# Role of Temperature on Alkali-Silica Reaction and the Efficacy of Supplementary Cementitious Materials

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**Highlights**

- Alkali release from aggregate to alkaline solution increases with temperature.
- Alkali leaching from concrete increases at higher temperatures.
- The binding capacity of cementing materials is higher at 38ºC compared to 60ºC and 23ºC.
- Concrete with SCM continues to expand at 60ºC until two years, unlike samples without SCM.

**Abstract**

Supplementary cementitious materials (SCM) are used in concrete to prevent expansion due to alkali-silica reaction. However, studies reported higher expansion in the field compared to that of laboratory samples, likely due to different exposure conditions. This paper investigates the effect of temperature on alkali release from aggregates, alkali leaching from concrete samples, and hydration and alkali-binding capacity of SCM. Aggregates contribute more alkalis to alkaline solutions at higher temperatures. Hydration of the tested cementing blends and their capacity to bind alkalis were highest at 38ºC, followed by 60ºC and 23ºC. The expansions of concrete cylinders at 60ºC are compared to those of the standard Concrete Prism Test.

**Keywords:** Alkali-silica reaction, alkali leaching, alkali release from aggregates, Supplementary Ceneting materials, hydration products, alkali binding capacity.

## 1. Introduction

Alkali-silica reaction (ASR) in concrete is a chemical reaction between the alkalis present in the concrete pore solution and the reactive silica in some aggregates [1,2]. This chemical reaction causes expansion, cracking, and other deleterious effects in concrete in the absence of preventive measures. The use of supplementary cementitious materials (SCM) is the method mostly implemented to prevent expansion due to ASR [3–5]. The right type and level of SCM required to reduce expansion are obtained based on the results of the Concrete Prism Test (CPT), described in the Canadian and American Standards, CSA A23.2-14A [6] and ASTM C1293 [7]. However, at later ages, the field expansions were found to be higher than the expansion obtained with the CPT at two years [8–10]. This is believed to be partly due to the excessive alkali leaching from the concrete samples during the CPT, leading to reduced pore solution alkalinity [4,11–13].

Studies have shown that paste samples without SCM cured at higher temperatures would lead to lower ultimate hydration due to the non-uniform distribution of the hydration products at early ages [14], although the rate of hydration was reported to be accelerated [14,15]. In addition, in the presence of fly ash, more hydration products were found at 40ºC and 60ºC, compared to 8ºC and 20ºC, and the lowest alkali concentration in the pore solution was obtained at 40ºC [15].

In addition, the testing temperature was found to affect the release of alkalis from the aggregates to the concrete pore solution. Some aggregates were shown to contribute significant amounts of alkalis to the pore solution [13,16]. Lu et al. [17] found that the alkali release from the aggregates increases exponentially with the increase in temperature between 20ºC and 80ºC. The alkali release might vary from one type of aggregate to another depending on the metamorphic alterations and mineralogical differences [17]. Another

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factor that was shown to be affected by temperature is the alkali leaching from concrete samples. Higher alkali leaching was obtained when testing concrete samples at 60ºC compared to 38ºC, which could be due to the increased diffusion at 60ºC [15]. The expansions of concrete samples without SCM at 60ºC reached lower ultimate values than the samples tested at 38°C [18]. However, research is needed to investigate the effect of temperature on the expansion of concrete samples containing SCM.

This paper investigates the effect of temperature on (i) the degree of hydration of SCM and the capacity of the hydration products to bind alkalis from pore solution, (ii) the alkali release from the aggregates, and (iii) the alkali leaching from concrete. These parameters are expected to help explain the different expansion results of the concrete samples tested under different lab and field conditions. Different concrete samples are investigated in this paper; however, the effect of sample shape on expansion was discussed elsewhere [13].

## 2. Materials and Experimental Methods

### 2.1. <u>Materials</u>

#### 2.1.1. Cementing Materials

General use Portland cement (GU-PC) having an alkali content of 0.99% $Na_2O_e$ was used in this study. Two supplementary cementitious materials were investigated: low calcium fly ash (FA) and slag. In addition, a blended cement consisting of 92% Portland cement (PC) and 8% silica fume (GUB-8SF) was used. The chemical compositions of the cementing materials are summarized in Table 1.

**Table 1.** Chemical compositions of cementing materials determined by XRF (% mass).

| Oxide | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $Na_2O$ | $K_2O$ | $Na_2O_e$ | Loss on Ignition | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| GU-PC | 19.54 | 5.21 | 2.16 | 62.39 | 2.39 | 4.03 | 0.24 | 1.14 | 0.99 | 2.36 | 99.46 |
| FA | 57.0 | 23.4 | 3.50 | 9.50 | 1.00 | 0.10 | 2.27 | 0.66 | 2.70 | 0.59 | 98.02 |
| Slag | 37.0 | 8.20 | 0.50 | 38.5 | 10.5 | 2.70 | 0.33 | 0.52 | 0.67 | 2.10 | 100.3 |
| GUB-8SF | 26.26 | 4.69 | 2.15 | 56.06 | 2.06 | 4.08 | 0.20 | 1.13 | 0.94 | 2.61 | 99.24 |

#### 2.1.2. Aggregates

Three coarse aggregates with different reactivity were investigated: (1) Sudbury (greywacke and argillite) from Sudbury, Ontario, Canada; (2) Spratt (siliceous limestone) from Ottawa, Ontario, Canada and (3) Springhill (greywacke and argillite) from Fredericton, New Brunswick, Canada. A non-reactive fine aggregate obtained from Caledon, Ontario, Canada, was used with all the concrete samples. The physical properties of the different aggregates and the 1-year CPT expansions of the concrete cast with these aggregates [13,19] are presented in Table 2.

**Table 2.** Physical properties of aggregates.

| Aggregate | Bulk Relative Density | Absorption (%) | 1-Year CPT Expansion (%) |
|---|---|---|---|
| Sudbury | 2.552 | 0.56 | 0.17 |
| Spratt | 2.691 | 0.52 | 0.21 |
| Springhill | 2.723 | 0.85 | 0.22 |
| Non-Reactive Sand | 2.538 | 1.30 | - |

### 2.2. <u>Experimental Program</u>

#### 2.2.1. Concrete Expansion Samples

Three concrete samples with different geometry were cast in this study: standard prisms (75x75x285 mm), cylinders (Ø100x285 mm), and 150-mm cubes. Since molds for cylinders and cubes with inserts to measure length change are not available commercially, they were fabricated in the laboratory. Mold fabrication and installation of the studs for length measurements were presented in more detail in [13].

Concrete samples were cast following the mix requirements specified in CSA A23.2-14A [6]. GU-PC cement was used, and its alkalinity was boosted to 1.25% $Na_2O_e$ by adding sodium hydroxide pellets. A water to

cementing materials ratio (w/cm) of 0.42 and a coarse to fine aggregates mass ratio of 60:40 were adopted as per the CSA standard [6]. The coarse aggregate gradation consisted of three equal portions of the following sizes: 19.5-13.2 mm, 13.2-9.5 mm, and 9.5-4.75 mm. The cubes were cast in three layers while cylinders in four layers; each layer was rodded 25 times. After 24 hours, samples were demolded, and zero readings were obtained. Cylinders were measured in a similar way as the prisms using a length comparator. For cubes, the measurements were performed diagonally on two faces, and the average expansion was reported. More details about the casting procedure of the concrete samples with different shapes and their corresponding storage containers can be found in Sinno and Shehata [13]. Each set of samples consisted of three prisms, three cylinders, or three cubes. The average expansion of three specimens of the same shape is reported here. Two sets from the same mix were cast: one stored in a heat room at 38⁰C and the other in an oven at 60⁰C. The samples were kept in containers above water as shown in Fig. 1 and stored at their designated temperatures.



<div align="center">(a)            (b)</div>

**Fig. 1.** Storage containers for (a) prisms and cylinders and (b) cubes.

### 2.2.2. Alkali Leaching from Concrete Samples

Alkali leaching from selected concrete samples was evaluated at 1.5 years. A 10-mL sample was obtained from the water at the bottom of the container and measured for sodium and potassium ion concentrations by flame photometry. The results are converted to sodium oxide equivalent ($Na_2O_e$) and reported as percent of cementing materials (CM) mass and as a percent of the initial alkali content in the mix, which is 1.25% $Na_2O_e$ by mass of Portland cement.

### 2.2.3. Alkali Contribution from the Aggregates

Alkali contribution from aggregates to alkaline solutions was studied at three different temperatures: 23⁰C, 38⁰C, and 60⁰C to examine the effect of temperature on the values of alkalis released from the three aggregates: Sudbury, Spratt, and Springhill. A 100 g sample consisting of 50 g with a size between 4.75 mm and 2.36 mm and 50 g with a size between 2.36 mm and 1.18 mm was obtained. This gradation was used since it will allow reasonable acceleration of the alkali release from the aggregates while maintaining the microstructural characteristics of the coarse aggregates [17]. The dry samples were soaked in alkaline solutions of different concentrations: 0.25 M NaOH, 0.25 M KOH, 0.70 NaOH, and 0.70 KOH. The release of $Na^+$ ions from the aggregate was measured in KOH solutions and that of $K^+$ ions in NaOH solutions. The aggregate to solution ratio was 1:1, similar to a study by Bérubé et al. [16]. After four weeks of soaking, a 2-mL sample was collected from the solution and tested for $Na^+$ and $K^+$ concentrations by flame photometry. Then, the aggregate samples soaked in alkaline solution were returned to their designated temperatures and measured once every four weeks until twelve weeks. Three replicates were used for each sample, and the average results with the min/max bar are presented.

### 2.2.4. Paste Samples

Paste cylindrical samples (Ø50x100 mm) were cast with slag or FA using different replacement levels and a w/cm ratio of 0.42 similar to that used with the concrete samples. A high-shear blender was used for mixing. First, cementing materials are added to the blender containing water. They were allowed to mix for three minutes at low speed. After, they were allowed to rest for two minutes, followed by another two minutes of mixing at medium speed. Then, a final two-minute rest followed by one-minute mixing was applied. Following the total of ten minutes of mixing and rest periods, the samples were cast and allowed to cure for 24 hours in a standard curing room at a temperature of 21 ± 2ºC and a relative humidity > 95%. After one day, they were demolded, and the paste cylinders were stored above water at their designated temperatures until the testing age. The paste samples were tested at three different temperatures: 23ºC, 38ºC, and 60ºC. This part of the study aims at investigating the effect of temperature on the pozzolanic activity of SCM and their ability to bind and retain alkalis. The samples were tested after 1, 3, 7, 28, and 92 days of curing at their designated temperatures.

At the age of testing, the cylinders were crushed to chunks in preparation for the alkali leaching test and Scanning Electron Microscopy (SEM) analysis and to fragments of size between 4.75 mm and 2.36 mm in preparation for the thermal gravimetric analysis (TGA). For the TGA, the samples were soaked in acetone for one week to remove the water from the pores and stop further hydration, followed by one week in a desiccator at 38ºC. The samples were kept in a desiccator with silica gel at room temperature in a $CO_2$-free environment - using soda lime - until the TGA was conducted. For the alkali leaching test and SEM, the paste chunks were dried in an oven at 100ºC until constant mass, after which they were stored in a desiccator with silica gel at room temperature in a $CO_2$-free environment until the time of running the test.

### 2.2.5. Thermal Gravimetric Analysis (TGA) on Paste Samples

Prior to running the test, the dry paste samples were collected from the desiccator and crushed to powder of size less than 80 μm using a pestle and mortar. TGA was then performed using a Mettler Toledo TGA/DSC 1 thermogravimetric analyzer. Two important quantities were obtained from the mass loss and heat flow curves generated at the end of the test. First, the non-evaporable water (NEW), i.e. chemically bound water, was obtained from the mass loss between 105ºC and 1050ºC expressed as a percent of the ignited mass. The calculated NEW was corrected for the initial loss on ignition of the raw cementing materials.

The second important quantity is the amount of calcium hydroxide ($Ca(OH)_2$). The decomposition of $Ca(OH)_2$ occurs in the range between 350ºC and 550ºC depending on the sample fineness and its mass [19,20]. In this study, the start temperature at which $Ca(OH)_2$ begins to decompose is the temperature at which the maximum energy is reached, which was obtained from the heat flow curve. In another study [19], the start temperature was obtained from the second derivative of the mass loss curve, which was found to give similar results to the method described here. The end temperature at which the decomposition of $Ca(OH)_2$ is completed was obtained from the maximum point on the first derivative curve of the mass loss. The mass loss between the start and end temperatures is attributed to the water loss during $Ca(OH)_2$ decomposition. The amount of $Ca(OH)_2$ is then calculated by stoichiometry and reported as a percent of the ignited mass. This quantity corresponds to the $Ca(OH)_2$ produced by cement in the case of control samples, or $Ca(OH)_2$ remained after pozzolanic reaction of SCM in the case of samples cast with SCM.

### 2.2.6. Powder Leaching Test on Paste Samples

Prior to testing, the dried paste samples were crushed to a size between 2.36 mm and 1.18 mm and then immersed in an alkaline solution of 0.25 M in sealed vials. This gradation was used similar to an earlier study by Kandasamy and Shehata [5]. The solution was prepared with the same $Na_2O$ to $K_2O$ ratio as that of the cementing materials (PC+SCM) of the samples being tested, and the ratio of solid to solution was 1:10 [5,21]. The paste samples soaked in alkaline solution were agitated for one week, and then the concentrations of sodium and potassium ions were obtained by flame photometry. The initial and final masses of the sealed vials were measured to make sure no evaporation had occurred. The alkalis released

from the cementing materials to the leaching solutions are the average of two specimens (two separate vials of powder and solution) and were expressed as % of the cementing materials (PC+SCM) mass.

### 2.2.7. Scanning Electron Microscopy (SEM) Examination on Paste Samples

Particles of size between 2.36 mm and 1.18 mm from the paste samples were examined by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analysis. Mature paste samples with 35% slag were tested at the three different temperatures (23ºC, 38ºC, and 60ºC). The dry paste particles were impregnated with epoxy and polished using a 0.3-μm diamond grade. Following that, the samples were sputtered with carbon using Edwards Vacuum Coating System. The polished sections were then examined under a JEOL JSM-6380 LV scanning electron microscope operated at 20 kV in backscattered electron imaging mode (BSE).

## 3. Results

### 3.1. Alkali Leaching from Concrete Samples

As shown in Fig. 2, the alkali leached from concrete samples stored at 60ºC was measured at 1.5 years and compared to samples tested at 38ºC. The leached alkalis are presented in Fig. 2(a-1) and Fig. 2(a-2) as a percentage of cementing materials (CM) mass (420 kg/m$^3$) and in Fig. 2(b-1) and Fig. 2(b-2) as a percentage of original alkalis in the mix, which is 1.25% Na$_2$O$_e$/mass of Portland cement (without SCM).
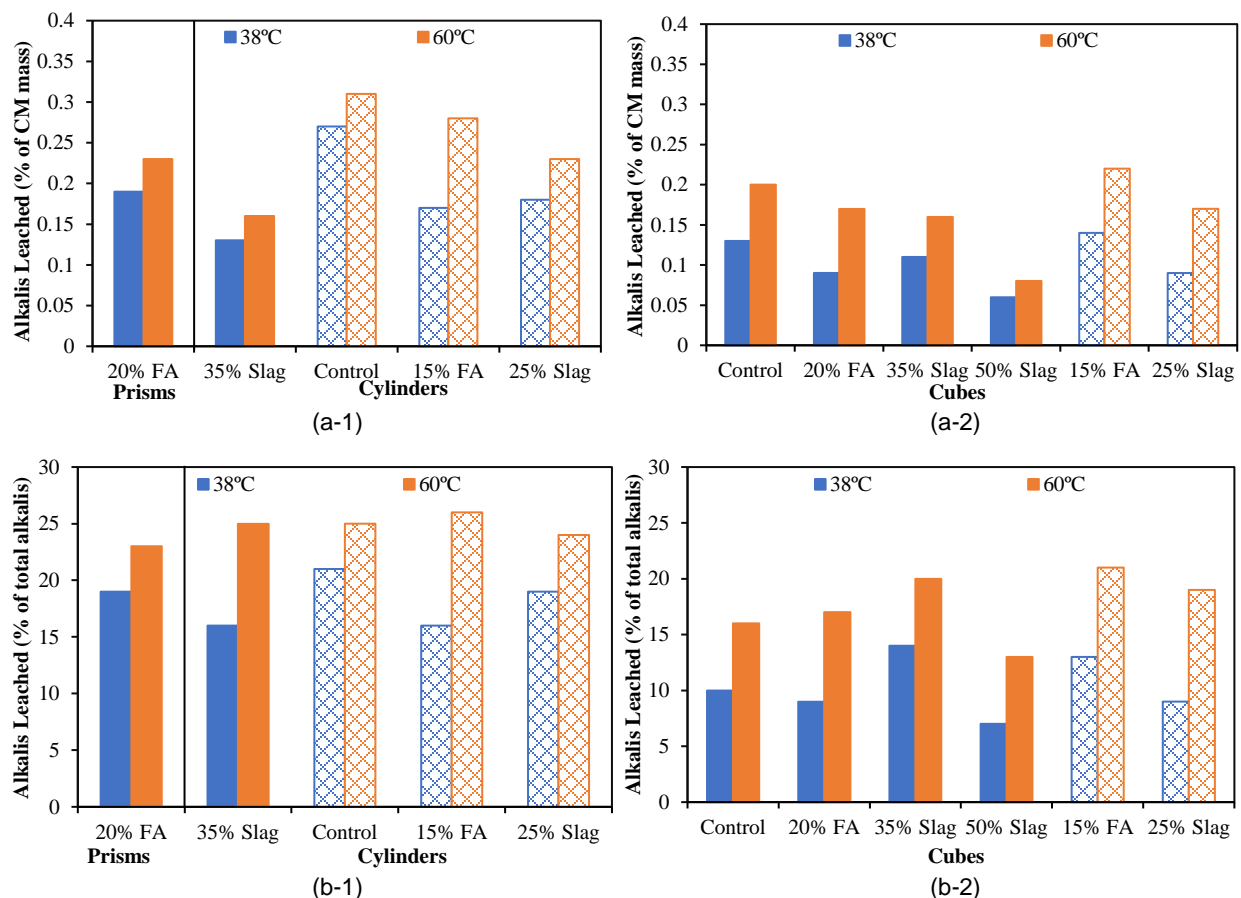


**Fig. 2.** Alkalis leached from concrete (1) prisms or cylinders and (2) cubes tested at 38ºC and 60ºC at 1.5 years expressed as % of (a) Cementing Materials (CM) mass and (b) total alkalis. (The solid and hatched filled bars correspond to concrete samples cast with Spratt and Sudbury aggregates, respectively).

Higher alkali leaching from concrete samples at 60ºC compared to 38ºC was obtained for all the different sample geometry and different aggregate/SCM combinations. The higher leaching at elevated temperature could be due to a higher diffusivity of alkalis [15]. The higher leaching obtained at 60ºC leads to a lower pore solution alkalinity. In terms of sample shape, it has been demonstrated that the leached alkalis are larger in concrete prisms, followed by cylinders and cubes [13].

The addition of SCM reduces the leached alkalis, as shown in Fig 2(a-1) and 2(a-2). It is also clear that the amount of leached alkalis is further reduced at higher SCM levels, likely due to the refined pore structure associated with the use of SCM. When the leached alkalis are normalized to the original alkalis in the mix, Fig 2(b-1) and 2(b-2), the normalized leached alkalis are reduced at higher replacement levels of SCM, as is clear from the case of cubes containing slag at 50%. As far as ASR is concerned, the authors believe that the amount of alkalis expressed as % of CM is more relevant to the reaction. Fig 2(b-1) and 2(b-2) are presented here to demonstrate that at higher levels of SCM, the leached alkalis are reduced to the extent that the value is low, even when normalized to the low initial alkalis in a mix with high SCM (or low PC). Collectively, the results show that for samples with SCM - particularly higher levels - alkali leaching might not be that significant or having the same impact on the expansion as the case of samples without SCM.

### 3.2.     Alkali Release from Aggregates

Alkali release from aggregates to solutions of different alkalinity was studied at three different temperatures: 23ºC, 38ºC, and 60ºC. Sodium ions are measured in KOH solutions as it is easier to trigger changes in $Na^+$ concentration in KOH solution. Similarly, $K^+$ concentration was measured in NaOH solutions. Alkaline solutions with concentrations of 0.25 M and 0.70 M were used as the 0.70 M corresponds to concrete pore solution before significant ASR has occurred, and 0.25 M represents the alkalinity after significant ASR has taken place [5,21]. Results of alkali release from aggregates to alkaline solutions correspond to the average of three samples, are presented in Fig. 3 along with the min/max error bars. Higher alkali release was obtained in the solution of higher alkalinity (Fig. 3(a) vs. Fig. 3(b)) due to the fact that higher pH favors the attack of the reactive silica and liberation of the alkalis from the aggregates, as explained in [13].
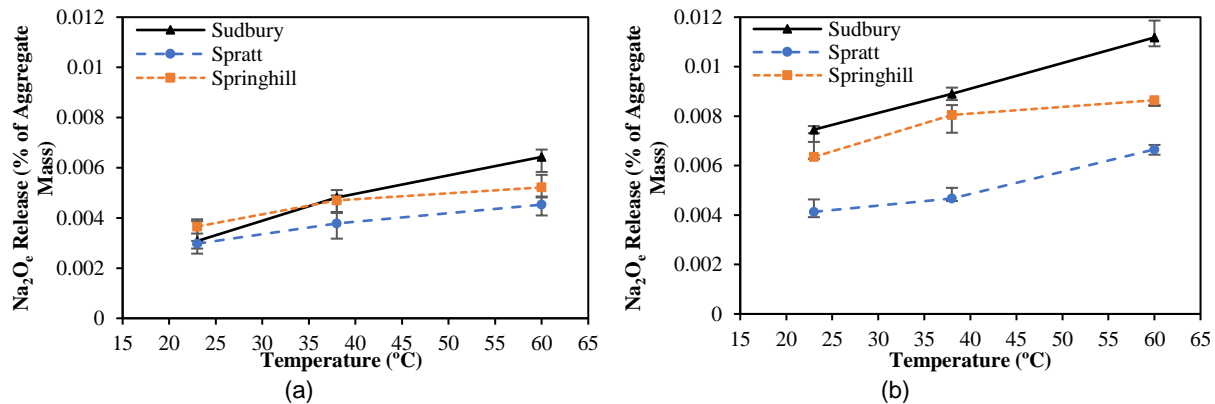


(a)                                             (b)

**Fig. 3.** Total alkalis released from aggregate to alkaline solution of (a) 0.25 M and (b) 0.70 M after 12 weeks with min/max error bars.

Higher release of total alkalis from the three tested aggregates to the alkaline solution is obtained with increased temperatures showing the highest release at 60ºC. This might aid in increasing the pore solution alkalinity of concrete samples tested at elevated temperatures. The maximum alkali contribution obtained - when tested in 0.70 M alkaline solution for 12 weeks – are 0.011% $Na_2O_e$ for Sudbury, 0.009% for Springhill, and 0.007% for Spratt. To put these values in context, the alkali contribution from aggregates in a concrete mixture with 1000 kg of coarse aggregate per $m^3$ would be 0.11, 0.09, and 0.07 kg of $Na_2O_e$ for Sudbury, Springhill, and Spratt, respectively. A concrete mix with 420 kg of PC with $Na_2O_e$ of 1.0% would have a total alkali of 4.20 kg $Na_2O_e$. With SCM replacing part of the PC, the alkalis from the PC would be less. So, one can argue that the alkalis from the aggregates might not be that significant. Nevertheless, the

results show that alkalis are more readily available from aggregates at higher temperatures and in a solution of high alkalinity, representing concrete before significant ASR takes place.

### 3.3. The capacity of SCM to bind alkalis

#### 3.3.1. Hydration of Cement without SCM

Fig. 4 shows the $Ca(OH)_2$ contents of paste samples without SCM up to 92 days at 23ºC, 38ºC, and 60ºC. The results reflect the degree of hydration of cement at different temperatures as more $Ca(OH)_2$ content indicates more hydration in cement pastes. The non-evaporable water contents of the paste samples with no SCM followed the same trend as the $Ca(OH)_2$ content.
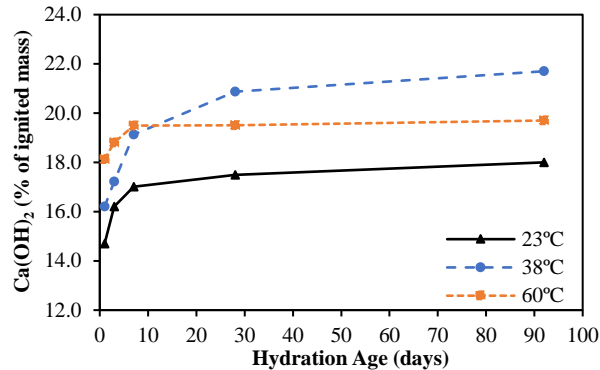


**Fig. 4.** $Ca(OH)_2$ formed in paste samples without SCM at different temperatures.

At 92 days, samples stored at 38ºC and 60ºC showed higher $Ca(OH)_2$ compared to 23ºC, indicating that more hydration is occurring at temperatures higher than 23ºC. The samples tested at 60ºC showed accelerated results until seven days; however, the hydration started to slow down after that; at 92 days, the $Ca(OH)_2$ reached a lower value compared to samples tested at 38ºC. The reason could be that at early ages of testing at 60ºC, the distribution of the hydration products is not uniform, with a dense product formed around the unreacted cement particles, preventing further hydration [14]. This is in line with the non-evaporable water content results where higher values were obtained for samples tested at 38ºC followed by 60ºC and then 23ºC. This explains that at early ages, the hydration is accelerated at 60ºC. However, at a later age, the hydration is slowed down at 60ºC, leading to lower ultimate $Ca(OH)_2$ compared to that at 38ºC.

#### 3.3.2. Pozzolanic Reaction and Alkali-binding Capacity of SCM

The non-evaporable water (NEW) contents of paste samples incorporating different SCM are shown in Fig. 5 for samples with FA and slag. Increasing the temperature seems to promote early hydration as reflected by high NEW. However, the ultimate degree of hydration at 92 days was highest at 38ºC followed by 60ºC and 23ºC, although the values at 60ºC and 23ºC were close. The obtained NEW reflects the hydration of both PC and SCM. The $Ca(OH)_2$ consumption of these cementing blends - shown in Fig. 6 and 7 - can shed light on the degree of hydration of SCM alone. The $Ca(OH)_2$ content of FA shown in Fig. 6 shows a lower $Ca(OH)_2$ content at 38ºC, although the paste with only PC shows the highest $Ca(OH)_2$ content at that temperature. In other words, the $Ca(OH)_2$ consumption by FA is highest at 38ºC, suggesting a higher pozzolanic activity or degree of hydration of SCM at that temperature. The consumption of $Ca(OH)_2$ at the other two temperatures is not much different. These results are in agreement with the NEW results and collectively show a higher degree of hydration for both PC and PC + FA at 38ºC. The difference in $Ca(OH)_2$ content between 23ºC, 38ºC, and 60ºC is not very evident for samples with slag, shown in Fig. 7, although the NEW for samples with slag was highest at 38ºC as shown in Fig. 5. The similar $Ca(OH)_2$ content in pastes with slag is attributable to its high calcium content compared to the low-calcium FA, which adds to the calcium availability in the system, resulting in more available $Ca(OH)_2$ after the reaction.
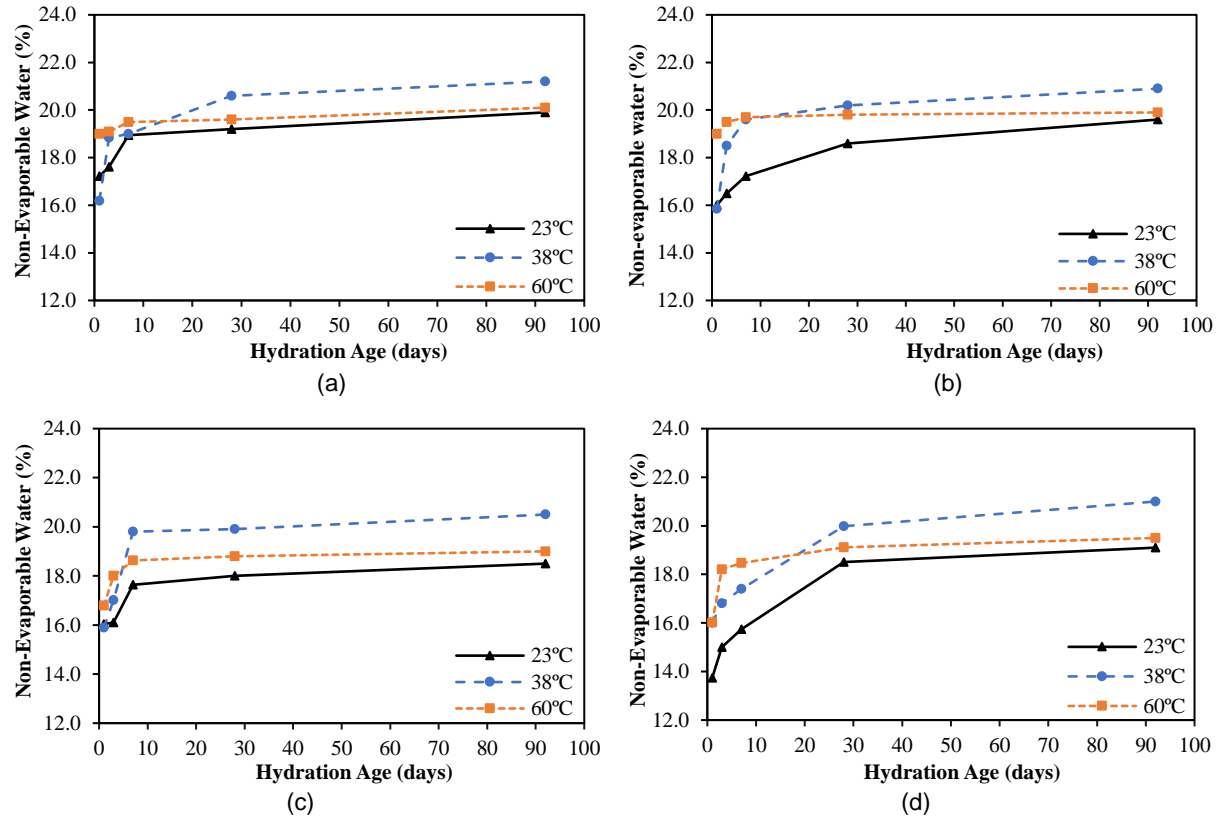
**Fig. 5.** Non-evaporable water at different temperatures for paste samples with (a) 15%FA, (b) 25% FA, (c) 25% slag, and (d) 35% slag.
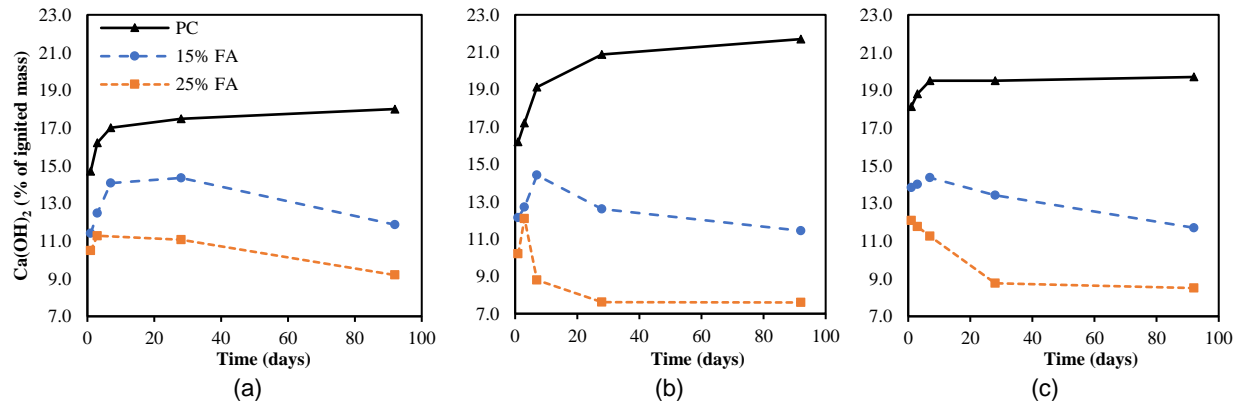


**Fig. 6.** Ca(OH)$_2$ in paste with 15% and 20% FA at (a) 23ºC, (b) 38ºC and (c) 60ºC.
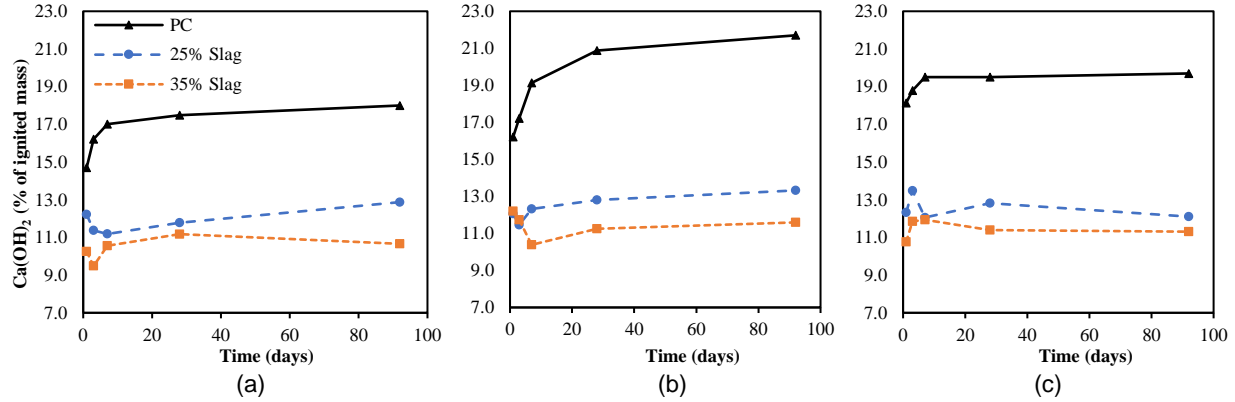
**Fig. 7.** Ca(OH)$_2$ in paste with 25% and 35% FA at (a) 23ºC, (b) 38ºC and (c) 60ºC.

The next step in this experimental program was to evaluate the effect of temperature on the ability of the cementing blends to bind and retain alkalis at different temperatures by determining the alkali released from the dried paste samples to a 0.25 M alkaline solution. The 0.25 M solution corresponds to the lowest alkalinity the concrete could reach due to the alkali consumption by reactive aggregates [22]. A lower value of contributed alkalis indicates a high efficacy of the blend to bind and retain alkalis. Such high efficacy is due to more hydration products, a hydrate composition that increases its ability to bind alkalis, or a combination thereof. At 92 days, higher alkali release from samples at 23ºC was obtained compared to 38ºC and 60ºC, as shown in Fig. 8. The alkali released from SCM to the test solution was the lowest in samples tested at 38ºC followed by 60ºC then 23ºC, which is in line with the Ca(OH)$_2$ consumption and degree of hydration (NEW) presented earlier.
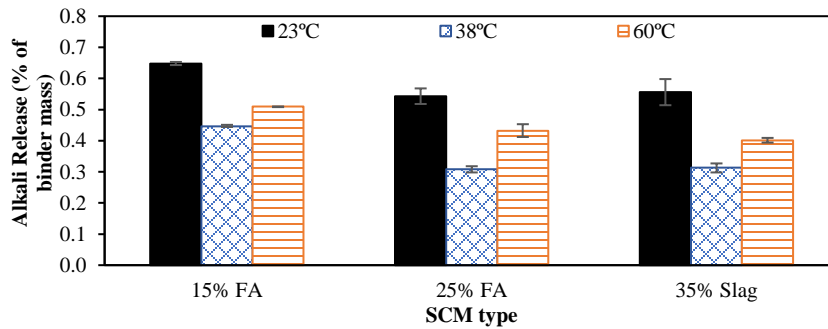


**Fig. 8.** Alkali release by SCM into 0.25 M solution at 92 days with min/max error bars.

### 3.3.3. SEM Analysis

Scanning electron microscopy (SEM) was performed on paste samples with slag at a 35% replacement level to study the effect of temperature on the inner hydrates' composition. The elements of interest are calcium, silica (and Ca/Si), alumina, potassium, and sodium of the inner hydrates of PC. Outer hydrates could not be analyzed as they were found mixed with other hydration products. Images obtained from the SEM analysis for paste samples containing 35% slag are shown in Fig. 9. For each sample, ten points were analyzed at different sites (inner hydrates surrounding a calcium silicate grain) with two to three measurements taken in each site. Looking at Fig. 9(d), the limited results show that there is no well-defined trend on the effect of temperature on Ca/Si ratio, although the sample cured at 23ºC seems to have more points at the lower end of the Ca/Si as defined by the red circle on the graph. Hydrates of lower Ca/Si are known to bind more alkalis [23,24]. The other finding is that the level of Al in the hydrates is higher at a higher temperature, perhaps due to a higher dissolution of alumina from the slag. Higher Al/Si can result in higher alkali binding since replacing Si with Al increases the hydrates' negative charge, raising their capacity to bind the positively-charged alkali cations [25].
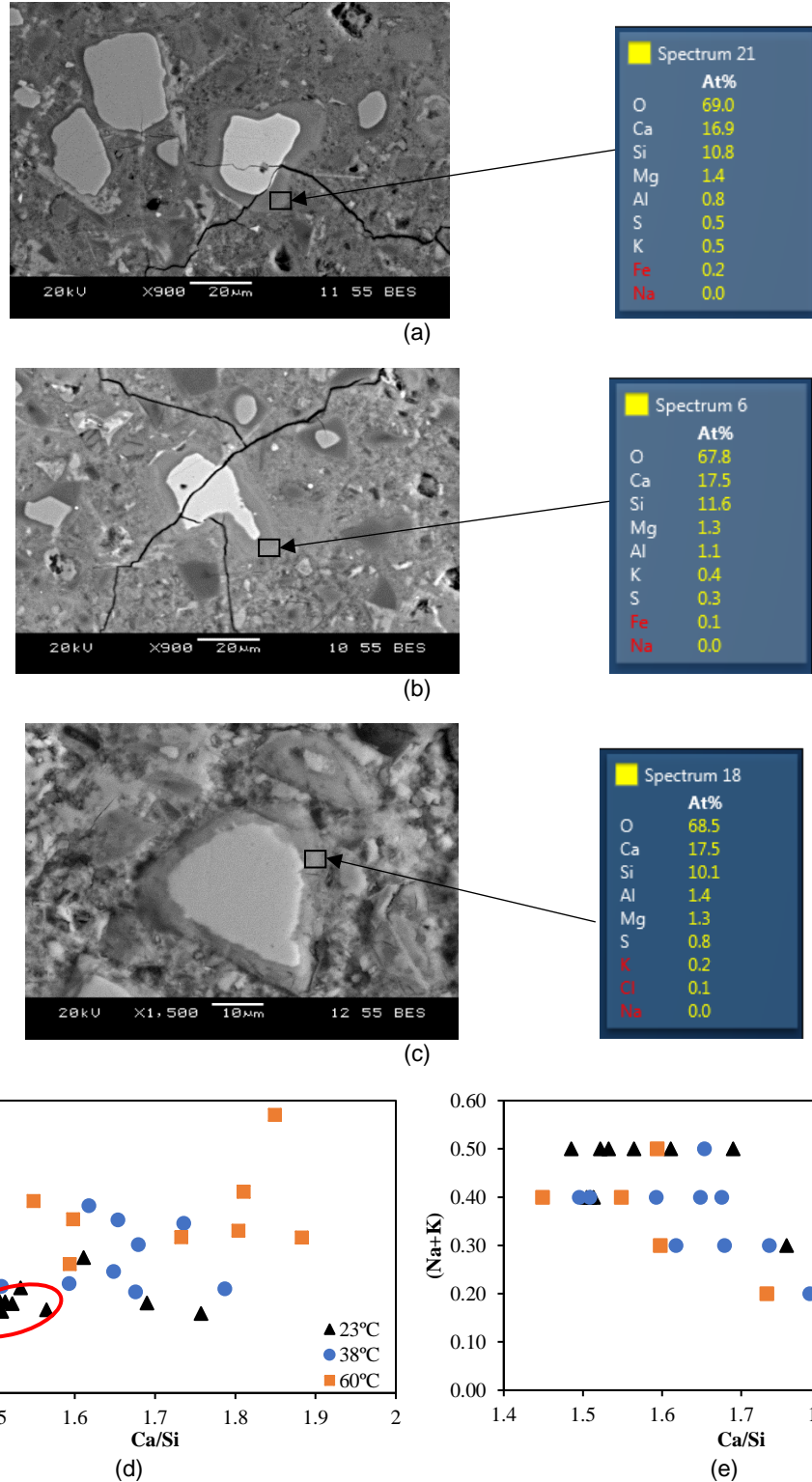
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Spectrum 21

| | At% |
|---|---|
| O | 69.0 |
| Ca | 16.9 |
| Si | 10.8 |
| Mg | 1.4 |
| Al | 0.8 |
| S | 0.5 |
| K | 0.5 |
| Fe | 0.2 |
| Na | 0.0 |

(a)



Spectrum 6

| | At% |
|---|---|
| O | 67.8 |
| Ca | 17.5 |
| Si | 11.6 |
| Mg | 1.3 |
| Al | 1.1 |
| K | 0.4 |
| S | 0.3 |
| Fe | 0.1 |
| Na | 0.0 |

(b)



Spectrum 18

| | At% |
|---|---|
| O | 68.5 |
| Ca | 17.5 |
| Si | 10.1 |
| Al | 1.4 |
| Mg | 1.3 |
| S | 0.8 |
| K | 0.2 |
| Cl | 0.1 |
| Na | 0.0 |

(c)



(d)



(e)

**Fig. 9.** SEM of paste with 35% slag tested at 2 years of curing at (a) 23⁰C, (b) 38⁰C, (c) 60⁰C, (d) Al/Ca vs. Ca/Si and (e) (Na+K) vs. Ca/Si for the corresponding samples.

Although there was no specific trend in Fig. 9(e) between Ca/Si and the measured alkalis in the hydrates, most of the test points taken in the sample cured at 23⁰C showed relatively high alkali content. This is likely attributable to these hydrates' low Ca/Si, as shown in Fig. 9(d). In any case, the SEM study carried out

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here is somewhat limited. The authors believe that the thermal analysis and alkali release investigations provide more comprehensive results on the amount and composition of all hydration products (inner and outer) rather than the limited number of spot analyses carried out in the SEM analysis. Nevertheless, the increased alumina in the hydration products of the sample cured at 60ºC can help explain the lower alkali release from this sample compared to that of the sample cured at 23ºC (Fig. 8), although the NEW contents and Ca(OH)$_2$ consumptions at the two temperatures were not much different.

### 3.4.    Expansion of Concrete Samples

This section covers the expansion of concrete samples tested at 38ºC and 60ºC to evaluate how the factors investigated in the previous sections might affect the expansion results.

#### 3.4.1. Concrete without SCM

Fig. 10 shows the expansions of prisms, cylinders, and cubes tested at 38ºC and 60ºC for Sudbury, and Spratt aggregates without SCM. The effect of sample geometry on expansion due to ASR was explained in [13] in which cylinders produced higher expansion than prisms - with cubes being the lowest - when tested at 38°C.  In the current study, and as shown in Fig 11., the 1-year expansions of samples tested at 38ºC were higher than that of samples tested at 60ºC for all the different sample shapes and aggregates. This is likely due to higher alkali leaching from the concrete samples at 60ºC compared to 38ºC. It is interesting to note that higher temperatures accelerate expansion at early ages. However, the expansion at 60 °C reached a plateau after 18 weeks, likely due to excessive leaching. While alkali release from aggregate to concrete is higher at a higher temperature (Fig. 3), the amount of the released alkalis was not enough to sustain the expansion at 60ºC.
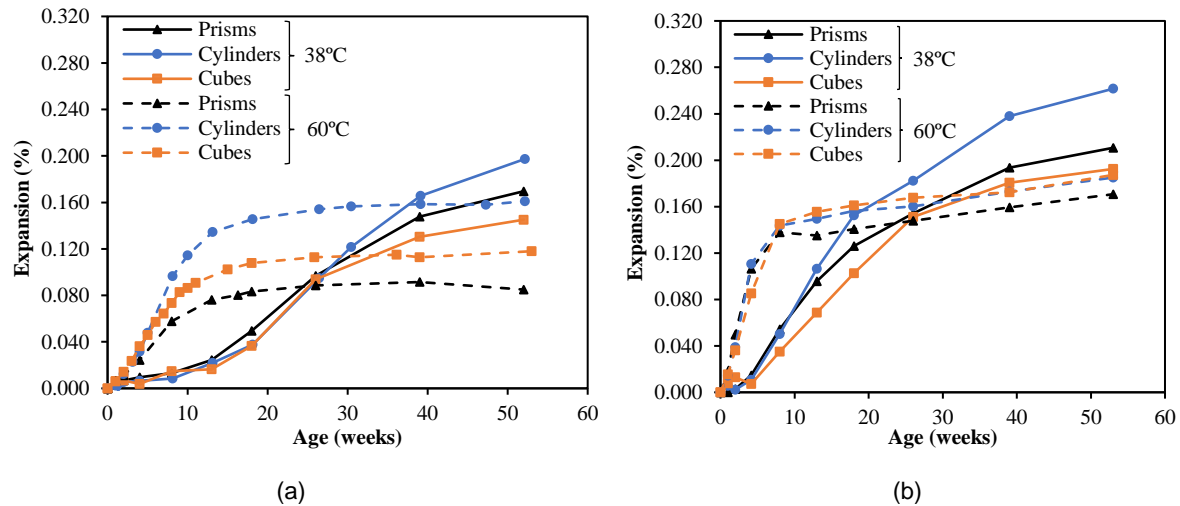


(a)                                                          (b)

**Fig. 10.** Expansion of concrete cast with (a) Sudbury and (b) Spratt aggregates.

#### 3.4.2. Concrete with SCM

The 2-year expansions of concrete samples cast with Sudbury aggregates with SCM are presented in Fig. 11 and Fig. 12. Contrary to the case of samples without SCM, the expansions of Sudbury samples with SCM show similar 2-year results at 38ºC and 60ºC for all different sample shapes, except for the cylindrical sample with Sudbury and 25% slag.
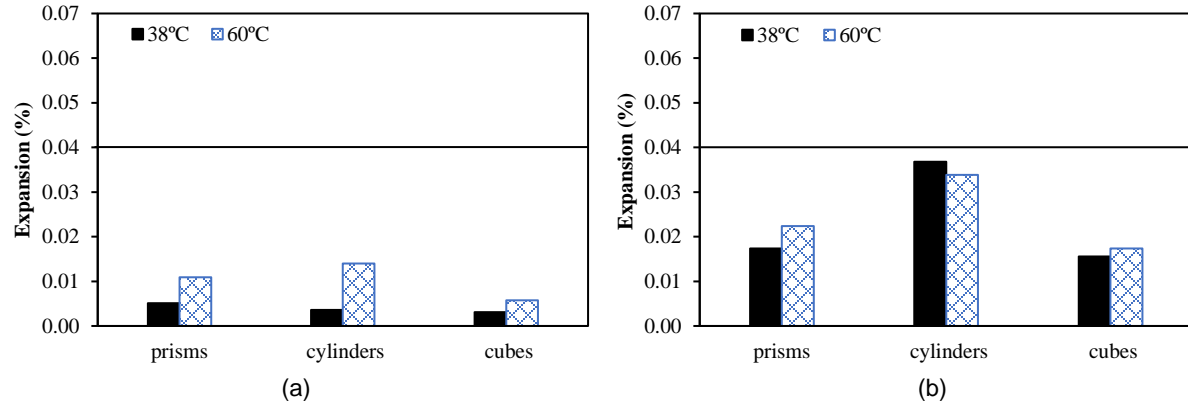
**Fig. 11.** Expansion of concrete cast with Sudbury aggregate and 15% FA at (a) 1 year and (b) 2 years.
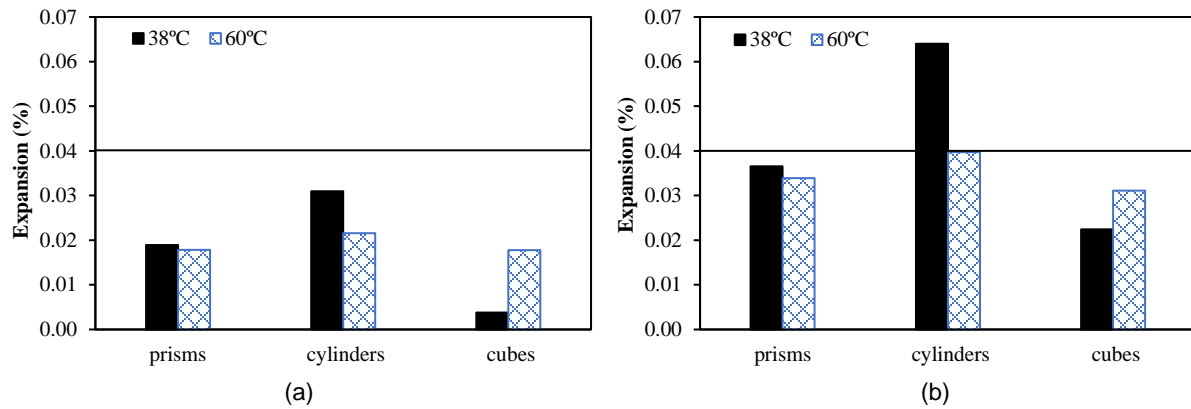


**Fig. 12.** Expansion of concrete cast with Sudbury aggregate and 25% Slag at (a) 1 year and (b) 2 years.

The one-year and two-year expansions of Spratt samples cast with 15% FA at 38ºC and 60ºC are presented in Fig. 13. The 2-year expansions at 38ºC and 60ºC did not show any statistical difference for all the different sample shapes, which was concluded by taking a two-tail t-test with a significance level of 0.05. At one year, however, the expansions at 60°C were higher than at 38ºC.
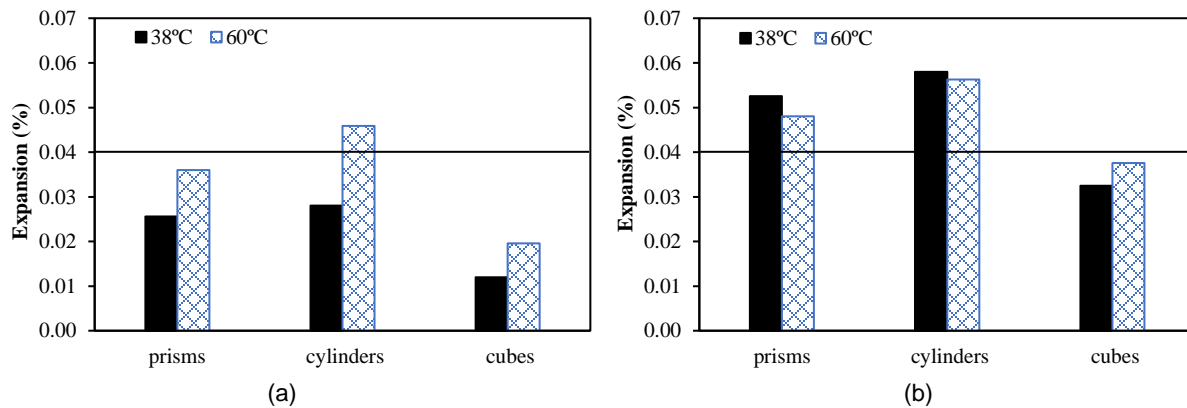


**Fig. 13.** Expansion of concrete cast with Spratt aggregate and 15% FA at (a) 1 year and (b) 2 years.

At a higher replacement level, Spratt sample cast with 20% FA showed a slightly higher expansion at 60ºC compared to 38ºC for all the different sample shapes, as shown in Fig. 14. At higher levels of SCM, slag at 35% and 50%, the higher expansion at 60ºC became more evident, as shown in Fig. 15 and Fig. 16.
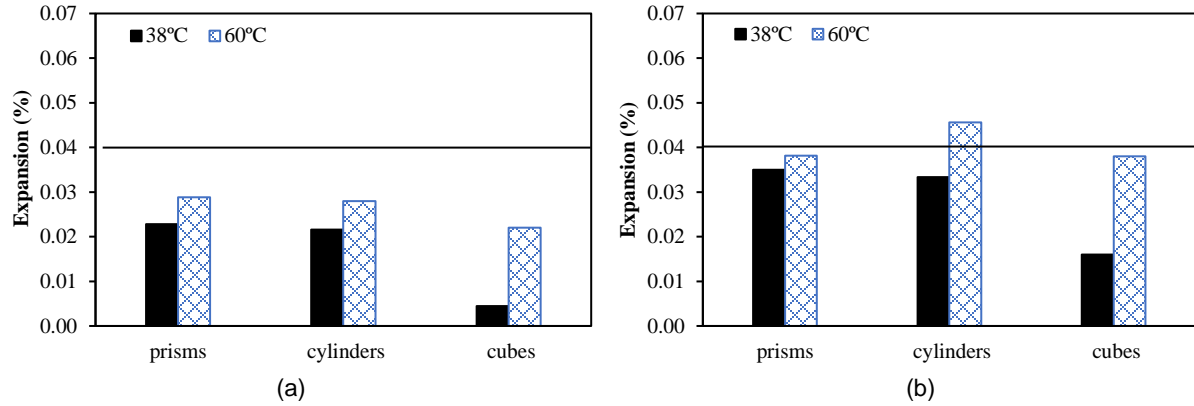
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**Fig. 14.** Expansion of concrete cast with Spratt aggregate and 20% FA at (a) 1 year and (b) 2 years.
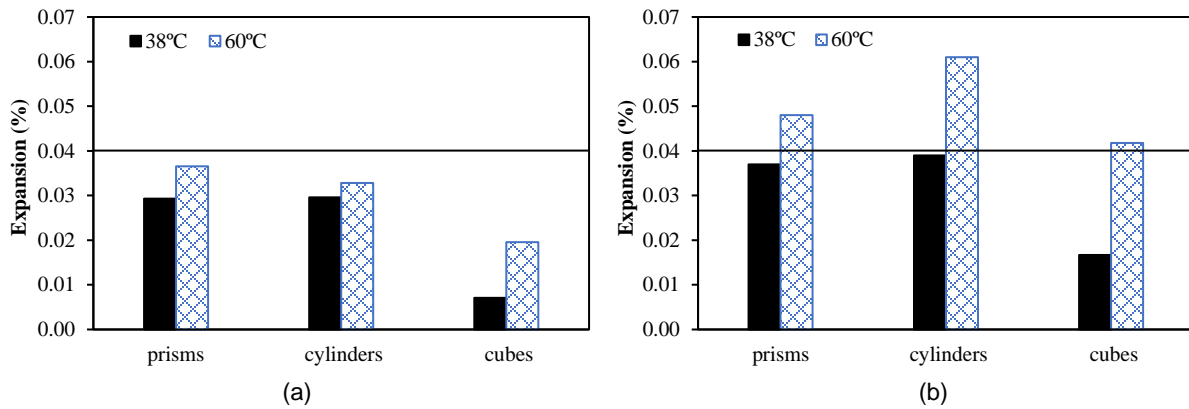


**Fig. 15.** Expansion of concrete cast with Spratt aggregate and 35% Slag at (a) 1 year and (b) 2 years.
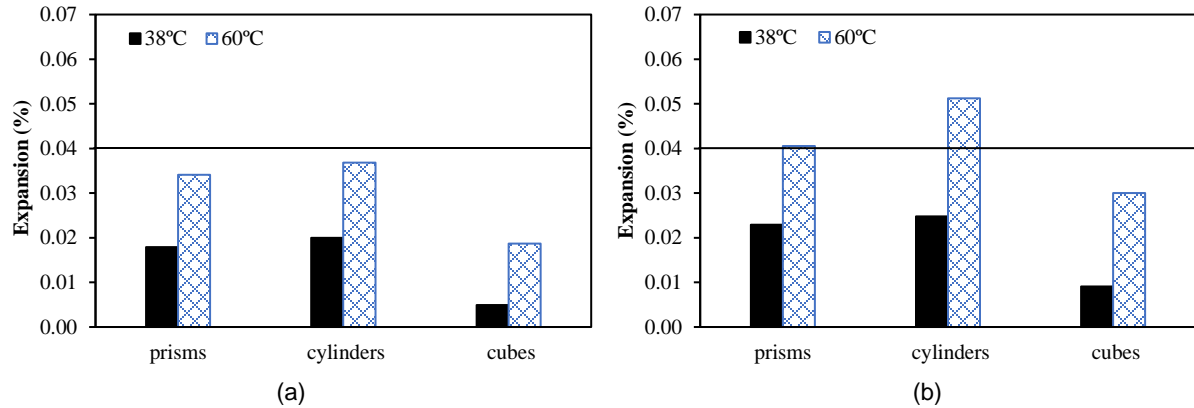


**Fig. 16.** Expansion of concrete cast with Spratt aggregate and 50% Slag at (a) 1 year and (b) 2 years.

Looking collectively at the expansion results, it is clear that expansions are higher at 60 °C, particularly at two years, for samples with high levels of SCM. This observation is contrary to the case of samples without or with lower levels of SCM, which is likely due to: (i) reduced alkali leaching at high replacement levels of SCM, leaving more alkalis in the samples for expansion to continue, and (ii) lower efficacy of SCM to bind and retain alkalis at 60 °C compared to 38 °C, which is better manifested at higher SCM levels. It should be noted that testing at 60 °C accelerates the ASR itself; however, testing samples for two years at such temperature might be too aggressive compared to conditions that are encountered during the service life of structures.

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Another way to look at the results is the possibility to shorten the test duration of concrete with SCM from two years at 38ºC to one year at 60ºC. Although there is still higher alkali leaching at 60ºC compared to 38ºC even with SCM, the use of cylinders rather than prisms would reduce leaching [13].

As an investigation on testing at 60ºC for 50% of the duration of the standard CPT, Table 4 shows the expansions of prisms at 38ºC and cylinders at 60ºC for different aggregates/SCM combinations. All samples showed a pass/pass or fail/fail relationship. However, it seems that the approach is safer - or perhaps overestimates the expansion – in samples with cementing systems that significantly enhance pore structure or reduce leaching such as high level of SCM or ternary blends. For cementing blends of low level of SCM, the 2-year expansion of CPT at 38ºC is slightly higher, likely due to considerable alkali leaching for these blends at 60ºC. It is also interesting to see that the difference between expansions of Sprat samples with 35% and 50% slag is not that significant when testing at 60ºC, likely due to less alkali leaching from samples with 50% slag. More samples need to be tested and compared to long-term expansions from the field to evaluate the possibility of evaluating SCM at 60ºC.

**Table 4:** Comparison of prisms expansion at 38ºC and cylinders at 60ºC.

| Sample type | | Expansion of cylinders at 60ºC* | Expansion of prisms at 38ºC** | Exp. at 38 °C – Exp. at 60 °C (%) | Pass/Fail Criterion |
|---|---|---|---|---|---|
| Sudbury | Control | 0.154 | 0.170 | 0.016 | Fail/Fail |
| | 15% FA | 0.014 | 0.017 | 0.003 | Pass/Pass |
| | 25% Slag | 0.022 | 0.037 | 0.015 | Pass/Pass |
| Spratt | Control | 0.160 | 0.211 | 0.051 | Fail/Fail |
| | 15% FA | 0.046 | 0.053 | 0.007 | Fail/Fail |
| | 20% FA | 0.028 | 0.035 | 0.007 | Pass/Pass |
| | 35% Slag | 0.033 | 0.037 | 0.004 | Pass/Pass |
| | 50% Slag | 0.037 | 0.023 | -0.014 | Pass/Pass |
| | GUB-8SF+15% FA | 0.021 | 0.012 | -0.009 | Pass/Pass |

*6-month expansion for control samples and 1-year expansion for samples with SCM.
**1-year expansion for control samples and 2-year expansion for samples with SCM.

## 4. Discussion

The findings of this research could explain - at least partly - the observed discrepancies in expansions obtained between the field and laboratory testing. In the field, the average temperatures are lower than the CPT standard testing temperature of 38ºC. The current work shows that at 38ºC, SCMs have a higher level of hydration and alkali binding capacity which might lead to lower expansions compared to those obtained in the field. In addition, the reduced alkali leaching in the field compared to laboratory samples contributes to the high expansion and cracking observed in the field at later ages [10], despite meeting the 2-year expansion limit of the CPT.

Based on the results obtained in this paper, testing SCM at 60ºC might offer some benefits. At 60ºC, more alkalis are released from the aggregates, particularly at the start of the testing, at which time the pore solution alkalinity is still high (section 3.2). This release of alkalis might address the concern that alkalis might be contributed from aggregates during the service life of structures, leading to late expansion. Compared to testing at 38°C, the hydration of SCM and their alkali binding capacity at 60 °C are closer to those at 23°C; hence, closer to hydration under in-service temperature in many locations. Testing at 38°C provides optimized hydration products in terms of the degree of hydration and alkali binding capacity. However, comparing expansion results from standard prisms at 38ºC at 2 years and cylinder at 60ºC at 1 year revealed that alkali leaching at 60ºC plays a significant role in the obtained expansions. Based on the results, samples with high levels of SCM are likely to show higher 1-year expansion at 60ºC, while those with a low level of SCM are likely to produce lower expansion. This finding is important to consider as when

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SCM is investigated for ASR mitigation, the interest is on finding the minimum level that prevents expansion which is likely to be in the range of the low levels investigated here. Also, the effects of SCM level on alkali leaching might render testing at 60ºC unsuitable for comparing different SCM levels - as was shown when comparing Spratt samples with 35% slag to samples with 50%. In summary, the results shed light on the effect of testing temperature on the parameters that affect expansions.  More expansion testing of different aggregates/SCM combinations needs to be carried out to establish the validity of testing at 60ºC. Also, ways to minimize alkali leaching at 60ºC can help to enhance the test outcomes.

## 5. Conclusions

The following conclusions could be drawn from this study:

a) Aggregates contribute more alkalis to concrete pore solution at higher temperatures.
b) Alkali leaching from concrete samples increases at higher temperatures leading to reduced concrete pore solution alkalinity and expansion. This observation explains the lower ultimate expansions at 60ºC compared to 38ºC for samples without SCM.
c) The degree of hydration and alkali-binding capacity of the tested SCM was highest at 38°C, followed by 60°C and 23°C.
d) Concrete samples cast with SCM - particularly high level - expanded more at 60ºC compared to 38ºC – unlike samples without or with low level of SCM.
e) The discrepancies between field and standard laboratory results at 38°C could be partly explained by the finding that the hydration of SCM is enhanced under laboratory testing as compared to the field where the average temperatures in many regions are lower than 38ºC.
f) Testing cylinders at 60ºC showed some benefits in reducing the test duration, but more testing is needed

## CRediT authorship contribution statement

**Noura Sinno:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Visualization. **Medhat H. Shehata:** Supervision, Conceptualization, Methodology, Project administration, Funding acquisition.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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