

## Physicochemical properties of synthetic alkali-silica reaction (ASR) gels

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### Abstract

Synthetic ASR gels produced via a new sol-gel method incorporating silicon, calcium, sodium, potassium and lithium with a broad range of compositions were synthesized using sol-gel method. The rheological and chemical properties of the gels were characterized as a function of gel composition. The primary objective of this research was to find out which chemical components affect the gelation, alkalinity, yield stress and osmotic pressure of the gels, which are argued to be the governing factors affecting the deleterious behavior of ASR gels in concrete. The results suggest that calcium is the predominant factor promoting the gelation and yield stress of the gels while sodium and potassium have opposite effects. Moreover, the presence of lithium was found to soften the structure of the gels and reduce the hydroxide concentration in the gels by up to a factor of seven for highly alkaline gels, which partly explains the suppressing effect of this element on ASR in concrete.

**Keywords:** alkali-silica reaction; osmotic pressure; sol-gel; synthetic ASR gel; yield stress

## 1. INTRODUCTION

Alkali-silica reaction (ASR) is the reaction between portland cement alkali-hydroxides and meta-stable silicates in aggregates which results in the formation of a hygroscopic alkali-silicate gel either within the aggregate micro-cracks or on their exterior surfaces [1,2,3,4]. While its basic chemistry is well-known, the reaction and damage mechanism(s) are still not adequately understood. Different theories have been proposed for explaining the mechanism of ASR damage. The  $Q_4 \rightarrow Q_3$  depolymerization of silicates in aggregates due to hydroxide attack followed by autogenous aggregate pore volume increase [3], ion diffusion [5,6], and electrical double-layer repulsion [2,7,8] are among such theories. Water imbibition due to osmotic action is also a mechanism that has been proposed and supported by many researchers [9,10,11,12]. The total ASR damage is most likely the result of the combined action of the above phenomena. However, since ASR expansion is closely related to the presence of an external source of water (or relative humidity >80%), it can be concluded that excessive water imbibition by ASR gel (which is promoted by the osmotic action) is a major underlying cause for ASR damage.

Previous research suggests that ASR gels are amorphous alkaline-alkaline earth-silicate hydrogels with a general formula  $(Na_2O)_n.(K_2O)_k.(CaO)_c.(SiO_2).(H_2O)_x$  where n, k, and c (expressed in molar ratios to  $SiO_2$ ) range from 0.05 – 0.5, 0 – 0.15, and 0.05 – 0.5, respectively [13]. The alkalis are generally known to enhance the gel's tendency towards swelling both through increasing the double-layer repulsive forces and water imbibition potential (the latter which is the focus of this research can be assessed by osmotic pressure as explained later). Calcium is also reported to act as a pH buffer which helps ASR to continue through alkali-recycling [14]. On the other hand, synthetic ASR gels with excessive amounts of alkalis have been concluded to not have sufficient mechanical resistance against confining pressure of the surrounding cement matrix and thus flow into the pores and micro-cracks [15]. Such mechanical resistance can be assessed by the yield stress of the gels. It appears that the physicochemical properties of ASR gels as the primary source of expansion and damage play an important role in quantifying the underlying causes of damage. Proper characterization of the effects of gel composition on the important characteristics such as osmotic pressure and yield stress help not only with identifying the deleterious gel compositions, but also engineering the composition of the gel towards less deleterious combinations.

Furthermore, tweaking the composition through utilization of lithium-based admixtures are found to be a very effective means to mitigate ASR damage. McCoy and Caldwell (1951) were first to conduct a comprehensive research on the effect of different lithium-based compounds on expansion of concrete

due to ASR. They concluded that LiCl, Li<sub>2</sub>CO<sub>3</sub>, LiF, lithium silicate (Li<sub>2</sub>SiO<sub>3</sub>), LiNO<sub>3</sub>, and lithium sulfate (Li<sub>2</sub>SO<sub>4</sub>) are the most effective compounds in allaying ASR, if used in sufficient quantities [16]. It should always be noted that the use of lithium in small amounts (e.g., LiOH.H<sub>2</sub>O-to-cement < 0.3% – wt./wt.) does not lead to any considerable suppression of ASR, since part of the lithium is always consumed in hydration reactions. However, addition of the same compound up to 0.83% of the cement mass was reported to reduce ASR expansion to 6% or its original value [17]. The molar ratio of lithium to alkalis (i.e., Li/(Na + K)) is usually used as the measure of the dosage of lithium compounds. A number of theories are proposed for justifying the suppressing effect of lithium on ASR expansion. Formation of less-expansive/non-expansive ASR gel due to the presence of lithium, reduction in the dissolution rate of silica/formation of less ASR gel, and decreased repolymerization are among the most viable mechanisms listed in FHWA report RD-03-047 under Chapter 3 [16].

The objective of this paper is to investigate the relationships between the batched composition of lithium-admixed ASR gels and their rheological properties (i.e., gelation time and yield stress), and liquid phase characteristics (solutes concentration, pH and osmotic pressure). The main test variables in this research are the batched Ca/Si, Na/Si, K/Si, and Li/Si atomic ratios as well as the batched water content of the gels.

## 2. EXPERIMENTAL PROGRAM

Thirty-two different compositions of ASR gels were synthesized and tested to determine their physicochemical properties. Below, the materials used for gel synthesis, the design of experiments, and the test methods for characterizing the abovementioned properties of the gels are laid out.

### 2.1 Materials

Reagent grade calcium hydroxide powder, sodium and potassium hydroxide pellets, and lithium hydroxide monohydrate (LiOH.H<sub>2</sub>O) were used as raw materials in synthesizing ASR gels. For the source of silicon, colloidal silicon dioxide IV (50% H<sub>2</sub>O) with an average particle size of 20 nm was used.

### 2.2 Design of experiments (DoE)

Five gel composition (input) variables (i.e., Ca/Si, Na/Si, K/Si, Li/Si and water content) were studied in the ranges shown in Table 2.1. The studied ranges selected for Ca/Si, Na/Si and K/Si were chosen based on the outcomes of the statistical analyses performed on the chemical compositions of 100 different in-situ ASR gel samples reported in the literature [18]. The lower and upper bounds chosen for Li/Si were selected to render an Li/(Na + K) of 0.0 to 0.8 which is found to be enough for full ASR mitigation [17]. Finally, the selected 65–75% was the workable range of water content which yielded gels that could be properly synthesized and tested. However, ASR gels formed on site can have considerably higher concentrations compared to what was studied in this research (i.e., 25–35%). Nevertheless, the selected ranges for the chemical composition of ASR gels are comprehensive and basically cover all compositions at which ASR gels form in concrete.

Previous research suggests that the influence of composition (input) variables (i.e., Ca/Si, Na/Si, etc.) on the properties of ASR gels are very interactive and complicated [13,15,18]. As such, a design of experiments capable of capturing the linear and non-linear effects of the input variables, along with their interactions in the entire studied ranges is needed.

Table 2.1: The studied ranges of the ASR gel composition (input) variables

Variable	Note	Lower bound	Upper bound
C: Ca/Si	Atomic ratio	0.05	0.4
N: Na/Si	Atomic ratio	0.2	1.0
K: K/Si	Atomic ratio	0.0	0.3
L: Li/Si	Atomic ratio	0.0	0.5
W: water content	wt./wt. of gel%	65	75

Similar to previous studies [13,18], the concepts of response surface methodology [19] were implemented in designing the experiments. The selection of experimental units was made using the central composite design (CCD) approach [19]. Five distinct levels were defined for each input variable; referred to as Low (L), Intermediate Low (IL), Intermediate (I), Intermediate High (IH), and High (H).

These levels were calculated for each input variable and shown in Table 2.2 along with the coded levels. Please refer to [19] for more details regarding the implementation of the CCD concepts in design of similar experiments.

Table 2.2: The coded and natural levels of the input variables

Coded levels	Categorical	Low (L)	Intermediate Low (IL)	Intermediate (I)	Intermediate High (IH)	High (H)
	Numerical	-2	-1	0	+1	+2
Input variables		Corresponding natural levels				
Ca/Si: C		0.05	0.1375	0.225	0.3125	0.4
Na/Si: N		0.2	0.4	0.6	0.8	1.0
K/Si: K		0.0	0.075	0.15	0.225	0.3
Li/Si: L		0.0	0.125	0.25	0.375	0.5
Water content: W		0.65	0.675	0.7	0.725	0.75

Table 2.3: The experimental units representing the batching composition of studied gels

Run order	Gel label	Ca/Si	Na/Si	K/Si	Li/Si	Water content (wt./wt.)	(H <sub>2</sub> O)/Si Molar ratio
1	C <sub>IH</sub> N <sub>IL</sub> K <sub>IH</sub> L <sub>IH</sub> W <sub>IL</sub>	0.3125	0.4	0.225	0.375	0.675	12.2
2	C <sub>IH</sub> N <sub>IH</sub> K <sub>IL</sub> L <sub>IL</sub> W <sub>IH</sub>	0.3125	0.8	0.075	0.125	0.725	15.8
3	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> W <sub>H</sub>	0.225	0.6	0.15	0.25	0.75	17.0
4	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> L <sub>IL</sub> W <sub>I</sub>	0.225	0.6	0.15	0	0.7	12.7
5	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> L <sub>IL</sub> W <sub>I</sub>	0.225	0.6	0	0.25	0.7	12.3
6	C <sub>IH</sub> N <sub>IH</sub> K <sub>IH</sub> L <sub>IL</sub> W <sub>IL</sub>	0.3125	0.8	0.225	0.125	0.675	13.2
7	C <sub>IL</sub> N <sub>IH</sub> K <sub>IL</sub> L <sub>IL</sub> W <sub>IL</sub>	0.1375	0.8	0.075	0.125	0.675	11.3
8	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> W <sub>I</sub>	0.225	0.6	0.15	0.25	0.7	13.2
9	C <sub>IL</sub> N <sub>IH</sub> K <sub>IL</sub> L <sub>IH</sub> W <sub>IH</sub>	0.1375	0.8	0.075	0.375	0.725	14.9
10	C <sub>IH</sub> N <sub>IL</sub> K <sub>IL</sub> L <sub>IH</sub> W <sub>IH</sub>	0.3125	0.4	0.075	0.375	0.725	14.5
11	C <sub>IH</sub> N <sub>IH</sub> K <sub>IH</sub> L <sub>IH</sub> W <sub>IH</sub>	0.3125	0.8	0.225	0.375	0.725	17.4
12	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> L <sub>IH</sub> W <sub>IL</sub>	0.1375	0.4	0.075	0.375	0.675	10.3
13	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> L <sub>IH</sub> W <sub>I</sub>	0.225	0.6	0.15	0.5	0.7	13.7
14	C <sub>IL</sub> N <sub>IH</sub> K <sub>IH</sub> L <sub>IL</sub> W <sub>IH</sub>	0.1375	0.8	0.225	0.125	0.725	15.4
15	C <sub>IH</sub> N <sub>IL</sub> K <sub>IH</sub> L <sub>IL</sub> W <sub>IH</sub>	0.3125	0.4	0.225	0.125	0.725	15.0
16	C <sub>H</sub> N <sub>IL</sub> K <sub>IL</sub> W <sub>I</sub>	0.4	0.6	0.15	0.25	0.7	14.5
17	C <sub>IL</sub> N <sub>IL</sub> K <sub>IH</sub> L <sub>IL</sub> W <sub>IL</sub>	0.1375	0.4	0.225	0.125	0.675	10.7
18	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> W <sub>I</sub>	0.225	0.2	0.15	0.25	0.7	11.6
19	C <sub>IL</sub> N <sub>IH</sub> K <sub>IL</sub> W <sub>I</sub>	0.225	1	0.15	0.25	0.7	14.8
20	C <sub>IH</sub> N <sub>IH</sub> K <sub>IL</sub> L <sub>IH</sub> W <sub>IL</sub>	0.3125	0.8	0.075	0.375	0.675	12.9
21	C <sub>L</sub> N <sub>IL</sub> K <sub>IL</sub> W <sub>I</sub>	0.05	0.6	0.15	0.25	0.7	12.0
22	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> W <sub>I</sub>	0.225	0.6	0.15	0.25	0.7	13.2
23	C <sub>IL</sub> N <sub>IL</sub> K <sub>IH</sub> L <sub>IH</sub> W <sub>IH</sub>	0.1375	0.4	0.225	0.375	0.725	14.1
24	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> W <sub>I</sub>	0.225	0.6	0.15	0.25	0.7	13.2
25	C <sub>IL</sub> N <sub>IH</sub> K <sub>IH</sub> L <sub>IH</sub> W <sub>IL</sub>	0.1375	0.8	0.225	0.375	0.675	12.5
26	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> L <sub>IL</sub> W <sub>IH</sub>	0.1375	0.4	0.075	0.125	0.725	12.5
27	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> W <sub>I</sub>	0.225	0.6	0.15	0.25	0.7	13.2
28	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> W <sub>I</sub>	0.225	0.6	0.15	0.25	0.7	13.2
29	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> W <sub>I</sub>	0.225	0.6	0.3	0.25	0.7	14.1
30	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> W <sub>L</sub>	0.225	0.6	0.15	0.25	0.65	10.5
31	C <sub>IH</sub> N <sub>IL</sub> K <sub>IL</sub> L <sub>IL</sub> W <sub>IL</sub>	0.3125	0.4	0.075	0.125	0.675	11.0
32	C <sub>IL</sub> N <sub>IL</sub> K <sub>IL</sub> W <sub>I</sub>	0.225	0.6	0.15	0.25	0.7	13.2

Table 2.3 shows the full list of the gel compositions that were synthesized and tested in this research. The water contents of the gels are reported in both mass and molar ratios. The designed experiments enable us in developing polynomial regression models for predicting each response parameter (e.g., yield stress) as a function of the input variables per Equation (1). In this equation, y is the response parameter,  $\epsilon$  is the prediction error, and X<sub>i</sub> is the i<sup>th</sup> input variable (among the 5 variables). X<sub>i</sub>×X<sub>j</sub> represents the interaction term between the i<sup>th</sup> and j<sup>th</sup> variable. The statistical significance of each

regression term is determined by testing the significance of their coefficients using a t–test. A P–Value smaller than 0.05 indicates the significance of the corresponding term. The regression model is constructed by compiling all significant and necessary terms into an equation similar to Equation (1).

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i < j} \sum_{j=1}^k \beta_{ij} x_i x_j + \sum_{i=1}^k \beta_{ii} x_i^2 + \varepsilon \quad (1)$$

### 2.3 Gel synthesis method

Table 2.4 shows the masses of different components needed to be batched for rendering gels with the target compositions as listed in Table 2.3. Our studies suggest that colloidal silica as the main precursor of the gels, if merely added with other components (i.e., Ca(OH)<sub>2</sub>, NaOH, etc.), will undergo ‘flash’ gelation and convert to large clusters of silicates without allowing for proper mixing of the ingredients. The resultant will have a heterogeneous chemistry and very slow gelation. As such, a protocol was developed for the synthesis of ASR gels using colloidal silica such that all components are properly introduced and incorporated to the gel’s structure. Lithium hydroxide monohydrate (LiOH.H<sub>2</sub>O) was first dissolved in 20 grams of the distilled mixing water. NaOH and KOH pellets were then weighed and added to the lithium hydroxide solution. The resultant was then added to the weighed colloidal silica followed by sufficient mixing on a shaking table for thorough mixing of all species and dissipation of the generated heat.

Table 2.4: The mixture proportions of the synthesized ASR gels (the reported masses are for each 1000 grams of the batched gel)

No.	Gel label	Ca(OH) <sub>2</sub> (gr)	NaOH (gr)	KOH (gr)	LiOH.H <sub>2</sub> O (gr)	Colloidal silica (gr)	H <sub>2</sub> O (gr)
1	C <sub>I</sub> H <sub>N</sub> ILK <sub>I</sub> H <sub>L</sub> I <sub>H</sub> W <sub>I</sub> L	70.84	46.31	38.60	48.24	371.76	424.25
2	C <sub>I</sub> H <sub>N</sub> I <sub>H</sub> K <sub>I</sub> L <sub>L</sub> I <sub>L</sub> W <sub>I</sub> H	59.05	79.46	10.72	13.41	309.89	527.47
3	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>I</sub> W <sub>H</sub>	40.81	56.67	20.59	25.74	297.46	558.74
4	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	50.84	70.60	25.65	0.00	370.58	482.34
5	C <sub>I</sub> N <sub>I</sub> K <sub>L</sub> L <sub>L</sub> W <sub>I</sub>	52.61	73.05	0.00	33.18	383.46	457.71
6	C <sub>I</sub> H <sub>N</sub> I <sub>H</sub> K <sub>I</sub> H <sub>L</sub> L <sub>L</sub> W <sub>I</sub> L	65.50	88.14	35.69	14.87	343.73	452.08
7	C <sub>I</sub> L <sub>N</sub> I <sub>H</sub> K <sub>I</sub> L <sub>L</sub> I <sub>L</sub> W <sub>I</sub> L	33.78	103.31	13.94	17.43	402.89	428.65
8	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	48.97	68.00	24.71	30.88	356.95	470.49
9	C <sub>I</sub> L <sub>N</sub> I <sub>H</sub> K <sub>I</sub> L <sub>L</sub> I <sub>H</sub> W <sub>I</sub> H	27.53	84.19	11.36	42.61	328.33	505.98
10	C <sub>I</sub> H <sub>N</sub> ILK <sub>I</sub> L <sub>L</sub> I <sub>H</sub> W <sub>I</sub> H	64.20	41.98	11.66	43.73	336.95	501.48
11	C <sub>I</sub> H <sub>N</sub> I <sub>H</sub> K <sub>I</sub> H <sub>L</sub> I <sub>H</sub> W <sub>I</sub> H	53.67	72.22	29.24	36.55	281.65	526.68
12	C <sub>I</sub> L <sub>N</sub> ILK <sub>I</sub> L <sub>L</sub> I <sub>H</sub> W <sub>I</sub> L	37.05	55.06	15.29	57.35	441.94	393.30
13	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	47.23	65.59	23.83	59.57	344.30	459.48
14	C <sub>I</sub> L <sub>N</sub> I <sub>H</sub> K <sub>I</sub> H <sub>L</sub> L <sub>L</sub> W <sub>I</sub> H	26.66	81.54	33.02	13.76	318.01	527.01
15	C <sub>I</sub> H <sub>N</sub> ILK <sub>I</sub> H <sub>L</sub> L <sub>L</sub> W <sub>I</sub> H	62.13	40.63	33.85	14.11	326.09	523.19
16	C <sub>H</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	79.43	62.04	22.54	28.18	325.66	482.15
17	C <sub>I</sub> L <sub>N</sub> ILK <sub>I</sub> H <sub>L</sub> L <sub>L</sub> W <sub>I</sub> L	35.73	53.10	44.25	18.44	426.18	422.31
18	C <sub>I</sub> N <sub>L</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	55.75	23.84	28.13	35.16	406.35	450.78
19	C <sub>I</sub> N <sub>H</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	43.66	102.59	22.03	27.53	318.26	485.92
20	C <sub>I</sub> H <sub>N</sub> I <sub>H</sub> K <sub>I</sub> L <sub>L</sub> I <sub>H</sub> W <sub>I</sub> L	67.43	90.75	12.25	45.93	353.91	429.73
21	C <sub>L</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	12.04	75.23	27.33	34.16	394.89	456.34
22	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	48.97	68.00	24.71	30.88	356.95	470.49
23	C <sub>I</sub> L <sub>N</sub> ILK <sub>I</sub> H <sub>L</sub> I <sub>H</sub> W <sub>I</sub> H	29.06	43.18	35.98	44.98	346.57	500.23
24	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	48.97	68.00	24.71	30.88	356.95	470.49
25	C <sub>I</sub> L <sub>N</sub> I <sub>H</sub> K <sub>I</sub> H <sub>L</sub> I <sub>H</sub> W <sub>I</sub> L	30.42	93.05	37.67	47.09	362.86	428.91
26	C <sub>I</sub> L <sub>N</sub> ILK <sub>I</sub> L <sub>L</sub> I <sub>L</sub> W <sub>I</sub> H	32.73	48.63	13.51	16.89	390.35	497.90
27	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	48.97	68.00	24.71	30.88	356.95	470.49
28	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	48.97	68.00	24.71	30.88	356.95	470.49
29	C <sub>I</sub> N <sub>I</sub> K <sub>H</sub> L <sub>L</sub> W <sub>I</sub>	45.80	63.60	46.22	28.89	333.88	481.61
30	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>L</sub>	57.13	79.33	28.82	36.03	416.45	382.24
31	C <sub>I</sub> H <sub>N</sub> ILK <sub>I</sub> L <sub>L</sub> I <sub>L</sub> W <sub>I</sub> L	78.86	51.56	14.32	17.90	413.89	423.46
32	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	48.97	68.00	24.71	30.88	356.95	470.49

The introduction of calcium hydroxide to the system was decided to be carried out towards the end of the procedure, since it causes rapid and permanent gelation upon addition to the silicate solutions due to its divalency and high field strength. Therefore, calcium hydroxide was added to the remaining amount of mixing water, and the obtained limewater was added to the sol and the system was mixed using a hand-held homogenizer at 7000 rpm for 3–5 sec to ensure complete blending of the two portions. The appearance of the resultant was found to range from light translucent to solid white instantly after the addition of limewater. The transparency of the mixture inversely correlated with the calcium content, while the alkalis tended to shift the gel's appearance towards translucent. For instance, solid white colors were found in the case of gels with low alkalis and high calcium, while the ones with opposite combination of alkalis and calcium appeared to be translucent.

## 2.4 Rheological measurements

### 2.4.1 Gelation time measurements

Gelation time is an approximate measure of the kinetics of reactions and it helps us understand how different components promote or delay formation of gels in concrete. Lithium (as a modifier) in particular can be investigated to see whether its ASR suppressing effect [20,21] has to do with how it alters kinetics/extent of gelation reactions and/or repolymerization. The gels were tested for their gelation time upon completion of the synthesis process. The gelation time (or the gel point) is the time at which the sol (for the most part) converts to gel through spatial cross-linking of a sufficient number of silicate clusters [22]. On a macroscopic level, the gel point is considered to be the point at which the sol starts to show growing resistance against shear deformations [23]. As such, the gel's viscosity starts to rapidly increase around the gel point, the rate of which will depend on the chemistry and solid concentration of the gel.

A Brookfield DV3–T rheometer with a V–73 spindle ( $D = 12.67$  mm and  $L = 25.35$  mm) was used for monitoring the evolution of viscosity in the gels. The plastic bottles containing the sols were mounted to the rheometer and the spindle was inserted into the sol and started rotating at 0.5 rpm. The torsional moment generated by the sol was monitored over time and the gelation time was determined as the time at which the torsional moment starts to grow.

### 2.4.2 Yield stress measurement

The yield stress of the gels were measured and compared in order to see the effect of each composition variable and lithium in particular on this parameter. Due to its high reliability and straightforwardness, the stress growth concept was used for testing the gels for their yield stress [24]. In this approach, the shear stress is applied and increased in the gels at a constant (slow) rate and the maximum tolerated stress is considered to be the yield stress of the material. Such shear stress can be applied to the media via different methods, and the vane geometry (adopted here) is known to be the most reliable one, due to its straightforward concept and minimum disturbance that it imposes on the media [25,26]. Therefore, same instrument used for the measurement of the gelation time of the specimens was used for yield stress measurements. The spindle used for applying the shear stress was either V–73 (for gels with low yield stress) or V–74 ( $D = 5.89$  mm and  $L = 11.76$  mm) otherwise. Please refer to [15] and [25] for detailed information about this experiment.

In the case of certain gels with yield stresses greater than 40 kPa, the torsional moment required to successfully test the gels using the rheometer exceeded beyond the rheometer capacity. In the case of such gels, the V–74 spindle was attached to a high precision torque driver model TD24 (THORLABS, 0–170 N.mm) via a manufactured connector. The yield stress of those gels was measured using such torque meter via inserting the spindle into the gel and slowly applying torque by hand. For both methods, six to eight measurements were taken from each gel specimen and the results were found to have high reliability.

## 2.5 Chemical characterization techniques

The chemical characteristics of the gels investigated in this research are the alkalinity (i.e., pH), chemical composition and osmotic pressure of the liquid phase (theoretically calculated per Morse equation). The liquid extraction was performed by applying hydraulic compressive pressure on representative samples of the gels inside a pressurized stainless steel capsule equipped with a multilayer filtering system. The extracted liquids were further filtered using 0.2  $\mu\text{m}$  syringe filter discs. The pH of the gels' liquid phase was measured by the acid titration method using a 0.1M HCl acid solution. The chemical compositions of the liquids were determined using Perkin-Elmer Optima 5300 UV inductively coupled plasma–atomic

emission spectroscopy (ICP–AES) technique. The detection limits of Ca, K, Li, Na and Si of the instrument were 0.01, 0.2, 0.01, 0.01, and 0.01 µg/mL, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1 Gelation time and yield stress results

Table 3.1 shows the gelation time ( $T_G$ ) and yield stress ( $\tau_y$ ) results of the 32 experimented gels. Notice how variations in composition results in drastic changes in these parameters. The gelation time changes across four orders of magnitude (comparing rows 14 and 15 as the maximum and minimum observations), and the yield stress shows near two orders of magnitude variation (comparing rows 16 and 21). In both cases, the effects of Ca/Si, Na/Si and K/Si are evident. Ca/Si seems to be significantly decreasing the gelation time and increasing the yield stress of the gels, while the opposite is found for Na/Si and K/Si. Short gelation times were observed in the case of gels with intermediate to high Ca/Si and low Na/Si (and/or K/Si). Furthermore, gels with such compositions were found to have more solid textures and higher yield stresses. The opposite properties were observed in the case of gels with low Ca/Si and high such alkalis. The effects of lithium and water are more subtle and need statistical analyses. As such, regression functions per Equation (1) were fit to the data to statistically evaluate the effects and interactions of each variable on these two rheological parameters.

Table 3.1: The gelation time ( $T_G$ ) and yield stress ( $\tau_y$ ) results of the gels

No.	Gel label	$T_G$ (min)	$\tau_y$ (kPa)	No.	Gel label	$T_G$ (min)	$\tau_y$ (kPa)
1	C <sub>H</sub> N <sub>L</sub> K <sub>H</sub> L <sub>H</sub> W <sub>L</sub>	0.9	127	17	C <sub>L</sub> N <sub>L</sub> K <sub>H</sub> L <sub>L</sub> W <sub>L</sub>	5.7	96
2	C <sub>H</sub> N <sub>H</sub> K <sub>L</sub> L <sub>L</sub> W <sub>H</sub>	2.2	71	18	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	0.7	89
3	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>H</sub>	2.6	24	19	C <sub>L</sub> N <sub>H</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	507	7.3
4	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	1.3	64	20	C <sub>H</sub> N <sub>H</sub> K <sub>L</sub> L <sub>H</sub> W <sub>L</sub>	6.5	67
5	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	1.4	57	21	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	328	2.7
6	C <sub>H</sub> N <sub>H</sub> K <sub>H</sub> L <sub>L</sub> W <sub>L</sub>	13.3	42	22	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	3.8	22
7	C <sub>L</sub> N <sub>H</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	342	8.7	23	C <sub>L</sub> N <sub>L</sub> K <sub>H</sub> L <sub>H</sub> W <sub>H</sub>	4.3	26
8	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	3.8	27	24	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	3.5	29
9	C <sub>L</sub> N <sub>H</sub> K <sub>L</sub> L <sub>H</sub> W <sub>H</sub>	30	7.3	25	C <sub>L</sub> N <sub>H</sub> K <sub>H</sub> L <sub>H</sub> W <sub>L</sub>	3678	6.8
10	C <sub>H</sub> N <sub>L</sub> K <sub>L</sub> L <sub>H</sub> W <sub>H</sub>	0.5	110	26	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>H</sub>	11	80
11	C <sub>H</sub> N <sub>H</sub> K <sub>H</sub> L <sub>H</sub> W <sub>H</sub>	12	23	27	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	3.5	22
12	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>H</sub> W <sub>L</sub>	2.3	78	28	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	3.6	27
13	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>H</sub> W <sub>L</sub>	6.0	21	29	C <sub>L</sub> N <sub>L</sub> K <sub>H</sub> L <sub>L</sub> W <sub>L</sub>	18	38
14	C <sub>L</sub> N <sub>H</sub> K <sub>H</sub> L <sub>L</sub> W <sub>H</sub>	4320	7.7	30	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	6.5	23
15	C <sub>H</sub> N <sub>L</sub> K <sub>H</sub> L <sub>L</sub> W <sub>H</sub>	0.4	71	31	C <sub>H</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	0.6	101
16	C <sub>H</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	1.0	214	32	C <sub>L</sub> N <sub>L</sub> K <sub>L</sub> L <sub>L</sub> W <sub>L</sub>	3.8	27

The regression function of gelation time is shown in Equation (2). The regression coefficient of determination ( $R^2$ ) was found to be 93.28%. Moreover, the prediction  $R^2$  of the developed regression model, which represents the accuracy of the model in predicting new observations, is 87.47%. A Box–Cox transformation of the response ( $\lambda = -1/3$ ) was needed in order to normalize the residuals of regression and stabilize their variations across the fitted values (which are two core assumptions of multiple linear regression). The terms included in the regression model are the significant predictors of gelation time. Other terms (e.g., W, (Ca/Si)<sup>2</sup>, (Na/Si)×(K/Si) etc.) did not prove significant. The regression model suggests that Ca/Si is by far the most important factor (P–Value < 0.0005) promoting the gelation of the studied ASR gels (compare the coefficients), while Na/Si and K/Si showed delaying effects (P–Values = 0.069 and < 0.0005, respectively).

Na/Si has a significant interaction with Ca/Si (P–Value = 0.033). As shown in Figure 3.1, the reducing effect of Ca/Si on  $T_G$  is more evident at higher levels of Na/Si. The increasing effect of sodium on the gelation time of ASR gels is due to the fact that sodium as a monovalent cation forms bonds with the non-bridging oxygens (NBOs) preventing them from making molecular chains with the adjacent silicate molecules. This will result in a decline in the development of longer molecular chains and their spatial cross–linking, which will then lead to longer gelation times. Calcium, on the other hand, is a divalent cation with a high affinity with oxygen and bonds silicates together thus promoting gelation. Due to its

higher field strength, it can replace sodium at the O-Na<sup>+</sup> sites and form bonds with the adjacent silicates, which is why it has a more pronounced decreasing effect on gelation time of high-sodium gels.

$$(T_G(\text{min}))^{-1/3} = 0.316 + 6.0 \frac{\text{Ca}}{\text{Si}} - 0.639 \frac{\text{Na}}{\text{Si}} - 1.107 \frac{\text{K}}{\text{Si}} + 1.005 \frac{\text{Li}}{\text{Si}} - 3.21 \frac{\text{Ca}}{\text{Si}} \times \frac{\text{Na}}{\text{Si}} - 5.30 \frac{\text{Ca}}{\text{Si}} \times \frac{\text{Li}}{\text{Si}} \quad (2)$$

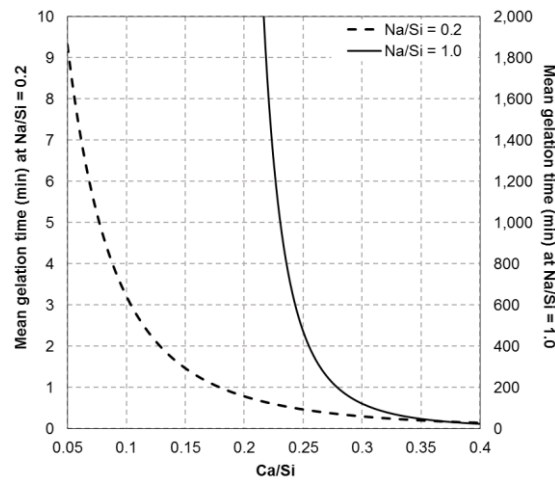


Figure 3.1: The interaction plot of Ca/Si and Na/Si on the gelation time; Ca/Si has a promoting effect on gelation especially at high Na/Si levels

Li/Si also showed a marginally significant effect on gelation time (P-Value = 0.074). However, it was found to have a significant interaction with Ca/Si (P-Value = 0.028). Figure 3.2 shows the interaction plot of Li/Si and Ca/Si. It is observed that at a low Ca/Si level (0.05), an increase in Li/Si leads to a drastic reduction in the gelation time, while it shows little to no effect on gelation time at high Ca/Si (> 0.2). Therefore, it can be concluded that lithium generally has an accelerating effect on the gelation of ASR gels. As shown later in the results, the presence of lithium causes significant drop in gel pH, which is known to act as a catalyst in gelation (i.e., lowering the pH) [1]. One of the few existing theories explaining the ASR suppressing effect of lithium hold that the presence of lithium reduces the repolymerization of silicate after dissolution [16]. However, the gelation time results obtained in this research suggest otherwise. Interestingly, the water content did not prove to significantly affect the gelation time in the studied range. While the effect of water on gelation time is intuitive, the results suggest that the diluting effect of water content variations (in the relatively narrow range 65–75%) on the gelation time is not statistically meaningful when compared to the inherent fluctuations in the results.

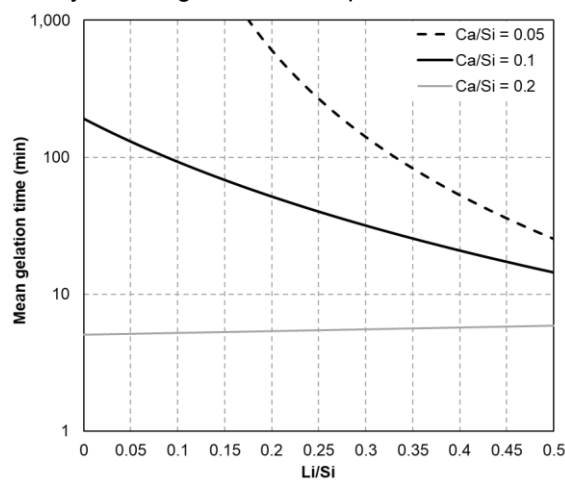


Figure 3.2: The interaction plot of Li/Si and Ca/Si on the gelation time; Li/Si has a promoting effect on gelation especially at low Ca/Si levels, while its effect is less evident at high Ca/Si

Equation (3) shows the regression model of the gels' yield stress with respect to their chemical composition. It is observed that the effect of chemistry on the yield stress of the gels is more complex

compared to the gelation time, and there are many terms involved in the variations of this parameter. The regular and prediction coefficients of determination for the developed regression model were calculated as 96.46% and 73.28%, respectively.

$$\ln(\tau_y(\text{Pa})) = -0.15 + 31.71 \frac{\text{Ca}}{\text{Si}} - 7.748 \frac{\text{Na}}{\text{Si}} + 43.0 \frac{\text{K}}{\text{Si}} + 24.0 \frac{\text{Li}}{\text{Si}} + 18.51W - 174.6 \times \left(\frac{\text{Ca}}{\text{Si}}\right)^2 \quad (3)$$

$$+ 32.76 \left(\frac{\text{K}}{\text{Si}}\right)^2 + 7.94 \left(\frac{\text{Li}}{\text{Si}}\right)^2 + 19.10 \frac{\text{Ca}}{\text{Si}} \times \frac{\text{Na}}{\text{Si}} - 78.4 \frac{\text{K}}{\text{Si}} \times W - 41.8 \frac{\text{Li}}{\text{Si}} \times W + 262.4 \left(\frac{\text{Ca}}{\text{Si}}\right)^3$$

While all input variables proved to be significantly affecting the yield stress, the patterns of their influence on yields stress cannot be easily realized due to the presence of non-linear terms and interactions. As such, the factorial plots of the average fitted yield stress versus different input variables were prepared and are shown in Figure 3.3. The factorial plots are obtained by plotting the fitted yield stress (per Equation (3)) as a function of each input variable while other variables are all at their intermediate levels. For instance, the factorial plot for Ca/Si is obtained by replacing Na/Si, K/Si, Li/Si and W with 0.6, 0.15, 0.25, and 0.7 respectively in the regression equation and plotting  $\tau_y$  as a function of Ca/Si. It is observed that an increase in Ca/Si from 0.05 to 0.4 results in ~80 times increase in the yield stress, which can be attributed to its divalency and high cross-linking potential. The increasing effect of Ca/Si is more pronounced once it exceeds 0.3.

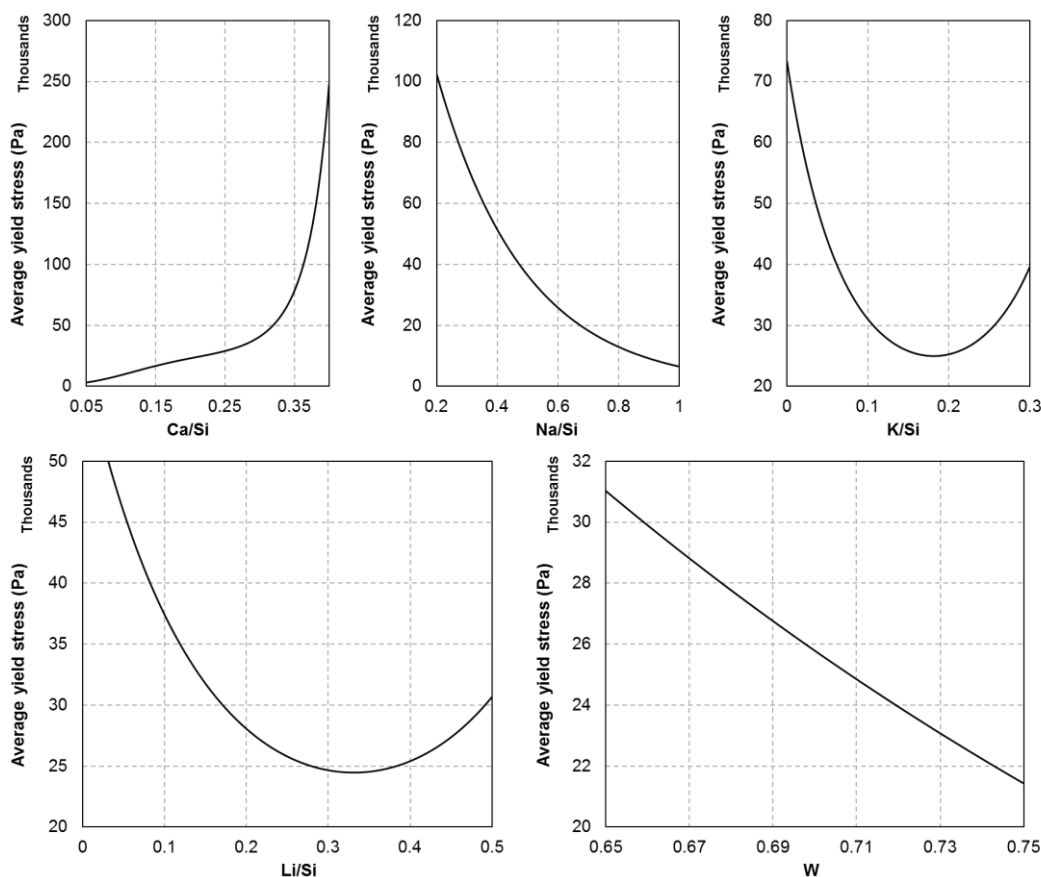


Figure 3.3: The factorial plots of the average fitted yield stress versus different input variables; increase in Ca/Si promotes the yield stress of ASR gels while other chemical components generally have a decreasing effect

Na/Si, on the other hand, has a drastic reducing effect on yield stress, causing a reduction in this parameter by a factor of 16 as it changes from 0.2 to 1.0. The effect of potassium appears to be complicated. It reduces the yield stress by a factor of 3 as it changes from 0.0 to 0.18, but it leads to a 58% increase as it increases from 0.18 to 0.3. This pattern of behavior is not only suggested by the regression function, but it is also clearly observed in the raw data. Therefore, the impacts of K/Si and Na/Si as two alkali elements are not similar, which might have to do with their different atomic sizes and field strengths. Li/Si has a more or less similar (but less intense) influence on the yields stress as K/Si.



It causes 58% decrease in the yield stress as it changes from 0.0 to 0.33, followed by a 25% increase as it increases from 0.33 to 0.5. The decreasing effect of lithium on yield stress is due to the fact that the NBO sites occupied by lithium do not contribute to mechanical strength of the gel. However, the significant reduction in pH (results are provided below) that occurs at high dosages of lithium results in more gelation reactions (thus more solid phase). Moreover, the increase in the solubility of calcium (due to lowering of pH) promotes its incorporation in the gel structure and thus the yield stress. The above two reasons probably justify the increase in yield stress of ASR gels as Li/Si exceeds 0.33.

According to Equation (3), Ca/Si and Na/Si have an interactive effect on yield stress, which is plotted in Figure 3.4. It is observed that at low levels of Na/Si (e.g., 0.2), Ca/Si has a generally increasing effect on yield stress with an episode of reducing effect in the range of 0.16 to 0.28. However, the Ca/Si has a monotonic increasing effect on yield at high levels of Na/Si.

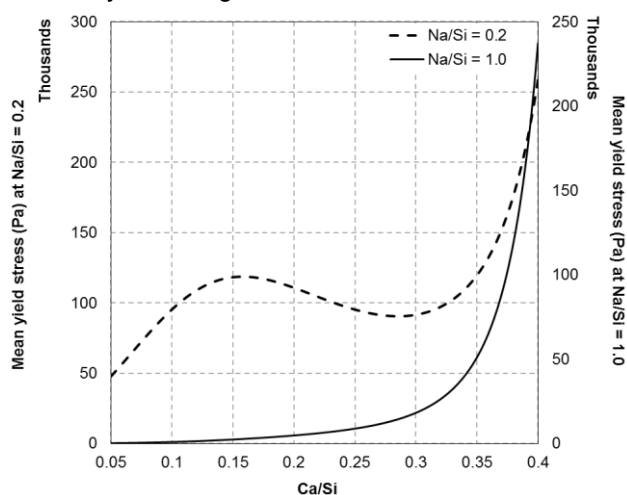


Figure 3.4: The interaction plot of Ca/Si and Na/Si on the yield stress

### 3.2 Chemical measurements and analyses results

The ICP chemical analyses results of the gels' liquid phases are shown in Table 3.2. These results reveal how much of the different species have remained in the dissolved state, as opposed to being chemically incorporated in the gels. Using Morse equation, the osmotic pressure of the gels liquid phase could be theoretically calculated. The ICP-AES results as well as the osmotic pressure and  $[\text{OH}^-]$  values are reported in Table 3.2. The lowest osmotic pressure was found to belong to the low-sodium gel (i.e., Na/Si = 0.2), which is due to the low concentration of sodium and silicates in the liquid phase. The highest osmotic pressure, however, was detected in the case of low-calcium gel where the high concentration of residual sodium-silicates in the liquid phase (due to lack of sufficient calcium to bind the silicates) results in a very high osmotic pressure.

Ca/Si, Na/Si and Li/Si are the three important variables controlling the pH of the gels' liquid phase. While calcium was found to have a marginally significant decreasing effect on pH, sodium and lithium showed a strong interactive effect on this parameter. In the case of gels with no lithium, Na/Si was found to have a linear increasing effect on pH. However, Na/Si seems to actually have a decreasing effect on the pH in the case of gels with Li/Si greater than 0.48. Also, lithium has a reducing effect on pH for the gels incorporating average to high sodium contents.

The immediate effect of lithium on pH and its altering influence on the impact of sodium on pH might be one of the contributing factors explaining why lithium has suppressing effects on ASR. As shown in Figure 3.5, gels with high Na/Si experience an over seven-fold drop in the  $\text{OH}^-$  concentration of their liquid phase when lithium is introduced up to a Li/Si of 0.5. Such drop in the pH could drastically reduce the rate of ASR reaction.

It can be argued that once a layer of ASR gel is formed around or within a reactive aggregate, the presence of lithium in considerable concentrations results in a significant decrease in the pH of the surrounding ASR gel's liquid phase, leading to substantial decline in the rate and extent of alkali attack on the remaining unreacted aggregates. A possible explanation for the observed influence of lithium on the pH of ASR gels has been provided as follows. The arguments assumes an ample presence of portlandite in the system, which is almost always the case in concrete. In the absence of lithium (i.e., Li/Si = 0.0), increase in sodium concentration results in the formation of more NBOs, which will be readily

occupied by the dissolved  $\text{Ca}^{2+}$ . The drop in the  $\text{Ca}^{2+}$  concentration calls for further dissolution of portlandite into the liquid phase, which releases not only  $\text{Ca}^{2+}$  but also  $\text{OH}^-$ , which leads to an increase in the pH (see Figure 3.5 for the difference in the  $\text{OH}^-$  concentration of the low-sodium ( $\text{Na}/\text{Si} = 0.2$ ; dashed line) and high-sodium ( $\text{Na}/\text{Si} = 1.0$ ; solid line) gels at  $\text{Li}/\text{Si} = 0.0$ ). However, in the presence of lithium, although increase in sodium concentration will still result in the formation of more NBOs, those endings will not be necessarily occupied by  $\text{Ca}^{2+}$ , because  $\text{Li}^+$  as a small and much more mobile and soluble cation compared to  $\text{Ca}^{2+}$  will occupy those NBOs. Once attached to oxygen,  $\text{Ca}^{2+}$  cannot replace for  $\text{Li}^+$  because these two elements (i.e.,  $\text{Ca}^{2+}$  and  $\text{Na}^+$ ) have similar electronegativity and the significantly larger cation size of  $\text{Ca}^{2+}$  will be a barrier in breaking the bond between  $\text{O}^-$  and  $\text{Li}^+$ . As such, no drop in the  $\text{Ca}^{2+}$  concentration will occur in the liquid phase and no dissolution of portlandite will be needed, which means no increase in the pH (see Figure 3.5 for the difference in the  $\text{OH}^-$  concentration of the low-sodium ( $\text{Na}/\text{Si} = 0.2$ ; dashed line) and high-sodium ( $\text{Na}/\text{Si} = 1.0$ ; solid line) at  $\text{Li}/\text{Si} = 0.5$ ).

Table 3.2: The ICP chemical measurements, alkalinity and osmotic potential of ASR gels

No.	Gel label	Liquid phase composition (moles per liter of liquid phase)							pH	Osmotic pressure (MPa)
		$[\text{Ca}^{2+}]$	$[\text{Na}^+]$	$[\text{K}^+]$	$[\text{Li}^+]$	$[\text{Si}_{\text{Tot}}]$	$[\text{OH}^-]$			
1	C <sub>I</sub> H <sub>N</sub> L <sub>K</sub> I <sub>H</sub> L <sub>I</sub> H <sub>W</sub> I <sub>L</sub>	0.018	1.074	0.443	0.712	1.226	2.116	14.33	13.6	
2	C <sub>I</sub> H <sub>N</sub> I <sub>H</sub> K <sub>I</sub> L <sub>L</sub> I <sub>L</sub> W <sub>I</sub> H	0.006	1.697	0.188	0.407	1.245	2.000	14.30	13.5	
3	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>H</sub>	0.006	2.128	0.350	0.652	2.051	1.887	14.28	17.2	
4	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	0.007	1.914	0.339	0.010	2.080	1.807	14.26	15.0	
5	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	0.000	1.407	0.008	0.431	1.368	1.867	14.27	12.4	
6	C <sub>I</sub> H <sub>N</sub> I <sub>H</sub> K <sub>I</sub> H <sub>L</sub> I <sub>L</sub> W <sub>I</sub> L	0.002	2.136	0.500	0.318	1.855	2.793	14.45	18.5	
7	C <sub>I</sub> L <sub>N</sub> I <sub>H</sub> K <sub>I</sub> L <sub>L</sub> I <sub>L</sub> W <sub>I</sub> L	0.058	2.427	0.212	0.322	2.735	2.845	14.45	21.0	
8	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	0.021	1.424	0.278	0.440	1.490	2.052	14.31	13.9	
9	C <sub>I</sub> L <sub>N</sub> I <sub>H</sub> K <sub>I</sub> L <sub>L</sub> I <sub>H</sub> W <sub>I</sub> H	0.010	1.541	0.145	0.194	1.366	1.977	14.30	12.8	
10	C <sub>I</sub> H <sub>N</sub> I <sub>L</sub> K <sub>I</sub> L <sub>L</sub> I <sub>H</sub> W <sub>I</sub> H	0.000	0.722	0.083	0.515	0.732	1.176	14.07	7.9	
11	C <sub>I</sub> H <sub>N</sub> I <sub>H</sub> K <sub>I</sub> H <sub>L</sub> I <sub>H</sub> W <sub>I</sub> H	0.000	1.165	0.267	0.072	0.609	1.493	14.17	8.8	
12	C <sub>I</sub> L <sub>N</sub> I <sub>L</sub> K <sub>I</sub> L <sub>L</sub> I <sub>H</sub> W <sub>I</sub> L	0.001	1.082	0.134	0.767	1.938	1.812	14.26	14.0	
13	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>H</sub> W <sub>I</sub>	0.003	1.417	0.299	0.199	1.182	2.067	14.32	12.6	
14	C <sub>I</sub> L <sub>N</sub> I <sub>H</sub> K <sub>I</sub> H <sub>L</sub> I <sub>L</sub> W <sub>I</sub> H	0.032	1.380	0.346	0.218	1.567	2.056	14.31	13.6	
15	C <sub>I</sub> H <sub>N</sub> I <sub>L</sub> K <sub>I</sub> H <sub>L</sub> I <sub>L</sub> W <sub>I</sub> H	0.001	0.695	0.227	0.121	0.538	0.956	13.98	6.2	
16	C <sub>H</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	0.000	1.167	0.261	0.392	0.880	1.822	14.26	11.0	
17	C <sub>I</sub> L <sub>N</sub> I <sub>L</sub> K <sub>I</sub> H <sub>L</sub> I <sub>L</sub> W <sub>I</sub> L	0.001	1.354	0.534	0.288	2.420	1.792	14.25	15.6	
18	C <sub>I</sub> N <sub>L</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	0.000	0.334	0.091	0.242	0.441	0.551	13.74	4.0	
19	C <sub>I</sub> N <sub>H</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	0.006	2.599	0.357	0.092	1.633	3.404	14.53	19.7	
20	C <sub>I</sub> H <sub>N</sub> I <sub>H</sub> K <sub>I</sub> L <sub>L</sub> I <sub>H</sub> W <sub>I</sub> L	0.000	1.264	0.103	0.061	0.650	0.879	13.94	7.2	
21	C <sub>L</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	0.018	2.342	0.474	0.927	2.950	3.133	14.50	26.0	
22	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	0.020	1.273	0.239	0.398	1.327	1.982	14.30	12.8	
23	C <sub>I</sub> L <sub>N</sub> I <sub>L</sub> K <sub>I</sub> H <sub>L</sub> I <sub>H</sub> W <sub>I</sub> H	0.003	0.860	0.352	0.578	1.494	1.782	14.25	12.4	
24	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	0.026	1.857	0.344	0.585	2.009	1.892	14.28	16.4	
25	C <sub>I</sub> L <sub>N</sub> I <sub>H</sub> K <sub>I</sub> H <sub>L</sub> I <sub>H</sub> W <sub>I</sub> L	0.002	1.020	0.226	0.060	0.869	1.290	14.11	8.5	
26	C <sub>I</sub> L <sub>N</sub> I <sub>L</sub> K <sub>I</sub> L <sub>L</sub> I <sub>L</sub> W <sub>I</sub> H	0.001	1.252	0.146	0.334	2.468	1.221	14.09	13.2	
27	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	0.027	1.572	0.292	0.475	1.701	2.207	14.34	15.3	
28	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	0.043	2.300	0.424	0.780	2.753	2.302	14.36	21.5	
29	C <sub>I</sub> N <sub>I</sub> K <sub>H</sub> L <sub>L</sub> W <sub>I</sub>	0.018	1.536	0.661	0.320	1.739	2.648	14.42	16.9	
30	C <sub>I</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>L</sub>	0.198	2.258	0.435	0.786	2.825	4.079	14.61	25.8	
31	C <sub>I</sub> H <sub>N</sub> I <sub>L</sub> K <sub>I</sub> L <sub>L</sub> I <sub>L</sub> W <sub>I</sub> L	0.000	0.680	0.056	0.123	0.546	0.796	13.90	5.4	
32	C <sub>H</sub> N <sub>I</sub> K <sub>I</sub> L <sub>L</sub> W <sub>I</sub>	0.033	1.896	0.316	0.571	2.013	2.137	14.33	17.0	

The findings of this research can promote the understanding of the roles and interactions of different chemical components on 1) the kinetics of gelation reactions, 2) mechanical properties of the gels (yield stress), 3) alkalinity of the gels liquid phase (which can be correlated with rate of ASR) and 4) their tendency to imbibe water (i.e., osmotic pressure). The reducing effect of lithium on yield stress of the gels, and on their pH are arguably two of the important underlying reasons why the presence of lithium can suppress the extent of ASR damage.

It should be noted that while using a system model for investigation of the behavior of synthetic ASR gels and the effects of different chemical components on their physicochemical properties offers several advantages and is arguably the most suitable way for understanding the chemistry of ASR gels in concrete, there are several differences between the studied model systems and the real life concrete. For instance, the developed model requires the chemical composition of the gels to be known for estimation of their properties while this is not necessarily available in real concrete and is affected by the composition of the cement and aggregates, and the location of the gel in concrete. Moreover, the chemical composition of ASR gels tend to vary over their life time in concrete, and they also endure physical and chemical influences such as confinement and carbonation in their life cycle, which can alter the properties and behavior of the gels in profound ways. Also, additives such as lithium may not fully integrate with the gels due to being consumed during hydration reactions, etc. Nonetheless, the observations of this research about lithium can generally explain the underlying cause of its ASR-inhibiting behavior.

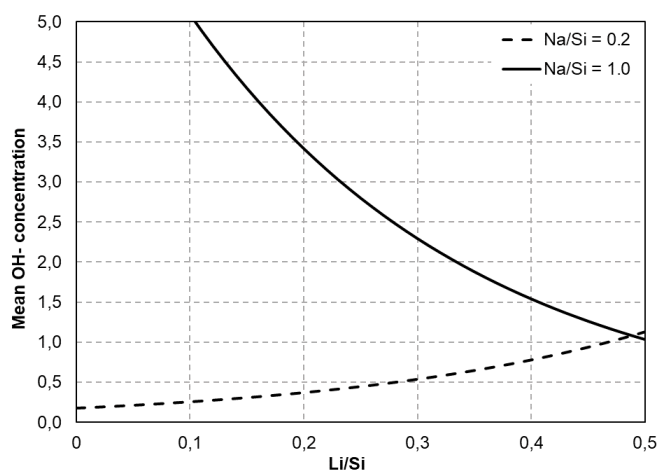


Figure 3.5: The interaction plot of Na/Si and Li/Si on the hydroxide concentration

#### 4. SUMMARY AND CONCLUSIONS

In the present study, synthetic lithium–admixed ASR gels with a broad range of compositions were produced using a new sol–gel method. The effects of gel chemistry on its rheological and chemical properties were investigated with the following conclusions:

- The presence of lithium was found to expedite gelation, which is attributed to the reducing effect of lithium on the pH of the liquid phase.
- The presence of lithium (up to Li/Si = 0.33) was found to reduce the yield stress of ASR gels thus reducing their capability in resisting against confining pressures, which is argued to result in less deleterious gels.
- Ca/Si was found to be the most important factor in promoting yield stress of ASR gel. Na/Si, on the other hand, showed the opposite effect on this parameter. Similar effects on yield stress were observed for K/Si.
- One of the most significant findings of this research was that at high Na/Si levels (> 0.50, which is usually the case in aggregates), an increase in Li/Si results in significant drop in the OH<sup>-</sup> concentration in the gels' liquid phase (up to 7 times), which can lead to a drastic decline in the aggregate dissolution rate and extent.

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