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Alkali silica reactivity of agglomerated silica fume

Andrew J. Maas [a], Jason H. Ideker [b], Maria C.G. Juenger [b,*]

[a] The Structural Alliance, 9401 LBJ Freeway, Suite 107, Dallas, TX 75243, USA
[b] Department of Civil, Architectural, and Environmental Engineering, The University of Texas at Austin, 1 University Station C 1748, Austin, TX 78712, USA

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Abstract

It is commonly accepted that replacement of a portion of cement in mortar or concrete with well-dispersed silica fume reduces expansion caused by alkali silica reaction. Recently there has been much discussion that large, agglomerated particles of silica fume may actually act as alkali silica reactive aggregates, thereby increasing expansion rather than reducing it. The data in the literature, from both field and laboratory studies, are inconsistent. This prompted an extensive laboratory investigation into the alkali silica reactivity of silica fume. Results from accelerated expansion testing and microscopic investigations are presented. It was seen that some agglomerated silica fumes participate in ASR while others do not. Factors determining the reactivity of silica fume agglomerates are suggested.

Keywords: Accelerated testing; Alkali–aggregate reaction; Mortar; Pozzolan; Silica fume; SEM

1. Introduction

Alkali silica reaction (ASR) causes premature deterioration in concrete. Alkali hydroxides present in concrete pore solution react with amorphous or poorly crystalline silica phases in aggregates, forming a gel which imbibes water and expands. Alkali silica reaction was first recognized in the field in 1940 by Stanton [1] and cases have since been documented around the world. It is easily reproduced in the laboratory and can be monitored in a variety of ways, the most common being through expansion measurements on mortar or concrete prisms and petrographic analysis.

Some of the most effective methods of mitigating expansion due to ASR involve replacement of a portion of cement with one or more pozzolanic materials. Silica fume, though not often used solely for this purpose, can be used to reduce ASR expansion. Laboratory studies have found ASR expansion to decrease with increasing amounts of silica fume (see Ref. [2], for example). This may seem contrary to logic because silica fume is made of amorphous silica, as are many reactive aggregates. It would seem that silica fume should react with alkali hydroxides to form ASR gel. However, silica fume and reactive aggregates are significantly different in size. Individual silica fume particles have an average diameter of 0.1 μm. Aggregates range in size from a few micrometers to several centimeters. Silica fume reacts in a pozzolanic manner with cement pore solution to form non-expansive calcium silicate hydrate (C–S–H), while siliceous aggregates react with alkali hydroxides in the pore solution to form expansive ASR gel. In fact, it has been observed that alkali silica reactive aggregates will behave as pozzolans when finely ground [3]. One of the more commonly accepted mechanisms for the reduction of ASR expansion by supplementary cementing materials (SCM), including silica fume, is based on this pozzolanic reaction. It has been suggested that the C–S–H formed by the pozzolanic reaction has a low ratio of CaO to SiO_2 (C/S). The formation of this C–S–H depletes calcium hydroxide (CH) in the cement paste and the low C/S enables entrapment of alkalis, both of which reduce the amount of hydroxyl ions available to participate in the alkali silica reaction [4].

One of the greatest advantages of using silica fume in concrete results from its small size; the addition of silica fume widens the size distribution of the cementitious particles in concrete, allowing more efficient particle packing, densifying the interfacial transition zone and converting CH into C–S–H, thus increasing strength. However, this small particle size makes silica fume difficult to transport and distribute. Producers

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* Corresponding author.
E-mail address: mjuenger@mail.utexas.edu (M.C.G. Juenger).

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Table 1
Composition and properties of cement and silica fume

Oxide percent	Cement A	Cement B	Cement C	Silica fume A	Silica fume B	Silica fume C	Silica fume D
SiO_2	19.71	20.1	19.27	84.02	94.28	94.69	93.47
Al_2O_3	5.13	5.36	5.08	0.37	0.04	0.21	0.30
Fe_2O_3	2.81	2.62	3.08	4.44	0.06	0.12	0.12
CaO	62.07	62.15	61.45	0.64	0.51	0.71	0.52
MgO	2.56	2.94	2.64	0.80	0.57	0.29	0.29
Na_2O	–	–	0.24	0.38	0.06	0.05	0.24
K_2O	–	–	0.93	1.73	0.99	0.62	0.38
Na_2O eq.*	0.89	0.91	0.85	1.52	0.71	0.46	0.49
TiO_2	–	–	0.22	0.03	0.02	0.01	0.02
MnO_2	–	–	0.07	0.22	0.07	0.05	0.03
P_2O_5	–	–	0.17	0.04	0.12	0.08	0.07
SrO	–	–	0.20	0.01	0.01	0.01	0.01
BaO	–	–	0.03	0.02	0.02	0.02	0.01
SO_3	3.94	4.03	4.19	0.79	0.16	0.10	0.05
Loss on ignition (%)	1.94	1.03	2.41	6.51	3.01	3.05	4.50
Bulk density (kg/m^3)	–	–	–	196.43	827.28	702.31	–

*Na_2O equivalent=% Na_2O+0.658·% K_2O.

therefore generally pelletize or densify the silica fume, agglomerating the small individual particles into relatively large clumps containing millions of particles and measuring up to several millimeters in size. Pelletized silica fume is always interground with cement before use, thereby eliminating large clumps. Densified silica fume is added to concrete as is. The large, agglomerated particles are generally assumed to break apart during the mixing of concrete, but this is not always the case [5,6], particularly in the absence of superplasticizers.

It has been suggested that these large silica fume agglomerates behave as reactive aggregates rather than as pozzolans, and actually aggravate ASR [6,7]. Several laboratory and field investigations have been conducted, with many conflicting results. These have been reviewed by the authors elsewhere [8,9]. Briefly, many tests have shown evidence of reactions in silica fume agglomerates through microscopy, the product of which may be ASR gel or a form of low-calcium C–S–H [6,8,10–16]. Some have shown cracking when agglomerates are present [10–14]. A few have shown increased expansion in laboratory specimens due to silica fume [14,17–19]. Yet some show decreased expansion in laboratory specimens with agglomerated silica fume [8,14,15,19–22]. The inconsistency in results indicates that perhaps silica fume agglomerates only participate in ASR under certain conditions, or only certain types of agglomerates are reactive. Given the serious consequences of damage in concrete structures due to alkali silica reaction involving silica fume agglomerates, it is certainly an area that merits further investigation.

In this paper, data are presented for three types of silica fume using known reactive and non-reactive aggregates. Mortar prisms were subjected to accelerated testing conditions for alkali silica reaction (ASTM C 1260 [23] and ASTM C 227 [24]) and expansions were measured. The agglomerates and mortars were also examined using scanning electron microscopy (SEM).

2. Experimental materials and methods

Mortar prisms were made according to the procedures in ASTM C 1260 [23] and ASTM C 227 [24]. The cement used in this study was a Type I, according to ASTM C 150 [25] classification. An oxide analysis of the cement, from the supplier's mill sheet, is presented in Table 1, labeled cement A. Cements B and C in Table 1 were used in previous and follow-up studies, respectively. These are from the same supplier as cement A but were from different batches because testing was performed at different times. The oxide analysis for cement B is from the supplier's mill sheet. The oxide analysis for cement C was performed by an independent testing lab using X-ray fluorescence. Results using different cements will be presented and discussed separately.

Aggregates from several sources were chosen for their different levels of reactivity in ASTM C 1260 testing. Two non-reactive aggregates were tested and labeled NR-1 and NR-2. NR-1 was used for most of the testing described herein and is a manufactured dolomitic sand. NR-2 was used in selected testing; it is a natural dolomitic carbonate sand. A reactive aggregate, labeled R, was used; it is a siliceous and limestone sand. A highly reactive aggregate, HR, was used in selected testing; it is a siliceous natural sand.

The aggregate gradation is specified by ASTM C 1260 and ASTM C 227 and is shown in Table 2. The aggregate-to-cement ratio specified by both standard test methods is 2.25 (by mass). The water-to-cement ratio (*w*/*c*) is specified by ASTM C 1260 as 0.47 (by mass). ASTM C 227 specifies a variable *w*/*c* be used, with mortar flow being constant. However, a *w*/*c* of 0.47 (by mass) was used for both test methods for consistency.

Three types of silica fume were tested for this study; oxide analyses of these materials are presented in Table 1 (X-ray fluorescence testing was performed by an independent laboratory). Silica fume A is undensified. Silica fume B is a commercially available densified silica fume. Silica fume C is also densified, but from a different supplier. The bulk densities listed in Table 1 were measured using ASTM C 29 [26]. Size distributions for the silica fumes are shown in Table 2; these were obtained by dry-sieving. The undensified silica fume was used as is, and all of the particles passed the No. 100 sieve (100 μm). Silica fume B contained agglomerates; the particle size distribution is shown in Table 2. Silica fume C was agglomerated with the particles having a very tight size distribution. The smallest agglomerates were removed so that all agglomerates used in testing passed the No. 30 sieve

Table 2
Particle size distribution of silica fume (SF) and aggregate (percent retained on sieve)

ASTM sieve size	SF A (%)	SF B (%)	SF C (%)	SF D (%)	Aggregate (all) (%)
No. 8 (2.36 mm)	0	0.2	0	10	10
No. 16 (1.18 mm)	0	0.3	0	25	25
No. 30 (600 μm)	0	0.3	0	25	25
No. 50 (300 μm)	0	2.9	100	25	25
No. 100 (150 μm)	0	37	0	15	15

(600 μm) and were retained on the No. 50 sieve (300 μm). The original dry-sieved size distribution for this silica fume had less than 0.10% of agglomerates retained on the No. 8, No. 16 and No. 30 sieves; 62% retained on the No. 50 sieve; and 30% retained on the No. 100 sieve.

Silica fume was used as 2, 4, 6, or 10% replacement of cement by mass. Silica fumes A and B were mixed-in with the cement, while silica fume C was mixed-in gently after the specified mixing procedures were complete [27]. It was assumed that some, but not all, of the agglomerates would break apart on gentle mixing. This was confirmed by microscopy where many intact agglomerates were observed.

ASTM C 1260 testing involves making mortar prisms, curing them at room temperature for 24 h, immersing them in room temperature water that is brought to 80 °C and maintained for 24 h, then immersing them in 1 N NaOH at 80 °C for 14 d. Length measurements on the prisms are taken periodically. Each mortar batch produced 3 or 4 prisms, whose 14-day expansion measurements were averaged. Generally, only one batch was tested for each sample type. Tests with silica fumes B and C were repeated; the results from these tests are reported separately because a different cement was used (cement C in Table 1).

ASTM C 1260 has been shown to be effective in examining the effects of SCM on expansion due to ASR in spite of the excessive amounts of alkali and hydroxyl ions present in the testing solution. Research [28] has shown that SCM are effective in reducing alkali ions in solution and reducing pH during the 14 d of the test. Therefore, it is an appropriate test for examining the role of silica fume in ASR expansion. However, ASTM C 227 testing was also done to provide an assessment of the reactions under testing conditions that are accelerated without using excessive alkali hydroxides.

ASTM C 227 testing involves storing prisms under moist conditions at 38 °C for 6 months. Length measurements are taken periodically. Only one batch of 3 or 4 mortar prisms was tested for each sample type; expansion values of the prisms in each batch were averaged.

Scanning electron microscopy (SEM) was used to examine the agglomeration of the silica fumes and the alkali silica reaction products in the mortars after testing. Silica fume was examined in powder-mounts by dusting the particles on carbon tape, sputter-coating with a gold–palladium mixture, and examining in secondary electron (SE) imaging mode. Agglomerates and mortars were infiltrated with epoxy under vacuum, polished, coated with either carbon or gold–palladium, and examined in backscatter electron (BSE) imaging mode. Select areas of ASR gel were examined for composition using energy dispersive spectroscopy (EDS). For most imaging, the SEM used was a Hitachi S-4500. For EDS analysis, a LEO 1530 scanning electron microscope and a JEOL 733 microprobe were used.

Data from an older series of silica fume agglomerate tests are also presented in this paper. In this series, cement B and silica fume D (Table 1) were used. Results are presented separately because the testing parameters were slightly different. Silica fume was added to the mortar as a 5% replacement of aggregate, which is approximately equivalent to a 10% addition to cement. This was done in keeping with an earlier study by one of the authors with the same silica fume [8]. Silica fume D had many large agglomerates, so it was sieved into the same particle size distribution as aggregates (Table 2).

3. Experimental results

3.1. ASTM C 1260

Table 3 shows results from ASTM C 1260 testing. ASTM C 1260 classifies aggregates with 14-day expansions greater than 0.2% as reactive and those with expansions between 0.1 and 0.2% as potentially reactive. Although ASTM C 1260 was originally designed for quickly identifying reactive aggregates, it has been shown to be effective in determining the ability of supplementary cementing materials to mitigate ASR-related expansion [28,29]. For the purposes of this study, ASTM C 1260 testing should demonstrate the ability of silica fume to either control expansion from reactive aggregates, or contribute to expansion itself. Tests were run for 28 d to determine if any specimens classified as non-reactive at 14 d would demonstrate further expansion between 14 and 28 d, indicating a potentially deleterious reaction. This was not the case; 28-day expansions were consistent with 14-day results, so only 14-day results are reported.

The undensified silica fume, A, did not increase expansion of the non-reactive aggregate, NR-1, at any cement replacement level and effectively controlled the expansion of the reactive aggregate, R, at the higher replacement levels. Silica fume A did not eliminate expansion when the highly reactive aggregate, HR, was used, but it did lower the expansion significantly. Densified silica fume B did not increase the expansion when used with the non-reactive aggregate. It did not effectively control expansion of the reactive aggregates either. In effect, silica fume B could be considered inert. Densified silica fume C, in which only agglomerates between 300 and 600 μm were used, substantially increased expansion and resulted in visible cracking in the mortar bars when used with both NR-1 and R, with the degree of expansion depending on the amount of silica fume used. Expansion results with the non-reactive aggregate NR-2 agree with those from the non-reactive aggregate NR-1

Table 3
ASTM C 1260 average 14-day expansions for mortar bars made with cement A; expansions exceeding the limit of 0.1% are indicated by boldface print

Aggregate	Silica fume	Average 14-day expansion (%)				
		0% SF	2% SF	4% SF	6% SF	10% SF
NR-1	A	0.03	0.04	0.03	0.03	0.02
	B		0.02	0.03	0.03	0.02
	C		0.06	**0.44**	**0.20**	**0.19**
NR-2	A	0.04	–	–	–	0.03
	B		–	–	–	0.02
	C		–	–	–	**0.17**
R	A	**0.23**	**0.20**	**0.15**	0.10	0.06
	B		**0.24**	**0.24**	**0.22**	**0.24**
	C		**0.35**	**0.29**	**0.24**	**0.24**
HR	A	**0.69**	–	–	–	**0.20**
	B		–	–	–	**0.56**
	C		–	–	–	**0.69**

Table 4
ASTM C 227 average 6-month expansions for mortar bars made with cement A

Aggregate	Silica fume	Average 6-month expansion (%)				
		0% SF	2% SF	4% SF	6% SF	10% SF
NR-1	A	0.01	0.01	0.01	0.01	0.01
	B		0.01	0.01	0.01	0.02
	C		0.03	0.03	0.03	–
R	A	0.01	0.02	0.02	0.01	0.01
	B		0.01	0.01	0.01	0.02
	C		0.04	0.04	0.03	–

when tested at a 10% replacement level, indicating that the results are not aggregate dependent.

3.2. ASTM C 227

Table 4 shows results from ASTM C 227 testing. Expansions shown are 6-month readings. ASTM C 227 is designed to identify potentially deleterious aggregate-cement combinations. ASTM C 33 [30] specifies that the aggregate-cement combination is benign if 6-month expansion values are less than 0.1% in ASTM C 227 testing. Since it has been suggested that finely divided silica fume may only delay expansion rather than prevent it [31], testing was continued for 1 year. The 1-year results were identical to the 6-month results, so only the 6-month results are reported.

ASTM C 227 is a less aggressive test for alkali silica reaction than ASTM C 1260. It was chosen to verify that effects shown in ASTM C 1260 were not artifacts of the testing conditions. Both aggregates R and NR-1 had 6-month expansion values of 0.01%, and are thus classified as non-reactive. They were identified as reactive and non-reactive on the basis of ASTM C 1260 test results, but ASTM C 227 results are identical for both. Correspondingly, the silica fumes had similar effects with both aggregates in ASTM C 227 tests. Undensified silica fume A and densified silica fume B did not affect expansion. Silica fume C increased expansion slightly with both aggregates at all replacement levels (10% replacement was not tested), but expansions are still significantly lower than the limit specified as deleterious by the test method.

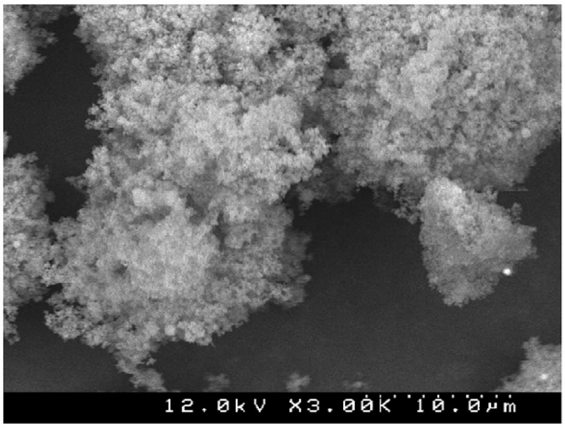

Fig. 1. SE image of silica fume A (undensified).

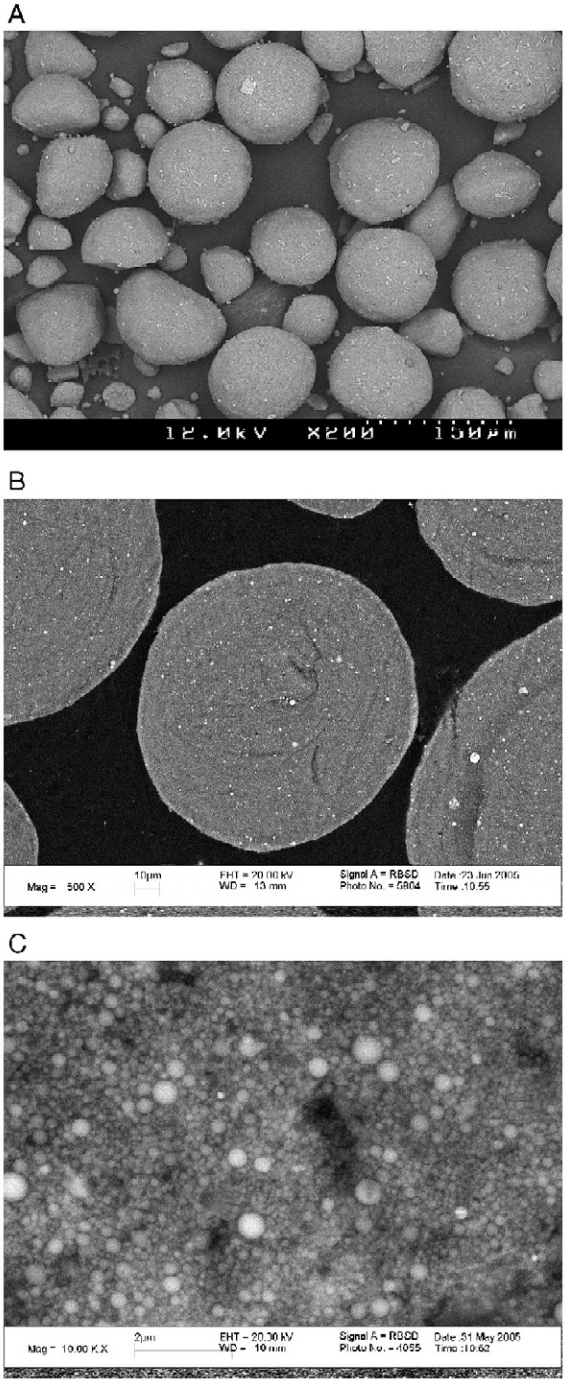

Fig. 2. SE powder-mount (A) and BSE cross-sectional (B, C) images of silica fume B.

3.3. Microscopy

Scanning electron microscope (SEM) images of the three different forms of silica fume are shown in Figs. 1–3. In Fig. 1, the undensified silica fume (A) was dusted on a piece of carbon tape and imaged in the microscope using secondary electron (SE) mode. It is clear from this high-magnification image that the individual silica fume particles are highly dispersed and not agglomerated. Figs. 2 and 3 show SEM images of silica fumes B and C, respectively. The low-magnification powder-mounted

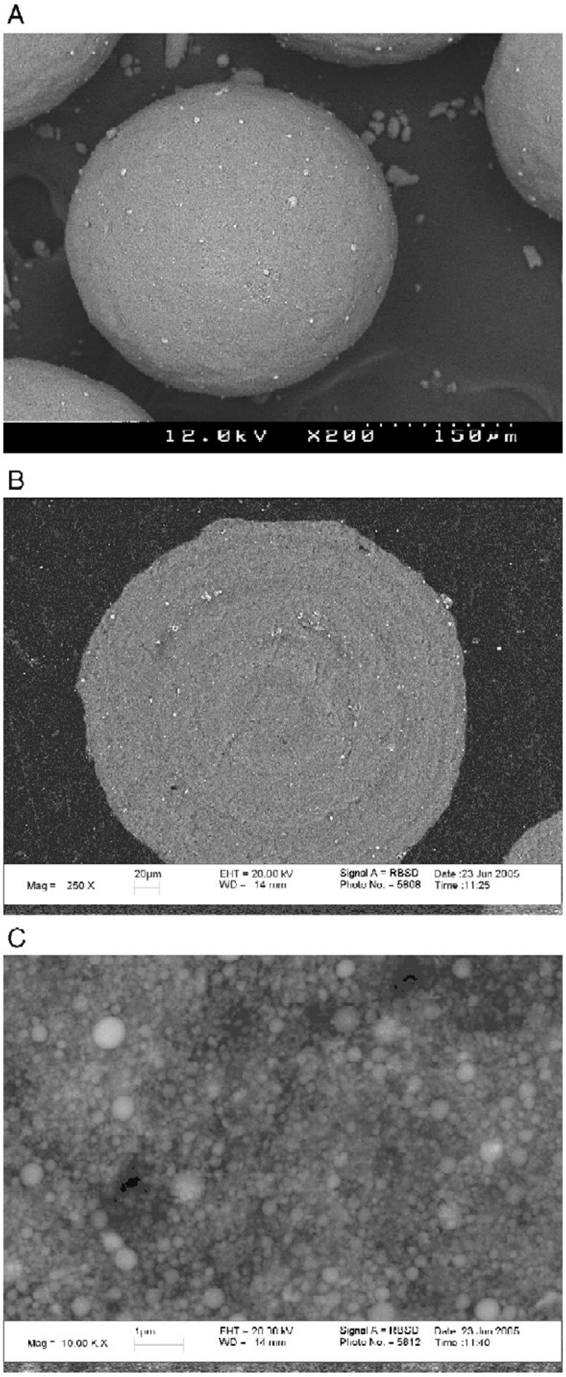

Fig. 3. SE powder-mount (A) and BSE cross-sectional (B, C) images of silica fume C.

images in Figs. 2A and 3A show the size and shape of the agglomerates, but individual silica particles cannot be distinguished. Silica fumes B and C were also infiltrated with epoxy under vacuum, polished, and imaged in backscattered electron (BSE) mode. These images are shown in Figs. 2B, C and 3B, C. Note that the magnifications in Figs. 2B and 3B are different in order to fit an entire agglomerate within the field of view. Silica fume C agglomerates are larger and more spherical than silica fume B, but the density of agglomeration is similar.

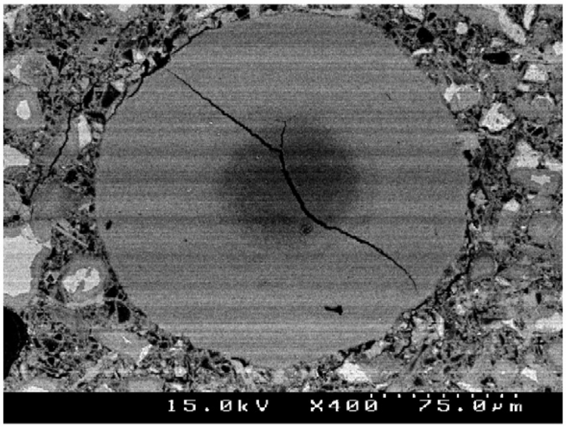

Fig. 4. BSE image of silica fume C agglomerate in mortar with aggregate NR-1 after ASTM C 1260 testing.

SEM was also used to image the mortars after ASTM C 1260 testing. These images are shown in Figs. 4–6. Only specimens with silica fume C are shown because these were the agglomerates that were observed to react expansively under ASTM C 1260 conditions and therefore merited further investigation. Fig. 4 shows a silica fume C agglomerate in mortar with the non-reactive aggregate NR-1. This agglomerate has a different morphology than most of the others in this type of specimen and is probably not alkali silica reactive. This will be addressed further in the Discussion section. Fig. 5 also shows a silica fume C agglomerate in mortar with NR-1 aggregates; this agglomerate has reacted to form ASR gel. The gel has expanded into cracks emanating from the agglomerate. In Fig. 6, silica fume C is shown in mortar with the non-reactive aggregate NR-2. This agglomerate also contains ASR gel.

3.4. Silica fume D

Results from ASTM C 1260 and ASTM C 227 testing with cement B and silica fume D are shown in Table 5. These results are presented separately because different cement was used and the method of silica fume replacement was different. Table 5

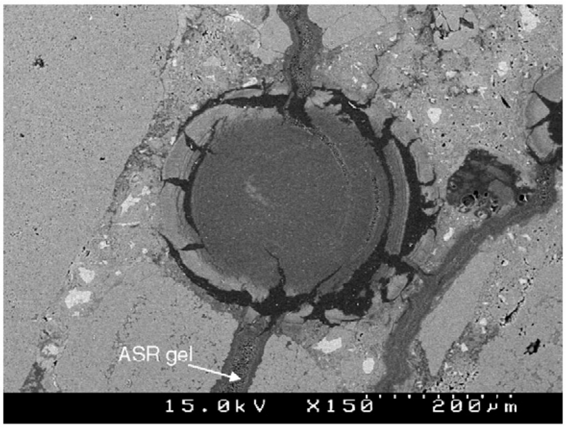

Fig. 5. BSE image of silica fume C agglomerate in mortar with aggregate NR-1 after ASTM C 1260 testing.

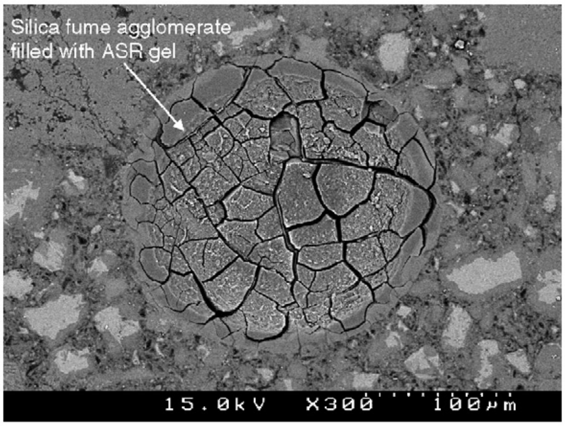

Fig. 6. BSE image of silica fume C agglomerate in mortar with aggregate NR-2 after ASTM C 1260 testing.

shows that silica fume D decreases expansion in ASTM C 1260 with reactive aggregates R and HR, although not below the critical limit with the latter. It does not significantly affect expansion when used with the non-reactive aggregate NR-2 in ASTM C 1260. In ASTM C 227 it has no effect on NR-2 or R, and effectively decreases expansion of HR below the critical expansion limit.

4. Discussion

The behavior of silica fume under accelerated testing conditions for alkali silica reaction is strongly dependent on the silica fume used. Undensified silica fume A controlled expansion of a reactive aggregate under ASTM C 1260 conditions at cement replacement levels greater than 6%. Densified silica fume B was inert under all tests performed. Densified silica fume C was expansive under ASTM C 1260 testing conditions, yet inert in ASTM C 227 conditions. Densified silica fume D effectively reduced expansion in both ASTM C 1260 and ASTM C 227. Factors contributing to the disparities in results are discussed here.

4.1. ASTM C 227

Silica fume C caused deleterious expansion in ASTM C 1260 but not in ASTM C 227 testing. This disparity may be the result of the testing conditions in ASTM C 227. ASTM C 227 was used to determine if expansions seen in ASTM C 1260 resulted from artifacts in this more accelerated testing method. What may be concluded is that artifacts in the ASTM C 227 test make it inappropriate as a method for confirming ASTM C 1260 results. It should be noted that aggregate R did not cause deleterious expansion in this test, even though it is reactive in ASTM C 1260, in ASTM C 1293 [32,33], and in outdoor exposure-site testing [34]. (Note: aggregate R is represented as “F4” in Refs. [33,34].) Other researchers have found that many known reactive aggregates appear non-reactive under ASTM C 227 conditions [35]. This is because alkalis are leached from the bars at a rate faster than they can be consumed by the alkali-aggregate reaction [36]. This may be happening with the silica fume and with aggregate R in this study, particularly given the alkalinity of the cement used (Na_2O eq. of 0.85–0.89). In fact, a better test to confirm ASTM C 1260 results would be the concrete prism test, ASTM C 1293 [32]. This test could not be performed, however, because of limited available quantities of some of the silica fumes.

4.2. Differences in silica fume

Given the questions regarding the reliability of the ASTM C 227 test results, discussion will focus on the ASTM C 1260 results. Silica fume C caused significant expansion with both non-reactive and reactive aggregates under ASTM C 1260 conditions. This behavior is so dramatically different from that of silica fumes A, B, and D, it suggests that the alkali silica reactivity of silica fume may have to do with the form and/or composition of silica fume.

There can be three principal differences between silica fumes: 1. composition, 2. density of silica fume particle packing within agglomerates, and 3. agglomerate size distribution. The composition of silica fumes B, C, and D are very similar, yet they exhibit dramatically different behavior. The composition of silica fume A is significantly different from the others, but this silica fume reduced expansion in spite of its low silica content because it was very finely divided. Composition on its own cannot, therefore, be used to explain why some silica fumes are alkali silica reactive. The density of silica particles within the agglomerates is the same for silica fumes B and C (Figs. 2 and 3), yet they have very different behaviors, so this cannot be the determining factor for alkali silica reactivity.

The agglomerate size distributions are dramatically different for all of the silica fumes tested (Table 2). It is often suggested that agglomeration of silica fume is the determining factor for its alkali silica reactivity. This is clearly not the case, as silica fumes B and D are agglomerated, yet do not cause expansion. The answer may have more to do with the distribution of agglomerate sizes. For example, silica fume B has very small agglomerates and silica fume D has very large agglomerates. Silica fume C has a very narrow range of intermediate sized agglomerates.

In order to compare “apples to apples” so to speak, the portion of silica fume C that was discarded for the earlier testing was used in follow-up testing, passed through a 150 µm sieve, and mixed into mortar along with the cement. Additionally, silica fume B was re-tested, folding in the agglomerates gently

Table 5
ASTM C 1260 and C 227 average expansions for silica fume D used as 5% replacement of aggregate by mass; mortars made with cement B; expansions exceeding the limit of 0.1% are indicated by boldface print

Test method	Aggregate					
	NR-2	NR-2+ SF D	R	R+ SF D	HR	HR+ SF D
ASTM C 1260 14-day expansion (%)	0.07	0.04	**0.28**	0.08	**0.69**	**0.27**
ASTM C 227 6-mo. expansion (%)	0.03	0.03	0.03	0.02	**0.40**	0.02

at the end of the mixing period in the follow-up test to preserve as many of the larger agglomerates (~ 150 µm) as possible. Cement C was used in both test series.

The results from these test series are striking (Table 6). When silica fume C particles are less than 150 µm, they are not alkali silica reactive. In fact, they slightly reduce the expansion of the reactive aggregate R. This is surprising because this silica fume is still highly agglomerated, not finely divided like silica fume A; the agglomerates are simply smaller than in the previous testing. These agglomerates behave in a similar manner to silica fume B in the original test series, 60% of which are smaller than 150 µm.

Silica fume B behaves differently when folded gently into the mortars after mixing instead of mixed-in with cement (Table 6). There is no change when the reactive aggregate R is used. However, when silica fume B was tested with NR-1, the silica fume increased expansion, with the expansions just exceeding the limit in the cases of 6% and 10% replacements.

These follow-up tests demonstrate that silica fume from the same source can have different alkali silica reactivity depending on its particle size distribution. Agglomeration itself is not enough to condemn a silica fume as being prone to ASR, as demonstrated by the ability of silica fume D to reduce expansion rather than increase it when very large agglomerates are used. In previous work [8], silica fume D also reduced expansion when entirely in large agglomerates of 150–300 µm, as well as in the aggregate-like size distribution used for testing in the present work and in small sizes of less than 75 µm.

More likely it is the distribution of agglomerate sizes that affects reactivity. Silica fume B was slightly reactive when mixed-in gently, preserving its larger (~ 150 µm) agglomerates. It was inert when mixed-in with the cement, in which case the larger agglomerates were likely dispersed. Silica fume C was highly reactive when 300–600 µm agglomerates were mixed-in gently, preserving their size. It was non-reactive when agglomerate size was reduced below 150 µm and the silica fume was mixed-in with the cement. Rangaraju and Olek [17] saw similar results with silica fume sieved into different size ranges under ASTM C 1260 testing. Silica fume less than 75 µm did not affect expansion, and that above 150 µm increased expansion.

From these data, it appears that keeping agglomerate sizes below 150 µm and using good dispersal techniques (shear mixing and superplasticizers) may be a good strategy for eliminating the possibility of ASR due to silica fume. However, it is also clear that agglomerates >150 µm are not necessarily alkali silica reactive (as in the case of silica fume D) and their mere presence is not indicative of compromised concrete.

Table 6
ASTM C 1260 average 14-day expansions for mortar bars made with cement C; expansions exceeding the limit of 0.1% are indicated by boldface print

Aggregate	Silica Fume	Average 6-month expansion (%)				
		0% SF	2% SF	4% SF	6% SF	10% SF
NR-1	B (gentle mixing)	0.04	0.05	**0.11**	0.08	**0.12**
	C (<150 µm)		0.05	0.04	0.03	0.03
R	B (gentle mixing)	**0.32**	**0.33**	**0.35**	**0.34**	**0.35**
	C (<150 µm)		**0.25**	**0.23**	**0.22**	**0.25**

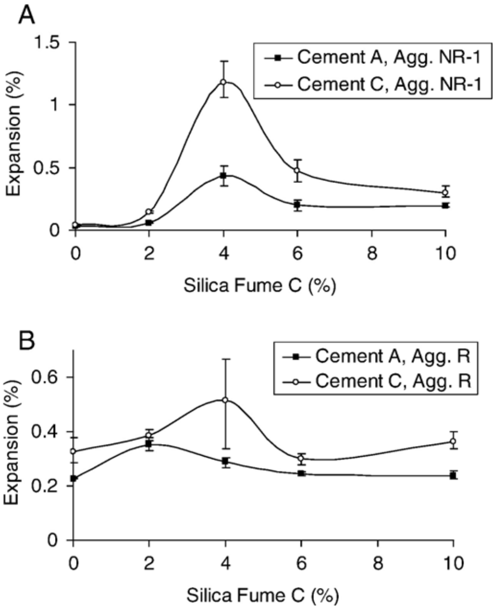

Fig. 7. ASTM C 1260 expansion results for duplicate tests using silica fume C, A. aggregate NR-1, B. aggregate R.

4.3. Pessimum effect

It is interesting to observe in Table 3 that the reactive silica fume C seems to exhibit a "pessimum" effect, meaning that the expansion peaks at a low percentage of silica fume rather than increasing linearly with replacement amount. The pessimum effect has been observed with many reactive aggregates. It has been shown that there is a ratio of reactive silica to alkalis that produces a maximum expansion [37]. When the ratio of silica-to-alkalis is too high, expansions are lowered. Likewise, when the ratio of silica-to-alkalis is too low, expansions are also lowered. It is because of both of these effects that we often see pessimum expansions in ASTM C 1260 testing. Pessimum expansions can be seen in ASTM C 1260 testing when the concentration of the NaOH soak solution is held constant and the reactive silica content is varied. Pessimums can also be seen when the NaOH of the soak solution is altered, but the reactive silica content is held constant [38].

To verify that the pessimum effect with silica fume C is real and not due to inherent variability in the expansion results, the tests were repeated. Cement C (Table 1) was used since the replicate tests were run at a later date. Results from this second batch of tests are shown in Fig. 7, along with the original test results. Error bars represent the range in measured data. The duplicate tests have higher expansions across the board compared to the original, but still exhibit a clear pessimum effect.

A pessimum effect with silica fume was also observed by Perry and Gillot [18] under modified ASTM C 441 testing using opal as the reactive phase; 5% silica increased expansion while higher cement replacement levels decreased expansion compared to the control. Kawamura et al. [19] observed a similar pessimum effect under ASTM C 227 testing with silica fume.

Higher expansions have been seen in ASTM C 1260 testing when the alkali content of the cement is lowered [39,40], and the results in Fig. 7 are another dramatic example of this phenomenon. This is the reason why ASTM C 1260 results using cements A, B, and C were presented separately in this study even though the cements were from the same supplier.

4.4. Reaction products

Results presented in this paper have shown that silica fume can exhibit a variety of behaviors with respect to alkali silica reaction. It is also interesting to note that within one silica fume type, a variety of reaction morphologies seem to occur. Many researchers have examined silica fume agglomerates in mortar and/or concrete with scanning electron microscopy [6,8,10–16], and all have observed that the silica fume has reacted, assuming a morphology different from that of the original agglomerated particle. Some have performed energy or wavelength dispersive spectroscopy on these particles and have shown that the reaction products contain large amounts of silica, but also significant amounts of calcium and sodium or potassium [6,8,10,12–16]. It has been previously observed that these reaction products are not necessarily expansive, and may be, instead, a form of low-calcium C–S–H that has absorbed alkalis [8,16]. Silica fume agglomerates forming this low-calcium C–S–H are different morphologically than those forming expansive alkali silica gel [16], and the reaction mechanisms are different in the two cases [8,16]. In the present study, Fig. 4 shows an example of this. The agglomerate from silica fume C in Fig. 4 has reacted to form a low-calcium C–S–H, which is not expansive. It is similar in morphology to the non-reactive silica fume D agglomerates published previously [8]. The crack in the agglomerate is likely a result of vacuum drying during SEM sample preparation. The agglomerates in Figs. 5 and 6 exhibit different morphologies, characteristic of classic ASR gel. It is clear, therefore, that not all of the silica fume agglomerates within a sample are alkali silica reactive.

5. Conclusions

In this study, silica fumes from four sources were tested under accelerated conditions for alkali silica reaction. The densified silica fumes tested had very different particle size distributions, and very different behaviors under the testing conditions.

- It was observed with the silica fumes examined in this study, that when agglomerates are smaller than 150 μm, the silica fume does not contribute to ASR-related expansion. This statement is not mutually exclusive — that is to say, silica fume with agglomerates larger than 150 μm are not necessarily reactive. For example, silica fume D has agglomerates much larger than 150 μm, but actually reduced expansion of reactive aggregates.
- Therefore, the presence of large silica fume agglomerates in field concrete cannot be used to assign blame in cases of cracking due to ASR. However, it appears that an appropriate means of preventing future problems due to silica fume agglomerates would be to keep agglomerates smaller than 150 μm.
- It appears that when silica fume is alkali silica reactive, there is a pessimum effect with expansion related to the percentage of silica fume used; smaller amounts of silica fume result in higher expansions than larger amounts.
- Slight differences in the alkali content of cement used in ASTM C 1260 testing can have a significant effect on expansion results.
- All silica fume agglomerates appear to react with pore solution under scanning electron microscopy. However, the reaction products are not necessarily expansive.

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