ALKALI-SILICA REACTIVITY AND THE ROLE OF ALUMINA

Skyler Warner[1*], Jason H. Ideker[1], Kelsea Schumacher[2]

[1]Oregon State University, Corvallis, OR, USA

[2]Duffield Associates, Inc., Wilmington, DE, USA

skywarner2@gmail.com

Abstract

In this study, the effect of alumina on mortar expansion when using the accelerated mortar bar test method (AMBT) to assess the behavior of a highly reactive aggregate was investigated. The study was done using two types of ternary blends: high-alkali portland cement with fly ash and alumina powder, and high-alkali portland cement with fly ash and metakaolin. Results show that mixtures containing an overall higher level of alumina showed improved alkali-silica reaction (ASR) expansion mitigation capabilities when analyzed using AMBT. The results here in show the improved potential for blends containing an overall higher level of alumina to suppress expansion due to ASR.

Keywords: Alkali-silica reaction, alkali binding, alumina, AMBT

1   INTRODUCTION

Alkali-silica reaction (ASR) is an internal chemical reaction in concrete that has resulted in premature deterioration of various concrete structures worldwide. The reaction is driven by a high pH concentration in the pore solution of the concrete (usually between 13.2 and 13.8). The presence of alkalis from Na_2O and K_2O produce an increased pH by disassociating in solution causing positively-charged Na^+ and K^+ to be balanced by negatively charged OH^- ions. The reaction is also dependent on the presence of reactive aggregate. An aggregate is considered expansive if mortar bar expansion containing the aggregate is greater than 0.10% at 14 days [1]. The increase in [OH] initiates an attack on the reactive aggregate that causes the dissolution of silicate species. A coagulation of this silicate species with the alkali ions produces a gel-like material that absorbs water, resulting in expansion that puts the concrete in tension internally. Previous studies have stated that the variable chemistry of this alkali-silica gel (ASG) is characterized by the dominance of Si^{4+}, with minor amounts of Ca^{2+}, Na^+, and/or K^+ [2, 3].

Production of cement not only consumes large amounts of energy, but could also account for approximately 10% of total anthropogenic CO_2 emissions in the close future [4]. The use of fly ash, a product of coal combustion that would otherwise be land filled, may be used as a supplementary cementitious material (SCM) to reduce energy demands and greenhouse gas emissions in addition to mitigating ASR damage. Fly ash is also preferred due to its added ability to improve workability as well as increase strength and long-term performance of hardened concrete. Particular fly ashes used at replacement levels of up to 40% have been found

effective in significantly reducing expansion and cracking of hardened concrete [5]. However, inconsistency in fly ash properties (due to combustion, collection processes, and differing sources of coal) and some unfavorable properties at higher replacement rates, such as delayed set times, have limited its use as a replacement for portland cement at replacement levels higher than 30%.

Metakaolin is a material that may be suitable to compliment fly ash for the purpose of ASR damage mitigation. Made up of primarily alumina and silica oxides, metakaolin is manufactured under a carefully controlled process by thermally activating purified kaolinite clay within a specific temperature range (650-800°C). The resulting anhydrous alumino-silicate ($Al_2Si_2O_7$) is mainly amorphous material that behaves as a highly reactive artificial pozzolan [6]. Metakaolin is capable of reacting with portlandite to form supplementary calcium-silicate-hydrate similar in composition and structure to those obtained from the hydration of portland cement [7].

This article reports on a study to evaluate the contribution of alumina oxides from SCMs and their role in controlling expansion due to ASR. Accelerated mortar bar tests were performed that incorporated five sources of fly ash. An alumina powder ternary blend or a metakaolin ternary blend (both with fly ash and portland cement) were employed in an attempt to increase the performance of fly ashes that previously displayed poor performance. The results showed that blends containing an overall higher level of alumina consistently performed better in ASR expansion mitigation when analyzed by the AMBT test method.

2   MATERIALS AND METHODS
2.1   Materials

Materials used for this project were selected to ensure a specific range of chemical constituents. The chemical composition as determined by an independent testing laboratory of the high alkali ASTM C 150 Type I cement, fly ashes, and metakaolin used are presented in Table 1. Properties provided by the manufacturer for the aluminum oxide powder used to augment the fly ash are listed in Table 2. The fine aggregate used was chosen to account for high reactivity as previously determined by the AMBT test method and is composed of natural volcanic sand.

2.2   Experimental Methods

ASTM C 1567 (AMBT plus SCMs for mitigation) was utilized as it has been proven to be a functional method for determining the effectiveness of SCMs to mitigate expansion due to alkali-silica reaction [8]. Length change is recorded to the nearest 0.002 mm and results are presented for the average of three or four mortar bars to the nearest 0.01% [9] and compared to an accepted expansion limit of 0.10% after 14 days [10].

For this investigation, four control mixtures were cast that had replacement levels of cement with fly ash of 0%, 25%, 35% and 45%. Expansions at 14-days were recorded and two fly ashes were considered to show poor performance. These two ashes were then augmented with aluminum oxide powder to increase their overall alumina content to 20%, 25%, or 30% and then used again at cement replacement levels of 25% and 35%. After 14 days, the expansion of these mortar bars were compared to the expansions obtained using the virgin ashes. The adjusted properties of the fly ash, required amount of alumina oxide powder and resulting mix proportions containing these altered fly ashes for 25% and 35% replacement of cement are listed in Table 3.

For investigating metakaolin, 5% or 10% of the least favorable virgin fly ash in terms of expansion reductions was replaced with metakaolin to create ternary blends for overall replacement of cement of 5%, 10%, 15% and 25%. The mix proportions for these ternary blends are listed in Table 4.

3 RESULTS AND DISCUSSION

3.1 Accelerated Mortar Bar Test (AMBT) Results

Expansion of mortar bar specimens containing fly ash that was replaced at levels of 0%, 25%, 35%, and 45% at 14 days for control mixtures is presented in Figure 1. It can be seen that FA2 and FA3 are less effective than FA1, FA4, and FA5 at the same replacement levels. Figure 2 shows the expansion of mortar bar specimens at 14 days for mixtures containing FA2 and FA3 that have an elevated alumina content of 20% and 25%. Although all of the mortar bars containing FA2 exceed the limit of 0.10% at 14 days, a reduction is seen for all blends containing fly ash that has been augmented with alumina oxide powder.

Expansion at 14 days of mortar bar specimens for mixtures that have a percentage of virgin fly ash replaced with metakaolin to create binary and ternary blends is presented in Figure 3. It is interesting to note that a replacement of only 5% metakaolin, which contains a considerably higher amount of alumina, reduced the expansion by 65% from 0.66% to 0.14%. Although this does not pass the 0.10% expansion limit, having such a reduction in expansion with only 5% replacement of cement is worth consideration. The expansion limit of 0.10% was not exceeded for any of the blends that contained both fly ash and metakaolin as long as 5% of the blend was made up of metakaolin.

3.2 Discussion

As evidenced in the AMBT results, the addition of SCMs as a replacement of cement in binary and ternary blends can result in reduction in ASR-induced expansion. While both fly ash and metakaolin reduced expansion, metakaolin displayed greater effectiveness when used at lower rates of cement replacement than fly ash. The influence of alumina content was evident in binary and ternary blends, where expansion decreased as the alumina content increased. When the oxide levels of the fly ashes were compared, as presented in Table 1, a proposed correlation was noticed between expansion and alumina content. Although FA4 exhibits similar alumina content to FA2 and FA3, it was not used in continued investigation beyond the control mixtures because of its ability to reduce expansion to an acceptable level of less than 0.10% at 14 days. Previous research would state that this is true due to its lower calcium content [11]. However, if that was the primary factor for forecasting the efficacy of a fly ash, then FA1 should exhibit poor performance. On the other hand, FA1 has a calcium oxide level higher than FA3 coupled with a comparably higher alumina content to the other fly ashes and displays some of the best results. The objective from this point was to analyze FA2 and FA3 and determine if an alteration in their chemical composition, particularly an increase in alumina, would improve their performance.

The greater relative effectiveness of fly ashes that contain higher amounts of alumina and metakaolin may be related to their elevated aluminosiliceous chemical composition. Mechanisms such as the alteration in the alkali adsorption capacity of the paste fraction and alkali activation of pozzolanic SCMs may contribute to the reduction in expansion [12]. It is still unclear which solid phase or phases of the concrete matrix may be responsible for binding alkalis. In the past, suggestion has been given to calcium silicate hydrate (C-S-H), the most copious phase in paste. Additionally, an increase in alkali binding has been seen to be responsive to the reduction of the Ca/Si ratio of the gel. Research by Hong and Glasser suggests that alkalis can be bound into C-S-H at acidic silanol, Si-OH, sites. It has been further suggested that alkali binding can be intensified through the incorporation of tetrahedral Al into C-S-H which results in acidity at those sites. When physically dispersed into C-S-H, alumina reacts slowly to form C-A-S-H. With further dispersion into solid solution, the alkali sorption potential increases. This mechanism proposed by Hong and Glasser suggests that Al replaces Si at tetrahedral sites creating a negative charge region that that may be capable of binding a positively charged alkali ion [13, 14].

A second mechanism that may be responsible for alkali sorption is borrowed from research related to alkali activated fly ash concrete (concrete without cement). The process involves geopolymerization development between a material rich in aluminosilicate oxides and an alkali solution under highly alkaline conditions. According to Glukhovsky, breakdown of the covalent bonds Si-O-Si occurs when the pH of the alkaline solution is raised. An accumulation of the destroyed products forms a gel like structure and the generation of a condensed structure. This gel is the primary structure that results in ASR gel expansion. When alumina is present, geopolymerization results from condensation and cross linking of –Si-O-Al-O sialate links into a three dimensional network [15]. The structure type of this geopolymer framework would be made up of [SiO$_4$] and [AlO$_4$] tetrahedral molecules. Similar to C-A-S-H, the incorporation of tetrahedral Al may result in an acidic location that would be charged balanced by the adsorption of alkali ions. Unlike the C-S-H phases, where structural details are based on crystal structure, details of geopolymer formation in the binder phase are particularly unidentified [16].

Paralleled to this possible geopolymer gel formation, the presence of calcium and the corresponding development of C-S-H and C-A-S-H results in water deficiency and a rise in alkalinity. The increased alkalinity accelerates the dissolution of silicate and aluminate species which in turn increases the rate of poly-condensation and geopolymerization. As a result, the presence of calcium contributes to the mechanical strength of the resulting hardened matrix not only be forming C-S-H and C-A-S-H but also by enhancing the geopolymerization process[17]. However, the geopolymerization and binding of alkalis is limited by the availability of Al to form tetrahedral bonds and cross linking of –Si-O-Al-O sialate links into a three dimensional network. Figure 4 shows how the geopolymer and C-A-S-H development may occur within the concrete matrix. This mechanism may be responsible for a lack of correlation between differing test methods used to evaluate various highly reactive aggregates. The NaOH soak solution used in this investigation has the potential to act as an activator solution with the fly ash to promote geopolymerization of –Si-O-Al-O sialate links and result in alkali binding mechanisms that do not exist in other test methods or in field applications.

A final mechanism to possibly describe the role of alumina in ASR expansion mitigation is its ability to lower the rate of dissolution of silica into solution. The availability of dissolved alumina has been found to hinder silica dissolution by the sorption of dissolved alumina onto silica particles in geopolymer gel formation [18]. It is unclear if this would apply to alumina adsorbing to the surfaces of damaged siliceous reactive aggregate or to coagulated species of dissolved silica around the aggregate or in the pore solution. In either case, it is believed that the presence of alumina may play a role in slowing down or even blocking the rate of silica dissolution. A major factor in the ability of alumina to hinder the dissolution of silica is directly related to its rate of participation in the network. From the data in this study, it appears that the alumina is contributed at a rapid rate by the SCMs that were used. In other words, the impact of alumina content in a blend is noticeable within the 14 days of AMBT test method. Whether this impacts the service life of a structure long term is another question since the driving forces of ASR may be capable of overcoming the initial suppressive nature of alumina on silica dissolution.

It seems that the most favorable alumina content for the fly ashes that have been augmented with alumina powder should be around 20% since a further increase in alumina does not produce further reduction in expansion. It is unclear if the form of the alumina from the powder properly simulates the alumina contained by the fly ashes and if it is working with similar mechanics to reducing ASR expansion. Due to this uncertainty an alternative source of alumina, in this case contributed by metakaolin, was obtained to evaluate other ternary blends. The incorporation of alumina powder or metakaolin both improved the expansive mitigation potential of

the fly ashes when ternary blends were utilized. This shows that fly ashes that were once deemed unusable for ASR expansion mitigation may be supplemented with other materials to increase the effectiveness. This could result in a large impact on the use of fly ash as an SCM because it would allow a greater range of fly ashes to be used. This would decrease the amount diverted to landfills and possibly also increase its use in areas where superior fly ashes are not readily/locally available.

4. CONCLUSION

Binary and ternary blends of fly ash with alumina oxide powder or metakaolin were examined for their ability to resist expansion by ASR using the AMBT while incorporating a highly reactive aggregate. It was determined that alumina plays a role in the mitigation of alkali-silica reaction in the following ways:

- Data showed that alumina contributed from alumina oxide powder correlates to lower expansion. An alumina content of 20% or higher is recommended when fly ash is used to mitigate ASR expansion based on the results of this study.
- The two types of ternary blends, high-alkali portland cement with fly ash and alumina powder, and high-alkali portland cement with fly ash and metakaolin, show that higher alumina content improved mitigation of ASR expansion.
- Metakaolin displayed an elevated ability to suppress ASR expansion due to its primarily alumino-siliceous composition. Lower levels of metakaolin were needed to control expansion below 0.1% in this study when compared to the amount of fly ash required to achieve the same result.
- Artificially increasing the alumina content of a fly ash through the incorporation of alumina oxide powder or metakaolin improved the effectiveness of certain fly ashes in this study to mitigate ASR expansion.
- The degree at which alumina is available when contributed by SCMs may play a role in suppressing the dissolution of silica into solution from reactive aggregates potentially delaying the rate of ASR gel formation.
- Analysis of pore solution to evaluate the efficacy of blends containing a range of alumina to bind alkalis should be conducted.

5. REFERENCES

[1]   AASHTO, (2010): Highway Subcommittee on Material; AASHTO provisional standards. AASHTO provisional standards. 65.1-65.20.
[2]   Peterson, K., Gress, D., Van Dam, T., and Sutter, L., (2006): Crystallized alkali-silica gel in concrete from the late 1890s. Cement and Concrete Research. 36(8): 1523-1532.
[3]   Glasser, L.S.D. and Kataoka, N., (1981): The Chemistry of Alkali-Aggregate Reaction. Cement and Concrete Research. 11(1): 1-9.
[4]   Habert, G., de Lacaillerie, J.B.D., and Roussel, N., (2011): An environmental evaluation of geopolymer based concrete production: reviewing current research trends. Journal of Cleaner Production. 19(11): 1229-1238.
[5]   Thomas, M., Dunster, A., Nixon, P., and Blackwell, B., (2011): Effect of fly ash on the expansion of concrete due to alkali-silica reaction - Exposure site studies. Cement & Concrete Composites. 33(3): 359-367.
[6]   Ramlochan, T., Thomas, M., and Gruber, K.A., (2000): The effect of metakaolin on alkali-silica reaction in concrete. Cement and Concrete Research. 30(3): 339-344.

[7]   De Silva, P.S. and Glasser, F.P., (1992): Pozzolanic activation of metakaolin. Advances in Cement Research. 4(16): 167-178.

[8]   Thomas, M.D.A. and Innis, F.A., (1999): Use of the accelerated mortar bar test for evaluating the efficacy of mineral admixtures for controlling expansion due to alkali-silica reaction. Cement Concrete and Aggregates. 21(2): 157-164.

[9]   Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method), in *ASTM C1260-07*, A. International, Editor. 2009, ASTM Int'l West Conshohocken, PA.

[10]   Thomas, M.D.A., Fournier, B., Folliard, K.J., Shehata, M., Ideker, J.H., and Rogers, C., (2007): Performance Limits for Evaluating Supplementary Cementing Materials using the Accelerated Mortar Bar Test. ACI Materials Journal. 104(2): 115-122.

[11]   Leemann, A., Le Saout, G., Winnefeld, F., Rentsch, D., and Lothenbach, B., (2011): Alkali-Silica Reaction: the Influence of Calcium on Silica Dissolution and the Formation of Reaction Products. Journal of the American Ceramic Society. 94(4): 1243-1249.

[12]   Moser, R.D., Jayapalan, A.R., Garas, V.Y., and Kurtis, K.E., (2010): Assessment of binary and ternary blends of metakaolin and Class C fly ash for alkali-silica reaction mitigation in concrete. Cement and Concrete Research. 40(12): 1664-1672.

[13]   Hong, S.-Y. and Glasser, F.P., (1999): Alkali binding in cement pastes: Part I. The C-S-H phase. Cement and Concrete Research. 29(12): 1893-1903.

[14]   Hong, S.U. and Glasser, F.P., (2002): Alkali sorption by C-S-H and C-A-S-H gels Part II. Role of alumina. Cement and Concrete Research. 32: 1101-1111.

[15]   Mikoc, M.M.M., Bjelobrk, I., and Korajac, J., (2011): Alkali-Activated Fly Ash Concrete (Concrete without cement). Tehnicki Vjesnik-Technical Gazette. 18(1): 99-102.

[16]   Ruscher, C.H., Mielcarek, E.M., Wongpa, J., Jaturapitakkul, C., Jirasit, F., and Lohaus, L., (2011): Silicate-, aluminosilicate and calciumsilicate gels for building materials: chemical and mechanical properties during ageing. European Journal of Mineralogy. 23(1): 111-124.

[17]   Diaz-Loya, E.I., Allouche, E.N., and Vaidya, S., (2011): Mechanical Properties of Fly-Ash-Based Geopolymer Concrete. ACI Materials Journal. 108(3): 300-306.

[18]   Hajimohammadi, A., Provis, J.L., and van Deventer, J.S.J., (2010): Effect of Alumina Release Rate on the Mechanism of Geopolymer Gel Formation. Chemistry of Materials. 22(18): 5199-5208.

[19]   Harrison, J. Tec-Cement Technologis and Geopolymers. in World Congress Geopolymer. 2005. Saint-Quentin, France: Institut Geoplymere.

Table 1: Fly ash, metakaolin, and portland cement composition.							
Constituents (Wt%, dry basis)	**FA1**	**FA2**	**FA3**	**FA4**	**FA5**	**MK**	**Cement**
Silicon Dioxide, SiO2	47.66	33.70	53.15	63.95	59.36	51.11	20.08
Aluminum Oxide, Al_2O_3	21.58	16.97	16.84	16.54	25.14	45.71	5.61
Iron Oxide, Fe_2O_3	4.21	4.89	6.13	4.43	5.56	0.39	2.51
Total ($SiO_2 + Al_2O_3 + Fe_2O_3$)	73.45	55.56	76.12	84.92	90.06	97.21	28.20
Calcium Oxide, CaO	12.30	27.08	11.33	6.16	5.63	0.01	63.79
Magnesium Oxide, MgO	2.70	4.63	3.93	2.38	0.94	0.00	1.22
Sodium Oxide, Na_2O	6.02	4.81	3.34	2.31	0.40	0.29	0.13
Potassium Oxide, K_2O	0.89	0.79	1.99	1.47	0.97	0.18	1.00
Na_2O_{eq}[a]	6.61	5.33	4.65	3.28	1.04	0.41	0.79
Titanium Dioxide, TiO2	0.97	1.13	1.08	0.90	1.09	1.69	0.24
Manganese Dioxide, MnO2	0.02	0.05	0.10	0.05	0.08	0.00	0.05
Phosphorus Pentoxide, P_2O_5	0.47	0.48	0.31	0.30	0.03	0.07	0.29
Strontium Oxide, SrO	0.42	0.60	0.33	0.21	0.11	0.01	0.09
Barium Oxide, BaO	0.80	1.12	0.56	0.46	0.16	0.02	0.02
Sulfur Trioxide, SO_3	1.20	2.92	0.64	0.54	0.37	0.08	3.39
Loss on Ignition	0.76	0.83	0.27	0.31	0.16	0.44	1.59
Moisture, as received	0.09	0.03	0.04	0.04	0.04	0.28	
Available Na_2O[b]	1.93	3.15	1.08	0.95	0.15	0.09	0.12
Available K_2O[b]	0.29	0.49	0.49	0.52	0.31	0.00	0.71
Available Na_2O_{eq}[a]	2.12	3.47	1.40	1.29	0.35	0.09	0.59
C_3S							56.20
C_3A							10.61
C_2S							15.17
C_4AF							7.64

[a] Total alkalis ($Na_2O+0.658K_2O$)

[b] Available alkalis, as per ASTM C311

Table 2: Properties of aluminum oxide powder.	
Assay (Al_2O_3)	99.6
Loss of Ignition	0.2
Chloride (Cl)	0.005
Solfate (SO_4)	<0.003
Heavy Metals	<0.0005
Iron (Fe)	<0.01

Table 3: Mix proportions and composition of mortar bars augmented with aluminum oxide (%).						
	25FA	25FA_20	25FA_25	25FA_30	35FA_20	35FA_25
Percent Replacement of Cement	25%	25%	25%	25%	35%	35%
Total Weight of Cement (g)	440.00	440.00	440.00	440.00	381.34	381.34
Total Weight of Supplementary Material (g)	146.67	146.67	146.67	146.67	205.33	205.33
Weight of Al2O3 Powder (g)	0.00	5.35	14.18	23.02	7.49	19.86
Weight of Bell River Fly Ash (g)	146.67	141.32	132.49	123.65	197.84	185.47
Aluminum Oxide (Al_2O_3)	16.97	20.00	25.00	30.00	20.00	25.00
Silicon Dioxide (SiO_2)	33.7	32.47	30.44	28.41	32.47	30.44
Calcium Oxide (CaO)	27.08	26.09	24.46	22.83	26.09	24.46
Sodium Oxide (Na_2O)	4.81	4.63	4.34	4.06	4.63	4.34
Potassium Oxide (K_2O)	0.79	0.76	0.71	0.67	0.76	0.71
Available alkalies (Na_2O)	3.15	3.04	2.85	2.66	3.04	2.85
Available alkalies (K_2O)	0.49	0.47	0.44	0.41	0.47	0.44
Total alkalies (Na_2O)	3.47	3.34	3.13	2.93	3.34	3.13

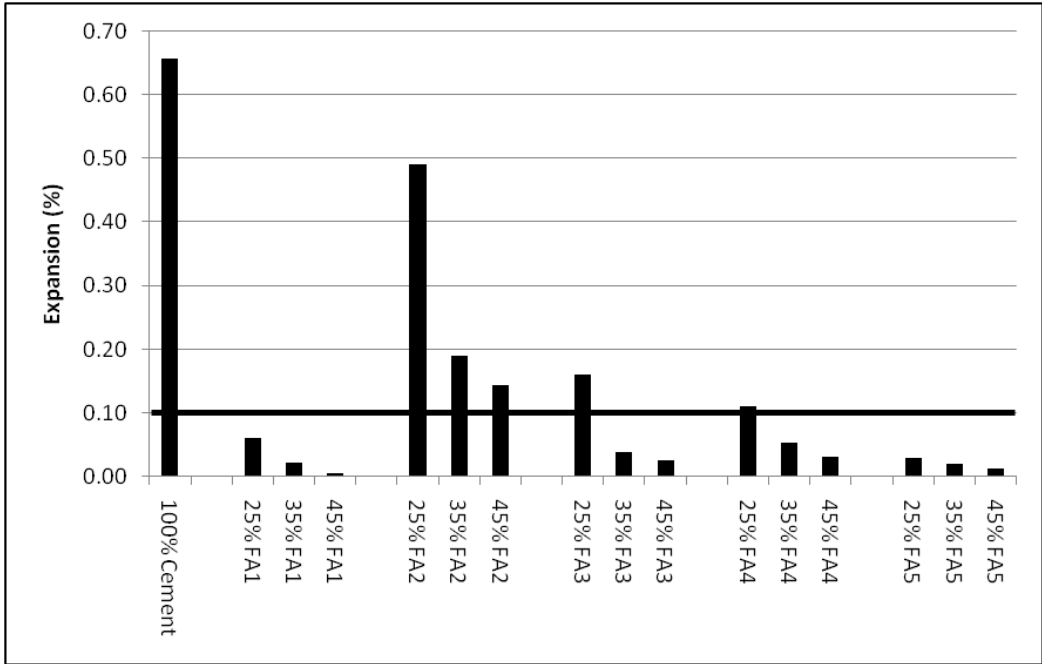| Table 4: Mix proportions of blends containing FA2 and metakaolin.				
	Percent Replacement of Cement (%)	Total Weight of Fly Ash (g)	Total Weight of Metakaolin (g)	Total Weight of Cement (g)
35FA2	35	205.33	0.00	381.34
45FA2	45	264.00	0.00	322.67
5MK	5	0.00	29.33	557.34
5MK_10FA2	15	58.67	29.33	498.67
10MK	10	0.00	58.67	528.00
10MK_15FA2	25	88.00	58.67	440.00

Figure 1: AMBT expansion results at 14 days for mortar bars containing cement supplemented with fly ash at replacement levels of 25%, 35%, and 45%.
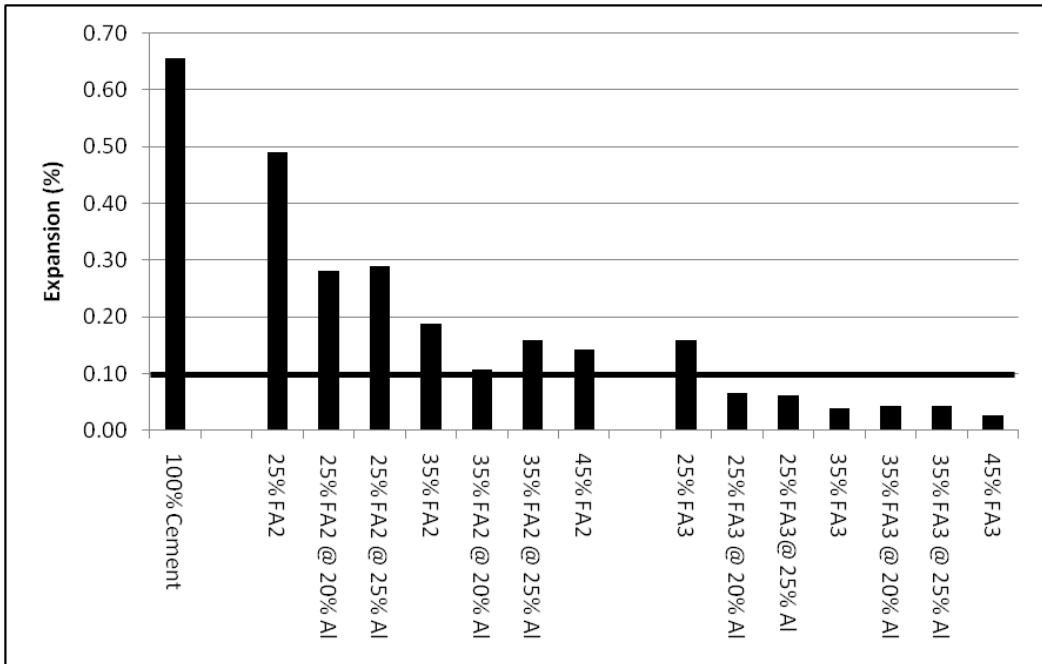

Figure 2: AMBT expansion at 14 days for mortar bars containing FA2 and FA3 that has alumina contents augmented to 20% and 25%.

Figure 3: AMBT expansion at 14 days for mortar bars containing binary and ternary blends of FA2 and metakaolin.

Figure 4: Development of –Si-O-Al-O geopolymer network and C-A-S-H (Inspired by [15] and [19]).