

# TRACKING ALKALI MIGRATION AND LEACHING IN THE AUTOCLAVED CONCRETE PRISM TEST

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## Abstract

The progression of alkali-silica reaction consumes alkalis to form reaction product, leading to a reduction in hydroxide and alkali concentrations in the pore solution over time. However, for specimens in the ASTM C1293 concrete prism test (CPT), the reduction in pore solution alkalinity is strongly influenced by alkali leaching.

An autoclaved concrete prism test has shown promise in correctly classifying aggregates that the CPT fails to identify as reactive. Specimens are identical to those of the CPT with the exception that the equivalent alkali content is boosted to 3.0% by mass of cement. Prisms are autoclaved at a temperature of 133 °C for 24 hours, providing final results in just four days.

The amount of alkali leaching is determined by analyzing samples of autoclave water and expressed pore solution using ICP-OES. Results show alkali leaching of only 4-11%, which is significantly lower than the 12-25% alkali leaching in the CPT.

**Keywords:** alkali-silica reaction, alkalis, pore solution, autoclave, alkali leaching

## 1 INTRODUCTION

Pore solution analysis, in conjunction with other methods, has been used for tracking the progress of alkali-silica reaction (ASR) in concrete. In the analysis, the concentrations of hydroxides (OH<sup>-</sup>) and alkalis are determined. Because the OH<sup>-</sup> ions, primarily supplied by the portlandite in cement paste, roughly balance the alkali ions, namely sodium (Na<sup>+</sup>) and potassium (K<sup>+</sup>), within the pore solution, the concentrations of the anion and cations should be proportional in a chemical analysis [1,2]. The progression of ASR consumes increasingly more alkalis to form reaction product, leading to a reduction in both [OH<sup>-</sup>] and [Na<sup>+</sup> + K<sup>+</sup>] in the pore solution over time [3-5].

Although some alkalis are consumed by the ASR product, Rivard et al. [2,6] determined that for specimens used to conduct the Canadian CSA A23.2-14A [7] or ASTM C1293 concrete prism test (CPT) [8], the decrease in pore solution alkalis was mainly caused by alkali leaching. Leaching of alkalis occurs when mortar bars or concrete specimens are stored in a moist environment where condensation occurs on the surface of the specimens, drawing out alkalis and consequently depositing them in water contained below. This phenomenon was first observed by Blanks and Meissner [9] in 1946 when they noticed an increase in alkali concentration in the water at the bottom of mortar bar storage containers. Ideker et al. [10] also noted that temperature affects the amount of leaching; storage temperatures of 60 °C in the accelerated concrete prism test caused more alkali leaching than the standard 38 °C used in the CPT.

The autoclaved concrete prism test (ACPT) is a new, ultra-rapid test method for determining the reactivity of both coarse and fine aggregates for ASR currently being evaluated at The University of Alabama (UA) [11,12]. This test involves casting concrete prisms with the same dimensions as those required by ASTM C1293 and, after 24 hours of remaining in the molds in ambient laboratory temperatures and 24 hours moist curing, autoclaving them at temperature of 133 °C (0.20 MPa gage pressure) for 24 hours. Expansions of the concrete prisms are measured and used as an indicator of aggregate reactivity. No pore solution analysis, nor analysis of autoclave water, have previously been conducted on autoclaved concrete prisms.

The objective of this study is to track the migration of alkalis by analyzing the pore solution and autoclave water of autoclaved concrete prisms used in the ACPT via an inductively-coupled plasma optical emission spectrometer (ICP-OES). Results of this analysis determine the potential for alkali leaching in the new test method. Additionally, findings, along with results obtained from petrographic examination, could help to confirm ASR as the mechanism of expansions observed in the test.

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## 2 MATERIALS AND METHODS

### 2.1 General

This research builds upon previous work on the ACPT in which autoclaved concrete prism expansions were measured and compared to expansion results from the ASTM C1260 accelerated mortar-bar test (AMBT), CPT, and field behavior [11,12]. The aggregates tested in the ACPT were of varying reactivities from different locations across the United States and were tested against a non-reactive crushed limestone from San Antonio, Texas that was used as both the fine and coarse counterpart.

After the concrete prisms were conditioned in the autoclave, the pore solutions of the prisms and the bottom water inside the autoclave were analyzed to determine alkali concentrations. Chemical analyses of pore solution and autoclave water samples from concrete prisms using five different aggregates are presented here along with the measured expansions of the prisms.

### 2.2 Materials and Mixture Proportions

Aggregate abbreviations, source locations, mineralogies, and reactivity classifications are given in Table 1. Reactivity classifications are based on field performance, CPT data, and AMBT results. Coarse aggregates are indicated by a C-designation, and fine aggregates are indicated by an F-designation. The specimen size (75 x 75 x 285 mm) and aggregate gradations in this study matched those specified in ASTM C1293. The equivalent alkali content ( $\text{Na}_2\text{O}_{\text{eq}}$ ) of each mixture was boosted to 3.0% of the cement mass by adding sodium hydroxide (NaOH) to the mixing water, and the w/cm was 0.42. Three cements with  $\text{Na}_2\text{O}_{\text{eq}}$  ranging from 0.46% to 0.99% were used in this research in an effort to determine the effect, if any, of alkalis provided by the cement versus alkalis provided by NaOH on prism expansion, pore solution chemistry, and alkali leaching. Chemical analyses of the cements are provided in Table 2. All mixtures had a cement content of 420 kg/m<sup>3</sup> and bulk volume of coarse aggregate equal to 0.70. Fine aggregate proportions were calculated using the absolute-volume method [14].

### 2.3 Methodology

#### *General*

Three concrete prisms and three 100 x 200-mm concrete cylinders were cast from each mixture. Stainless steel gage studs were embedded in the tops and bottoms of the prisms for length change measurements. The mixing procedure was as follows:

1. Add all of the aggregate and half of the mixing water (with NaOH added).
2. Mix for 1 minute.
3. Stop mixer and add all of the cement.
4. Mix for 30 seconds.
5. Add the remaining water over a 30-second period while mixer is running.
6. Mix for 2 minutes.
7. Stop and cover mixer for 3 minutes.
8. Mix for 2 minutes and sample.

Prisms and cylinders were covered with plastic and remained in molds for 24 hours in the laboratory before they were demolded and moist-cured until testing at an age of 48 hours for the prisms and 28 days for the cylinders.

After curing, concrete prisms were measured using a length change comparator before being conditioned in a commercially-available autoclave for 24 hours at 133 °C (0.20 MPa gauge pressure). Prisms were placed upright inside the autoclave chamber in a wire basket so that they were not resting on the embedded metal studs. The wire basket sat upon a steel plate which was suspended above deionized water used to create a steam environment. A schematic of the autoclave chamber interior is provided in Figure 1.

The prisms were removed from the autoclave once the unit reached 90 °C and were cooled upright in a tap water bath over approximately 1 hour until prism temperatures reached 23 °C. They were once again measured using the comparator, and expansions were calculated. The proposed expansion limit for the ACPT is 0.08%; an aggregate with an expansion at or above this value is considered reactive.

The autoclave water was sampled at the time that the prisms were removed and was immediately refrigerated at 4 °C until chemical analysis was performed. Bérubé and Tremblay [4] demonstrated that freezing concrete prisms for two weeks prior to pore solution expression had no significant influence on  $[\text{K}^+ + \text{Na}^+]$  in the pore solution; they concluded that freezing specimens and

thawing them before pore solution expression was a viable storage method to prevent further progress of ASR in specimens if the pore solution could not be immediately expressed at a desired age. Therefore, after the final length measurement, one prism from each batch was covered in plastic cling wrap and placed in a freezer at about -18 °C. Specimens were thawed one day prior to pore solution expression.

#### *Pore Solution Expression*

Pore solution samples were expressed from the concrete prisms using a high-pressure die similar to the one used by Longuet et al. [15]. Prisms were pre-crushed, and the coarse aggregate was removed by hand, leaving 200-250 g of broken mortar. The sample was placed inside the die and subjected to a pressure of approximately 700 MPa to express the pore solution. About 6 mL of solution was obtained from each concrete prism. Vials of pore solution were immediately sealed and refrigerated to prevent carbonation, leaching, and dilution prior to analysis, which was performed within 12 hours of expression.

#### *ICP-OES*

ICP-OES was used to determine the concentrations of alkalis in the concrete pore solution and autoclave water samples. Calcium ( $\text{Ca}^{2+}$ ), silicon ( $\text{Si}^{4+}$ ), potassium ( $\text{K}^+$ ), and sodium ( $\text{Na}^+$ ) concentrations were measured. Shortly before the samples were diluted and analysed, nitric acid was added to obtain a 2% nitric acid solution. ICP-OES was first performed on pore solution samples diluted at a ratio of 100:1 with deionized water, but because  $\text{K}^+$  and  $\text{Na}^+$  concentrations were so high, the dilution ratio was increased to 1000:1 to obtain accurate values for those alkali concentrations. Autoclave water samples were also brought to a 2% nitric acid solution prior to dilution and ICP-OES analysis. The autoclave water samples were diluted at a ratio of 10:1 or 20:1 with deionized water, depending on the amount of  $\text{K}^+$  and  $\text{Na}^+$  present in the samples.

#### *Titration*

Titrations were performed on selected pore solution and autoclave water samples using phenolphthalein as the indicator and a 0.05 M hydrochloric acid (HCl) solution as the titrant. Pore solution samples were initially diluted 100:1 with deionized water, but the amount of titrant used to achieve equilibrium was low in these samples, so the dilution ratio was changed to 50:1. All dilutions used deionized water with a resistivity of at least 18.0 M $\Omega$ . Autoclave water samples were not diluted for titration except for mixture C5-2 because the sample supply was low; that autoclave water sample was diluted 2:1.

### **3 RESULTS**

Table 3 shows average prism expansions for each concrete mixture. Mixture names correlate to the test aggregate abbreviations and the cement used. For example, mixture C1-2 was composed of aggregate C1 and cement 2. The average prism expansion for F3 mixtures, 0.51%, far exceeds expansions exhibited by the other mixtures. In fact, the second-most expansive mixtures, which used aggregate F4, only expanded half as much as the F3 mixtures, averaging 0.25% expansion. Overall, cement alkalinity did not predictably influence the degree of prism expansion in this study. Not all of the mixtures listed in Table 3 were analysed for pore solution and autoclave water alkalinity.

Pore solution expression calculations indicated that at least 35% of evaporable water from the crushed concrete samples was extracted. This percentage is lower than the actual percentage of solution that was expressed, however, because the 6-mL vials were overflowing each time solution was expressed.

Concentrations of  $\text{K}^+$  and  $\text{Na}^+$  and  $\text{Si}^{4+}$  and  $\text{Ca}^{2+}$  in the pore solutions, determined by ICP-OES, are shown in Figure 2 and Figure 3, respectively. Pore solution alkalinity, represented as  $[\text{K}^+ + \text{Na}^+]$ , ranged from about 800 to 1400 mmol/L for these samples. Reactive mixtures containing aggregates F3 and C5 revealed higher levels of  $\text{Si}^{4+}$  and lower levels of  $\text{Ca}^{2+}$  in the pore solutions compared to the other samples. Mixture F3-3, far surpassed all other mixtures in expansion and contained the lowest concentrations of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  in the pore solution. Concretes using aggregate F4, which demonstrated expansions between those of concretes using aggregates F3 and C5, did not produce high concentrations of  $\text{Si}^{4+}$  in the pore solutions but exhibited higher levels of  $\text{Ca}^{2+}$  compared to the F3 and C5 mixtures. In fact,  $\text{Si}^{4+}$  and  $\text{Ca}^{2+}$  concentrations in pore solutions of F4 mixtures were almost equal; this was also the case with the pore solution sample from the C2 concrete. Overall, alkalinity of the pore solution did not appear to be directly related to prism expansion.

Concentrations of  $K^+$  and  $Na^+$  in the autoclave water, determined by ICP-OES, are illustrated in Figure 4 and shown in Table 4 along with calculated alkali leaching percentages. The percentage of leached alkalis was calculated based on the initial alkali content of the concrete, which was  $12.6 \text{ kg/m}^3 \text{ Na}_2\text{O}_{\text{eq}}$  for all mixtures. The concentrations of  $K^+$  and  $Na^+$  were used to calculate the  $\text{Na}_2\text{O}_{\text{eq}}$  of the autoclave water in  $\text{mg/L}$ . That number was then multiplied by the volume of deionized water initially added to the autoclave (7 L) and divided by the number of prisms being conditioned at once (3 prisms), giving a mass of alkalis ( $K^+$  and  $Na^+$ ) per prism, which was compared to the initial alkali content. Alkali leaching in these samples ranged from about 4 to 11% per prism. There was no discernible correlation between prism expansion and degree of alkali leaching.

Concentrations of  $Si^{4+}$  and  $Ca^{2+}$  in the autoclave water samples are shown in Figure 5. As with the pore solution samples, autoclave water samples from mixtures containing aggregates F3 and C5 contained higher levels of  $Si^{4+}$ . In both pore solution and autoclave water samples, the concentrations of  $Ca^{2+}$  and  $Si^{4+}$  were trivial compared to those of  $K^+$  and  $Na^+$ , and concentrations of  $Na^+$  were at least three times  $K^+$  concentrations in both types of samples.

Titration results for pore solution and some autoclave water samples are shown in Table 5 and Table 6, respectively. Each sample was titrated three times unless indicated otherwise, and pH values were calculated using the determined  $OH^-$  concentrations. For the pore solution samples, concentrations of  $OH^-$  from titration were compared to the combined concentrations of  $K^+$  and  $Na^+$  from ICP-OES analysis because these values should be approximately equal in high pH systems [1,2]. However, the alkali concentrations far exceeded the hydroxide concentrations in pore solutions from this study. Other autoclave water samples were titrated but not before the samples were altered by age, so those titrations were not included in this paper. The samples presented here were tested at 1 and 17 days after sampling from the autoclave.

#### 4 DISCUSSION

Based on aggregate mineralogies and established reactivity classifications via other test methods and field behaviour, the prism expansions obtained were not surprising. No clear correlation between cement alkalinity and prism expansion in the ACPT could be found in this work and other ongoing, unpublished work by the authors. With the high quantities of added NaOH to mixtures in this study, the influence of cement alkalinity was expectedly negligible.

The amount of pore solution expressed from the concrete prisms exceeded amounts commonly reported in the literature [2,4,6]. However, certain factors such as specimen age, w/cm, and applied expression pressure varied in the literature and were not always similar to factors in this study. Bérubé and Tremblay [4], applying constants most comparable to those used here, expressed only about 20% of evaporable water from cement paste cylinders aged 3 days with a w/cm equal to 0.42 using up to 1000 MPa of pressure for expression. The greater amounts of pore solution expressed in this study (at least 35% of evaporable water) could be attributed to a somewhat higher pressure exerted on the prisms inside the autoclave; the higher pressure may reduce the amount of water leached from the prisms, resulting in more pore solution expressed.

Overall, pore solution alkalinity,  $[K^++Na^+]$ , was higher in this study than what has been documented in the literature [2,4,6]. Concentrations of  $K^+$ , ranging from 100 to 200 mmol/L in this study, were typical, but  $Na^+$  concentrations, ranging from 700 to 1200 mmol/L, were much higher than those found other works. This dissonance is due to the relatively large amount of NaOH added to the mixing water to achieve a 3.0%  $\text{Na}_2\text{O}_{\text{eq}}$  in these mixtures; studies in the literature did not involve  $\text{Na}_2\text{O}_{\text{eq}}$  above 1.25%.

No other definitive conclusions can be drawn from the observed  $K^+$  and  $Na^+$  concentrations in the pore solutions in this study. However, it should be noted that the mixture for which average prism expansion far exceeded expansions of the other mixtures, mixture F3-3, contained the lowest  $[Na^+]$  in the pore solution. This is likely due to the incorporation of  $Na^+$  in the reaction product within the concrete. The well-known behaviour of this particular aggregate in both laboratory and field conditions supports this theory.

Mixtures containing aggregates F3 and C5 demonstrated patterns similar to each other regarding  $[Si^{4+}]$  and  $[Ca^{2+}]$  in pore solutions; there were significantly higher  $Si^{4+}$  concentrations and significantly lower  $Ca^{2+}$  concentrations in the pore solutions from these mixtures compared to the other mixtures. Also in common between these two aggregates is the presence of feldspars, which have been shown to contribute to alkalis to the pore solution over time [16-18]. The release of  $Si^{4+}$  from the aggregates into the pore solution would explain the elevated concentrations of  $Si^{4+}$  for these concretes if ASR is indeed the cause of prism expansion.

Alkali leaching in the ACPT, 4 to 11% per prism, is relatively low compared to the amount of leaching observed in the CPT, which is between 12 and 25% per prism [2,6]. The duration of conditioning is likely a significant factor here because alkali leaching occurs over time; the ACPT is completed in only four days while the CPT takes 1 year or more. If the ACPT concretes were conditioned for as long as the CPT concretes, then increased alkali leaching would be expected.

As stated in the literature, at high pH, the summed concentrations of  $K^+$  and  $Na^+$  has been found to be approximately equal to the concentration of hydroxides in pore solution for concretes cured in standard laboratory conditions and without added alkalis [1,2]. However, this relationship did not exist in the titrated samples from this research. Diamond and Ong [19] demonstrated an increase in sulfate concentrations and decrease in  $OH^-$  concentrations for mortar bars with added alkali hydroxides.  $SO_4^{2-}$  concentrations on the order of 250 mmol/L have been reported for concretes exposed to high curing temperatures (up to 80 °C to 90 °C) and would balance 500 mmol/L of  $Na^+_{eq}$  [20-23]. If similar sulfate concentrations were present in the pore solution of the autoclaved specimens, this would explain a substantial portion of the observed imbalance between  $[K^++Na^+]$  and  $[OH^-]$ .

## 5 CONCLUSIONS

Based on the results from this study, the following conclusions can be made:

- With the high quantities of added NaOH to mixtures in this study, the influence of cement alkalinity was expectedly negligible.
- Pore solution alkalinity,  $[K^++Na^+]$ , was higher in this study than what has been documented in the literature. Significantly higher concentrations of  $Na^+$  found in the pore solutions were responsible for this increased alkalinity, which was caused by the relatively large amount of NaOH added to the mixing water to achieve a 3.0%  $Na_2O_{eq}$  in these mixtures.  $K^+$  concentrations were typical to those in other works.
- The most expansive mixture, F3-3, showed the lowest level of  $Na^+$  in the pore solution compared to the other mixtures. Based on the well-known behaviour of this aggregate, it is likely that  $Na^+$  was incorporated into the ASR product within these prisms.
- Mixtures incorporating the known reactive aggregates, F3 and C5, showed higher levels of  $Si^{4+}$  and lower levels of  $Ca^{2+}$  in the pore solutions. The release of  $Si^{4+}$  from the aggregates into the pore solution would explain the concentrations of  $Si^{4+}$  for these concretes if ASR is indeed the cause of prism expansion.
- Alkali leaching in the ACPT, 4 to 11% per prism, is relatively low compared to the amount of leaching observed in the CPT, which was between 12 and 25% per prism. Low alkali leaching in the ACPT is probably most related to the short testing duration because leaching typically occurs over longer periods of time as it does in the CPT.
- The summed concentrations of  $K^+$  and  $Na^+$  and the concentrations of  $OH^-$  in the pore solutions analysed in this study were not approximately equal as they are in the literature. This is most likely due to an increase in sulfates in the pore solution brought about by the addition of NaOH and exposure to high-temperature conditions in the autoclave.
- Therefore, sulfates should be measured in future pore solution analyses of ACPT specimens and other concretes and mortars subjected to autoclaving conditions.

In further evaluation of the ACPT, it is advised that the autoclave water samples be chemically tested shortly after being sampled. One autoclave water sample in this study was 161 days old before it was chemically analysed. Four samples were around 60 days old, and the remaining samples were less than 30 days old. Only a couple of aggregates that were used more than once for autoclave water analysis, aggregates F4 and C5, demonstrated a range of sample age. In comparing chemical compositions of these samples to their ages, there appeared to be no significant change brought about by age of the sample. However, data for this is quite limited because there were only two F4 mixtures and three C5 mixtures. Therefore, any conclusions based on the effect of sample age on chemical composition or alkali concentrations are impractical at this point.

Additionally, pore solutions of concrete prisms should be expressed in a timelier manner. Four prisms were around a year old, two prisms were close to 200 days old, and the other two prisms were less than 25 days old prior to pore solution expression in this study. Concretes using aggregates F4 and C5 were the only repeat tests in which sample ages varied substantially, and comparison of alkali concentrations versus prism age revealed no significant effect caused by age. However, as in the case of the autoclave water samples, current data are not enough to draw conclusions at this time.

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TABLE 1: Aggregate abbreviations, source locations, mineralogies, and reactivity classifications. Reactivities are based on CPT data and field behaviour.

Aggregate Abbreviation	Source Location	Mineralogy	Reactivity
C1	Adairsville, Georgia	Dolostone	Borderline reactive
C2	Helena, Alabama	Dolomitic limestone	Non-reactive
F3	El Paso, Texas	Natural sand; quartz, feldspars, volcanics, chert	Highly reactive
F4	Sumter, South Carolina	Natural sand; quartz, strained quartz, quartzite	Potentially reactive
C5	Wells, Maine	Micas, feldspars	Reactive

TABLE 2: Cement oxide analyses.

Oxide Shorthand Notation	% by Weight		
	Cement 1	Cement 2	Cement 3
SiO <sub>2</sub>	20.1	20.2	19.8
Al <sub>2</sub> O <sub>3</sub>	4.07	4.7	5.3
Fe <sub>2</sub> O <sub>3</sub>	3.18	2.9	2.4
CaO	63.74	62.8	63.1
MgO	2.53	2.4	2.9
SO <sub>3</sub>	3.17	3.0	3.8
Loss on Ignition	2.40	2.5	0.8
Na <sub>2</sub> O <sub>eq</sub>	0.46	0.56	0.99

TABLE 3: Average concrete prism expansions grouped by aggregate.

Mixture	Avg. Prism Expansion, %
C1-1	0.06
C1-2	0.08
C1-3	0.06
C2-1	0.06
C2-2	0.05
C2-3	0.05
F3-1	0.50
F3-2	0.48
F3-3	0.55
F4-1	0.28
F4-2	0.28
F4-3	0.18
C5-1	0.15
C5-2	0.14
C5-3	0.13

TABLE 4: Autoclave water concentrations from ICP-OES analysis and calculated percent leached alkalis per concrete prism.

Mixture	Autoclave Water Concentration, mg/L			Leached Alkalis, %
	K <sup>+</sup>	Na <sup>+</sup>	Na <sub>2</sub> O <sub>eq</sub>	
C1-2	72.35	280.45	435.74	4.86
C2-1	75.28	30.55	475.99	5.31
C2-2	69.16	249.07	390.86	4.36
F3-3	107.05	238.05	405.90	4.53
F4-1	76.46	305.93	473.37	5.28
F4-3	206.82	403.25	707.70	7.90
C5-1	145.96	636.41	974.40	10.88
C5-2	136.70	518.05	807.31	9.01
C5-3	165.69	328.91	574.85	6.42

TABLE 5: Titration results for pore solution samples.  $[\text{Na}^+ + \text{K}^+]$  was determined via ICP-OES. Samples were titrated three times unless indicated otherwise.

Mixture	$[\text{Na}^+ + \text{K}^+]$ , mmol/L	Average $[\text{OH}^-]$ , mmol/L	Average pH
C1-2	1014	427	13.63
F4-1	1191	423	13.62
C5-1*	1162	405	13.61
C5-2	1338	500	13.69

\* Titrated twice.

TABLE 6: Titration results for autoclave water samples. Samples were titrated three times unless indicated otherwise.

Mixture	Average $[\text{OH}^-]$ , mmol/L	Average pH
C5-1*	15.32	12.19
C5-2	15.80	12.20

\* Titrated twice.

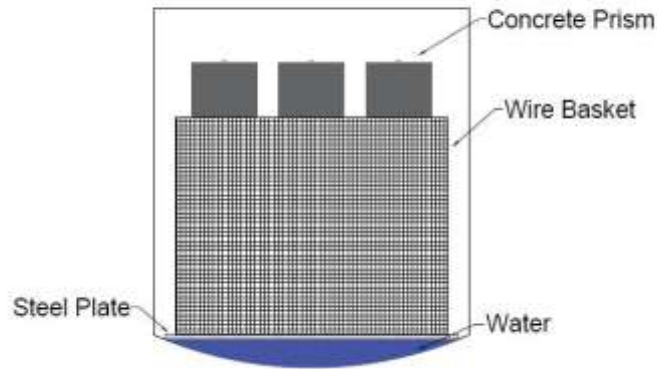


FIGURE 1: Schematic of the autoclave chamber with concrete prisms.

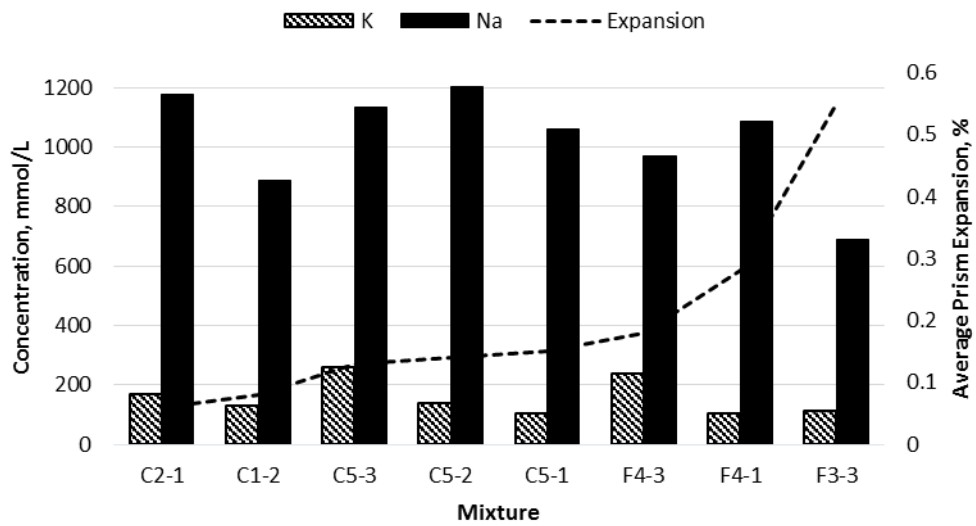


FIGURE 2: Pore solution concentrations of  $\text{K}^+$  and  $\text{Na}^+$  determined by ICP-OES. The dashed line shows average concrete prism expansions in the ACPT.



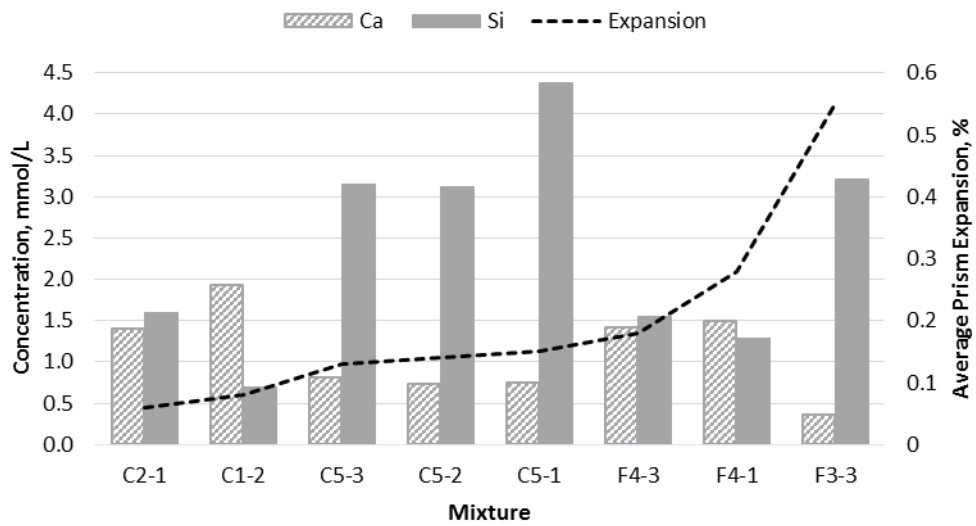


FIGURE 3: Pore solution concentrations of Ca<sup>2+</sup> and Si<sup>4+</sup> determined by ICP-OES. The dashed line shows average concrete prism expansions in the ACPT.

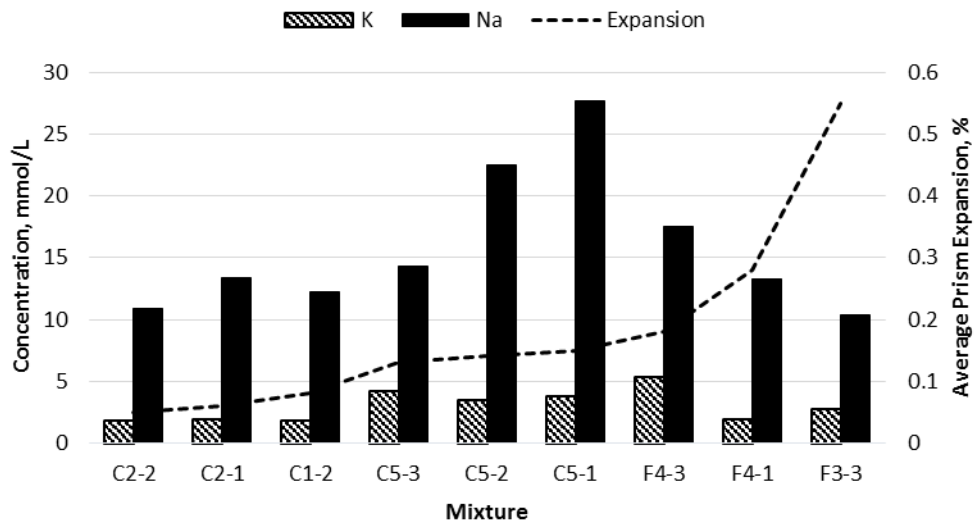


FIGURE 4: Autoclave water concentrations of K<sup>+</sup> and Na<sup>+</sup> determined by ICP-OES. The dashed line shows average concrete prism expansions in the ACPT.

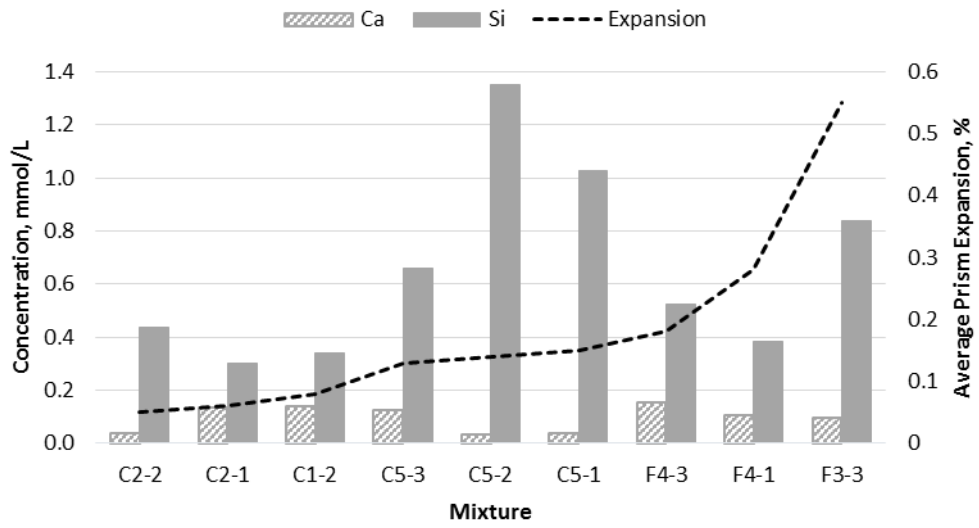


FIGURE 5: Autoclave water concentrations of  $\text{Ca}^{2+}$  and  $\text{Si}^{4+}$  determined by ICP-OES. The dashed line shows average concrete prism expansions in the ACPT.