

## A study on the effect of aggregate type on pore solution composition

Krishna Siva Teja Chopperla <sup>(1)</sup>, Jason H. Ideker <sup>(2)</sup>

(1) Oregon State University, Corvallis, USA, [chopperk@oregonstate.edu](mailto:chopperk@oregonstate.edu)

(2) Oregon State University, Corvallis, USA, [jason.ideker@oregonstate.edu](mailto:jason.ideker@oregonstate.edu)

### Abstract

The study of pore solution has become a critical tool to track the chemical reactions and ion exchange in concrete subject to alkali-silica reaction (ASR). The study of pore solution is used to indicate the process of ASR and the efficacy of supplementary cementitious materials (SCMs) to mitigate ASR by analyzing the change in alkalinity and ion concentrations. High-pressure pore solution expression devices have been widely used to express pore solution from hardened cementitious materials to determine the efficacy of SCMs, chemical admixtures, and alkali supply from aggregates. Even though there were studies on the effect of maximum load and load rate on the pore solution chemistry, the method is not yet standardized. In addition, most studies focused on analyzing the pore solution of cement pastes; the influence of aggregates on pore solution chemistry is not well characterized in the literature. Therefore, there is a need to understand the influence of aggregates on the pore solution chemistry. In this study, the influence of two types of non-reactive aggregate (siliceous and limestone) and two alkali-silica reactive aggregates (very-highly reactive fine aggregates as per ASTM C1778) on pore solutions expressed from mortars were investigated. The samples were seal cured at two different temperatures – 23°C and 80°C for 28 and 15 days respectively. At 23°C, no significant difference in ion concentrations and pH between the pastes and the mortars with non-reactive aggregates was observed. Whereas, at 80°C, a slight reduction in ion concentrations and pH was observed for the mortars with limestone non-reactive aggregate. A significant difference in ion concentrations and pH was observed between the pastes and the mortars with reactive fine aggregates at both the temperatures owing to ASR.

**Keywords:** alkali-silica reaction; pore solution analysis; reactive aggregates

## 1. INTRODUCTION

Over the past ~40 years, there have been many studies on the pore solution of hardened cementitious materials, mostly after the study by Barneyback and Diamond [1]. Pore solution can be defined as the free liquid that exists in the pores of cementitious materials. Even though pore solution is a free liquid, it continuously interacts with surrounding solid phases to be in equilibrium with the phase assemblage. Therefore, the composition of pore solution changes as the degree of hydration of cementitious material changes. The ionic composition of pore solution of hardened cementitious materials at various ages and after various types of curing is determined to better understand the interactions between solid and liquid phases inside cementitious materials as well as cement hydration.

Pore solution analysis is important for studying concrete durability as well. It is used to study the interaction of cementitious materials with external agents (such as deicing salts and sea water) and concrete aggregates (in the case of alkali-silica reaction). Therefore, it acts as an important tool to study deleterious reactions such as alkali-silica reaction, reinforcement corrosion, and delayed ettringite formation [2]. In the presence of reactive aggregates in concrete, pore solution analysis is used to study the process of alkali-silica reaction by analyzing the change in alkalinity, pH and other ion concentrations such as calcium, silicon and aluminum in pore solution. Expansion tests are usually done along with pore solution analysis to better understand the mitigation strategies such as required minimum replacement of supplementary cementitious materials (SCMs) [3-5]. As the reduction in pore solution alkalinity when SCMs are used is not just from the dilution due to partial replacement of cement but it is also from alkali-binding and from consumption of calcium hydroxide, pore solution analysis becomes a critical tool to evaluate alkali-binding.

The pore solution expression (PSE) is the most used method to express pore solution and analyze it using various analytical techniques. It involves applying very high-pressures to specimens to squeeze

the pore solution out of them. The device for this was initially developed by Longuet et al. [6]. The maximum pressure applied in the PSE method by the authors varied based up on the type of sample (hardened cement paste, mortar, or concrete). It ranges from 170 to 1000 MPa. Typically, lower pressures are used for hardened cement pastes, moderate pressures for mortar samples, and higher pressures for concrete samples. The increase in pressures for mortar and concrete samples are for increasing the yield of the expressed pore solution owing to the smaller volume of paste in the overall system. The majority of pore solution extractions using the PSE method were done on pastes mostly to study hydration process and determine pore solution pH. Relatively less studies were done on mortars and even fewer studies on concrete samples. Only a limited number of studies compared pore solutions expressed from pastes, mortars, and concrete.

## 1.1 Impact of Aggregates

Duchesne and Berube [7] compared the pore solutions expressed from hardened cement pastes and mortars. The mortar samples were cast with both reactive and non-reactive limestone aggregates. Both the pastes and mortars were cast with the same water to cementitious material ratio (w/cm). The alkali concentrations of the expressed pore solutions after 7 and 28 days of seal curing at 38°C were compared, and the authors concluded that they were not affected by the presence of aggregates. However, it should be noted that the influence of aggregates on the other ion concentrations were not studied. In addition, the study only included two aggregates.

Leemann et al. [8] studied pore solution compositions of pastes of w/cm of 0.31 and mortars of w/cm 0.47 and compared them. The specimens were seal cured at 60°C. It was observed that the ion concentrations of sodium, potassium, and sulfur were higher in pastes because of the lower w/cm of paste. Calcium and aluminum concentrations were observed to be similar in both mortar and pastes. It was observed that the silicon concentration in mortars steadily increased after one day, whereas it was relatively constant in pastes after one day. This could be due to the presence of reactive aggregate. However, this conclusion may not be applicable for all types of aggregates as only one aggregate was used in the study, and it was not an equal comparison as the w/cm of the pastes and mortars were different.

There is a need to extensively study the influence of aggregates on pore solution compositions with different types of non-reactive and reactive aggregates as only a few studies were done regarding this topic. This paper includes the study on comparing the ion compositions of the pore solutions expressed using the PSE method from hardened cement pastes and mortars with two non-reactive aggregates and two reactive aggregates, which were cured at two different temperatures.

## 2. MATERIALS, MIXTURES, AND EXPERIMENTAL METHODS

### 2.1 Materials

#### 2.1.1 Cements and SCM

Three cements and a class F fly ash were used in this study. The chemical compositions of the materials are listed in Table 2.1. The cements were labelled as A, B, and B\_L15. Cement A is a high-alkali cement with 0.96% Na<sub>2</sub>O<sub>e</sub>. Cement B is an ASTM type II/V cement with 0.62% Na<sub>2</sub>O<sub>e</sub>. Cement B\_L13 is an interground portland limestone cement with 13% limestone and was prepared from the same clinker as cement B.

#### 2.1.2 Aggregates

Two very-highly reactive fine aggregates (according to ASTM C1778) labelled as R1 and R2 were used in the study. The average 14-day expansion of the reactive sands, R1 and R2, according to ASTM C1260 were 0.54% and 0.47% respectively. Two non-reactive fine aggregates – a limestone sand (NR1) and a siliceous sand (NR2) were used. NR2 sand is the graded standard Ottawa (ASTM C778) sand. Absorption capacities of R1, R2, and NR1 were determined according to ASTM C128 and the values were 0.64%, 4.58%, and 0.37% respectively. NR2, the standard Ottawa sand, has very low (<0.10%) absorption capacity.

Table 2.1: The chemical compositions, d50, and d90 of the cements and fly ash used in the study

% wt	A	B (Type II/V)	B_L13	Fly Ash (FA)
SiO <sub>2</sub>	20.51	20.54	18.46	51.86
Al <sub>2</sub> O <sub>3</sub>	5.26	4.05	3.71	21.70
Fe <sub>2</sub> O <sub>3</sub>	2.11	3.62	3.46	5.04
CaO	64.20	61.72	60.45	8.61
MgO	1.40	2.52	2.28	2.58
SO <sub>3</sub>	4.28	1.80	1.71	0.78
Na <sub>2</sub> O	0.15	0.17	0.13	2.58
K <sub>2</sub> O	1.23	0.69	0.63	1.45
Na <sub>2</sub> O <sub>e</sub>	0.96	0.62	0.54	3.50
LOI	-	1.96	6.75	1.42
d50 (μm)	12.87	11.77	12.57	13.01
D90 (μm)	37.03	29.94	37.06	44.62

## 2.2 Mixing and molding procedure

Four cementitious material combinations used in this study were 100% A (100A), 100% B (100B), 75% B + 25% FA (B\_25FA), and 75% B\_L13 + 25% FA (B\_L13\_25FA). Both the pastes and mortars were prepared with water to cementitious materials ratio of 0.47 by mass. Cementitious materials to sand ratio was 2.25 by mass for all the mortars prepared. R1, R2, and NR1 sands were sieved according to the grading requirements shown in Table 2.2. After sieving, they were rinsed, oven-dried (at 105 C) for 24 hours and cooled them down to room temperature before using them to mix mortars. The absorption capacities of the aggregates were accounted for by increasing the mixing water content to maintain the same effective w/cm for all the mixtures. The mortars were mixed in accordance with the requirements of ASTM C305. The pastes were also mixed in the same way as the mortars to prevent any differences in the sample preparation process.

Table 2.2: Grading requirements used for R1, R2, and NR1 fine aggregates

Sieve size (Sieve number)	Mass retained, %
2.36 mm (No. 8)	10
1.18 mm (No. 16)	25
600 μm (No. 30)	25
300 μm (No. 50)	25
150 μm (No. 100)	15

The pastes and mortars were cast in 50 mm (diameter) x 100 mm (length) plastic cylinders. The cylinders were closed with air-tight fitting caps and further sealed with duct tape to prevent any leaks. The paste cylinders were rotated at 75 rpm for 24 hours after casting at room temperature to prevent bleeding. After 24 hours of casting, the cylinders were bagged in air-tight plastic bags and stored at two different temperatures: 23°C and 80°C. The bagged cylinders at 80°C were stored over water to prevent any evaporation for 15 days. The bagged cylinders at 23°C were stored in sealed plastic buckets for 28 days.

## 2.3 Test methods and matrix

### 2.3.1 Pore solution expression

The pore solution expression device used in the study works on the same principle as the one developed by Longuet et al. [6]. The assembly of the device is as shown in Figure 2.1. The device works based on a simple principle of applying high pressures on the sample to squeeze the solution out of it. A maximum pressure of 320 MPa was used for the paste samples and 520 MPa was used for the mortar samples. After the maximum pressure was attained, it was maintained for about a minute in order to increase the yield of the solution collected. The collected solutions in the vials were immediately transferred to syringes to minimize the exposure to air and prevent carbonation. The syringes were placed in air-tight bags at 5°C until further testing.

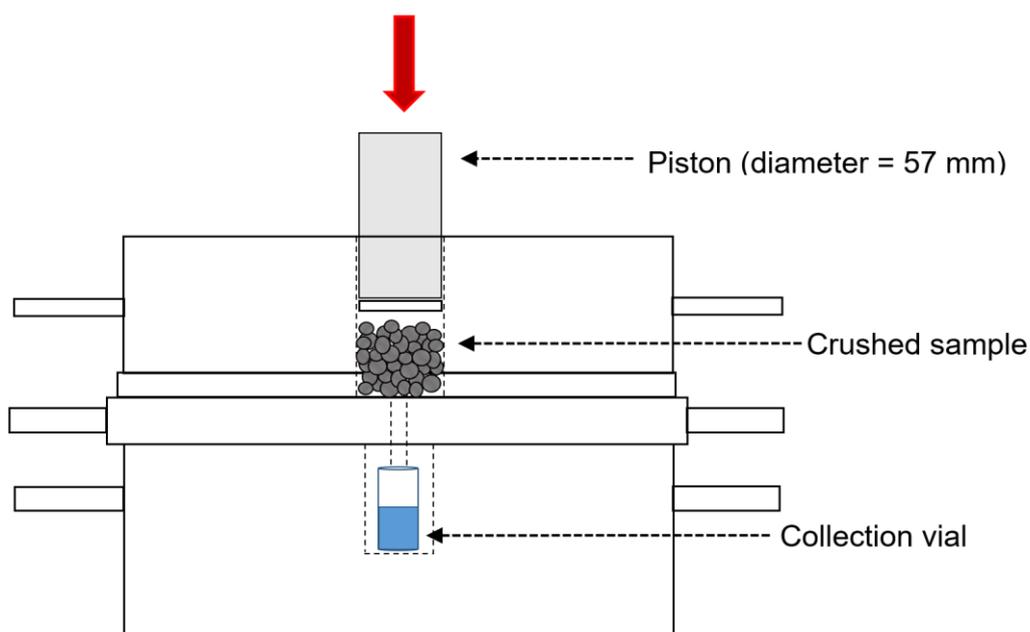


Figure 2.1: Assembly of the pore solution expression device

### 2.3.2 Pore solution analysis

The pH was measured using an electrode while the ion compositions were determined using inductive coupled plasma optical emission spectroscopy (ICP-OES) method. The pH of the solutions were measured at room temperature immediately after expression. The solutions were vacuum filtered through 0.45  $\mu\text{m}$  filter papers within two weeks after the expression. Then the solutions were diluted with 2% nitric acid at two different dilutions: 20x and 100x. The solutions were stored in new sealed syringes at 5°C and tested for their ion compositions in less than two weeks after they were expressed. Twenty (20x) dilution samples were used to determine their Ca, Al, and Si ion concentrations. One hundred (100x) dilution samples were used to determine their Na, K, and S ion concentrations.

### 2.3.3 Test matrix

A total of 28 samples were tested in the study. 12 samples were seal cured at 23°C and 16 samples were seal cured at 80°C. Table 2.3 shows the details of the test matrix of the study.

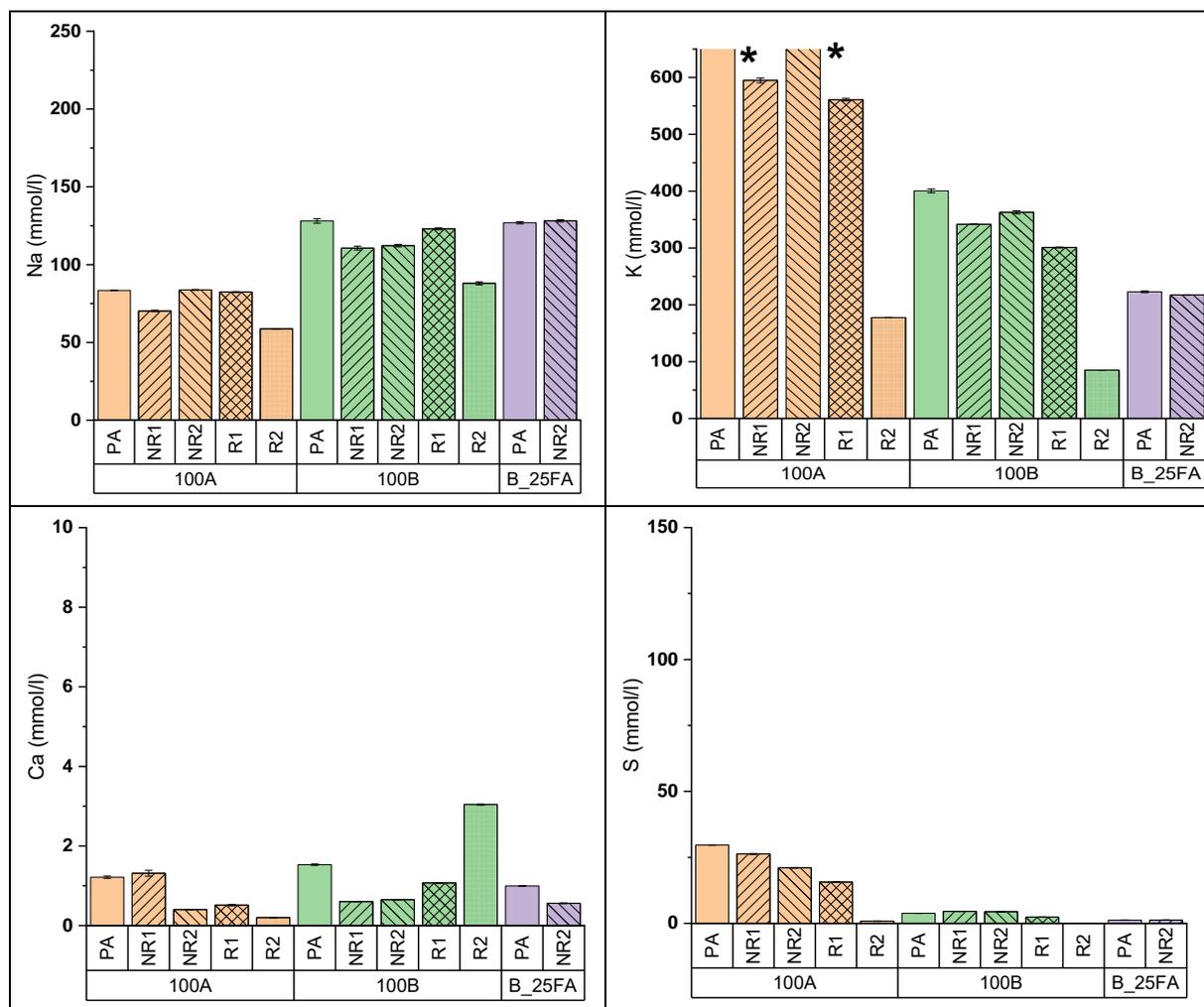
Table 2.3: Test matrix for the study (All the samples marked with 'X' were tested for pore solution analysis)

Mixture	Paste/Mortar	Aggregate	Curing temperature	
			23°C	80°C
100A	Paste	-	X	X
100B	Paste	-	X	X
B_25FA	Paste	-	X	X
B_L13_25FA	Paste	-	-	X
100A	Mortar	R1	X	X
100B	Mortar	R1	X	X
B_25FA	Mortar	R1	-	X
B_L13_25FA	Mortar	R1	-	X
100A	Mortar	R2	X	X
100B	Mortar	R2	X	X
B_25FA	Mortar	R2	-	X
B_L13_25FA	Mortar	R2	-	X
100A	Mortar	NR1	X	X
100B	Mortar	NR1	X	X
B_25FA	Mortar	NR1	-	X
B_L13_25FA	Mortar	NR1	-	X
100A	Mortar	NR2	X	-
100B	Mortar	NR2	X	-
B_25FA	Mortar	NR2	X	-

### 3. RESULTS AND DISCUSSION

#### 3.1 Pore solution analysis of samples stored at 23°C

Figure 3.1 shows the results of the pore solution analysis of the paste and mortar samples seal cured at 23°C for 28 days after demolding. In Figure 3.1, PA stands for paste. Please note that potassium ion concentration of the paste and mortar with NR2 of 100A mixture exceeded the maximum calibration range of 650 mmol/l.



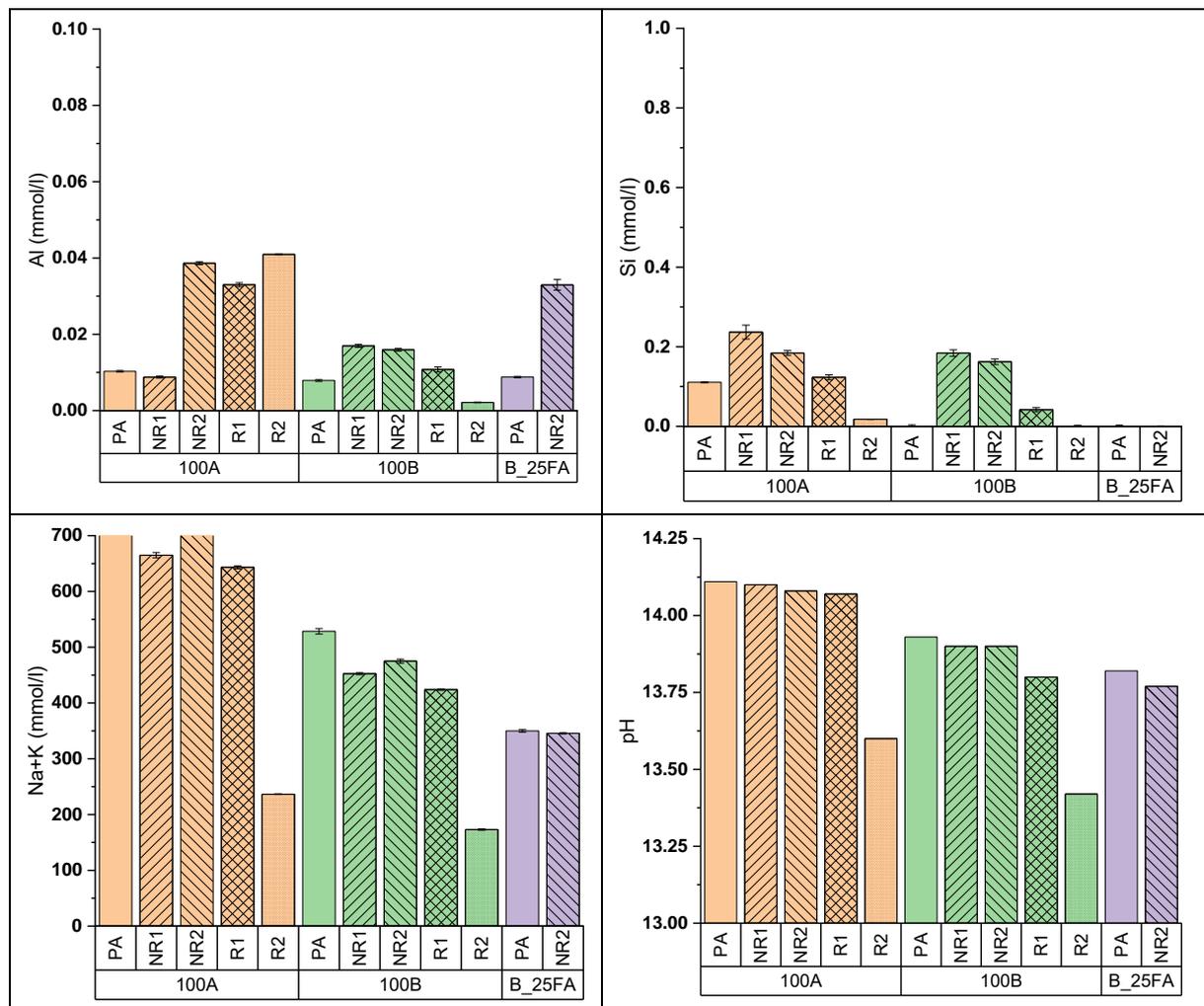


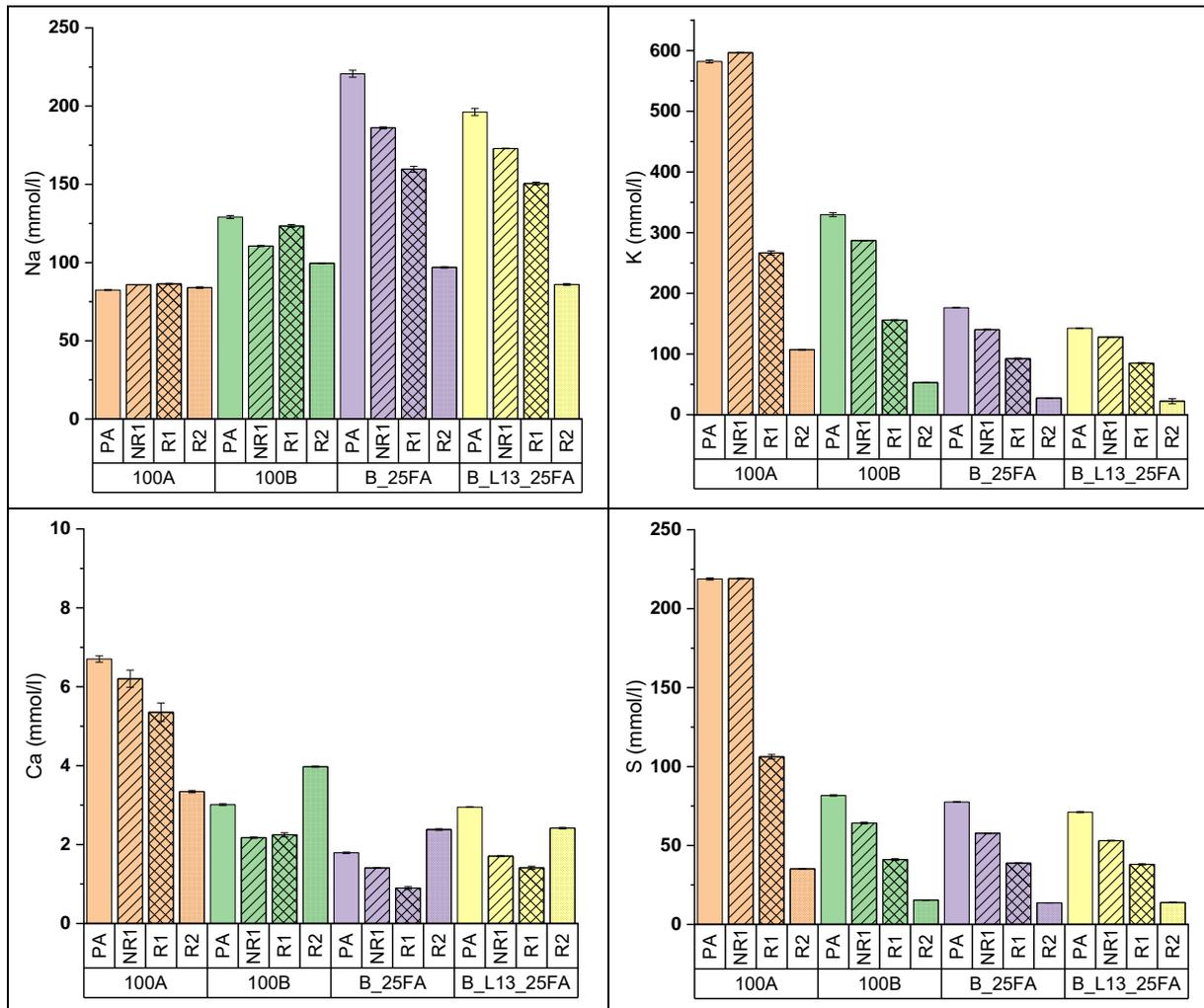
Figure 3.1: Ion concentrations and pH of the pore solutions expressed from the paste and mortar samples that were seal cured at 23°C for 28 days after demolding (PA: paste) [Note: Scale of Y-axis in all the plots is not the same] \* The potassium ion concentration of the paste and mortar with NR2 of 100A mixture exceeded the maximum calibration range of 650 mmol/l

From Figure 3.1, it was observed that no significant difference in pH between the paste pore solutions and the mortars with non-reactive aggregate pore solutions. However, a significant pH difference was observed between the paste and the mortar with R2 sand.

The maximum difference observed between the pastes and the mortars with NR1 and NR2 in Na ion concentration was 17.4 mmol/l, K ion concentration was 58.7 mmol/l, S ion concentration was 8.6 mmol/l, Ca ion concentration was 0.9 mmol/l, Al ion concentration was 0.03 mmol/l, and Si ion concentration was 0.18 mmol/l. Therefore, it can be concluded that no significant difference in ion concentrations was observed between the paste and mortars with non-reactive sands. However a significant difference was observed between the pastes and mortars with reactive aggregate. The highest difference in ion concentrations was observed between the paste and the mortar with R2 sand.

### 3.2 Pore solution analysis of samples stored at 80°C

Figure 3.2 shows the results of the pore solution analysis of the paste and mortar samples seal cured at 80°C for 15 days after demolding. In Figure 3.2, PA stands for paste.



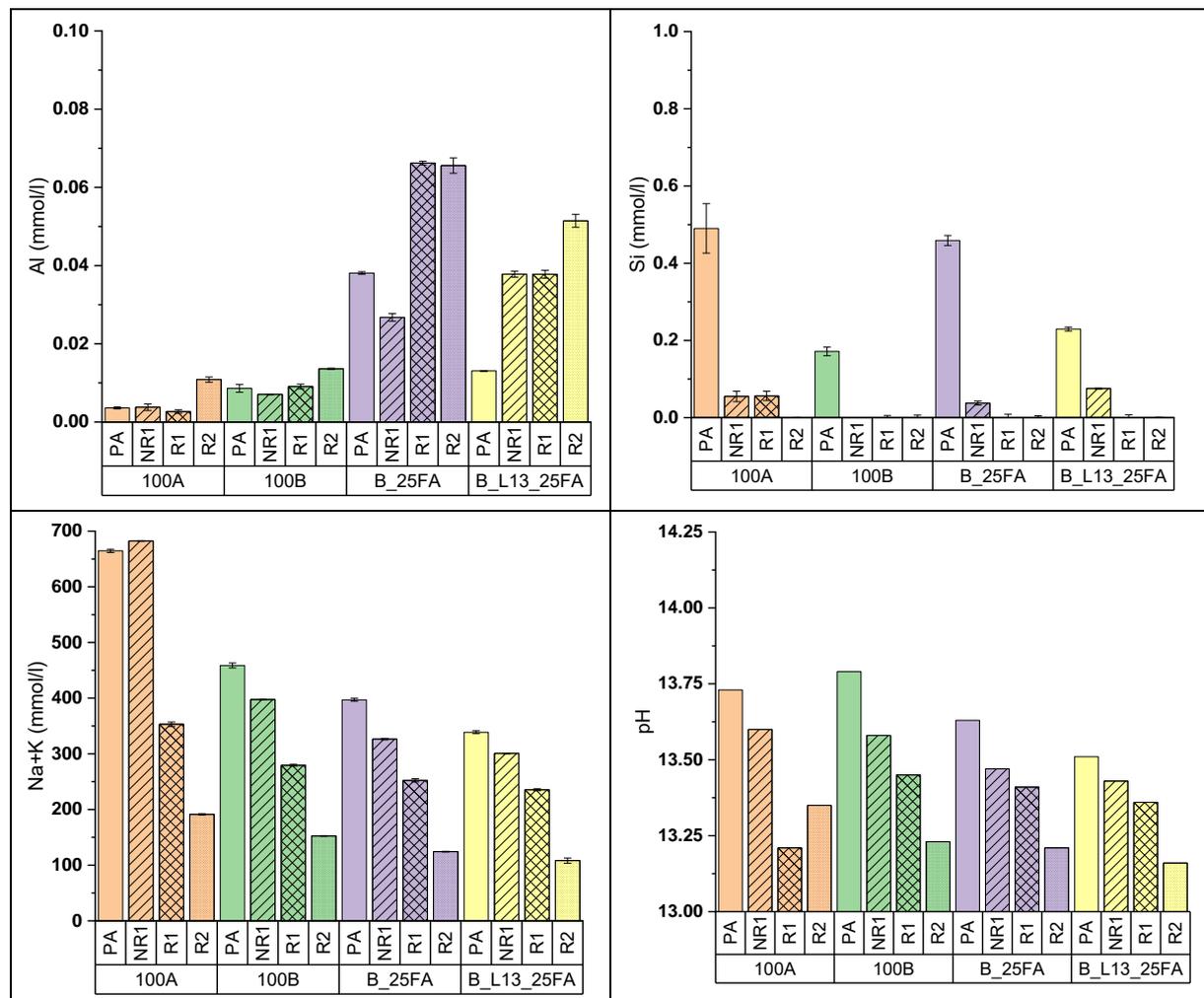


Figure 3.2: Ion concentrations and pH of the pore solutions expressed from the paste and mortar samples that were seal cured at 80°C for 15 days after demolding (PA: paste) [Note: Scale of Y-axis in all the plots is not the same]

From Figure 3.2, it was observed that no significant difference in alkali ion concentrations between the paste samples and the mortars with NR1 sand. The maximum difference observed was 42.6 mmol/l for K ion concentration of 100B mixture. The maximum difference in pH of 0.21 was observed between the pastes and the mortars with NR1 sand, which was lower than the maximum difference in pH of 0.56 between the pastes and the mortars with reactive sands. When NR1 is used in combination with reactive aggregates in concrete, the slight reduction in pH due to the presence of NR1 might affect the expansion of concrete fairly well as shown in previous research [9].

For the mortars with R1 and R2 sands, a significant difference in ion concentrations, especially alkalis, was observed as expected as the sands are very-highly reactive sands and the alkalis from the pore solutions are consumed to form alkali-silica gel. The maximum difference observed was 315 and 475 mmol/l respectively for K ion concentration of 100A mixture.

It was observed that there was a significant reduction in sulfur ion concentration in the mortars with R1 and R2 sands when compared to the pastes. This could be due to the charge balance as there was a reduction in both alkalis and hydroxide ions in the pore solutions of the mortars with reactive sands owing to the alkali-silica reaction. This reasoning cannot be generalized to mixtures that are not seal cured.

In addition, it was observed that the reduction in alkalis and sulfur ion concentrations was proportional to the absorption capacities of the sands. As the sands were added in oven-dry condition while mixing, there is a possibility of a slight dilution of ion concentrations due to the fact that the sands might have

not absorbed water to reach their saturated surface dry (SSD) conditions. This needs to be further investigated by analyzing the pore solutions of the mortars that were mixed with sands at their SSD condition.

Table 3.1 shows the  $R^2$  values of the linear correlations between ion concentrations of the paste and mortar samples seal cured at 80°C. Figure 3.3 shows the linear correlations between potassium ion concentrations of the paste and mortar samples seal cured at 80°C.

Table 3.1:  $R^2$  values of the linear correlations between ion concentrations of the paste and mortar samples seal cured at 80°C

$R^2$	Na	K	Ca	S	Al	Si	Na+K
NR1	0.9882	0.9921	0.9717	0.9998	0.7439	0.0977	0.9816
R1	0.9701	0.9983	0.9729	0.9991	0.8967	0.4018	0.9983
R2	0.0993	0.9957	0.1617	0.9973	0.2780	-	0.9661

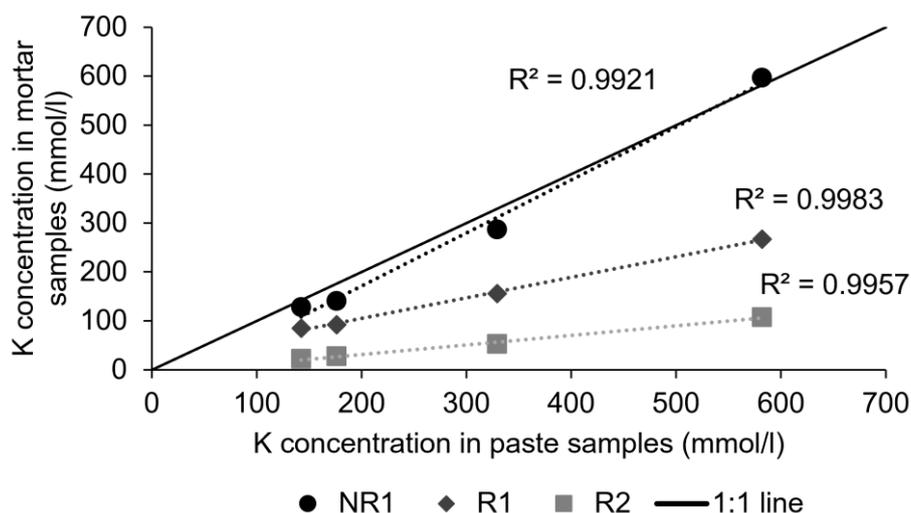


Figure 3.3: Linear correlations between potassium ion concentrations of the paste and mortar samples seal cured at 80°C

From Table 3.1, it was observed that a strong correlation ( $R^2 > 0.95$ ) exists between the dominant ion (Na, K, S, and Ca) concentrations of the pastes and the mortars with both non-reactive and reactive aggregates with two exceptions. The exceptions were Na and Ca ion concentrations of the mortar with R2 sand. No strong correlation exists between Al and Si ion concentrations of the pastes and mortars. However, it should be noted that Al and Si ion concentrations in the pore solutions were significantly lower compared to Na, K, and S ions. The correlations can be used to calculate the pore solution alkalinity of mortars if the pore solution alkalinity of the paste is known. This further helps to determine the efficacy of mixtures with SCMs and a certain reactive aggregate when the alkali threshold of the aggregate and the pore solution alkalinity of the paste with the same cementitious materials are known.

#### 4. CONCLUSIONS AND FUTURE WORK

No significant difference in pore solution chemistry was observed between the pastes and the mortars with non-reactive sands. However, a slight reduction ( $\leq 0.2$ ) in the measured pH values of the mortars with NR1 sand seal cured at 80°C was observed. The slight reduction in pH due to the presence of NR1 sand can affect the expansion of concrete when it used in combination with a reactive aggregate. A significant difference in ion concentrations, especially alkalis, was observed between the pastes and the mortars with reactive sands as expected due to the consumption of alkalis from pore solutions for the formation of alkali-silica gel. The dominant ion (Na, K, S, and Ca) concentrations of the pastes and

mortars (seal cured at 80°C) were well correlated. The correlations can be used to calculate the pore solution alkalinity of mortars when the pore solution alkalinity of the paste is known. The effect of sand moisture condition at the time of mixing mortar on the pore solution chemistry should be investigated. Several aggregates with different mineralogy need to be studied with the approach used in this paper to provide additional evidence to the inferences made in the study.

## 5. REFERENCES

- [1] Barneyback R, Diamond S (1981) Expression and analysis of pore fluids from hardened cement pastes and mortars. *Cement and Concrete Research* 11 (2):279-285
- [2] Thomas MDA, Hooton D, Ramlochan T (2010) Use of pore solution analysis in design for concrete durability. *Advances in Cement Research* 22:203-210. doi:10.1680/adcr.2010.22.4.203
- [3] Kawabata Y, Yamada K (2015) Evaluation of alkalinity of pore solution based on the phase composition of cement hydrates with supplementary cementitious materials and its relation to suppressing ASR expansion. *Journal of Advanced Concrete Technology* 13:538-553
- [4] M.H. Shehata MDAT (2002) Use of ternary blends containing silica fume and fly ash to suppress expansion due to alkali-silica reaction in concrete. *Cement and Concrete Research* 32 (3):341-349
- [5] Thomas M (2011) The effect of supplementary cementing materials on alkali-silica reaction: A review. *Cement and Concrete Research* 41 (12):1224-1231. doi:10.1016/j.cemconres.2010.11.003
- [6] Longuet P, Burglen L, Zelwer A (1973) The liquid phase of hydrated cement. *Rev Mater Constr* 676:35-41
- [7] Duchesne J, Berube, M.-A. (1994) The effectiveness of supplementary cementitious materials in suppressing expansion due to ASR: Another look at the reaction mechanisms part 2: Pore solution chemistry. *Cement and Concrete Research* 24 (2):221-230
- [8] Leemann A, Lothenbach B, Thalmann C (2011) Influence of superplasticizers on pore solution composition and on expansion of concrete due to alkali-silica reaction. *Construction and Building Materials* 25 (1):344-350. doi:https://doi.org/10.1016/j.conbuildmat.2010.06.019
- [9] Ideker JH, East BL, Folliard KJ, Thomas MDA, Fournier B (2010) The current state of the accelerated concrete prism test. *Cement and Concrete Research* 40 (4):550-555. doi:https://doi.org/10.1016/j.cemconres.2009.08.030

