



Decoupling the effects of chemical composition and fineness of fly ash in mitigating alkali-silica reaction



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ARTICLE INFO

Article history:

Received 23 December 2012

Received in revised form 25 June 2013

Accepted 28 June 2013

Available online 8 July 2013

Keywords:

Particle size

Fly ash

Chemical composition

Alkali-silica reaction

Durability

ABSTRACT

A comprehensive investigation was conducted to determine the individual effects of the chemical composition and particle size of fly ash on alkali-silica reaction (ASR). Test results indicated that the combined oxides content of fly ash showed a better correlation with the ASR expansions than its individual oxides. Mixtures containing finer fly ash fractions registered lower expansions than those containing the corresponding virgin fly ashes or its coarser fractions.

Within the usual range of average particle size of 10 to 30 microns, of fly ash, the chemical composition had a more dominant influence on ASR mitigation than the particle size. However, when the average particle size of fly ash decreases below 10 microns, the fineness of fly ash becomes significant in mitigating ASR. In addition, the fineness of fly ash had a more significant influence in mitigating ASR in mixtures containing high-lime fly ashes than those containing low-lime fly ashes. Hence, reducing the particle size of fly ash to finer fractions is an effective strategy to mitigate ASR. The decoupling of the chemical composition of fly ash from its particle size indicated that ASR mitigation can be achieved with any fly ash having a D_{50} below 5 μm . However, low-lime fly ashes were effective in mitigating ASR even without reducing their particle size.

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1. Introduction

Alkali silica reaction (ASR) is a well known durability distress in portland cement concrete. ASR is primarily caused by the reaction between the alkali hydroxides present in the pore solution and reactive silica found in some aggregates. This reaction produces alkali-silica gel. The ASR gel being hygroscopic in nature, absorbs moisture, producing deleterious tensile cracks in concrete structures such as pavements, bridge decks, dams, etc. [1–3]. The use of fly ash as a supplementary cementing material (SCM) to mitigate ASR has been well documented [4–7]. The principle mechanisms by which fly ash mitigates ASR has been extensively studied. The recognized mechanisms include (i) its pozzolanic reactivity resulting in the depletion of calcium hydroxide $[\text{Ca}(\text{OH})_2]$ produced during cement hydration [8–10], (ii) its alkali binding ability [6,11–13] and (iii) reduced permeability of the supplemental calcium-silicate-hydrates (C–S–H gel) produced as a result of pozzolanic reaction [14].

Fly ashes vary widely in their chemical composition and physical characteristics, and are classified based on their

$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and CaO contents as per the ASTM and Canadian standard specifications [15,16], respectively. Hence, the properties of concrete containing different fly ashes vary significantly. For example, low-lime fly ashes react slowly than high-lime fly ashes, especially during the early ages, primarily due to the presence of less or no calcium in the alumino-silicate glasses in the former. The calcium alumino-silicate glass in the fly ash is usually more reactive than the pure alumino-silicate glass and hence results in high early age strengths in concretes [17]. Similarly, mortars containing finer fly ashes were found to possess higher compressive strength than those containing coarser fly ashes, indicating the beneficial effects of lowering the particle size of fly ash [18]. Of the different oxides in the fly ash, the SiO_2 (or $\text{SiO}_2 + \text{Al}_2\text{O}_3$) and CaO are of prime importance [17]. Since the properties of concrete containing fly ashes are largely dependent on their oxide contents and fineness, the ability of fly ash to reduce expansions due to ASR in concrete are also dependent on these two factors.

Numerous investigations demonstrating the beneficial effect of fly ashes in mitigating ASR have been conducted. Among these studies, several of them have focused on correlating the effect of chemical composition of fly ashes on ASR mitigation [6,19–21]. Research conducted by Shehata and Thomas [6,21] to determine the effect of chemical composition of fly ash on ASR mitigation indicated that the low-lime fly ashes ($\text{CaO} < 8\%$) were more effective than the high-lime fly ashes ($\text{CaO} > 20\%$) and required lower

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replacement levels to mitigate ASR. In their study, the fly ashes were characterized based on their lime contents and the ASR expansions were found to be a direct function of it. However, characterizing the fly ashes on the basis of its lime content alone may not be appropriate as other oxides in fly ashes can also promote or reduce ASR expansion. Recent research performed by Malvar et al. [20] suggested that the efficacy of fly ash in mitigating ASR can be better characterized by considering a chemical index that is based on all the principal oxides in fly ash, rather than merely the lime content of the ash.

Studies conducted to determine the effect of fineness of fly ash on the properties of mortar or concrete have indicated that the finer size-fractions of fly ash resulted in higher pozzolanic activity index than the coarser size-fractions of fly ash when used in mortars [18]. The use of finer size-fractions of fly ash can also be beneficial in reducing the mortar bar expansions due to ASR in the sense that finer particles promote pozzolanic reactions faster than coarser particles. In addition, the use of such finer fly ash may also require lower replacement levels to mitigate ASR within permissible limits. For example, ultra-fine fly ash having a mean particle diameter of $\sim 3 \mu\text{m}$, and a CaO content of $\sim 11\%$ was found to mitigate ASR at a cement replacement level of $\sim 12\%$ by mass. This performance was found to be comparable with that of silica fume [22].

Though the importance of chemical composition of fly ash and its fineness for ASR mitigation has been established in literature, none of these studies were able to decouple the individual effects of chemical composition and fineness of fly ashes. The individual effects of oxide content and fineness of fly ash in ASR mitigation is important for the following reasons:

- To understand the effects of individual oxides, combined oxides and oxide ratios in ASR mitigation.
- To establish limits on the oxide contents of fly ash and its fineness for ASR mitigation in concrete.
- To predict the effectiveness of fly ashes in mitigating ASR directly from its oxide contents and average particle size.

In geographic locations having only high-lime fly ashes, which are usually known to be less effective in reducing ASR expansions,

available techniques such as grinding or sieving can be employed to reduce their average particle size to appropriate size so as to achieve ASR mitigation. The utilization of existing resources and techniques to mitigate ASR can avoid the need to transport other materials from other locations, thereby eliminating the associated material transportation cost, and thus providing a sustainable option for ASR mitigation.

In the current study, a detailed investigation was conducted with the principle objective to determine the individual effects of the oxide contents of the fly ash and its fineness on the ASR expansions. In addition, certain limits on the individual and combined oxide contents of fly ash based on its specific average particle size were established, which will provide a solution to choose specific fly ashes in specific geographical location while also achieving ASR mitigation. In this study, the standard ASTM C 1260 or C 1567 test method [23,24] was adopted to evaluate the effects of the chemical composition and the particle size of fly ashes on ASR mitigation. A mortar bar expansion of 0.10% or less at 14 days was considered to represent an effective mitigation in these studies. While this mortar bar expansion limit of 0.10% may not accurately represent the field performance of the ASR mitigation measures, it is considered as a standard metric for comparing the individual effects of chemical composition and particle size of fly ashes.

2. Experimental materials

2.1. Cement

In this study, a high-alkali ASTM Type I cement with a $\text{Na}_2\text{O}_{\text{equi}}$ of 0.82% was used. The chemical composition of this cement is shown in Table 1.

2.2. Fly ash

A total of thirteen fly ashes differing significantly in their lime content from 1% to 27.5% were used in this study. Of these fly ashes, four were high-lime fly ashes ($\text{CaO} > 20\%$), four others were

Table 1
Chemical composition of cement.

Material	Oxide composition by mass (%)							Specific gravity
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Total alkali [$\text{Na}_2\text{O}_{\text{equi}}$]	
Cement	19.78	4.98	3.13	61.84	2.54	4.15	0.82	3.15

Table 2
Chemical composition of fly ashes.

Fly ash (or) mixture ID	Oxide composition by mass (%)									Specific gravity
	SiO_2	Al_2O_3	Fe_2O_3	S + A + F*	CaO	MgO	SO_3	Total alkali, [$\text{Na}_2\text{O}_{\text{equi}}$]	LOI**	
LL1	60.30	28.60	3.20	92.10	1.00	0.00	0.00	1.60	1.30	2.20
LL2	61.63	24.86	4.56	91.05	1.40	0.23	0.21	2.61	1.05	2.09
LL3	58.67	20.86	11.51	91.04	3.35	1.15	0.40	1.20	0.04	2.44
LL4	57.49	29.29	2.95	89.73	6.06	1.36	0.41	2.44	0.45	1.97
LL5	54.53	26.29	5.03	85.85	7.31	1.60	0.39	0.96	0.73	2.17
IL1	52.97	22.25	5.39	80.61	10.45	2.33	0.52	1.66	0.78	2.40
IL2	56.26	19.88	4.48	80.62	12.25	2.76	0.48	1.21	0.29	2.41
IL3	49.69	15.03	6.60	71.32	15.63	4.92	0.90	3.93	0.01	2.55
IL4	41.91	21.08	5.61	68.60	18.94	4.21	0.98	2.59	0.54	2.57
HL1	39.66	20.42	5.51	65.59	22.85	4.22	1.21	1.90	0.27	–
HL2	37.60	18.80	6.00	62.40	24.20	4.50	2.30	1.99	0.30	2.50
HL3	34.90	19.50	5.70	60.10	26.60	5.00	2.00	2.09	0.30	2.61
HL4	34.55	18.10	5.68	58.33	27.50	5.04	2.80	1.83	0.18	2.63

* S + A + F denotes $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$.

** LOI – loss on ignition.

Table 3
Average particle size and fineness of fly ashes.

Fly ash ID	Avg. particle size, D_{50} (μm)	Specific surface area (m^2/kg) (laser particle size analyzer)
LL1	17.02	887
LL2	25.08	660
LL3	21.90	–
LL4	28.08	436
LL5	20.90	807
IL1	21.23	938
IL2	21.20	961
IL3	20.66	969
IL4	13.99	1490
HL1	10.92	1800
HL2	12.32	1550
HL3	14.48	1610
HL4	13.91	1310

intermediate-lime fly ashes ($\text{CaO} = 8\text{--}20\%$) and the remaining five were low-lime fly ashes ($\text{CaO} < 8\%$). Based on the ASTM C 618 specification, the low- and intermediate- lime fly ashes were together classified as Class F fly ash while the high-lime fly ashes were classified as Class C fly ash. The chemical composition of these fly ashes is provided in Table 2. The average particle size and fineness of the fly ashes as determined using Malvern Particle Size Analyzer are provided in Table 3. As this table shows, the average particle size of the as-obtained or virgin fly ashes was usually found to be in the range of $\sim 10\text{--}30\ \mu\text{m}$ and decreases with an increase in their lime content. For example, the high-lime fly ashes were found to be finer than the intermediate and low-lime fly ashes, perhaps due to the variation in the operational characteristics and the collection techniques used at a power plant [8].

2.3. Reactive aggregates

Four aggregates were used in this study which has an established history of being alkali-silica reactive. The basic properties of these aggregates are provided in Table 4.

3. Experimental program

A preliminary investigation was conducted to determine the effect of replacement level of fly ash on ASR mitigation in order to arrive at an optimal replacement level that can be used in mixtures for detailed investigation. In this study, three fly ashes (HL4, IL3 and LL3) were used to prepare mortars at four different cement replacement levels (by mass) of 0% (Control), 15%, 25% and 35%. Each of these fly ashes was used with all the four reactive aggregates to understand the effect of fly ash replacement level on aggregate reactivity.

A detailed investigation was conducted to study the effects of chemical composition and particle size of fly ash on ASR mitigation. In the first part, the effect of chemical composition of fly ashes on ASR mitigation was studied by correlating their oxide content

with the 14-day expansion of mortar bars in the ASTM C 1567 test. This was accomplished by using (a) individual oxide, (b) sum of specific oxides, (c) oxide equivalents calculated using molecular weight ratio and (d) ratios of oxides or oxide equivalents. A comparison of all the established correlations with the ASR expansion was performed and the minimum or maximum oxide or oxide equivalents required in the fly ash to achieve ASR mitigation was determined.

The second part involved investigation on the effect of the particle size of fly ash on ASR mitigation. In this study, the as-obtained fly ashes were fractionated using two different processes: (a) ultrasonic sieving and (b) grinding. In the sieving process, three fly ashes (HL3, IL3 and LL1) were sieved in a Gilsonic sieve shaker consisting of four sieves. Using these sieves, four particle size-fractions were obtained: S1 ($>45\ \mu\text{m}$), S2 ($25\text{--}45\ \mu\text{m}$), S3 ($15\text{--}25\ \mu\text{m}$) and S4 ($5\text{--}15\ \mu\text{m}$). Since significant quantity of these size fractions were obtained with LL1 fly ash, all four fractions were employed in the study. However with IL3 fly ash, only three size-fractions were employed, S1, S2 and a third combined fraction, S3S4 ($5\text{--}25\ \mu\text{m}$) obtained by blending S3 and S4 due to lack of sufficient quantity in either of the sieves by itself. In the case of HL3 fly ash, only two size-fractions (S1 and S2) were employed. Thus, a total of thirteen mixtures including one control (without fly ash) mixture, three high-lime fly ash mixtures (HL3, HL3–S1 and HL3–S2), four intermediate-lime fly ash mixtures (IL3, IL3–S1, IL3–S2 and IL3–S3S4) and five low-lime fly ash mixtures (LL1, LL1–S1, LL1–S2, LL1–S3 and LL1–S4) were prepared and the ASTM C 1260 and C 1567 test were conducted on these mixture to study the effect of fineness of sieved fly ashes on ASR mitigation.

Similarly in the grinding process, five fly ashes (HL1, HL4, IL3, IL4 and LL1) were selected and each fly ash was ground to two different size-fractions: (i) intermediate-ground (G1) and (ii) well-ground (G2), both using a Retsch Planetary Ball mill. To achieve these grinding levels, the grinding regimes of 250 rpm for 15 min and 250 rpm for 60 min were adopted. The ground fly ashes were then used to replace cement at specific replacement level. Thus, a total of sixteen mixtures including one control mixture (without fly ash), six high-lime fly ash mixtures (HL1, HL1–G1, HL1–G2, HL4, HL4–G1, HL4–G2), six intermediate-lime fly ash mixtures (IL3, IL3–G1, IL3–G2, IL4, IL4–G1, IL4–G2), and three low-lime fly ash mixtures (LL1, LL1–G1, LL1–G2) were prepared and the ASTM C 1567 test was conducted to determine ASR expansion in all mixtures. Since all the parameters were held constant except the different grinding levels of fly ash, the effect of ground fly ash size-fractions on ASR mitigation was then evaluated.

A particle size distribution analysis was conducted on virgin, sieved and ground fly ash size-fractions as shown in Fig. 1(i) through (v). The effective and average particle size (D_{10} and D_{50}) of the fly ash size fractions were determined and listed in Table 5. As this table shows, the D_{50} for the virgin, sieved and ground fly ashes range from $10.92\text{--}20.66\ \mu\text{m}$, $10.00\text{--}60.00\ \mu\text{m}$ and $4.20\text{--}10.69\ \mu\text{m}$, respectively. The average particle size of the ground fly ash size-fractions was then correlated to the 14-day mortar

Table 4
Basic properties of four reactive aggregates.

Aggregate property	Units	Aggregate type			
		Aggregate 1	Aggregate 2	Aggregate 3	Aggregate 4
Aggregate ID	SP	SD	NC	NM	
Source	–	Spratt quarry, Ontario	Dell Rapids quarry, South Dakota	Gold Hill quarry, North Carolina	Las Placitas Gravel pit, New Mexico
Major reactive mineral	–	Siliceous limestone (Chert)	Quartzite	Argillite	Rhyolite
Water absorption	%	0.456	0.42	0.344	1.09
Bulk specific gravity	–	2.69	2.51	2.75	2.60
Bulk specific gravity (SSD)	–	2.71	2.52	2.76	2.63
Dry-rodded unit weight	kg/m^3	1568	1557	1566	1585

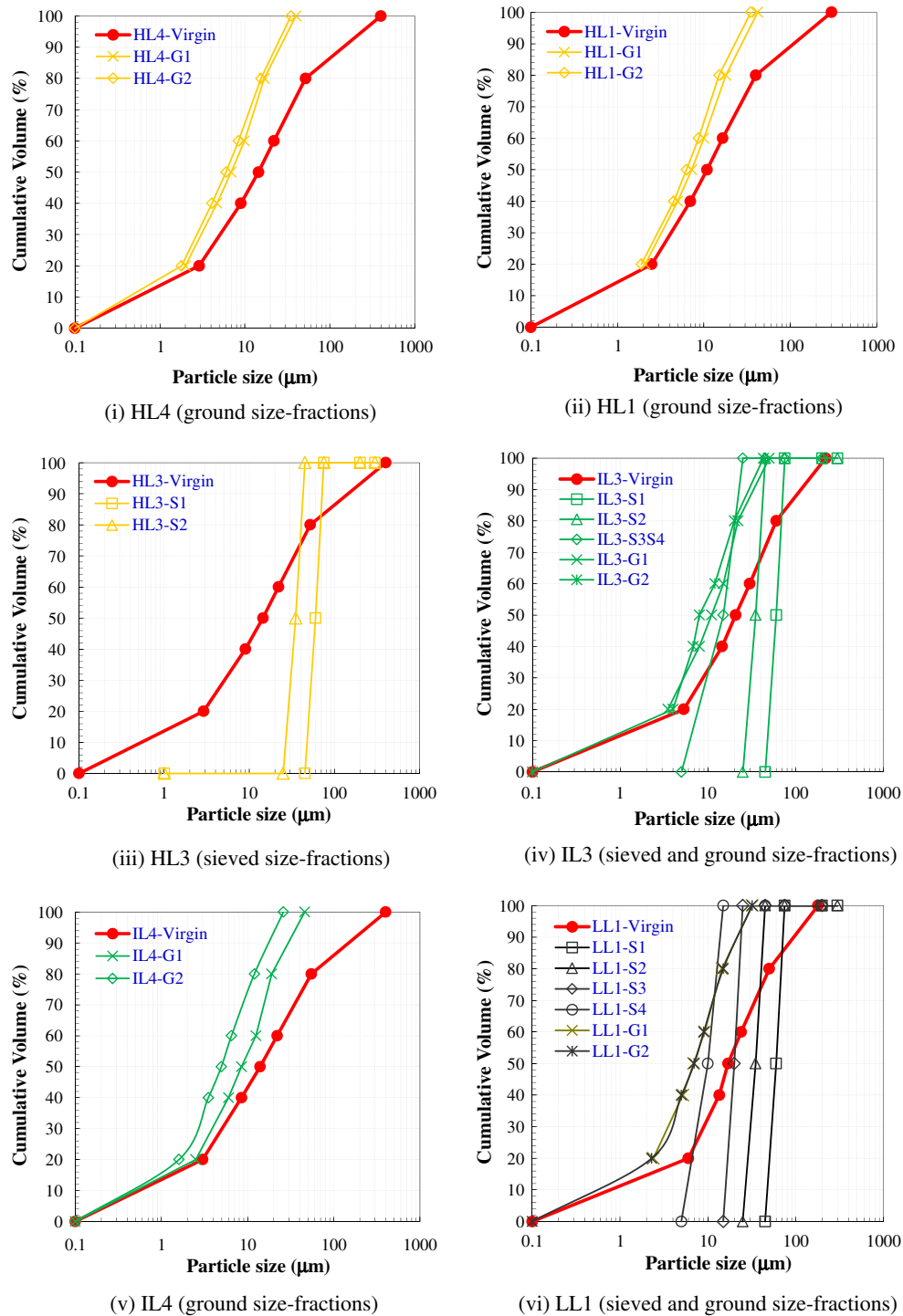


Fig. 1. Comparison of particle size distribution of virgin fly ash with their ground and/or sieved size-fractions.

bar expansion in order to understand the individual effect of particle size on ASR mitigation, independent of chemical composition. This correlation was used to establish the effect of the oxide composition of fly ash as a function of average particle size.

4. Experimental test methods

The efficacy of fly ashes in mitigating ASR in mortars containing reactive aggregate was conducted as per the ASTM C 1260/C 1567

test method. The mixture proportion as specified in this test procedure was used to prepare all the mortar mixtures. In these mixtures, a constant aggregate-to-cementitious materials ratio of 2.25 and a constant water-to-cementitious material ratio of 0.47 were used. The prepared mortar bars of size $25 \times 25 \times 285$ mm were initially moist-cured for 24 h before demolding and then cured in hot water for 24 h at 80°C before recording the reference reading using a standard comparator. The bars were then immersed in a standard 1 N sodium hydroxide solution at 80°C and their expansions were recorded at regular intervals, thereafter un-

Table 5
Particle size distribution data of fly ashes and its size fractions.

Description	Type of fly ash	Fly ash ID	Particle size distribution parameters	
			Effective Size, D_{10}	Average Size, D_{50}
Virgin fly ash	LL1	Virgin	0.80	17.02
		Virgin	0.70	20.66
		Virgin	1.55	13.99
		Virgin	0.50	10.92
		Virgin	0.50	14.48
		Virgin	1.80	13.91
Sieved fly ash	LL1	S1	48.00	60.00
		S2	27.00	35.00
		S3	16.00	20.00
		S4	6.00	10.00
	IL3	S1	48.00	60.00
		S2	27.00	35.00
		S3S4	7.00	15.00
	HL3	S1	48.00	60.00
		S2	27.00	35.00
Ground fly ash	LL1	G1	1.30	6.90
		G2	0.60	7.00
	IL3	G1	1.90	10.69
		G2	0.65	7.99
	IL4	G1	1.40	8.55
		G2	0.85	4.92
	HL1	G1	1.20	7.27
		G2	1.00	6.38
	HL4	G1	1.20	6.88
		G2	0.40	6.01

til 28 days of immersion period. The mortar containing no fly ash was considered as the control mortar and an expansion limit of 0.10% at 14 days immersion period was considered as a measure of effective ASR mitigation as specified by the ASTM C 33 specification [25].

5. Results and discussions

5.1. Effect of replacement level of fly ash on ASR mitigation

The effect of replacement level of low-lime, intermediate-lime and high-lime fly ash (LL1, IL3 and HL4) on the 14-day expansion of mortar bars containing different reactive aggregates is shown in Fig. 2(i), 2 (ii) and 2 (iii), respectively. As these figures show, the 14-day expansion of fly ash mortars decreases with an increase in the replacement level of fly ash, irrespective of the aggregate type used. With a low-lime fly ash, replacement levels required to achieve ASR mitigation was found to be 15–25% (by mass). With an intermediate-lime fly ash, this replacement levels for ASR mitigation were found to be relatively higher. However with a high-lime fly ash, ASR mitigation was not achievable even at a very high replacement level of 35%. This inefficacy of high-lime fly ashes to mitigate ASR has been reported in several past investigations [6,20]. In addition, it can be observed that an exponential function of the following form was found to closely fit all the data points.

$$y = ae^{-bx} \quad (1)$$

where “a” and “b” are constants depending on the aggregate reactivity and replacement level of fly ash.

5.2. Effect of oxide composition of fly ash on ASR mitigation (neglecting the variation in the particle size of fly ash)

In this study, 13 fly ashes as listed in Table 2 were chosen and the ASTM C 1567 test was conducted on fly ash mixtures contain-

ing aggregate 2. The replacement level of fly ash used in the mixture was maintained constant and equal to 25% by mass of cement and hence, the oxide composition of fly ash can be correlated directly to their 14-day mortar bar expansions. The oxide composition of fly ash was considered in two ways: (i) As individual oxide contents and (ii) As combined oxide contents.

5.2.1. Effect of individual oxides of fly ash on ASR expansion

The effect of individual oxides in fly ash which tend to inhibit and promote ASR is shown in Fig. 3(i) and (ii), respectively. As the Fig. 3(i) shows, an increase in the SiO_2 content of the fly ash caused a decrease in the 14-day mortar bar expansion. A good exponential fit (with $R^2 = 0.88$) existed between the SiO_2 content of the fly ash and 14-day expansion perhaps due to factors contributing directly to ASR mitigation such as pozzolanic reactivity and the alkali binding ability of the low C/S ratio C–S–H gel [5,6,11–13]. In the case of Al_2O_3 and Fe_2O_3 content of fly ash, a strong correlation with the 14-day expansion did not exist. The presence of Al_2O_3 in pozzolans such as metakaolin, however, has been found to result in the production of calcium aluminosilicate hydrates (C–S–A–H), which significantly improves the alkali binding ability of the fly ashes [26,27]. Similarly, the nature of iron oxide in the fly ashes is usually non-reactive and hence, its presence by itself was unimportant [20,28].

As the Fig. 3(ii) shows, an increase in the CaO content of the fly ash caused an increase in the 14-day expansion and hence, its quantity is often restricted by many organizations to 10% [19,29]. A good correlation with a high R^2 value was found to exist between the oxide contents and the 14-day expansion. The MgO and SO_3 contents of fly ash correlated well with the 14-day expansion, however, the degree of correlation for these oxides (by itself) is likely to be coincidental in nature, as there is not much evidence to suggest that these oxides affect the ASR mechanism. Fly ashes that contain high lime are likely to come from power plants that may employ lignitic or subbituminous coals or other sulfate scrubber systems which are likely to increase both the MgO and the SO_3 contents in the ash. In addition, these oxide contents in the fly ash are also very low. In the case of Na_2O_e content of fly ash, a weak trend was observed. This is because, the concentration of the total alkalis (Na_2O_e) in the fly ash is significantly lower than that is present in the soak solution of 1 N NaOH concentration during the ASTM C 1260/C 1567 test and hence, the effect of the alkali present in fly ash on mortar bar expansion is usually negligible. On the contrary, the high alkali contents in cement and fly ash have been found to increase the alkali-silica reactivity in concrete containing reactive aggregates when tested using the standard ASTM C 1293 test [13,21].

5.2.2. Effect of combined oxides of fly ash on ASR mitigation

The individual oxides of fly ash can be combined directly or based on a molar mass ratio to form oxide equivalents.

5.2.2.1. As combined oxides. The combined oxides of fly ash considered include $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and $\text{CaO} + \text{MgO} + \text{SO}_3$; their effect on the 14-day expansion is shown in Fig. 4(i) and 4 (ii). As the Fig. 4(i) shows, the 14-day expansion was found to vary inversely with the $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content of the fly ash. This combined oxide content of fly ash had a better correlation with the mortar bar expansion than the individual oxides (SiO_2 , Al_2O_3 and Fe_2O_3) by themselves. As the Fig. 4(ii) shows, the 14-day expansion was found to increase with increase in the $\text{CaO} + \text{MgO} + \text{SO}_3$ content of the fly ash. Similar to the $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content, the $\text{CaO} + \text{MgO} + \text{SO}_3$ content was found to have better correlation with the ASR expansion than the individual oxides of CaO, MgO and SO_3 by themselves. The sum quantity of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and

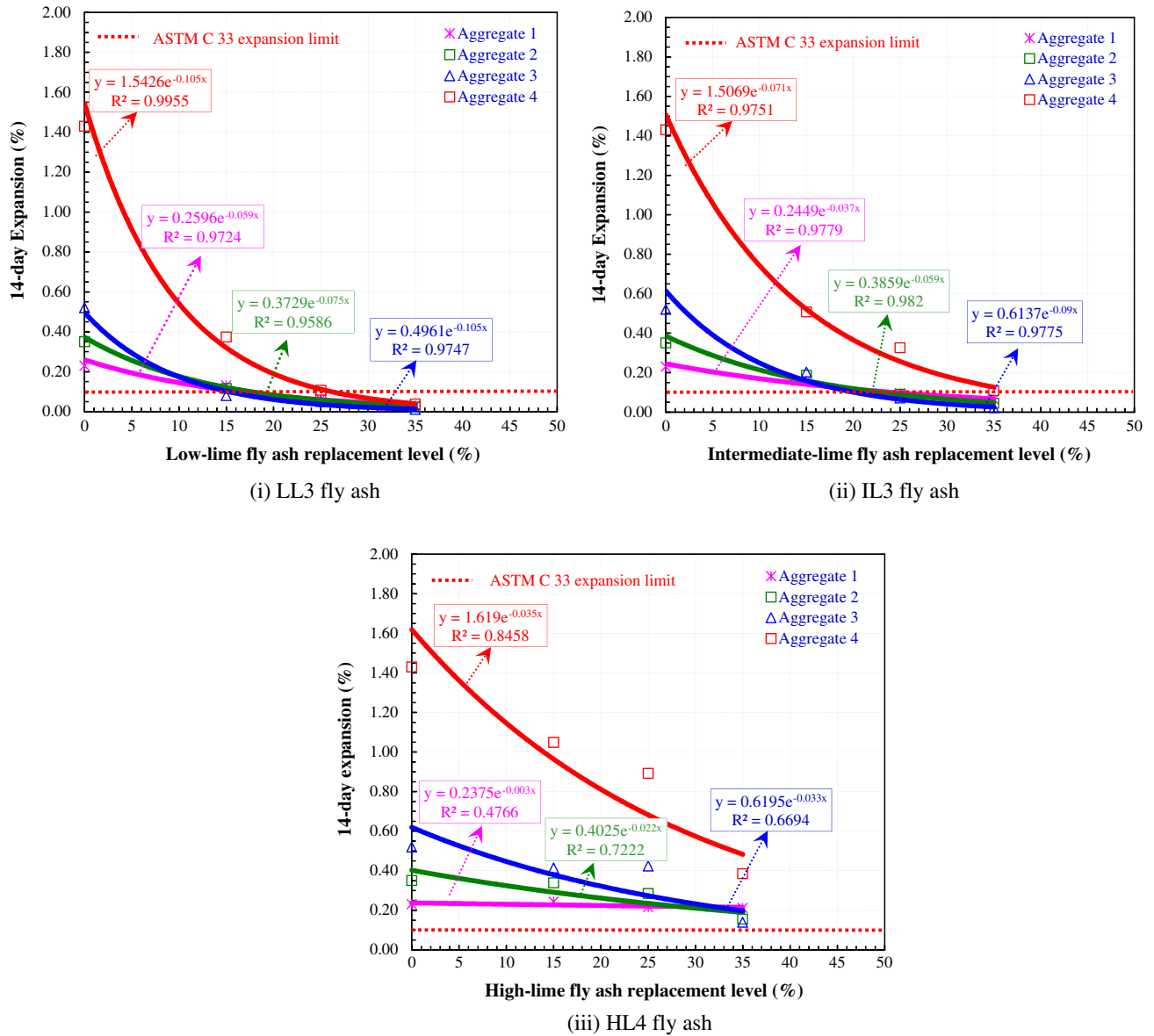


Fig. 2. Effect of replacement level of different fly ashes on 14-day expansion of mortars containing reactive aggregate.

CaO + MgO + SO₃ required for ASR mitigation below 0.10% was found to be 75% and 19.5%, respectively.

The combined effect of CaO + MgO + SO₃ and SiO₂ + Al₂O₃ + Fe₂O₃ on ASR mitigation was studied by determining the ratio of (CaO + MgO + SO₃)/(SiO₂ + Al₂O₃ + Fe₂O₃) and correlating it with the 14-day expansion as shown in Fig. 4(iii). As this figure shows, higher the CaO + MgO + SO₃ to SiO₂ + Al₂O₃ + Fe₂O₃ ratio higher is the expansion and a linear relationship exists between the two. For ASR mitigation below 0.10%, a CaO + MgO + SO₃ to SiO₂ + Al₂O₃ + Fe₂O₃ ratio of less than 0.22 in the fly ash were required.

5.2.2.2. As oxide equivalents. The oxide equivalents of fly ash considered include CaO_{equi} and SiO_{2equi}, which were calculated using the following formulas [20]:

$$\text{CaO}_{\text{equi}} = \text{CaO} + 0.905\text{Na}_2\text{O}_{\text{equi}} + 1.391\text{MgO} + 0.7\text{SO}_3 \quad (2)$$

$$\text{SiO}_{2\text{equi}} = \text{SiO}_2 + 0.589\text{Al}_2\text{O}_3 + 0.376\text{Fe}_2\text{O}_3 \quad (3)$$

where the co-efficients are molar ratios of CaO [in Eq.(2)] and SiO₂ [in Eq.(3)] to that of the individual oxides being considered.

The effect of these equivalents on the 14-day expansion is shown in Fig. 4(iv) and 4 (v). As these figures show, the 14-day expansion decreases with an increase in the SiO_{2equi} content and with a decrease in the CaO_{equi} content of the fly ash. Not only the trends of the SiO_{2equi} and CaO_{equi} of fly ash appear to be similar to that of the individual SiO₂ and CaO contents, respectively, but also the R-squared values were higher, indicating that oxide equivalents can be used as reliable indicators to estimate the 14-day expansion in fly ash mortars. For effective ASR mitigation in mortars containing fly ash at a cement replacement level of 25%, the quantity of SiO_{2equi} and CaO_{equi} shall be above 62% and below 22%, respectively. The effect of CaO_{equi} to SiO_{2equi} ratio on ASR mitigation as shown in Fig. 4(vi) indicated that the 14-day expansion increases with an increase in this ratio and effective ASR mitigation was achieved only when this ratio in the fly ash is below 0.30.

5.3. Effect of fineness of fly ash on ASR mitigation

In this section, results from investigation on evaluating the effect of fineness of fly ashes in mitigating ASR is presented and

discussed. Fly ashes with different fineness were obtained by using either ultrasonic sieving or planetary ball mill grinding operations. The mixtures containing the sieved and ground fly ash size-fractions are indexed with an S and a G notation in the graphs, respectively.

5.3.1. Sieving process

In this study, three fly ashes namely, HL3, IL3 and LL1 were considered. Upon ultrasonic sieving, the LL1 fly ash yielded four distinct size-fractions (S1 through S4), the IL3 fly ash yielded three size-fractions (S1, S2 and S3S4) and the HL3 fly ashes yielded two size-fractions (S1 and S2). Fig. 5(i), (iii) and (v) show the ASR expansion behavior of these sieved size-fractions of HL3, IL3 and LL1 fly ash mixtures and Fig. 5(ii), (iv) and (vi) show the comparison of their 14-day ASR expansion. In all these figures, the 14-day expansion of mortars containing the virgin fly ash and sieved fly ash size-fractions were found to be well below that of the control mortar.

As the Fig. 5(i) and 5 (ii) shows, within the high-lime fly ash mortars, the sieved fly ash size-fraction mortars (HL3–S1 and

HL3–S2) registered higher ASR expansion than their virgin fly ash (HL3) mortars, perhaps due to the higher average particle size of these size-fractions compared to that of their virgin fly ash. Within the two sieved size-fraction mortars, the finer fractions (HL3–S2) gave lower expansion than the coarser fraction (HL3–S1), indicating that the finer particles are more effective in ASR mitigation than the coarser ones. In addition, a ASR expansion below 0.10% was not achieved using any of the high-lime fly ash size-fractions. Since the finer fractions (HL3–S3S4 or HL3–S4) below HL3–S2 was not obtainable, the effect of particle size of high-lime fly ash on the ASR expansion cannot be clearly observed. Previous investigations have indicated that the addition of fine pozzolans in mortars or concrete improves the ability to bind alkalis, the dispersion ability and the pozzolanic reactivity, thereby improving the ASR mitigation potential in the mixture [6,13].

As the Fig. 5(iii) and 5 (iv) show, the virgin intermediate-lime fly ash registered a 14-day ASR expansion above the 0.10% limit. One of the mortars containing coarser size-fraction (IL3–S1) registered 45% higher expansion while the other containing finer size-fraction (IL3–S2 and IL3–S3S4) registered 17% and 58% lower expansions when compared to their virgin fly ash mortar. In addition, ASR mitigation was not achieved with coarser fly ash size-fraction (IL3–S1) while the same was achieved with finer fly ash size-fractions.

In the case of low-lime fly ash mortars as shown in Fig. 5(v) and 5 (vi), the expansion of the mortars containing virgin fly ash and its sieved size-fractions were below the expansion limit of 0.10% at 14 days immersion period. Mortars containing LL1–S1 and LL1–S2 fractions registered 164% and 32% higher expansion than their virgin fly ash mortars and those containing LL1–S3 and LL1–S4 fractions registered 3% and 29% lower expansion than their corresponding virgin fly ash mortars.

Overall from these findings, the smaller size-fractions of low-lime and intermediate-lime fly ashes (IL3 and LL1) not only appear to be more effective in reducing the ASR expansions than their larger size-fractions but also mitigated ASR, indicating that the sieving process can be considered beneficial in improving the ASR mitigation ability of both low-lime and intermediate-lime fly ashes. However, such a trend was not clearly observed with high-lime fly ashes due to difficulty in obtaining finer fractions through the ultra-sonic sieving method.

5.3.2. Grinding process

In this study, five fly ashes namely, LL1, IL3, IL4, HL1 and HL4 were considered. Each fly ash was ground to two levels of fineness (G1 and G2) by subjecting it to grinding in a planetary ball mill operating at a speed of 250 rpm for a period of 15 or 60 min. Fig. 6(i) through (v) shows the ASR expansion behavior of mortars containing ground fly ash size-fractions. These figures clearly indicate that regardless of the oxide content of the fly ash, the ground fly ashes performed better in reducing the ASR expansions than their corresponding virgin fly ashes. Between G1 and G2 levels of grinding, some fly ashes (HL4, IL4, and LL1) showed improved performance with higher fineness (G2). However with other fly ashes (HL1 and IL3), both levels of grinding provided similar levels of ASR mitigation. This could be because, higher grinding energy level (G2) is more effective in reducing the particle size of certain fly ashes beyond G1 while the same is less effective in reducing the particle size of some others primarily due to the variation in the hardness of the fly ash.

The effectiveness of grinding of fly ashes in mitigating ASR can be distinctly observed by comparing the 14-day expansion of mortars containing these ground fly ash size-fractions as shown in Fig. 7. As this figure shows, the 14-day expansion of mortars containing the ground fly ash size-fractions was found to be substantially lower than that of their respective virgin fly ashes. The

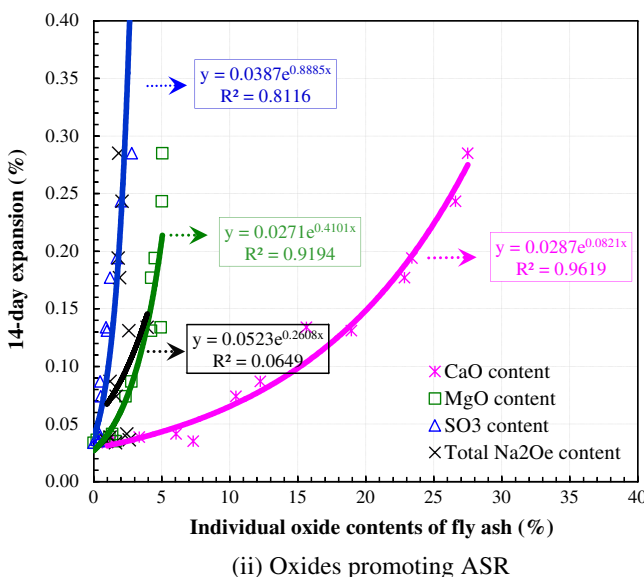
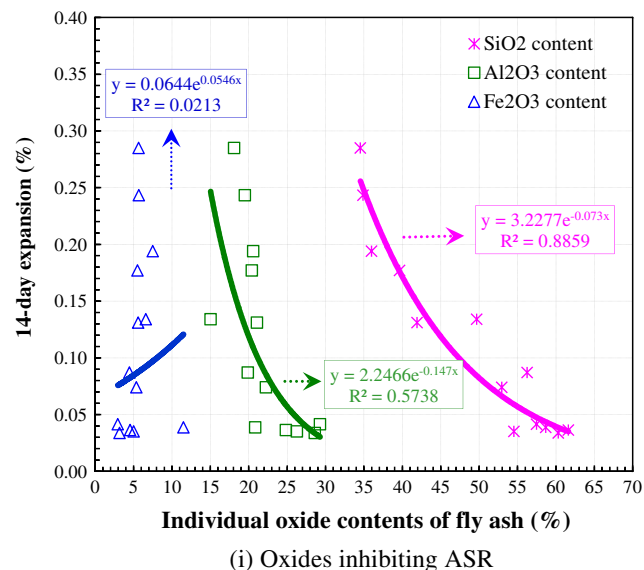


Fig. 3. Effect of individual oxides of fly ash that inhibit and promote ASR expansion in mortars containing 25% replacement level of fly ash for cement.

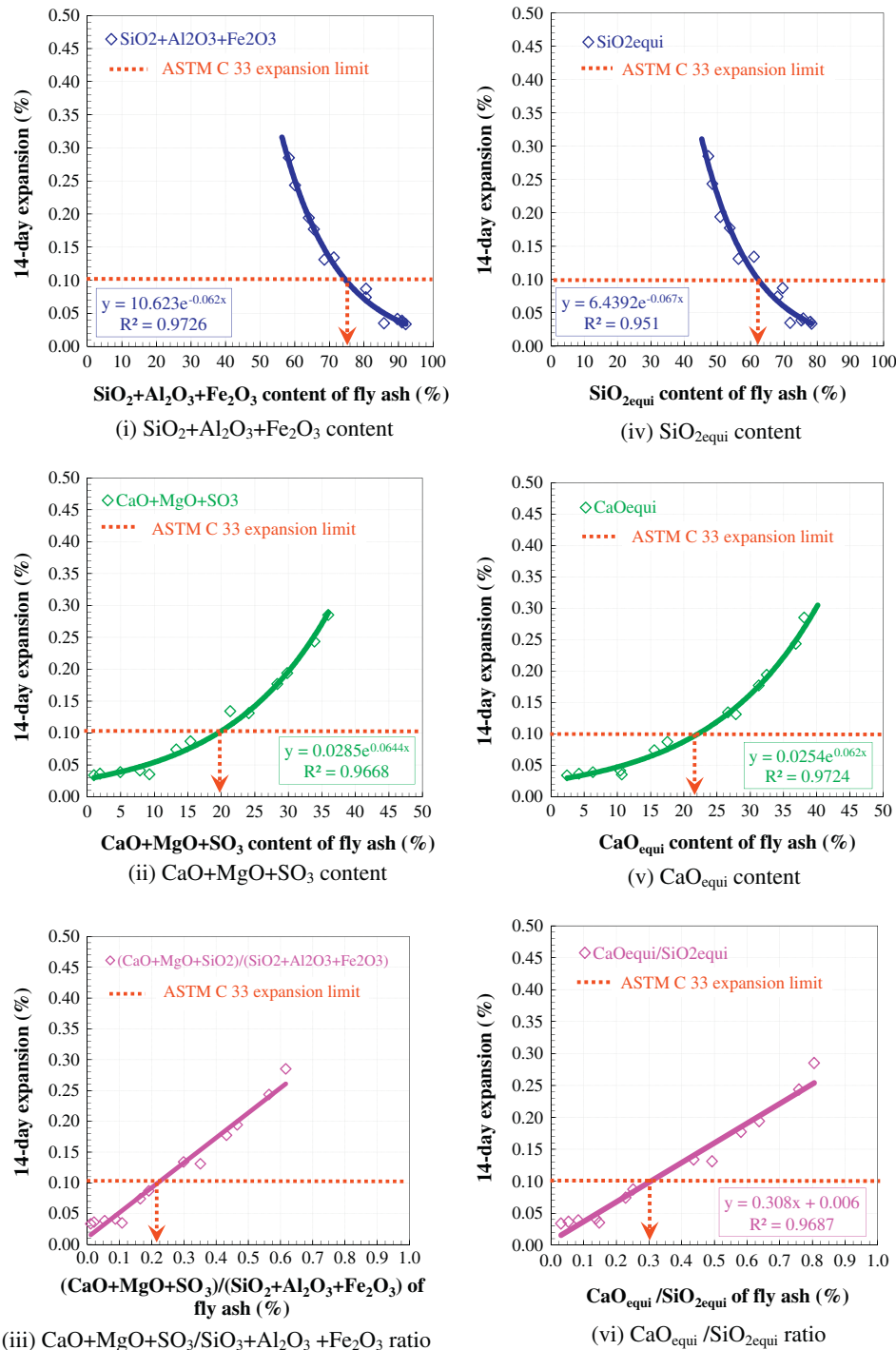


Fig. 4. Effect of combined oxides and oxide equivalents of fly ash on ASR expansion at a fly ash replacement level of 25%.

percentage reduction in the ASR expansion due to G1 and G2 levels of grinding was found to be 50% and 66% for HL4, 40% and 46% for HL1, 41% and 80% for IL3, 36% and 43% for IL4, and 12% and 79% for LL1, respectively. In addition, it is interesting to note that the ASR expansion below 0.10% limit was achievable with all the ground fly ash size-fractions, indicating that the process of grinding fly ash is beneficial in mitigating ASR in mortars containing fly ashes having any chemical composition.

In the case of high-lime fly ashes, ASR mitigation was observed only by using the well ground size-fractions (HL4-G2 and HL1-G2), indicating that higher grinding levels are required for mitiga-

tion in these fly ash mortars. In the case of intermediate-lime fly ashes, ASR mitigation was achieved using both the G1 and G2 ground size-fractions (IL3-G1, IL3-G2, IL4-G1 and IL4-G2), indicating that the ASR mitigation is possible even with lower grinding levels. In the case of low-lime fly ashes, ASR mitigation was achieved using both virgin and ground fly ash size-fractions, indicating that the grinding of fly ash is not required to mitigate ASR. Alternatively, the well ground size-fractions (G2) of the intermediate and low-lime fly ashes, which registered very low ASR expansion, can be used at a replacement level lower than 25% to mitigate ASR.

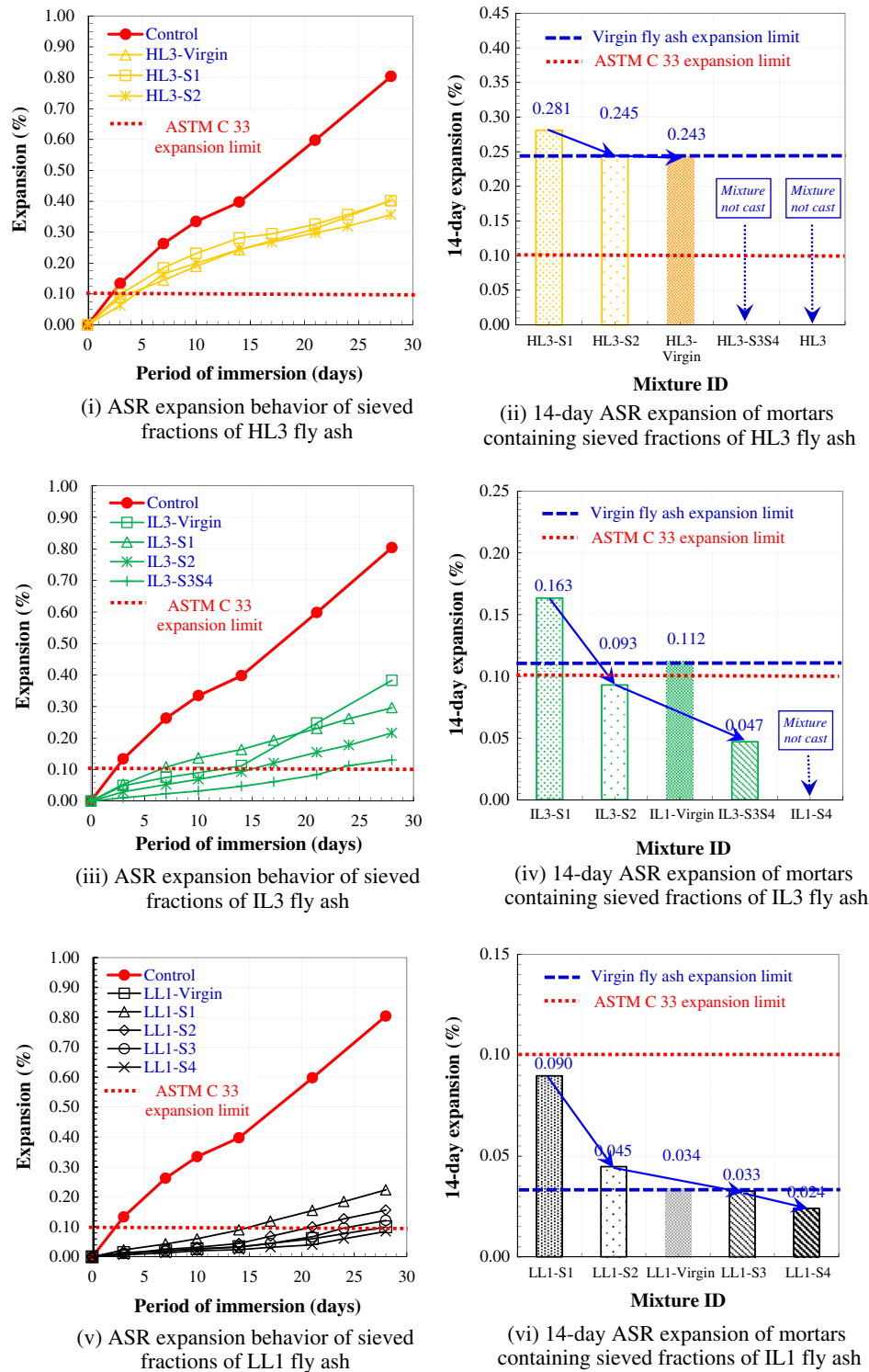


Fig. 5. ASR expansion behavior of mortars containing sieved fly ash fraction at a constant fly ash replacement level of 25%.

Based on the observations made in the previous sections, it can be assessed that both sieving and grinding of fly ashes had a very positive impact on their ability to mitigate mortar bar expansion in the ASTM C 1567 test. Considering the difficulty faced in sieving the fly ashes to achieve different size fractions and the relative ease with which fly ashes can be ground, the process of grinding fly ashes to required fineness appears to be a practical approach to facilitate the use of intermediate and high-lime fly ashes in ASR mitigation.

5.4. Effect of particle size of fly ash on ASR mitigation

The effect of average particle size of fly ash on the 14-day expansion of fly ash mortars is shown in Fig. 8(i). As this figure shows, the 14-day expansion was found to decrease with decrease in the average particle size of fly ash. An ASR expansion below 0.10% was observed with the HL4, HL1, IL3 and IL4 using particle sizes lower than 5.85, 6.64, 10.37 and 12.77 μm , respectively. For LL1, even the virgin fly ash was able to mitigate ASR below

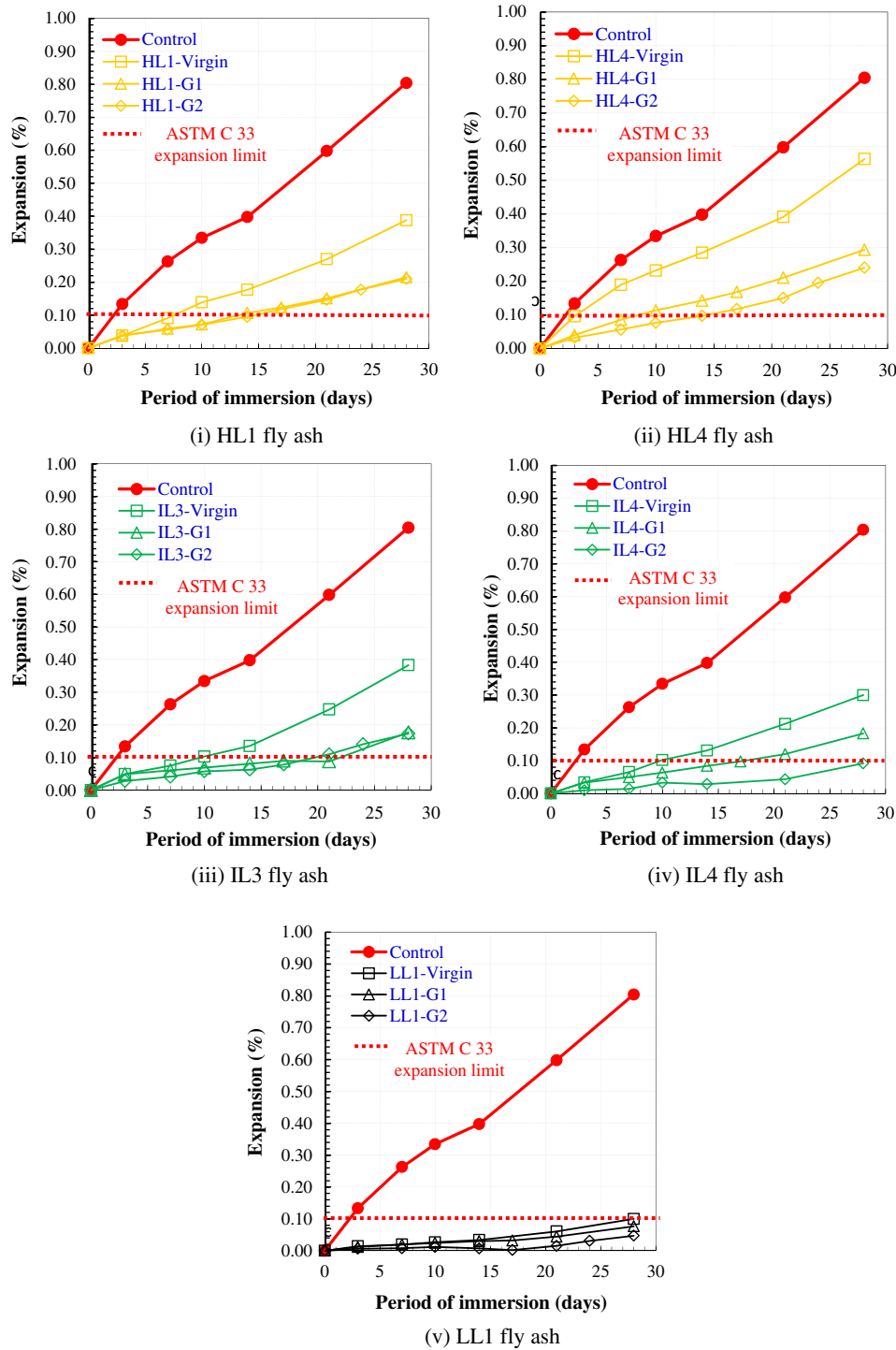


Fig. 6. ASR expansion behavior of mortars containing ground fly ash fractions at a constant fly ash replacement level of 25%.

0.10%. The maximum particle size required to mitigate ASR was also observed to increase with decrease in the lime-content of the fly ash, i.e., a fly ash containing higher lime content requires lower particle size while that containing lower lime content can mitigate ASR even at a higher particle size. In addition, a logarithmic trend was found to exist between the two by closely fitting all the data points, with highly reliable R -squared values ranging between 0.96 and 1.00. The general form of this trend can be written as follows:

$$y = a \cdot \ln(x) + b \quad (4)$$

where y is the 14-day ASR expansion of the fly ash mortars, x is the average particle size of fly ash particles and a and b are constants.

The trends observed within the five fly ashes, HL1, HL4, IL3, IL4 and LL1 having decreasing lime content appears to follow logarithmic pattern, with the only difference being in the values of their constant. The trends observed with all fly ashes except LL1, converge themselves at an approximate average particle size of 3 μm , where the 14-day mortar bar expansion is equal to 0%. In the case of LL1, a 0% 14-day mortar bar expansion was achieved with an average particle size of approximately 6 μm . A closer look at the constants 'a' and 'b' in the logarithmic expression for the

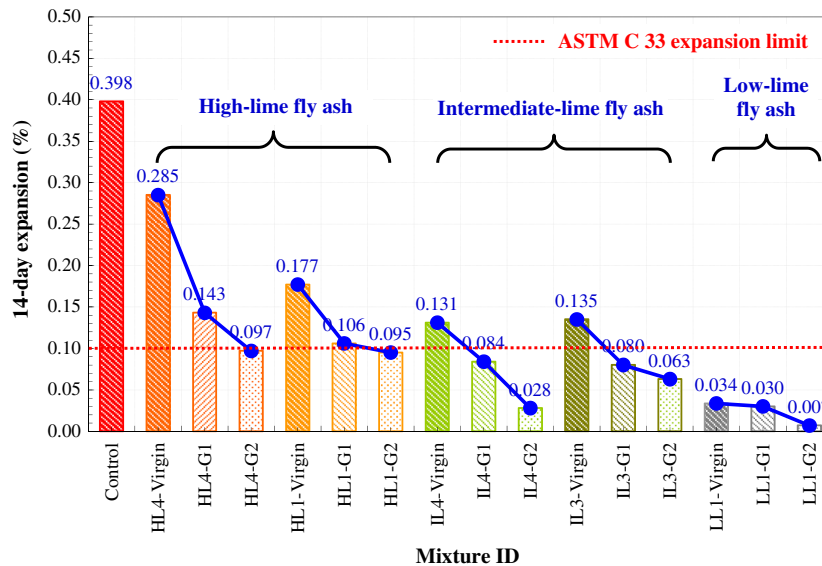


Fig. 7. Effect of grinding of fly ash on the 14-day mortar bar expansion.

mortars containing all the five fly ashes imply that these constants are primarily functions of the chemical composition (or lime content) of these fly ashes. In other words, by knowing the lime content of fly ash, it is possible to use interpolation for obtaining the value of these constants as shown in Fig. 8(ii). As this figure shows, the values of 'a' and 'b' do not change up to a lime content of 5%. Between a lime content of 5% and 10%, only a marginal change in their values was observed, indicating that the low-lime fly ashes are less influenced by these constants. However beyond 10%, a substantial increase or decrease in the values of 'a' or 'b' was observed, indicating that the expressions for the intermediate-lime and high-lime fly ashes were highly dependent on these constants. This figure can be helpful in individually separating the effect of particle size of fly ash from the effect of chemical composition of fly ash on ASR mitigation.

5.5. Individual effect of particle size and the chemical composition of fly ash on ASR mitigation

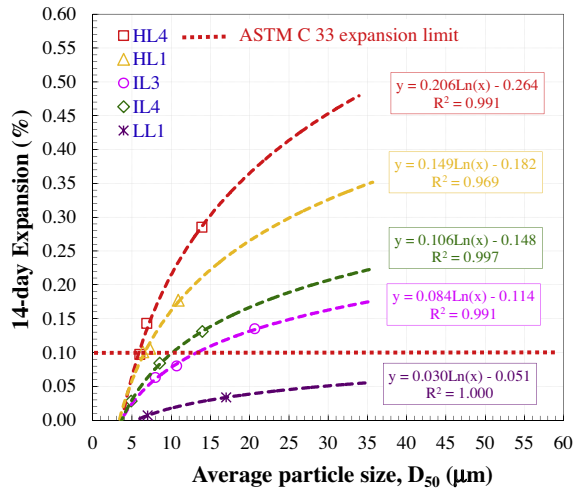
It is often misunderstood that the effect of variation in the particle size of virgin fly ashes from different coal power plants has negligible effect on the ASR expansion of mortars containing them. The previous section has clearly demonstrated the importance of particle size of fly ash on ASR mitigation and; hence, the effect of chemical composition of virgin fly ashes on ASR mitigation discussed in Section 5.2 can be strictly considered to be due to both their chemical composition and particle size. This is because the particle size of 13 virgin fly ashes used in that section was not the same and varied widely between ~ 10 and $30 \mu\text{m}$ as shown in Table 3. Understanding the individual effect of chemical composition and particle size of fly ash on ASR mitigation is important because the degree to which a fly ash needs to be ground to achieve ASR mitigation was found in the previous section to be a function of both. Specifically in the case of high-lime and intermediate-lime fly ashes where the mitigation is not usually possible at normal cement replacement levels of 25% (by mass), the process of grinding the fly ash to finer size-fractions can serve as an effective mitigation strategy.

Their individual effect on ASR mitigation was accomplished by fixing an average particle size for all the fly ashes and then determining the effect of their chemical composition on ASR mitigation

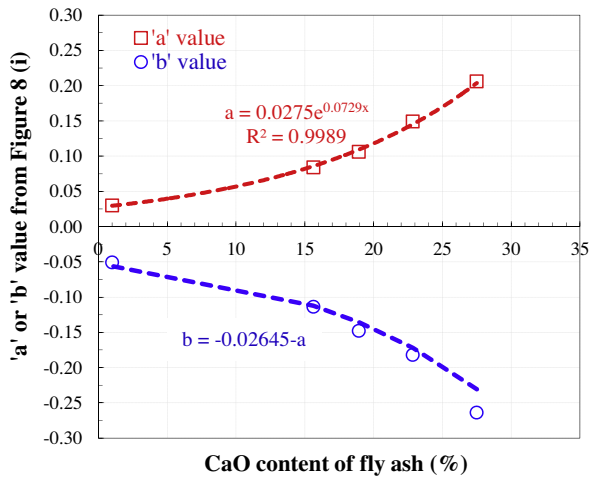
for that size. This is performed by determining the values of 'a' and 'b' as shown in the Fig. 8(ii) based on their lime content either through interpolation or extrapolation for each of the 13 fly ashes considered in Section 5.2. By this method, the 14-day expansion for each of the fly ash mortars namely, y_5 , y_{10} , y_{15} , y_{20} and y_{30} having a constant fly ash particle size of 5, 10, 15, 20 and $30 \mu\text{m}$, respectively, can be obtained as shown in Table 6. The values from this table was used to plot the individual effect of SiO_2 , CaO , $\text{SiO}_{2\text{equi}}$, CaO_{equi} , $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and $\text{CaO} + \text{MgO} + \text{SO}_3$ contents of fly ash on ASR expansions as shown in Fig. 9(i) through (vi). These specific individual and combined oxides were chosen as they were found in the previous sections to have a good relationship with the ASR expansions.

As the Fig. 9(i) shows, the 14-day ASR expansion of the fly ash mortars were found to decrease with an increase in the SiO_2 content of the fly ash as already observed in the Fig. 3(i). A comparison of these two figures indicate that the Fig. 9(i) is an improvised version of the Fig. 3(i), with highly reliable R -squared values obtained by appropriately considering and adjusting the expansions for a constant average particle size of fly ash. In addition, the 14-day ASR expansions appear to decrease with decrease in the average particle size of the fly ash from $30 \mu\text{m}$ to $5 \mu\text{m}$. For the fly ashes having average particle size ranging from $30 \mu\text{m}$ to $10 \mu\text{m}$, not only an exponential trend existed but also most part of the curve was found to be above the 14-day ASR expansion limit of 0.10%, indicating that high SiO_2 content in the fly ash is required for ASR mitigation. However for the fly ashes having average particle size below $10 \mu\text{m}$, the trend appears to change from exponential to logarithmic with highly reliable R -squared values and with most part of the curve below the limited expansion of 0.10%, indicating that low SiO_2 content in the fly ash is sufficient for ASR mitigation. The minimum quantity of SiO_2 content in the fly ash for ASR mitigation in mortars containing fly ashes having an average particle size of 30, 20, 15, 10 and $5 \mu\text{m}$ was found to be 54% 51% 49% 45% and 37%, respectively. This clearly implies that lower SiO_2 is sufficient to mitigate ASR especially when finer fly ash particles are used.

Fig. 9(iii) and (v) show the individual effect of $\text{SiO}_{2\text{equi}}$ and $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ contents of fly ash on the 14-day ASR expansion and this trend was found to be similar to the SiO_2 content of fly ash as shown in the Fig. 9(i) except that the $\text{SiO}_{2\text{equi}}$ and $\text{SiO}_2 +$



(i) Average particle size vs 14-day ASR expansion



(ii) Relationship between lime content and constants 'a' or 'b'

Fig. 8. Effect of particle size of different fly ashes of varying chemical composition on ASR expansion of mortars containing 25% replacement level of fly ash for cement.

$\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ contents of fly ash represent the combined oxides, with a higher R -squared values almost approaching unity. The minimum quantities of $\text{SiO}_{2\text{equi}}$ and $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ in the fly ash for ASR mitigation were found to decrease with an increase in its average particle size. For example, the minimum quantities of $\text{SiO}_{2\text{equi}}$ for ASR mitigation was found to be 69%, 67%, 64%, 60% and 50% while that of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ was found to be 83%,

79%, 77%, 72% and 62% for fly ashes having an average particle size of 30, 20, 15, 10 and 5 μm , respectively.

The Fig. 9(ii) shows the individual effect of CaO content of fly ash on the 14-day ASR expansion of its mortars. As this figure shows, the 14-day ASR expansion of the fly ash mortars were found to increase with an increase in the CaO content of the fly ash as already observed in the Fig. 3(ii). A comparison of these two figures indicates that the Fig. 9(ii) is an improvised version of the Fig. 3(ii), with higher R -squared values approaching unity. In addition, for the fly ashes having average particle size ranging from 30 μm to 10 μm , an exponential relationship exist and most part of the curve was above the limited 14-day ASR expansion of 0.10%, indicating that low CaO content in the fly ash is required for ASR mitigation. However for the fly ashes having average particle size below 10 μm , the exponential relationship appears to change to a linear one with most part of the curve below the limited expansion of 0.10%, indicating that ASR mitigation can be achieved even with fly ashes containing higher CaO content. This is especially beneficial when one has to consider using high-lime or intermediate-lime fly ashes for mitigating ASR. The maximum quantity of CaO content in the fly ash for ASR mitigation in mortars containing fly ashes having an average particle size of 30, 20, 15, 10 and 5 μm was found to be 9%, 11%, 13%, 16% and 25%, respectively. This clearly implies that ASR mitigation can be accomplished using fly ashes having higher CaO content by appropriately grinding them to suitable size-fractions.

The Fig. 9(iv) and (vi), showing the individual effect of CaO_{equi} and $\text{CaO} + \text{MgO} + \text{SO}_3$ contents of fly ash on the 14-day ASR expansion was found to be similar to that of the CaO content of fly ash except that the former represent the effect of combined oxides with more reliable R -squared values approaching unity. The maximum quantities of CaO_{equi} and $\text{CaO} + \text{MgO} + \text{SO}_3$ in the fly ash for ASR mitigation were found to decrease with an increase in its average particle size. For example, the maximum quantities of CaO_{equi} for ASR mitigation was found to be 14%, 17%, 20%, 24% and 35% while that of $\text{CaO} + \text{MgO} + \text{SO}_3$ was found to be 11%, 15%, 17%, 21% and 32% for fly ashes having an average particle size of 30, 20, 15, 10 and 5 μm , respectively.

The minimum and maximum quantity of the individual and combined oxides in the fly ash required for ASR mitigation is shown in Fig. 10. As this figure shows, the SiO_2 , $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and $\text{SiO}_{2\text{equi}}$ of the fly ash can be decreased or the CaO, $\text{CaO} + \text{MgO} + \text{SO}_3$ and CaO_{equi} of the fly ash can be increased while still achieving ASR mitigation below 0.10% by suitably altering the average particle size of the fly ash. Thus, this figure gives an option to the users to pick fly ash based on their oxide composition and appropriate average particle size depending up on the availability

Table 6

Data from the interpolation and extrapolation of Fig. 8.

Fly ash ID	Constant from the Fig. 8 (i)		Calculated 14-day ASR expansions for specific particle size of fly ash (%)				
	a	b	y_5	y_{10}	y_{15}	y_{20}	y_{30}
LL1	0.030	-0.052	-0.0029	0.0180	0.0303	0.0390	0.0512
LL2	0.030	-0.051	-0.0028	0.0181	0.0303	0.0390	0.0513
LL3	0.031	-0.052	-0.0015	0.0203	0.0330	0.0420	0.0548
LL4	0.037	-0.057	0.0027	0.0282	0.0432	0.0538	0.0687
LL5	0.041	-0.060	0.0055	0.0338	0.0504	0.0622	0.0788
IL1	0.055	-0.074	0.0151	0.0533	0.0756	0.0915	0.1138
IL2	0.066	-0.084	0.0222	0.0679	0.0947	0.1136	0.1404
IL3	0.091	-0.108	0.0388	0.1023	0.1394	0.1657	0.2028
IL4	0.123	-0.139	0.0591	0.1445	0.1945	0.2299	0.2798
HL1	0.169	-0.184	0.0883	0.2055	0.2740	0.3226	0.3912
HL2	0.187	-0.201	0.0996	0.2293	0.3051	0.3589	0.4348
HL3	0.222	-0.235	0.1215	0.2751	0.3650	0.4288	0.5187
HL4	0.236	-0.249	0.1302	0.2935	0.3890	0.4568	0.5523

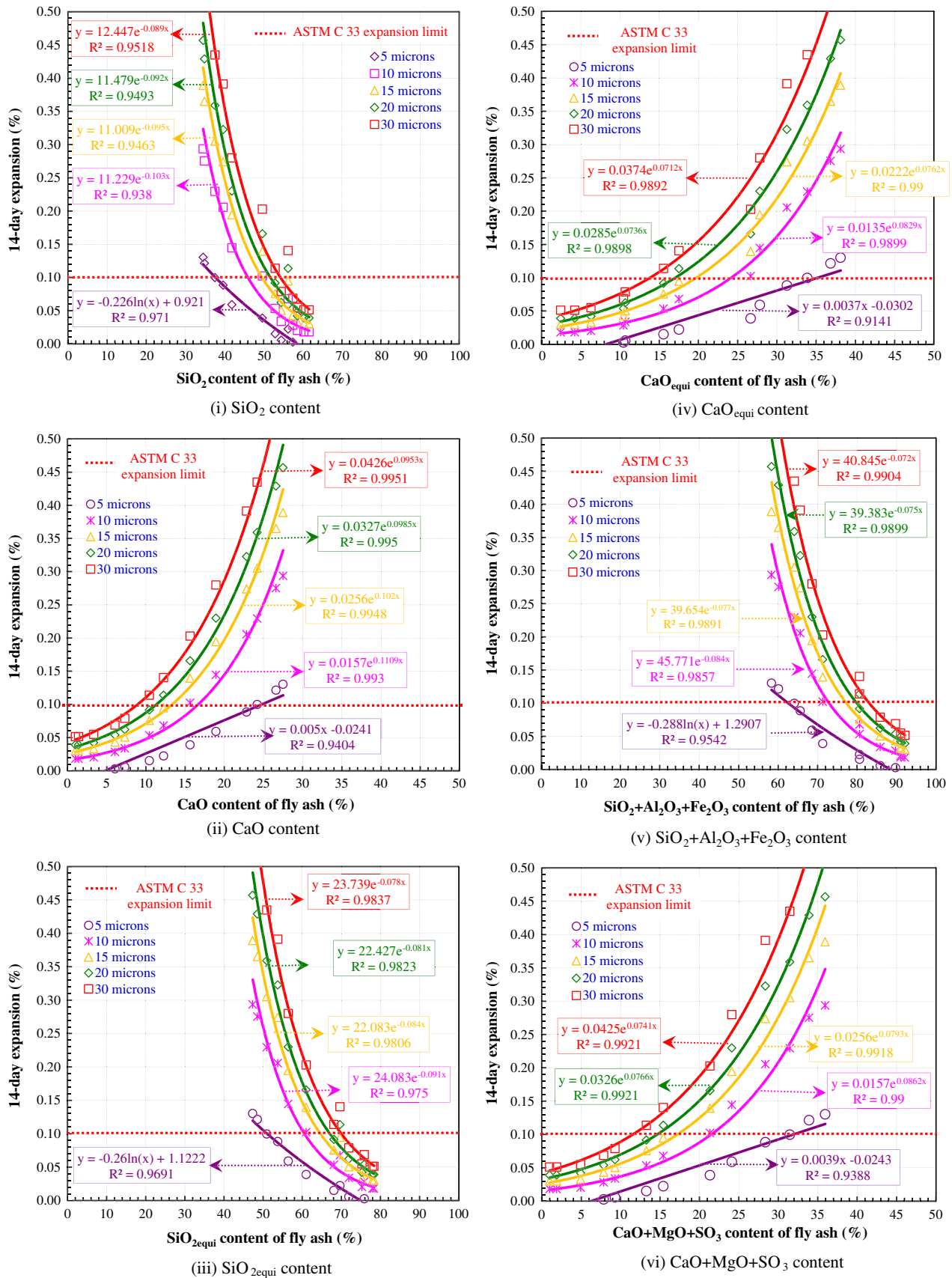


Fig. 9. Individual effects of particle size and chemical composition of fly ash on 14-day expansion of mortars containing 25% replacement level of fly ash for cement.

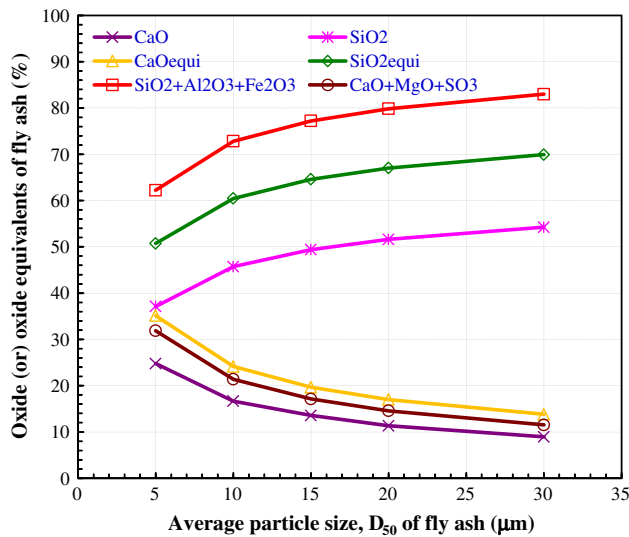


Fig. 10. Maximum or minimum allowable oxide content of fly ash based on particle size for ASR mitigation evaluated at a 25% replacement level of fly ash for cement.

of fly ash in a geographical location, its properties and the practicality of grinding it to finer fractions.

6. Conclusions

Fly ashes vary significantly in their oxide contents and fineness, and their ability to mitigate ASR distress has been found to be dependent on these properties. The main goal of this paper is to determine and decouple the individual effects of chemical composition and fineness of fly ashes in mitigating ASR. To accomplish the main objectives, 13 fly ashes of widely varying oxide contents and fineness were chosen to mitigate ASR in mortars containing Spratt reactive aggregate. Selected fly ashes were used in original, sieved and ground forms at a nominal replacement level of 25% by mass of cement. The ASTM C 1567 test method was used all throughout the study to determine the expansions in fly ash mortars. Correlations were then obtained based on least square best fitting. Having used different fly ashes, a standard reactive aggregate and a standard test method, this study can be expected to provide approximate solutions for ASR distress in many applications. However, it should be remembered that the correlations obtained are for the specific reactive aggregate and fly ash replacement level used in this study. Extension of these findings to other aggregates and other fly ashes may need additional validation. The salient conclusions from this study are listed below:

- (1) The effect of oxide composition of fly ash on ASR expansion suggested that specific oxides in fly ash such as SiO₂, CaO, MgO and SO₃ had a good correlation with the 14-day ASR expansion. In addition, the combined oxides in the fly ash had a better correlation with the ASR expansion than its individual oxides. Though other oxides in the fly ash such as Al₂O₃ and Fe₂O₃ individually were not found to correlate well with the ASR expansion, a better correlation was observed when these oxides were combined with others, indicating that these oxides indirectly contribute to reduction in ASR expansions.
- (2) The effect of fineness of fly ash on ASR expansion indicated the following:

- The finer size-fractions of sieved and ground fly ash gave lower expansions than their corresponding coarser size-fractions, indicating that the fineness of fly ash significantly influences ASR mitigation.

- In the case of sieved fly ash size-fractions, the beneficial effect of using a finer fly ash to mitigate ASR was observed only with low-lime and intermediate-lime fly ashes and not with high-lime fly ash.
- In the case of ground fly ash size-fractions, the beneficial effect of using a finer fly ash to mitigate ASR was observed with all the fly ashes used. This indicates that the process of grinding can be used as an effective strategy to employ a wide variety of fly ash compositions to help mitigate ASR. Also, grinding employs the entire fly ash and does not result in additional waste or residue of coarser fly ash as is the case with sieving fly ashes.

(3) From the individual effect of particle size and chemical composition of fly ash on ASR expansion, the following conclusions can be drawn:

- Within the usual range of the average particle size of fly ash between ~10 to 30 μm , the ASR expansion was observed to have an exponential relation with the specific oxides of fly ash namely, SiO₂, CaO, SiO₂ + Al₂O₃ + Fe₂O₃, CaO + MgO + SO₃, SiO_{2equi} and CaO_{equi}.
- For fly ashes having an average particle size below ~10 μm , the ASR expansion was observed to be a linear function of CaO, CaO + MgO + SO₃, and CaO_{equi} of fly ash and a logarithmic function of SiO₂, SiO₂ + Al₂O₃ + Fe₂O₃ and SiO_{2equi} of fly ash. For fly ashes having an average particle size below 5 μm , it can be concluded that the ASR expansion of almost all mortars containing fly ash were found to be below 0.10% expansion limit, indicating that ASR mitigation is possible with all fly ashes.

Acknowledgements

The authors would like to thank the Office of Naval Research and the Naval Facilities Engineering Service Center (NAVFAC ESC) for providing support to conduct this research. Also the authors would like to extend their gratitude to the fly ash suppliers for this project including Headwater Resources, DBA Salt River Materials Group, Nebraska Ash Company and Separation Technologies, LLC.

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