DEVELOPMENT OF ENHANCED TEST METHODS TO EVALUATE ALKALI-SILICA REACTION IN CONCRETE

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ABSTRACT

The research presented in this paper studies the effect of sample geometry and temperature on expansion due to alkali-silica reaction (ASR) in concrete. Expansions of cubes and cylinders are compared to those of the standard prisms. Control samples, samples with fly ash (FA) and others with slag are investigated at two temperatures, 38°C and 60°C. At 38°C, results showed that smaller samples have higher expansion at early ages. However, larger samples such as cubes and cylinders seem to reach higher expansion compared to prisms after 32 weeks for both control and samples with fly ash. In addition, the results showed that higher temperature accelerated the expansion of the different sample geometry. However, in the case of the samples with no supplementary cementing materials (SCM), the ultimate expansions at 60°C are not higher than that of the samples tested at 38°C. Secondly, the degree of hydration and pozzolanic reaction of different SCM were studied using thermal analysis to predict their alkali binding capacity at different temperatures. The results provide a better understanding of the evolution of their hydration products. The hydration of SCM was higher at temperature higher than 23°C, especially at ages earlier than 28 days.

Keywords: Alkali-silica reaction, alkali leaching, SCM, degree of hydration, pozzolanic reaction.

1. INTRODUCTION

Since 1940, alkali-silica reaction in concrete has been studied to understand its mechanism and to find preventive measures to mitigate it. ASR is a chemical reaction between the alkalis present in the cement and the reactive silica in some types of aggregate. In presence of water, a gel product is formed and swells with the absorption of moisture. The latter exerts pressure to the surrounding. If the swelling pressures exceed the tensile strength of the concrete, this will lead to the formation of cracks (Poole 1992). Many sources of alkali can be available in concrete such as aggregates, cement, chemical admixtures as well as external sources. However, the major contributor for the reaction is the Portland cement which normally has an alkali content in the range of 0.2 to 1.3% of Na_2O_e (Federal Highway Administration 2012). As for the silica, a form of reactive silica should be present in the aggregates so that the alkali-silica reaction occurs. SiO_2 is a component of many rocks but not all types of siliceous particles can react with alkalis (Federal Highway Administration 2012). Depending on their microstructure, some aggregates are unstable at high pH compared to others having the same chemical composition. As many other reactions, water is required for ASR to occur. Other than being a transport for the external alkalis, water is absorbed by the gel formed due to the reaction between alkalis and silica. Although below 70% there is minimal expansion but the dramatic change is whenever the relative humidity is higher than 80% (Poole 1992).

Preventive measures have been developed to mitigate ASR such as the use of lithium-based compound, sealers or supplementary cementing materials. The use of SCM, the mostly commonly used method, showed improved performance of concrete against ASR (Shehata and Thomas 2000, Thomas et al. 2006). The results are based on concrete prism test (CPT) described in the Canadian Standards, CSA A23.2-14A (2014). This test is the most reliable lab test to predict the levels of supplementary cementing materials to counteract ASR. However, many challenges are being faced while using this test such as the long testing time and the alkali leaching from the

samples. Many researchers studied the possibility to shorten the testing time for the concrete prism test by increasing the temperature to 60°C instead of 38°C. However, Ideker et al. found that some non-reactive fine aggregates at 38°C have shown expansion at 60°C (Ideker et al. 2008). Further, many studies were done to compare the field expansion to laboratory results. In 2012, Ideker et al. compared the expansion of CPT samples to site blocks, both tested with a variety of SCM, at 10 and 15 years. They established that there exists good correlation between CPT expansion results and prism samples at 10 years. However, that was not the case for the same samples tested at 15 years (Ideker et al. 2012). At later ages, the expansion of tested blocks under field conditions was much higher than the expansion found in CPT for samples with SCM (Fournier et al. 2008, Ideker et al. 2012). The leaching is being more revealed in the case of smaller samples compared to the blocks on site which lead to lower expansion results as compared to the site testing. Bérubé et al. studied the possibility of changing the diameter of the sample to reduce leaching. He found out that the higher the diameter of the cylinder samples, the more the expansion (Bérubé et al. 2012). Many attempts are being made to reduce leaching and testing time.

Many explanations have been suggested to explain the effect of SCM in preventing the expansion due to ASR. Although there is still some disagreement on the nature of the reactions, some proposed that the presence of SCM acts as a diluent for the Portland cement (Glasser 1992). Another explanation of the effect of SCM is their fineness, which will lower the permeability of the concrete thus making the migration of the alkali towards the reactive silica more difficult (Glasser 2012). In addition, studies have been done to understand the binding capacity of SCM. Researchers suggested that the hydration products of SCM have a higher binding power to alkalis than that of the silica in the aggregate (Glasser 1992). The silica present in SCM will react with the calcium hydroxide formed from the hydration of the calcium silicates through pozzolanic reaction. As a consequence, the produced calcium silicate hydrates (C-S-H) have a lower calcium-to-silica ratio (Shehata et al. 1999) which has a high tendency to bind alkalis (Shehata et al. 1999, Shehata and Thomas 2002, Shehata and Thomas 2006, Kandasamy and Shehata 2014). The removal of alkali from the pore solution into cement solids will result in less immediate potential for reaction with aggregates (Glasser 1992). The degree of pozzolanic reaction of SCM can thus be measured based on the consumption of $Ca(OH)_2$. The calcium silicate hydrates formed due to the pozzolanic reaction do not show any sign of expansion compared to the silica gel formed due to ASR expansion. This could be explained by the fact that the pozzolans are very fine materials which will distribute the C-S-H throughout the cement paste compared to the accumulation of large deposits of alkali-silica gel in discrete locations where the reactive silica aggregates are present (Federal Highway Administration 2012). Thus, the binding capacity of different pozzolans and their effect in reducing expansion due to ASR is still not clearly understood.

2. RESEARCH OBJECTIVES

Some preventive measures that limited the 2-year expansion in CPT produced late expansion at 15 years when tested in large blocks under field test. This triggered the need to identify the reasons behind this and to come up with a modified approach to determine the level of SCM required to mitigate long-term expansion in field. This paper will focus on studying two possible reasons:

(a) The sample size, geometry and temperature of CPT could underestimate the expansion. Smaller samples usually promote more leaching which reduces the expansion at late ages although their cores are usually of higher relative humidity which sustains the swelling gel.

(b) The rate and ultimate hydration of SCM, and hence their capacity to bind alkalis, under CPT conditions could be higher than those under field conditions.

The methodology followed to investigate the above possible reasons is composed of two experimental programs. The first one studies the effect of the geometry - cubes, cylinders and prisms - on expansion by casting different samples and measuring their expansions at different temperatures. The second experimental program focuses on developing a better understanding of the hydration and pozzolanic reactions of different cement blends at different temperatures through studying the hydration of cement paste samples over time.

3. MATERIALS AND EXPERIMENTAL DETAILS

3.1 Materials

3.1.1 Aggregates and Cementing Materials

The aggregate used in this study is Sudbury coarse aggregate, a moderately reactive aggregate, which is a gravel containing argillite, greywacke and quartz-wacke. The bulk relative density and absorption of Sudbury aggregates were tested in the lab and found to be 2688 kg/m^3 and 0.56% respectively. As for the cementing materials, Type GU Portland cement with 0.99% Na_2O_e was used for the different mixes along with Class F fly ash and slag. The chemical compositions of these materials are presented in Table 1.

Table 1: Chemical composition of cementing materials (Mass %)

Oxide	Cement	Fly ash	Slag
SiO_2	19.54	57.0	37.0
Al_2O_3	5.21	23.4	8.2
Fe_2O_3	2.16	3.5	0.5
CaO	62.39	9.5	38.5
MgO	2.39	1.0	10.5
SO_3	4.03	0.1	2.7
Na_2O_e	0.99	2.89	0.67
Loss on Ignition	2.36	0.59	2.1

3.1.2 Expansion Samples

The samples casted in this research are: (1) concrete prisms (75x75x285 mm), (2) cylinders of same height as the prisms to allow measuring them using the same length comparator (ø100 mm), and (3) 150 mm cubes. For prisms and cylinders, studs were placed on top and bottom of the specimen. As for the cubes, studs were inserted on two faces and expansion was measured diagonally using a demec style digital strain gauge. Each set of samples consists of 3 prisms, 3 cubes and 3 cylinders and were tested at two different temperatures, 38°C and 60°C, for a total of 18 specimens for each set. Three different sets were casted: a control with no SCM containing a reactive gravel from Sudbury, Sudbury with 15% FA and Sudbury with 35% slag. The fine aggregate used is non-reactive natural sand. The coarse to fine aggregate ratio is 60 to 40 by mass as per CSA A23.2-14A (2014). The coarse gradation for the samples is as specified in the CSA A23.2-14A (2014) and the amount of Portland cement and cementing materials is 420 kg/m^3. The alkalinity of the cement was boosted to 1.25% to compensate for the leaching that will occur during the test as explained in the CSA A23.2-14A (2014) guidelines of the concrete prism test. The moulds used for the cylinders and cubes are not commercially available because there is no current test method that uses these sample shape/size for monitoring length change. Figure 1 and 2 show the moulds that have been fabricated for cubes and cylinders respectively.

Figure 1: Moulds for cubes

Figure 2: Moulds for cylinders

3.1.3 Tested Samples for Degree of Hydration

Different paste samples of 50 mm x 100 mm were casted at a water cement ratio (w/cm) of 0.42 with several replacement levels of SCM, as follows:
- control samples with 100% Portland cement,
- samples with 15% low-calcium fly ash,
- samples with 35% slag.

Each set of samples consists of 6 specimens for testing at 7 and 28 days of curing at 100% relative humidity, and three different temperatures: 23°C, 38°C and 60°C. More testing at a later stage is also scheduled.

3.2 Experimental Procedures

3.2.1 Casting of Expansion Samples

The concrete prism test was followed as per CSA A23.2-14A (2014) to determine the expansion due to ASR. All procedures outlined in the standard were followed during casting. The samples were cast and put in the curing room at 100% relative humidity and room temperature for 24 hours and then demolded. They were measured for zero reading and then put in buckets lined with cloth. The samples were put above water and placed at the designated temperatures of 38°C and 60°C. The buckets and containers used for the different samples are shown in Figures 3, 4 and 5. The cube buckets at 38°C were put in a heat room; and the ones tested at 60°C were put in an oven. Thus, due to space constraint, the containers used for 60°C were smaller.

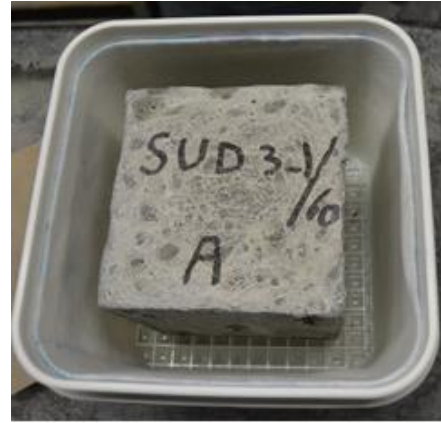Figure 3: Containers for cubes at 38°C
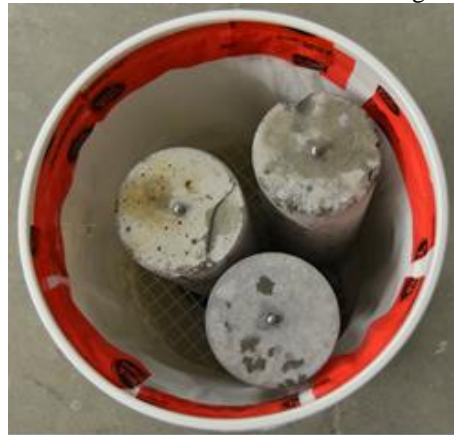

Figure 4: Containers for cubes at 60°C

Figure 5: Buckets for cylinders and prisms

3.2.2 Paste Samples and Thermal Analysis

Mixing the paste samples for thermal analysis was made using the high-shear blender. First, water was added to the mixer; the water cement ratio used is 0.42 similar to the one used for expansion samples. Then, cementing materials were added. The procedure consisted of three minutes of mixing at low speed, stopped as needed to remove the materials stuck on the surfaces of the blender. Following the three minutes of mixing, a two-minute rest was adopted, followed by two minutes of mixing at medium speed. Finally, a two-minute rest period followed by one minute of mixing was used. After this complete 10 minutes of mixing and rest periods, the samples were placed in their moulds. They were cured for 24 hours and then demolded. Each sample was put at its designated temperature in containers above water. At the testing age, the sample is taken and crushed into small chucks of 2-3 mm. The water was removed from the samples by solvent replacement method where they were soaked in acetone for 7 days. Following this, they were put in desiccators at 38°C to allow the evaporation of the acetone. These samples will be tested using thermogravimetric analysis (TGA) to determine the $Ca(OH)_2$ present in the sample. Another portion of the crushed sample was put into the oven at 105°C to remove all the free water in the sample. They will be tested for loss on ignition (LOI) to determine the amount of chemically bound water (CBW) in the sample. The samples are kept in the desiccators at room temperature until testing to avoid humidity and carbonation. During the tests, the samples were heated to 1050°C and loss on ignition as well as mass loss at 450°C was used to calculate the $Ca(OH)_2$ in the samples and the chemically bound water.

4. RESULTS AND DISCUSSION

Two sets of samples were measured for expansion in the lab until 52 weeks. Figure 6 and 7 present the expansion data for Sudbury control and Sudbury with 15% FA respectively. The data are based on the average of 3 different specimens of the same shape and mixture. It should be noted that the values of the 3 specimens, constituting one

sample, were close to each other. At 38°C, the expansions at 52 weeks are 0.170%, 0.145% for prisms and cubes respectively, and 0.166% for cylinders at 39 weeks. As for 60°C, the expansions are higher with 0.158%, 0.113% and 0.08% for cylinders, cubes and prisms respectively. The reaction at 60°C is faster and it seems to reach a plateau after about 26 weeks.
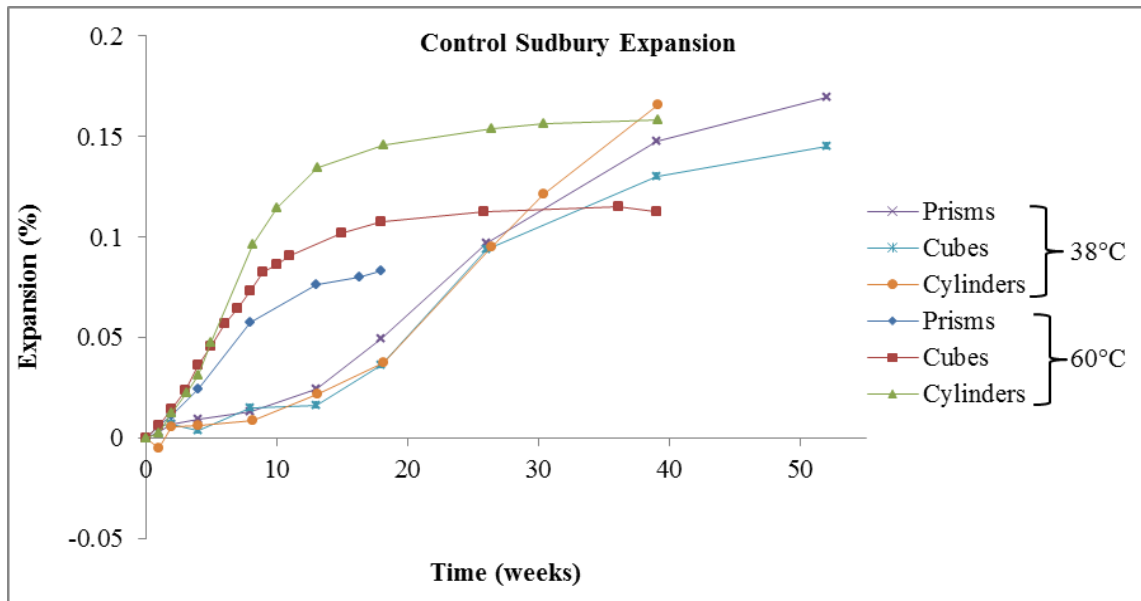

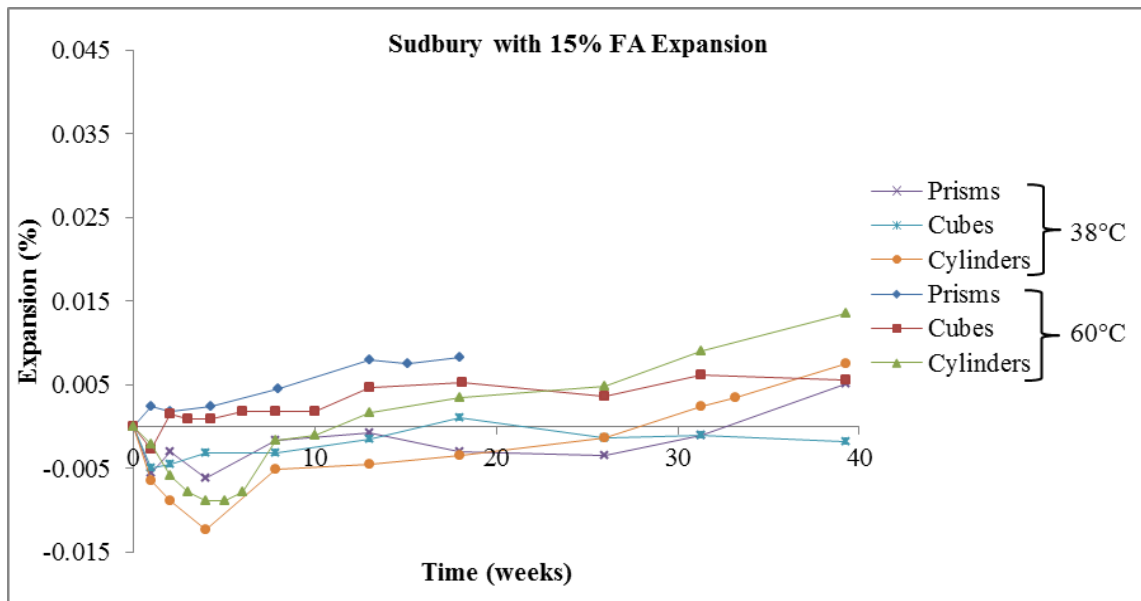Figure 6: Expansion data of samples of different shape and geometry containing Sudbury aggregate

Figure 7: Expansion data of samples of different shape and geometry containing Sudbury aggregate with 15% FA

For Sudbury with 15% FA, the expansions are well below the acceptable limit of 0.04%. At 39 weeks, the expansions are 0.007% for cylinders, 0.005% for prisms and -0.002% for cubes. As for 60°C, the cylinders have an expansion of 0.014% and 0.006% for cubes. Also, a set of samples was casted using 35% replacement of slag. The data was measured until 13 weeks. It seems that fly ash with 15% replacement level was more efficient in reducing the expansion as compared to 35% slag. At 8 weeks, the expansions at 60°C are 0.015%, 0.014% and 0.003% for prisms, cylinders and cubes, respectively as compared to 0.005%, 0.003% and -0.0016% for samples with 15% FA. The long-term expansions will be monitored to see the late rate of expansions obtained in different sample shape/size.
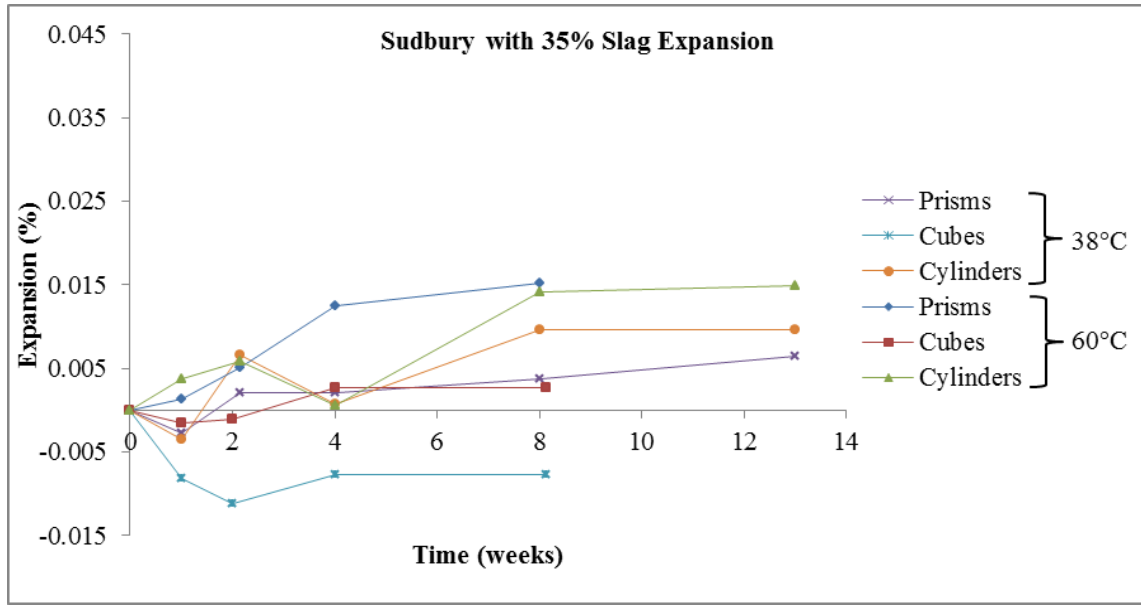
Figure 8: Expansion data of samples of different shape and geometry containing Sudbury aggregate with 35% Slag

4.1 Effect of Sample Shape on Expansion

Prisms seem at the beginning to have the highest expansion compared to cubes and cylinders as shown in Figure 6. At 18 weeks, the prisms had an expansion of 0.05% compared to 0.04% for cubes and cylinders of the control. As for the samples with fly ash, at 13 weeks, the expansion of the prisms was higher than those of the cubes and cylinders, although all the values are low. Same trend seems to be followed by the samples with 35% slag. This could be explained by the fact that the cores of smaller samples have higher relative humidity compared to larger samples, which accelerates the reaction. However, the late expansion may show different trend; for instance, it can be seen that at 26 weeks the cylinder expansions started catching with the other samples to reach higher values at 32 weeks of 0.12% for samples without SCM, Figure 6, and 0.002% for samples with fly ash, Figure 7. This suggests that perhaps more leaching is occurring in the prism samples, and this was shown at a later age when the level of alkalis drops. Also, it should be noted that the slope of the expansion curve of cylinders for the control seems to be steeper than that of the prisms which indicates that the rate of expansion is higher for the cylinders compared to prisms. On the other hand, the cubes seem to have an expansion almost similar to the prisms until 32 weeks. At later ages, it is anticipated that the cubes should reach higher expansion than that of the prisms. This is implied by the accelerated test at 60°C where the difference in expansion between the three samples is clear from the early ages with expansion values reaching 0.157%, 0.115% and around 0.08% for the cylinders, cubes and prisms respectively. It could be concluded that sample geometry has an effect on expansion. This might help explain the fact that in the field, expansions are higher due to their larger size compared to lab samples.

4.2 Effect of Temperature on Expansion

For the control sample with no SCM, it can be seen that the expansion at 60°C is much faster than the one at 38°C as shown in Figure 6. At 13 weeks, for the prisms at 60°C, the expansion is 0.08% which is around four times the expansion at 38°C. As for the cylinders, the expansion is 0.135% at 60°C compared to the low expansion of 0.022% at 38°C. Also, it is shown that the expansion at 60°C has almost reached its ultimate value at 26 weeks. However, it is clear that the expansion at 38°C will reach much higher ultimate values at later ages since at 36 weeks the cubes expansions at 38°C started having higher expansions than the ones at 60°C, which reached a plateau with a value of 0.115%. Same for the cylinders where at almost 39 weeks, the expansions are 0.158% and 0.165% at 38°C and 60°C, respectively. As for the samples with 15% FA, the same trend can be observed from Figure 7 where the expansions at 60°C are higher from the ones at 38°C by around 0.008% for all the samples. Same observations are shown in Figure 8 for the samples with 35% slag. Thus, it could be concluded that at higher temperatures, the expansion rate is faster. However, the ultimate expansions at 60°C are not higher than the ones at 38°C, perhaps partly due to the characteristics of the swelling gel. At lower temperatures, the period at which the gel exerts its

maximum pressure is prolonged compared to higher temperatures. The gel composition differs from temperature to temperature with the ability of the gel to exert higher swelling pressures at lower temperatures (Poole 1992).

4.3 Degree of Hydration and Pozzolanic Reaction of Blended Cement

The paste samples were tested by TGA and LOI tests. Two important quantities are obtained from the analysis. First is the chemically bound water which gives an indication of the degree of hydration of the cementing materials. It gives an explanation about the amount of water needed for the cement to react. The second important quantity is the decomposition of the calcium hydroxide which occurs in the range of 440°C and 550°C. This quantity shows how much $Ca(OH)_2$ is present in the sample. $Ca(OH)_2$ is a product of the cement hydration. In presence of SCM, this quantity should normally decrease since SCM consume $Ca(OH)_2$ through pozzolanic reaction. The results of chemically bound water present in each sample are presented in Table 2. It should be noted that the tests have not been completed yet for the samples at 60°C and 28 days.

Table 2: CBW results obtained from LOI test (% of dry mass)

Time (Days)	Temperature (°C)	Control	Fly ash (15%)	Slag (35%)
7	23	16.6	16.8	14.6
	38	16.9	17.1	15.8
	60	17.4	17.6	16.4
28	23	17.8	17.7	16.1
	38	18.9	17.9	17.2

As shown in Table 2, the chemically bound water of blended mixes as well as the control is higher at higher temperatures. For example, the CBW, in the case of 35% slag at 7 days, is 14.6% at 23°C as compared to 16.4% at 60°C. As for the control, it is 16.6% at 23°C compared to 17.4% at 60°C. The chemically bound water is related to the degree of hydration. The higher the chemically bound water means higher degree of hydration. Thus, at higher temperatures, the degree of hydration of the samples is higher. The CBW is higher in the samples with 15% fly ash compared to the ones with 35% slag at the same age and temperature. At 7 days and 38°C for example, the CBW of the sample with FA is 17.1% and that of slag is 15.8%. This could be related to the fact that the fly ash sample has 85% Portland cement while the slag sample has only 65% Portland cement. Cement hydration is faster and this could explain, partly, the higher CBW in fly ash samples.

Table 3 presents the $Ca(OH)_2$ content in the different samples obtained from TGA analysis. It can be seen that the control has higher $Ca(OH)_2$ as temperature increases which confirms the fact that the degree of hydration is higher at higher temperatures, since $Ca(OH)_2$ is a by-product of cement hydration. Also, the control has the highest percent of $Ca(OH)_2$ with 20.9% after 28 days at 38°C. This is because no SCM is present to consume the calcium hydroxide. For blended mixes, the $Ca(OH)_2$ present in the samples is less compared to the control for all temperatures and ages.

Table 3: $Ca(OH)_2$ results obtained from TGA analysis (% of dry mass)

Time (Days)	Temperature (°C)	Control	Fly ash (15%)	Slag (35%)
7	23	17.0	17.1	10.5
	38	19.1	14.8	10.4
	60	19.5	14.3	11.9
28	23	17.5	14.3	11.3
	38	20.9	12.6	11.4

For example, at 28 days and 23°C, the control has 17.5% of $Ca(OH)_2$ as compared to the lower values of 14.3% and 11.3% for samples with FA and slag respectively. This is reasonable because SCM consume $Ca(OH)_2$ through pozzolanic reaction. For the samples with FA, it should be noted that the $Ca(OH)_2$ present drops with increase in temperature, with 17.1% at 23°C and 14.3% at 60°C for 7 days and 14.3% at 23°C and 12.6% at 38°C for 28 days.

However, this is not the case with slag. For example, at 7 days, the slag samples showed higher $Ca(OH)_2$ when tested at 60 ℃. In addition, the $Ca(OH)_2$ content is also increasing with age when tested at the same temperature. This could indicate that the control is producing more $Ca(OH)_2$ as temperature increases while the 35% slag did not consume as much between 7 and 28 days. In any case, the limited samples tested here are not enough to reach conclusions and more testing is in progress.

5. CONCLUSIONS

(a) Samples of smaller cross section have higher expansion at early ages, likely due to the higher relative humidity in their cores.
(b) At later ages, larger samples showed higher expansion suggesting that less leaching is occurring.
(c) At higher temperatures, the expansion rate is accelerated; however, the ultimate expansions are lower than the ones tested at lower temperatures.
(d) The chemically bound water and thus the degree of hydration of cement as well as blended mixes are higher at higher temperatures.
(e) There is evidence from this study that larger samples are likely to have higher ultimate expansion at later age, suggesting that the issue of alkali leaching during lab testing can be minimized.

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