK$_b$15	MK$_b$	15	0	363.1		653.8		64.1	0.0	1.6
C/FA25	–	0	25	320.4	↓	653.2	↓	0.0	106.8	1.4
C/MK$_a$8/FA25	MK$_a$	8	25	286.2		644.9		34.2	106.8	1.3
C/MK$_b$8/FA25	MK$_b$	8	25	286.2		644.9		34.2	106.8	1.3

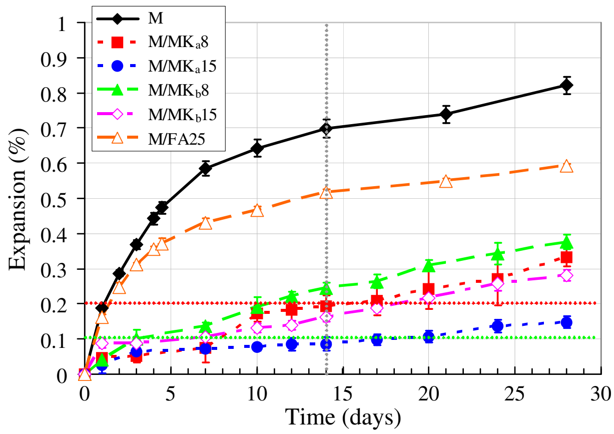

Fig. 2. AMBT expansion for binary blends and the control.

Table 4
14 and 28-day AMBT expansion results.

Mix	AMBT expansion (%)	
	14-day	28-day
M	0.699	0.821
M/MK$_a$8	0.242	0.333
M/MK$_a$15	0.107	0.148
M/MK$_b$8	0.310	0.376
M/MK$_b$15	0.215	0.281
M/FA25	0.519	0.592
M/MK$_a$3/FA25	0.336	0.485
M/MK$_a$5/FA25	0.331	0.452
M/MK$_a$8/FA25	0.129	0.229
M/MK$_b$3/FA25	0.201	0.368
M/MK$_b$5/FA25	0.158	0.278
M/MK$_b$8/FA25	0.149	0.251

and vibrated through a No. 200 sieve (75 μm opening) to remove aggregates. TGA was performed in a dry nitrogen environment from 25 °C to 600 °C with a heating rate of 10 °C per minute on approximately 15 mg samples using a Seiko TG/DTA system. CH content was determined using the percentage decrease in sample mass between 410 °C and 440 °C.

3. Results

3.1. Accelerated mortar bar test (AMBT)

AMBT expansion results for the control, binary blends, and ternary blends are shown in Figs. 2 and 3. 14 and 28 day AMBT expansion results have also been recorded in Table 4. The vertical dashed line indicates the standard 14 day AMBT testing duration. AMBT expansion of the ordinary Portland cement control mortar M was 0.70% at 14 days, supporting the historically high reactivity of this aggregate.

The use of metakaolin in binary blends at 8% and 15% replacement for cement was effective in reducing expansion by 55–85% compared to the control, with MK$_a$ providing a greater reduction in expansion than MK$_b$ in all metakaolin binary blends. Only M/MK$_a$15 yielded an expansion of less than 0.1% after 14 days of exposure. The use of 8% MK$_a$ and MK$_b$ as a binary blend was found to be ineffective at limiting expansion according to the AMBT, with expansion either near or greater than 0.2% at 14 days. M/FA25 had a 14 day expansion of 0.52%, with 0.25% occurring within the first two days of exposure. Further, expansion for all binary blends continued to increase beyond the 14 day measurement to the end of the 28 day test duration, indicating that the reaction continued to proceed with this highly reactive aggregate.

AMBT expansion results for ternary blends (Fig. 3) show that none of the compositions tested produced 14-day expansions less than 0.1%. However, the addition of metakaolin in ternary blends did yield a significant reduction in expansion compared to M/FA25. Ternary blended mortars showed moderate mitigation, with expansion between 0.1% and 0.2% at 14 days or a 71% to 82% reduction compared to control mortar M. Expansion of M/MK$_a$3/FA25 and M/MK$_a$5/FA25 were both approximately 0.33% at 14 days. Furthermore, approximately 50% of the 14 day expansion in M/MK$_a$3/FA25 and M/MK$_a$5/FA25 occurred during the first two days of exposure (similar to mortar M/FA25). Following the 2-day measurement, expansion trends for M/MK$_a$3/FA25 and M/MK$_a$5/FA25 followed those for the other ternary blends. It is also important to note that ternary blends with comparative compositions (e.g., 8% MK$_a$ vs. 8% MK$_b$ with 25% FA) were shown to provide moderate reductions in AMBT expansion when compared to equivalent binary blends. Similar to the metakaolin binary blends (Fig. 1), AMBT expansion for ternary blends continued beyond the 14-day measurement through the 28-day test duration. Unlike the AMBT results for binary blends, the MK$_b$ performed marginally better than MK$_a$ when used as a ternary blend with 25% FA.

3.2. Concrete prism test (CPT)

Expansion results determined using the CPT method for the control, binary blends, and ternary blends are shown in Figs. 4 and 5. One and 2 year CPT expansion results have also been recorded in Table 5. CPT expansion of the ordinary Portland cement concrete control C was 0.43% at 1 year and 0.46% at 2 years, approximately 11 times the acceptable expansion of 0.04%. The use of 25% FA (C/FA25)

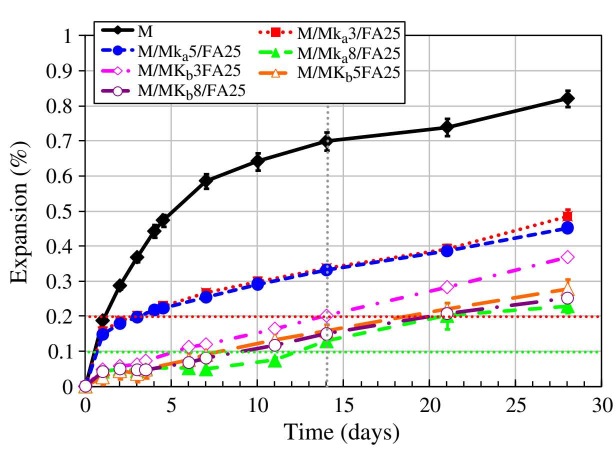

Fig. 3. AMBT expansion for ternary blends and the control.

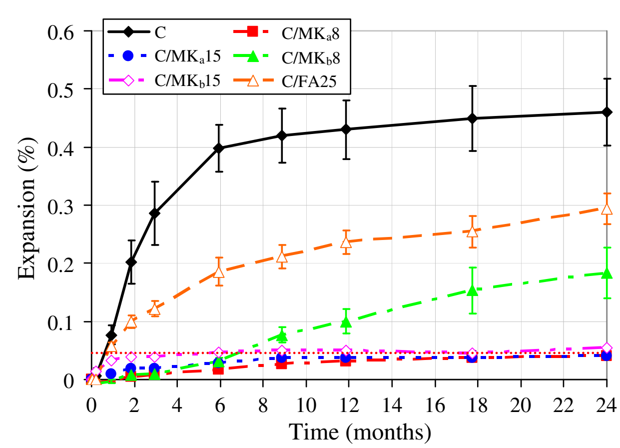

Fig. 4. CPT expansion for binary blends and the control.

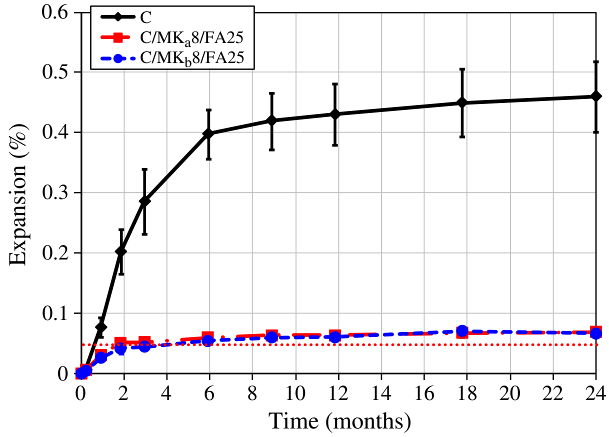

Fig. 5. CPT expansion for ternary blends and the control.

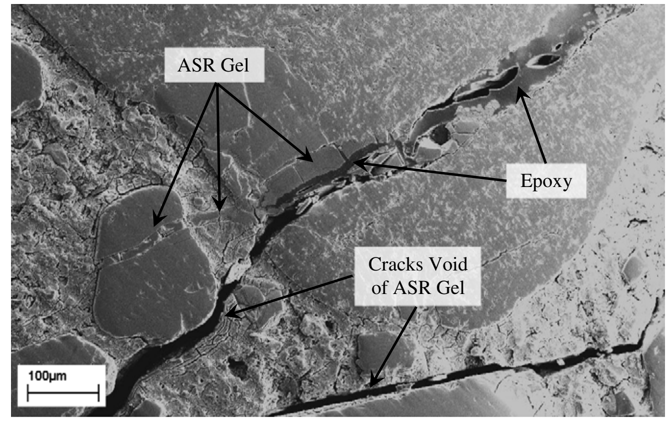

Fig. 6. Backscattered SEM image of concrete C after 2 year CPT duration.

reduced expansion to 0.29% at 2 years, still greater than 7 times the 0.04% limit. All concrete mixes utilizing metakaolin, with the exception of mix C/MK_b8 (8% MK_b mix), were effective in reducing CPT expansion to either near or below the 0.04% limit at 2 years. Corroborating AMBT results, binary blends incorporating MK_a showed lower expansion compared to MK_b blends at both 8% and 15% cement replacement.

The addition of metakaolin in ternary blends (Fig. 5) provided a significant reduction in expansion when compared to the C/FA25. When 8% metakaolin MK_a was used as a ternary blend with 25% FA concrete (C/MK_a8/FA25), greater expansion occurred when compared to the use of 8% metakaolin alone in a binary blend concrete (C/MK_a8). This result is contrary to that which occurred for comparative mixtures evaluated by the AMBT. However, it should be noted that, like AMBT mixtures M/MK_a3/FA25 and M/MK_a5/FA25, a majority of expansion in ternary blends occurred during the initial stages of the test (the first two months in this case). Expansion time histories for ternary blends C/MK_a8/FA25 and C/MK_b8/FA25 also showed there was little effect of the metakaolin's type.

Corresponding to its high expansion, the Portland cement concrete control exhibited cracking and exudation on the surface. When examined after 2 years of CPT using an SEM, widespread cracking was observed in the microstructure of the control sample. A typical SEM micrograph from concrete C is shown in Fig. 6. Cracks up to 85 μm wide were observed. Generally, cracks were observed at the interface or within reacted aggregates and in many cases spread into the paste adjacent to reacted aggregates. When in close proximity to reacted aggregates the cracks were generally filled with ASR gel, while further away from the aggregates the cracks were empty.

Examination of binary and ternary blends showed very little damage by ASR in aggregates and the paste after 2 years of exposure. Visual inspection of the surface of these prisms also indicated no visible damage. A typical SEM micrograph from binary blend C/MK_a8 is shown in Fig. 7. Cracks were much narrower and less extensive in these samples than in the control mixture C, with widths of 10 μm to 20 μm. Moreover, ASR-induced cracking present in reacted aggregates or the interfacial transition zone in binary blends did not spread throughout the paste. Other than minor drying shrinkage cracking (likely resulting from sample preparation procedures), no damage in aggregates or the paste resulting from ASR was evident in either of the ternary blends when investigated using SEM (Fig. 8).

Following the 2-year CPT expansion measurement, TGA was performed on concretes samples to determine the relative CH content in the pastes among these samples. CH contents for all concrete samples are recorded in Table 6. The correlation between CH content and 2-year CPT expansion is illustrated in Fig. 9. Control concrete C exhibited the highest CH content of 5.22%. As SCMs were added at greater rates of cement replacement, CH content generally decreased, with C/MK_a8/FA25 yielding the lowest CH content of 0.58%. While the general trend shown in Fig. 9 is that expansion increases with increasing CH content, many mixtures with similar CH contents showed significant differences in 2-year expansion (e.g., C/MK_a8 and C/FA25, both with CH contents near 2.3%). This would suggest that other mechanisms in addition to the consumption of CH may also be playing a role in reducing ASR-induced expansion.

Table 5
One and 2-year CPT expansion results.

Mix	CPT expansion (%)	
	1-year	2-year
C	0.430	0.460
C/MK_a8	0.031	0.041
C/MK_a15	0.037	0.040
C/MK_b8	0.100	0.184
C/MK_b15	0.050	0.054
C/FA25	0.236	0.294
C/MK_a8/FA25	0.064	0.069
C/MK_b8/FA25	0.061	0.066

4. Discussion

4.1. Influence of binary and ternary blends on ASR

As evidenced in both AMBT and CPT results, the addition of SCMs as a replacement for cement in binary and ternary blends resulted in a significant decrease in ASR-induced expansion. While both metakaolin and Class C fly ash reduced expansion, metakaolin was much more

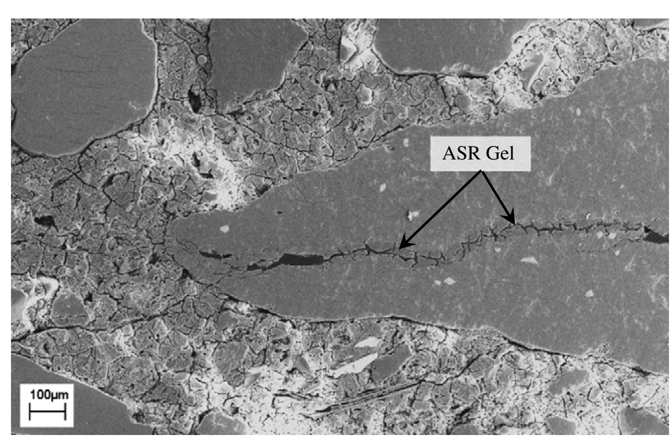

Fig. 7. Backscattered SEM image of concrete C/MK_a8 after 2 year CPT exposure.

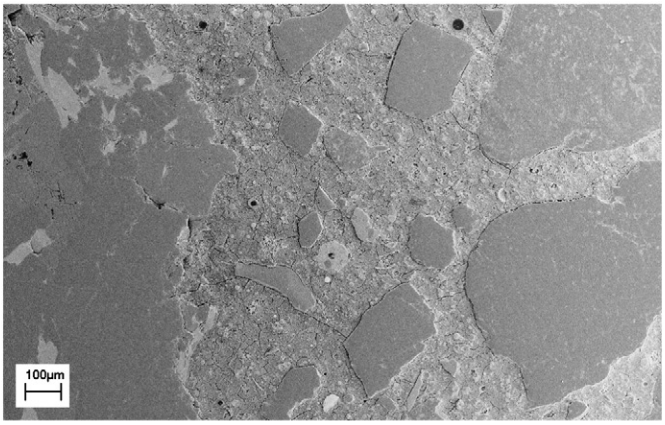

Fig. 8. Backscattered SEM image of concrete C/MK$_a$8/FA25 after 2 year CPT exposure.

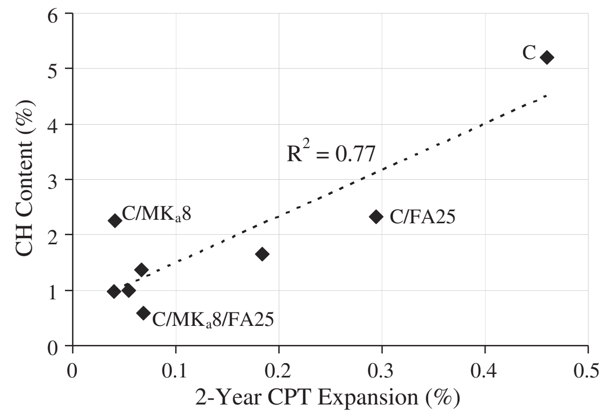

Fig. 9. CH content vs. expansion of 2-year CPT specimens.

effective even when used at lower rates of cement replacement than Class C fly ash. The influence of metakaolin surface area and particle size distribution (i.e., the behavior of MK$_a$ vs. MK$_b$) along with the procedures associated with the test methods was evident in binary and ternary blends and will be examined further in subsequent discussion sections.

The greater relative effectiveness of metakaolin when compared to Class C fly ash is likely related to its smaller particle size and primarily aluminosiliceous chemical composition, which results in its greater reactivity. Together, these should result in greater densification of the paste fraction and consumption of CH, yielding lower permeability [27,28] and decreased availability of calcium-containing reactants (e.g., solid CH, Ca^{2+} in pore solution) in metakaolin binary blends [12,13]. Other mechanisms such as alterations in the alkali adsorption capacity of the paste fraction and alkali activation of pozzolanic SCMs may have also contributed to decreases in expansion but were not investigated in the present study. It is also important to note that due to the facile reaction kinetics of metakaolin which almost fully reacts within the first week after mixing under normal curing conditions [29], ASR was suppressed even during the initial stages (approximately first 10% of test duration) of the AMBT and CPT in metakaolin binary blends, whereas the rate of expansion of Class C fly ash binary blends was high during the initial stages of the AMBT and CPT.

In the case of Class C fly ash binary blends, the addition of fly ash resulted in a high rate of expansion in the initial stages of the reaction, as shown in Fig. 2, but the rate of expansion decreased after the initial stages of the test duration. This behavior is likely a result of dilution effect at early ages (first 2–5 days of AMBT and 2 months of CPT) along with limited pozzolanic reactions, resulting in only a marginal reduction in expansion until pozzolanic reaction mechanisms start to influence microstructural development and pore solution composition. Prior studies have shown that even at extended curing temperatures of up to 60 °C, Class C fly ash does not provide quantifiable benefits (i.e., CH consumption and decreased permeability) to binary blends until approximately two weeks of age [17,30]. While this temperature is lower than the 80 °C curing used in the AMBT, it certainly indicates that

Table 6
CH content of 2-year CPT specimens.

Mix	CH content (%)
C	5.21
C/MK$_a$8	2.33
C/MK$_a$15	0.97
C/MK$_b$8	1.66
C/MK$_b$15	0.99
C/FA25	2.33
C/MK$_a$8/FA25	0.59
C/MK$_b$8/FA25	1.36

Class C fly ash provides little early strength and contributes little to early permeability, during the first week of the AMBT.

Due to the interaction between metakaolin and Class C fly ash, the behavior of ternary blends is quite different than that of binary blends. In both the AMBT and CPT, it was evident that the reduction in expansion of ternary blends is not a superposition of two equivalent binary blends, but is rather a mixture of the behavior of metakaolin and Class C fly ash. This is particularly evident when comparing expansion between 8% metakaolin binary blends and 8% metakaolin with 25% Class C fly ash ternary blends tested using the AMBT and CPT. For example in mortars, M/MK$_a$8 resulted in a 14-day AMBT expansion of 0.2%, while M/MK$_a$8/FA25 resulted in a 14-day AMBT expansion of 0.13%. However, the opposite behavior was observed in comparative concrete mixtures in the CPT. For example in concrete tests, 8% MK$_a$ binary blend (C/MK$_a$8) resulted in a 2-year CPT expansion of 0.04%, while the 8% MK$_a$ with 25% Class C fly ash ternary blend (C/MK$_a$8/FA25) resulted in a 2-year CPT expansion of 0.07%. These anomalous results suggest that the expansion behavior of ternary blends of metakaolin and Class C fly is particularly complex (especially at early ages), likely being influenced by dilution effects, early-age pozzolanic reactivity, and the procedures associated with the test methods (see discussion section 4.3). Additional research in the form of time-dependent permeability and CH content measurements will be required to better understand these mechanisms and their influence on expansion throughout the test duration of the AMBT and CPT.

4.2. Effect of metakaolin particle size distribution on ASR mitigation

A trend evident in both the AMBT and CPT binary blend expansion results is the influence of particle size distribution and surface area on the behavior of MK$_a$ when compared to that of MK$_b$. When comparing binary blended mortars and concretes containing metakaolin at the same dosage rates, the lower mean particle size and surface area MK$_a$ decreased expansion significantly more than the MK$_b$. For example, 14-day AMBT expansion for M/MK$_a$15 was 0.09% compared to 0.16% for M/MK$_b$15. The same trends also hold true for CPT binary blends. The most troubling example of this is C/MK$_b$8, whose rate of expansion was low until three months of age when it began to accelerate, ultimately resulting in a 2-year expansion of 0.18%; while C/MK$_a$8 had a 2-year expansion of 0.04%.

The influence of metakaolin surface area and particle size distribution was less obvious in ternary blends and in some cases the behavior was opposite, with expansion decreasing as surface area increased. For example in the AMBT, M/MK$_a$3/FA25 had a 14 day expansion of 0.33% compared to 0.20% for M/MK$_b$3/FA25. However, the influence of surface area and particle size distribution in ternary blends seems to diminish as the dosage rate of metakaolin increases to 8% and the capacity of both MK$_a$ and MK$_b$ to limit ASR-induced expansion is sufficient for the given mixture. Furthermore, the faster

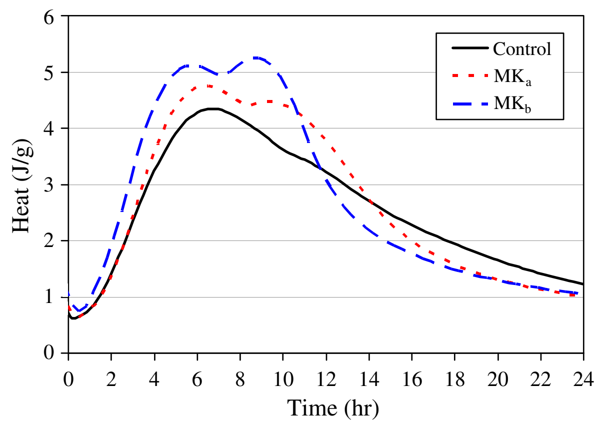

Fig. 10. Isothermal calorimetry of Control, 8% MK$_a$, and 8% MK$_b$ cement pastes.

reaction kinetics of MK$_b$ seem to be better able to overcome increased early age permeability and CH content resulting from the presence of Class C fly ash compared to MK$_a$ in ternary blends. This behavior in ternary blends is particularly clear in the first 2 days of M/MK$_a$3/FA25 and M/MK$_b$/FA25 (see Fig. 3) and 2 months of C/MK$_a$8/FA25 and C/MK$_b$8/FA25 (see Fig. 5), where the rate of expansion of MK$_a$ blends is higher than MK$_b$ until the two comparative expansion time histories continue in a parallel fashion through the duration of the test.

In order to elucidate the influence of metakaolin surface area and particle size distribution, additional studies were conducted by the authors examining permeability and composition of the paste fraction of mixtures incorporating MK$_a$ and MK$_b$ as a replacement for cement. From the heat of hydration curve shown in Fig. 10, obtained using isothermal calorimetry, it is clear that the increased surface area of MK$_b$ both accelerates the rate of reaction and amplifies the heat of hydration compared to MK$_a$ at early ages. Measurements of the chloride permeability (measured using the rapid chloride permeability method ASTM C 1202 [31]) in binary blends of 8% MK$_a$ and 8% MK$_b$ have shown the influence of surface area as well. For example with a w/cm of 0.50 tested at 28 days, 8% MK$_a$ had a lower chloride permeability (1044 Coulombs) compared to 8% MK$_b$ (1565 Coulombs) and the control (5200 Coulombs) [4,27]. Further, differential thermal analysis (DTA) was used to determine the CH content of cement pastes at early ages incorporating 8% MK$_a$ and 8% MK$_b$ with a w/cm of 0.40 [4,27]. DTA results from 4 h to 7 days of age (Fig. 11) demonstrate that MK$_a$ provided a greater decrease in the CH content at early ages. TGA conducted at 2 years on CPT specimens indicated that at late-ages (2 years in this case) metakaolin surface area has little influence on CH content (see C/MK$_a$8 and C/MK$_b$8 in Fig. 9).

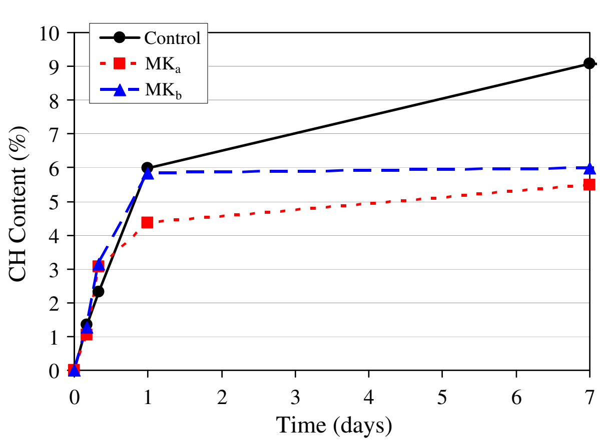

Fig. 11. Differential thermal analysis on Control, 8% MK$_a$, and 8% MK$_b$ cement pastes (Adapted from [4]).

In all cases (the experiments discussed above and expansion results presented herein), the relative behavior of these two metakaolins does not, perhaps at first examination, appear to follow the expected trends, considering their differences in surface area. For SCMs in general, higher surface area SCMs would be expected to produce decreases in permeability and CH content, particularly at earlier ages where rapid reaction of the more finely divided materials would be noticed [32,33]. However, with these two metakaolins, it is suggested that each material's particle size distribution may play a more significant role in its performance than initially considered. Recall from Section 2.1 Materials that the while the surface area of MK$_b$ is higher than MK$_a$, its mean particle size and overall particle size distribution is actually larger than MK$_a$ (see Fig. 1). It is only the "tail" of particles in MK$_b$ below 1 μm that contributes to its higher reactive surface area. When considering the overall particle size distribution, correlations between expansion and metakaolin type become much more clear. For example, MK$_b$ was found to have somewhat better performance at early ages (particularly when used in ternary blends, see Fig. 3) which corresponds well with its higher proportion of particles below 1 μm and higher early-age reactivity determined using calorimetric measurements compared to MK$_a$. However, the mean particle size proved to dominate overall expansion in the AMBT and CPT, with MK$_a$ (lower mean particle size) mixture generally exhibiting less expansion than mixtures incorporating MK$_b$.

4.3. Accelerated mortar bar test vs. concrete prism test

A final point warranting further discussion is the correlation between the AMBT and CPT results, particularly since both tests are currently used to define the acceptability of a given mix design for mitigation of potentially reactive aggregates. Both test methods have been fairly recently adopted by ASTM (AMBT was first approved in 1989 [24], but the use of SCMs in this test was approved much more recently, in 2004 [25]; CPT was first approved in 1995 [20]), and correlations between an aggregate/paste combination in these test environments and field performance remain under development. Most recently, the US Department of Transportation's Federal Highway Administration (FHWA) published a report [32] describing the sequence of testing for aggregates where field performance is not known. For the aggregate examined in this research, and using the results for AMBT and CPT on the control mixes (M and C), the report suggests that AMBT is adequate for assessing the ability of SCMs to mitigate expansion with this aggregate. However, closer comparison between AMBT and CPT results for the range of mixes examined leads to some ambiguity.

Fig. 12 compares AMBT expansion to CPT expansion for the specified test duration (14 days for the AMBT [24,25], 1 year for CPT controls, and

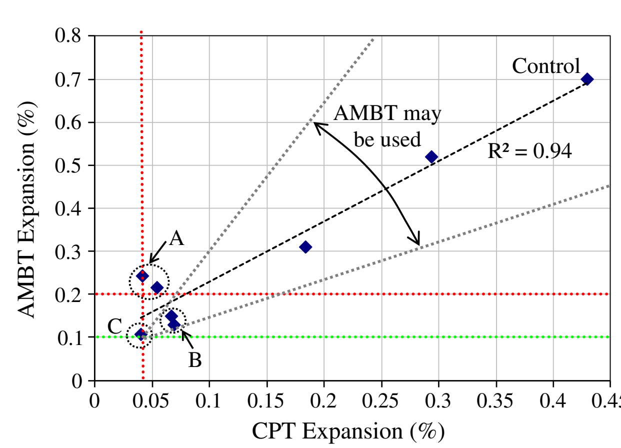

Fig. 12. AMBT vs. CPT expansion for specified test duration.

2 years for CPT binary and ternary blends [20]). Dotted horizontal lines represent the 0.1% and 0.2% expansion criteria for the AMBT and the vertical dotted line represents the 0.04% expansion criterion for the CPT. Diagonal lines indicating the acceptability of using the AMBT to evaluate various ASR mitigation strategies provided by FHWA [32] are also shown. For this highly reactive aggregate, the correlation between the acceptability of a cementitious composition for companion samples tested by the AMBT and the CPT is good at high levels of expansion but becomes poor as the mixture becomes more complex and expansion decreases towards the limits of acceptability. This decreasing resolution as the expansion approaches these limits is problematic in terms of providing confidence in the acceptance or rejection of an aggregate/paste combination.

Among these data, of particular interests are three cases, indicated by circles A, B, and C in Fig. 12:

- Case A: M,C/MK_a8 and M,C/MK_b15 which passes the CPT but fails the AMBT with a 14-day expansion just above the 0.2% limit.
- Case B: M,C/MK_a8/FA25 and M,C/MK_b8/FA25 which nearly passes the AMBT but fails the CPT.
- Case C: M,C/MK_a15 the only composition which passes both the AMBT and CPT.

Deviations between the acceptability of aggregates and mix designs when companion samples are tested using the AMBT and CPT have been documented previously [5,15,33,34]. In most studies, Case A occurs, where the AMBT is seemingly “too aggressive” and the composition is subsequently investigated and accepted using the CPT which is generally recognized as a better predictor of field performance. Case A also falls outside of the diagonal AMBT validity lines provided by FHWA [32], indicating that the AMBT may not be a suitable method for evaluating some ASR mitigation techniques. Case B is the most troubling, when a composition looks to be marginally acceptable by the AMBT but fails the CPT. According to a recent study which examined 182 aggregate and material combinations using the AMBT and CPT, only 7% of the compositions tested had results fall under Case B [34]. In many instances, Cases A and B are encountered when utilizing high dosage rates of SCMs [33]. Case C represents the ideal result of a comparative study, where correlation between both expansion and acceptability are strong.

In the case of binary and ternary blends used in the present study, pozzolanic and latent hydraulic reactions most certainly affect the time-dependent development of concrete properties, such as permeability, CH content, and alkali binding capacity among others, all of which directly affect ASR and expansion. In order to be applicable for the prediction of a concrete's field performance, laboratory based test methods must take into consideration the time-dependent nature of concrete properties. One can trace back many of the deviations between the AMBT and CPT comparative results to the differences in the test methods themselves, including the specimen preparation procedures and the curing regimes, which are the same regardless of the cementitious composition being evaluated.

In the AMBT, samples undergo standard 24 h curing, followed by an initial 24 h conditioning period submerged in 80 °C water prior to exposure to alkali solution at 80 °C. Even at this high temperature, most studies have shown that pozzolanic reactions of SCMs such as fly ash and slag can take up to one week to near completion [17,30], halfway through the standard duration of the AMBT. Further, studies on the reaction kinetics of metakaolin at various temperatures have also shown that increased curing temperatures can result in alterations in the phases formed through pozzolanic reactions with CH [35]. Both of these effects may influence expansion results for Class C fly ash and metakaolin in the present study.

It is also clear that the expansion time histories provided by the AMBT show no clear influence of permeability on limiting ASR-induced expansion, with the rate of expansion of all mixtures being approximately equal between 14 and 28 days (Figs. 2 and 3). This is likely due to the unlimited supply of alkali ions and small cross section of the mortar bars negating any effect of limiting access to moisture and external alkalis by decreases in permeability. As a result, when evaluating binary and ternary blends using the AMBT only chemical mechanisms of ASR mitigation are likely detected, and not alterations in permeability.

In the CPT with its larger specimen dimensions the influence of permeability is clearly shown, with the rate of expansion at 2 years approaching zero for mixtures with reduced permeability resulting from the addition of metakaolin and/or Class C fly ash. TGA results also support the theory that permeability plays a large role in reducing expansion along with CH content. The results in Fig. 9 clearly illustrate that even with similar CH contents expansion can vary significantly. For example, concrete C/MK_a8 and C/FA25 exhibited similar CH contents (of 2.26% and 2.34%) but had 2-year expansions of 0.041% and 0.294%, respectively. This result suggests that other mechanisms (e.g., reductions in permeability, alkali binding) in addition to CH consumption play an integral role in ASR mitigation and are better captured in the more realistic CPT than the AMBT.

However, while the CPT is generally considered to be a better predictor of field performance, it also utilizes a specimen preparation and curing regime that is generally unrealistic compared to actual field conditions. With alkalis contributed from the cement in addition to NaOH added to the mix water to bring the Na_2O_{eq} up to 1.25%, the mixture has a significant alkali loading from day one when the first expansion measurement is taken, prior to any significant initiation of mechanisms that may decrease permeability, bind alkalis, or consume CH. In reality, concrete that is proportioned to have a low intrinsic alkali content will typically not be exposed to a significant concentration of alkalis from external sources until well into the service life when hydration reactions have ceased and concrete properties have fully developed. While this will not affect faster reacting SCMs like silica fume and metakaolin, it would undoubtedly have a large influence on the early-age expansion of mixtures incorporating slower reacting SCMs such as fly ash (such as that found in the present study) and slag which may take weeks to months to fully react under the 38 °C storage conditions of CPT specimens [30].

Thus, while significant effort has focused on improving standard ASR test methods, these data demonstrate that limitations associated with the prescribed test methods and standard curing regimes remain. These limitations become particularly apparent when evaluating mixtures incorporating slower-reacting SCMs, such as fly ash and slag. For these test methods (AMBT, CPT, and others) to be used robustly for evaluating aggregate reactivity and methods to mitigate deleterious expansions, testing procedures must be developed which consider the time-dependent development of concrete properties and all possible mechanisms by which ASR may be mitigated. It is only when all of these factors are considered by ASR test methods that they may be used as a reliable means for predicting the field performance of given aggregate/matrix combinations.

5. Conclusions

Binary and ternary blends of two types of metakaolin (MK_a and MK_b with different particle size distributions) and Class C fly ash were examined for their ability to resist damage by ASR using the AMBT and CPT methods while incorporating a highly reactive fine aggregate.

(1) The use of metakaolin was universally more effective at limiting AMBT and CPT expansion than Class C fly ash. The relative effectiveness of metakaolin primarily results from the smaller particle size, higher degree of reactivity, and chemical composition. Data show that these contribute to a decrease in CH content, which correlates to lower expansion. It may also be proposed that contributions to lower permeability and increased alkali binding also play a role in mitigating ASR.

(2) MK_b with a higher surface area was less effective than MK_a decreasing ASR-induced expansion in binary blends. It is proposed that the increased performance of MK_a results its smaller mean particle size.
(3) According to AMBT and CPT test results, ternary blends of metakaolin with Class C fly ash seem to provide no benefit for the mitigation of ASR over metakaolin used alone in concrete. This result, however, is likely influenced by the increased early-age expansion associated with the addition of Class C fly ash in ternary blends.
(4) Correlation between the acceptability of the aggregate and cementitious compositions used in the present study when tested by the AMBT and CPT methods was good at high levels of expansion but poor as SCMs addition rates were increased and expansion approached the limits of acceptability
(5) In order to accurately and reliably predict the field performance of binary and ternary blends incorporating SCMs, test methods and curing regimes used to evaluate ASR susceptibility should consider the time-dependent development of concrete properties and all possible mechanisms by which ASR may be mitigated.

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