

THE INFLUENCE OF ASR GELS COMPOSITION ON THEIR SWELLING PROPERTIES

Asghar Gholizadeh Vayghan*, Farshad Rajabipour, Corey Arndt

The Pennsylvania State University, PA, UNITED STATES

Abstract

This paper investigates the effects of ASR gels chemical composition (represented as Ca/Si, Na/Si and K/Si molar ratios) on their free swelling capacity in contact with water vapor. Synthetic ASR gel minibars with twenty different chemical compositions similar to those of field ASR gels were produced and exposed to 95% relative humidity, and their free swelling strains were monitored over a period of four weeks. Response surface design concepts were implemented to design the experiments such that the non-linear effects and interactions of the test variables (i.e., Ca/Si, Na/Si and K/Si) on the swelling properties of the gels can be statistically evaluated. The results suggest that Na/Si and K/Si have linear positive effects on the free swelling of the gels, while Ca/Si shows suppressing effects when it ranges from 0.05 to 0.18, and also beyond 0.4. However, it promotes swelling as it increases in the range of 0.18 to 0.4.

KEYWORDS: ASR gels, free swelling strain, minibar expansion, response surface design

1 INTRODUCTION

Alkali-silica reaction (ASR) has been studied for decades in terms of its chemistry, mechanism, assessment and mitigation. However, studies systematically focusing on characterization and evaluation of ASR gels are scarce, especially when it comes to the role of the gels chemistry and its impact on their expansive behavior and hydrophilic properties. ASR damage is controlled by the expansion pressure induced by ASR gels. As such, ASR gels play a significant role on the magnitude of ASR damage, which is a function of the amount of formed gel and the swelling strain of the gel. The study of the rheological, chemical and swelling properties of synthetic alkali-silicate gels promotes (a) better understanding of the swelling behavior of ASR gels and the factors (i.e. chemistry and morphology) that control it, (b) developing chemical admixtures that suppress the swelling potential of the gels and, subsequently, damage in concrete, and (c) developing computer models to simulate and predict ASR damage in concrete.

Sodium, potassium and calcium are the most common metals observed in ASR gels. Other components (i.e., Mg, Al, Fe) are found in trace amounts and, as such, not investigated in this paper. The composition of ASR gels can be represented in the general form of $\text{SiO}_2 \cdot (\text{Na}_2\text{O})_n \cdot (\text{K}_2\text{O})_k \cdot (\text{CaO})_c \cdot (\text{H}_2\text{O})_x$. The important parameters in the chemistry of the gels, therefore, are the sodium to silica atomic ratio (Na/Si), as well as K/Si and Ca/Si [1,2]. ASR gels form in concrete in a variety of different compositions and behave differently in terms of expanding and inducing damage to the surrounding concrete. Although it is understood that calcium, sodium and potassium influence the expansive behavior of ASR gels, such effects have not been accurately quantified. Further, there is no information on the interactions between Ca, Na, K and Si on the properties of ASR gels. The most important characteristics of ASR gels are their swelling capacity and swelling pressure, mechanical and rheological properties (primarily yield stress as demonstrated in a previous work [3]), and the osmotic pressure of their pore solution. The free swelling capacity of a gel determines potentially how much a gel can freely swell if there is no resistance against its expansion. The swelling pressure is the maximum amount of pressure that the gel can exert to the surrounding concrete when its expansion is partially or fully restrained. Moreover, the osmotic pressure of the gel's pore solution explains part of their tendency towards water imbibition and expansion [4]. The study of free swelling capacity of the gels is the first necessary step towards understanding their swelling properties, because the capacity for freely swelling in humid environments is a prerequisite for deleteriousness of the gels. If a gel has a three-dimensionally connected atomic structure (resulting in a non-swelling gel), it will not be able to induce and maintain pressure to the surrounding concrete in an effective range. The objective of this research is therefore to study the effect of ASR gels composition (i.e., Na/Si, K/Si, Ca/Si) on their swelling properties in contact with water vapor (RH=95%).

* Correspondence to: a.v.gholizadeh@gmail.com

2 MATERIALS AND METHODS

2.1. Materials

The studied range of ASR gels composition

In order to develop a comprehensive understanding about the behavior of the gels, the commonly observed range of ASR gels composition in the field need to be determined. The compositions of one hundred ASR gel samples extracted from concrete bridges, dams, pavements, and sea walls, reported in the literature [5,6,7,8,9,10,11,12,13,14], are summarized in Figure 1. It is observed that sodium is usually present in the gels in larger quantities compared to potassium and calcium.

The study range of ASR gels for research purposes should differ with the range of chemical compositions reported in the literature in some aspects. This is because the compositions reported in the literature usually associate with ASR gel samples extracted from aged concrete structures and also were not necessarily taken from the vicinity of aggregates. The composition of the gels is known to change with time; increasing in Ca/Si and decreasing in Na/Si [15]. Also, the gels around or within the aggregates are richer in sodium and incorporate less calcium. Thomas [15] argued that ASR gels tend to undergo an ion exchange process, which he referred to as “alkali-recycling”, where the sodium ions in the gels are replaced with calcium ions dissolving from portlandite in the cement paste. This process maintains high alkalinity of the concrete pore solution and possibly reduce the swelling capacity of the gel. Many of the reported gels in the literature are aged and they seem to be in their post-ion-exchange state, where they show little further expansion and therefore are not of interest. According to Hou et al. [1], alkali and alkaline earth metals in the field ASR gels typically appear in the ranges $(\text{Na}+\text{K})/\text{Si}=0.1\sim 1.2$ and $(\text{Ca}+\text{Mg})/\text{Si}=0.0\sim 0.2$ (atomic ratios). As such, a lower range of Ca/Si and a higher range of Na/Si and K/Si compared to what Figure 1 suggests will be studied to better represent the “younger” gels that are responsible for concrete expansion and deterioration. Using all of the given information and in order to maintain the generality of the research, the ranges of chemical compositions studied are shown in Table 1. The gels water content was held at 40%.

Raw materials used for gel synthesis

Among other commercially available sources of silica (SiO_2), dried pulverized colloidal silica was found to be the most suitable for gel synthesis. Colloidal silica (50% H_2O) was dried at 110 °C for two days followed by 48 hours of grinding in a porcelain jar mill, which produced silica powder with an average particle size of 6.37 μm . Reagent grade NaOH and KOH pellets were used as alkali sources. Also, reagent grade $\text{Ca}(\text{OH})_2$ powder was used as the source of calcium.

2.2. Gel synthesis and experimentation methods

Gel synthesis

In the previous work, a sol-gel method was developed for gel synthesis [3]. The sol-gel method has been a commonly practiced method for ASR gel synthesis in the past [2,16]. However, it does not allow achieving high gel concentrations (i.e., the mass percent of the gel's solid skeleton). The maximum achievable solid concentration, using sol-gel method, for gels having intermediate calcium ($\text{Ca}/\text{Si}=0.2$) and low sodium ($\text{Na}/\text{Si}=0.2$) contents was found to be ~25%, while the concentration of the gels in the field may well exceed this level. As such, a new gel synthesis method was adopted in this paper. Dry SiO_2 powder was batched, using a Hobart mixer, with appropriate amounts of NaOH, KOH, $\text{Ca}(\text{OH})_2$ and water to render the designated Na/Si, K/Si, Ca/Si and a constant water content of 40%. The mixing protocol adopted for gel synthesis was as follows. First, the alkalis (i.e., NaOH and KOH) were dissolved in the mixing water in an airtight bottle, and the silica was weighed and dry-mixed with appropriate amount of $\text{Ca}(\text{OH})_2$. It is worth noting that mixing the alkaline solution with the silica-lime mixture in turn generates excessive heat (depending on the composition), which usually causes boiling of the mixture minutes after batching. In order to control the rate of initial reactions, the alkaline solution was stored in refrigerator at 2 °C, and the blended powder was stored in a freezer at -18 °C. After cooling down, the alkaline solution was transferred to the mixing bowl followed by addition of the silica-lime powder. The mixer was started at the low speed for 30 seconds, followed by scraping and mixing at the medium speed for 90 seconds. If necessary, the mixture was mixed up to 15 seconds at high speed to break up the residual lumps of powder. The resulting mixtures were molded in minibar molds and allowed to undergo natural silica dissolution and gelation similar to what occurs in concrete.

Design of Experiments (DOE)

In order to determine the linear and non-linear effects and interactions between the three variables, namely Ca/Si, Na/Si and K/Si, the concepts of response surface methodology (RSM) was implemented for designing the experiments. RSM is an efficient and very effective method for the design of experiments for

simultaneous estimation of the linear and quadratic effects as well as the interactions of the variables on the response parameters of interest as shown in Equation 1 (where Y is the response parameter (i.e., free swelling strain), X_1 , X_2 and X_3 are the three variables (i.e., Ca/Si, Na/Si and K/Si) and β_s are the coefficients of each term). $X_i \times X_j$ is the interaction term between X_i and X_j . The magnitude and statistical significance (evaluated by p-value) of each term indicates whether it has a meaningful influence on the response parameter. The advantage of RSM is that the cubic effects (i.e., X_i^3) and three-way interaction of the parameters (i.e., $X_1 \times X_2 \times X_3$) can also be evaluated. The regression model can be used to estimate the free swelling capacity of the gels with any given composition both within and outside the studied ranges.

$$Y = \beta_0 + \beta_1 \times X_1 + \beta_2 \times X_2 + \beta_3 \times X_3 + \beta_{12} \times X_1 \times X_2 + \beta_{13} \times X_1 \times X_3 + \beta_{23} \times X_2 \times X_3 + \beta_{11} \times X_1^2 + \beta_{22} \times X_2^2 + \beta_{33} \times X_3^2 \quad (1)$$

Central composite design (CCD) is a common RSM design method that is adopted in this paper. A 3-D demonstration of the combinations of different levels of the three variables (i.e., Ca/Si, Na/Si and K/Si) used for gel synthesis and experimentation is represented in Figure 2. CCD is comprised of three categories of variable combinations; namely axial, cube, and center points. The axial points (which along with the center points enable estimation of linear and quadratic terms) are the points on the surface of the pseudo-sphere where it intercepts each axis. The cube points (which enable estimation of interactions) are the points at the vertices of the cube encircled by the pseudo-sphere. Also, the center points are the ones collected at the origin. If the variable X_i is to be studied over the range of a to b in the experiments (e.g., Ca/Si is studied in the range of 0.05 to 0.50 here), the low (e.g., 0.05) and high (e.g., 0.5) levels are respectively coded as $-\alpha$ and $+\alpha$. The parameter α is a number (>1) equal to $n_c^{1/4}$, where n_c is the number of cube points. Two intermediate-low and intermediate-high levels are defined for each variable coded respectively as -1 and +1. All of the possible factorial combinations of the k variables on these levels (i.e., -1 and +1) constitute the cube points. As such, in a CCD with $k=3$ variables, there will be $n_c=2^k=8$ cube points. Hence, the parameter α in a 3-variable CCD is equal to 1.682. $n_a=2k=6$ axial points are defined in this design where one variable is set at its high or low level (i.e., $+\alpha$ or $-\alpha$) while others are at intermediate levels (i.e., 0). Also, a number of center points equal to n_0 are defined to produce replication in the experiments, where all variables are at their intermediate levels (e.g., Ca/Si has an intermediate level of 0.275, associated with coded level of 0). Considering 6 center points, 20 experiments will be necessary for estimating the linear and quadratic effects of the three variables as well as their two-way interactions.

Table 2 contains the coded and natural levels of the designed experiments with their labels and randomized run order (the gels were batched in a random order as shown in Table 2). The coded dosage levels of -1.682, -1, 0, +1 and +1.682 are respectively referred to as low (L), intermediate-low (IL), intermediate (I), intermediate-high (IH) and high (H). The gels are labeled by assigning the corresponding dosage levels of Ca/Si, Na/Si and K/Si as the lowercase suffixes to C, N and K, respectively. For instance, $C_{II}N_{II}K_{IH}$ is a gel having intermediate-low levels of Ca/Si and Na/Si (i.e., 0.141 and 0.282, respectively), and also intermediate-high level of K/Si (0.239). Therefore, $C_{IH}N_{I}K_{I}$ represents a gel with Ca/Si=0.275, Na/Si=0.55 and K/Si=0.15 and water content of 0.4. The mixture proportions are shown in Table 3. The source of silica contained an initial Na/Si of 0.022, which was taken into account in calculating the required NaOH content. Moreover, the water embedded in $Ca(OH)_2$, NaOH and KOH was subtracted from the total water content listed in the last column of Table 3.

Free swelling measurements in contact with water vapor

For each gel mixture, four 12.7 mm×12.7 mm×127 mm ($1/2" \times 1/2" \times 5"$) bars were cast and demolded after 24 to 72 hours. The specimens were vacuum sealed and stored at 25 ± 1 °C for two months. Then, the specimens were stored in a nitrogen purged chamber at 95% RH for monitoring their expansion over time using a digital gauge with accuracy 0.002 mm. The length change values were then converted to free swelling strain ($\epsilon_{g,fr}$) values. The weight changes were also monitored using a 0.0001 gr accuracy balance. The measurements were taken at 1, 4, 7, 14, 21 and 28 days.

3 RESULTS AND DISCUSSION

The free swelling experiments results are plotted in Figure 3 and Figure 4. Figure 3 shows the time dependent variations of $\epsilon_{g,fr}$ (i.e., free swelling strain) values of the ASR gel specimens. Notice that some gel compositions lead to shrinkage even at 95% RH, indicating that the equilibrium RH of those gels is probably greater than 95%. The greatest ultimate $\epsilon_{g,fr}$ values are observed in the case of $C_{IH}N_{IH}K_{IH}$ ($8.84 \pm 0.22\%$), followed by $C_{I}N_{IH}K_{I}$ ($7.87 \pm 0.67\%$), $C_{I}N_{I}K_{I}$ ($7.65 \pm 0.27\%$), $C_{II}N_{IH}K_{IH}$ ($3.96 \pm 0.44\%$) and $C_{IH}N_{IH}K_{IL}$ ($3.75 \pm 0.15\%$). Similarly, the greatest shrinkage (i.e., negative $\epsilon_{g,fr}$) values are found in the case of $C_{II}N_{II}K_{IL}$ ($-6.37 \pm 0.04\%$) followed by $C_{II}N_{II}K_{IH}$ ($-3.20 \pm 0.05\%$).

The general trend of data suggests that an increase in Na/Si and K/Si leads to increase in $\epsilon_{g,fr}$ values, which might be justified due to the fact that sodium and potassium are both monovalent ions and are often identified as “network breakers” for alkali-silicate structures [17]. They promote volumetric instability of the gels, due to reducing the structural connectivity [17] and increasing the surface charge density of the gels [18], and also increasing the osmotic pressure of their pore solution [3]. However, the effect of Ca/Si on $\epsilon_{g,fr}$ does not appear to be monotonic. It has three episodes of effect on the free swelling properties of the gels. The results as well as the regression model suggest that at low levels and high levels (i.e., from 0.05 to 0.18, and 0.4 and above, respectively), an increase in Ca/Si is accompanied by a decrease in $\epsilon_{g,fr}$. However, Ca/Si has an increasing effect on $\epsilon_{g,fr}$ when it ranges from 0.18 to 0.4. There seems to be at least three competing actions in effect; 1) decrease in osmotic pressure due to silicates-binding effect of calcium (suppressing free swelling—effective mostly in low ranges of Ca/Si), 2) increase in osmotic pressure due to alkali-recycling effect (promoting free swelling—effective at intermediate to high ranges), and 3) network-binding effect (suppressing and ultimately eliminating free swelling—effective at intermediate to high ranges). The reducing effect of Ca/Si on osmotic pressure due to silicates-binding effect has been observed in a previous work [3], evidenced by drop in the concentration of silicates and alkali species in the pore solution of the gels. It is a reasonable assumption that at low levels, Ca/Si does not recycle alkalis, since there are a lot of free O^- vacancies around silicates that calcium can readily occupy without confronting the alkali-occupied O^- endings. However, as Ca/Si increases (apparently beyond 0.18), it starts to show alkali-recycling effect, boosting alkali concentration in the pore solution and increasing the osmotic pressure. It is also reasonable to assume that calcium does not show considerable network-binding effect at low levels. However, as the calcium exceeds beyond 0.4, it gradually eliminates the capability of the gel to swell. The regression model suggests that regardless of alkali content, ASR gels with Ca/Si greater than 0.55 do not show any swelling capacity. Nevertheless, more investigation is needed on the pore solution and structure of the gels to confirm these hypotheses.

The trends found for the effects of calcium, sodium and potassium on the swelling capacity of the gels can be used in justifying the effects of pozzolans in reducing the swelling capacity of ASR gels. Pozzolans reduce the availability of alkalis in cement pore solution through alkali-binding action, which will lead to reductions in Na/Si and K/Si ratios. Such reductions will decrease the swelling capacity of the gels. Pozzolans will also consume the available portlandite (which are responsible for alkali-recycling and resisting pH reduction in the cement pore solution), and will therefore reduce the susceptibility of aggregates to undergo ASR. Therefore, it can be argued that the presence of pozzolans reduces the Ca/Si, Na/Si and K/Si in ASR gels, thus shifting the gels composition towards gels such as $C_{II}N_{II}K_{II}$, which have shown no swelling capacity ($6.37 \pm 0.04\%$ shrinkage at 95% RH).

The analysis of variance (ANOVA) suggests that there is no significant interaction between Ca/Si, Na/Si and K/Si (i.e., the p-values of the interaction terms is much greater than 0.05). The effects of Na/Si and K/Si are also linear positive. Table 4 shows the shorthand ANOVA output, the estimated coefficients associated with each term, their 95% confidence intervals (CI) and p-values. The terms that are not listed in the table are insignificant and, as such, dropped from the model. The 95% CI is the interval that the true value of the corresponding coefficient falls into with 95% probability. The p-value of each term also indicates the chance of that term not having a significant effect on the variations of $\epsilon_{g,fr}$. Any term with a p-value smaller than 0.05 is deemed significant, which is a common significance level in statistical analyses. The significant terms shown in Table 4 and their coefficients are compiled into the regression equation of free swelling strain ($\epsilon_{g,fr}$) shown in Equation 2. The regression equation explains 84.65% of total variations in $\epsilon_{g,fr}$ (i.e., $R^2=84.65\%$).

$$\epsilon_{g,fr} = 7.28 - 207.8Ca/Si + 11.05Na/Si + 12.31K/Si + 823(Ca/Si)^2 - 937(Ca/Si)^3 \quad (2)$$

Figure 4 shows the weight change (%) of the gel specimens over time. The ultimate (i.e., 28-day) weight change (%) data follow the same pattern as the ultimate free swelling strain data (i.e., there is a direct correlation between these two parameters). The coefficient of correlation between weight change (%) and $\epsilon_{g,fr}$ is 0.926, with p-value=0.000 indicating zero chance of lack of correlation. The order of gels showing greatest weight gain results, however, is somewhat different than observed for free swelling strain results. The greatest weight gain is observed in the case of $C_I N_I K_I$ ($18.08 \pm 0.19\%$), followed by $C_I N_{IH} K_{IL}$ ($15.25 \pm 3.18\%$), $C_{IH} N_{IH} K_{IH}$ ($12.56 \pm 1.38\%$), $C_{II} N_{IH} K_{IH}$ ($8.01 \pm 1.47\%$) and $C_{IH} N_{IH} K_{II}$ ($2.05 \pm 0.34\%$). Similar to free swelling results, $C_{II} N_{II} K_{II}$ showed the greatest weight loss ($-14.77 \pm 4.90\%$). It is worth noting that the relation between length change and weight change values is not linear. Some samples (e.g., $C_I N_{IH} K_I$) continued expanding while they showed some weight loss.

Notice that the obtained $\epsilon_{g,fr}$ and weight change (%) results are associated with gels having 40% water content. Change in initial water content of gels results in variations in the swelling/shrinkage and weight

gain/loss behavior of the gels. Preliminary test results indicate an inverse relation between the water content and the magnitudes of swelling and weight gain in the gels. Therefore, if ASR gels with lower water contents (and the same compositions) were produced, greater free swelling strains would be observed. Lower water content also promotes the mechanical properties (e.g., higher elastic modulus, etc.) of the gels, which contributes to the restrained swelling and deleteriousness of the gels as demonstrated in the next section. Further research is required on the effect of water content on the swelling and mechanical properties of the gels.

4 CONCLUSIONS

ASR gels form in concrete with a broad range of compositions (i.e., Na/Si=0.1–1.0, K/Si=0.0–0.3, and Ca/Si=0.0–0.5; atomic ratios). The free swelling strain results suggest that increase in Na/Si and K/Si ratios equally increase the swelling capacity of the gels in a linear fashion. The effect of Ca/Si on the swelling of the gels, however, is not monotonic. As it increases from 0.05 to 0.18, due possibly to the reduction in the osmotic pressure of gel's pore solution caused by silicates-binding effect of calcium, the swelling capacity of the gels is reduced. Ca/Si has an increasing effect on swelling when it exceeds 0.18, possibly due to calcium's alkali-recycling effect that increases the osmotic pressure in the gels. However, the network-binding effect of Ca becomes dominant when Ca/Si exceeds 0.4, and gradually eliminates the swelling capacity of the gels when it reaches 0.55.

5 ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the National Science Foundation (NSF) under CMMI CAREER Award# 1254333, awarded to the second author. Any opinions, findings, conclusions, or recommendations expressed in this manuscript are those of the authors solely and do not necessarily reflect the views of NSF.

6 REFERENCES

- [1] Hou, X, Kirkpatrick, RJ, Struble, LJ, and Monteiro, PJ (2005): Structural investigations of alkali silicate gels. *Journal of the American Ceramic Society* 88(4): 943-949.
- [2] Krogh, H (1975): Examination of synthetic alkali-silica gels. In: *Symposium on Alkali-aggregate Reaction, Preventive Measures*, Reykjavik, Iceland: 131-163.
- [3] Gholizadeh Vayghan, A, Rajabipour, F, and Rosenberger, JL (2015): Composition-Rheology Relationship of ASR Gels and Their Effects on the Extent of ASR damage, *Cement and Concrete Research* (Initial submission: Aug 2015).
- [4] Rajabipour, F, Giannini, E, Dunant, C, Ideker, JH, and Thomas, MDA (2015): Alkali – silica reaction : Current understanding of the reaction mechanisms and the knowledge gaps. *Cement and Concrete Research* (76): 130-146.
- [5] Stanton, TE (1942): Expansion of concrete through reaction between cement and aggregate. *Transactions of the American Society of Civil Engineers* 107(1): 54-84.
- [6] McConnell, D, Mielenz, RC, Holland, WY, and Greene, KT, (1947): Cement-Aggregate Reaction in Concrete. *Journal of the American Concrete Institute, JACIA, Proceedings* 44(10): 93-128.
- [7] Hester, JA, and Smith, OF (1958): The alkali-aggregate phase of chemical reactivity in concrete—Part II. *Special Technical Publication* (205): 74-90.
- [8] Idorn, GM (1961): Studies of Disintegrated Concrete-Part 1, Progress Report N2, Committee on Alkali Reactions in Concrete. The Danish National Institute of Building Research and the Academy of Technical Sciences: 27-30.
- [9] Buck, AD, and Mather, K (1969): Concrete Cores from Dry Dock No. 2, Charleston Naval Shipyard, SC (No. AEWES-MISC-PAPER-C-69-6). Army Engineer Waterways Experiment Station Vicksburg MS.
- [10] Poole AB (1975): Alkali-Silica Reactivity in Concrete from Dhekelia Cyprus. In *Symposium on Alkali-Aggregate Reaction, Proceedings*, Reykjavik, Finland: 101-112.
- [11] Gutteridge, WA, and Hobbs, DW (1980): Some chemical and physical properties of beltane opal rock and its gelatinous alkali silica reaction product. *Cement and Concrete Research* 10(2): 183-193.
- [12] Oberholster, RE (1983): Alkali reactivity of siliceous rock aggregates: diagnosis of the reaction, testing of cement and aggregate and prescription of preventative measures. *Alkali in Concrete, Research and Practice*: 419-433.
- [13] Visvesvaraya, HC, Mullick, AK, Samuel, G, Sinha, SK, and Wason, RC (1986, September). Alkali reactivity of granitic rock aggregates. In *Proceedings VIII International Congress on the Chemistry of Cement* (5): 206-213.

- [14] Šachlová, Š, Příkryl, R, and Pertold, Z (2010): Alkali-silica reaction products: Comparison between samples from concrete structures and laboratory test specimens. *Materials Characterization* 61(12): 1379-1393.
- [15] Thomas MDA (2001): The role of calcium hydroxide in alkali recycling in concrete. In: J. Skalný, J. Gebauer, I. Odler (Editors), *Materials Science of Concrete Special Volume on Calcium Hydroxide in Concrete*, American Ceramic Society, Westerville, Ohio: 269-280.
- [16] Struble, LJ, and Diamond, S (1981): Swelling properties of synthetic alkali silica gels. *Journal of the American ceramic society*, 64(11): 652-655.
- [17] Shelby, JE (2005): *Introduction to glass science and technology*. Royal Society of Chemistry.
- [18] Rodrigues, FA, Monteiro, PJ, and Sposito, G (2001): The alkali-silica reaction: the effect of monovalent and bivalent cations on the surface charge of opal. *Cement and Concrete Research*, 31(11): 1549-1552.

TABLE 1: The chemical composition range of the ASR gels under study (atomic ratios).

<i>Variable</i>	<i>Lower bound</i>	<i>Upper bound</i>
Ca/Si	0.05	0.5
Na/Si	0.1	1.0
K/Si	0.0	0.3

TABLE 2. The experimental design with the coded and natural levels of the variables.

<i>Run order</i>	<i>Point type</i>	<i>Label</i>	<i>Variable</i>						
			<i>Ca/Si</i>		<i>Na/Si</i>		<i>K/Si</i>		
			<i>Coded</i>	<i>Natural</i>	<i>Coded</i>	<i>Natural</i>	<i>Coded</i>	<i>Natural</i>	
5	Cube points	$C_{II}N_{II}K_{II}$	-1	0.141	-1	0.282	-1	0.061	
19		$C_{III}N_{II}K_{II}$	1	0.409	-1	0.282	-1	0.061	
18		$C_{II}N_{III}K_{II}$	-1	0.141	1	0.818	-1	0.061	
16		$C_{III}N_{III}K_{II}$	1	0.409	1	0.818	-1	0.061	
2		$C_{II}N_{II}K_{III}$	-1	0.141	-1	0.282	1	0.239	
9		$C_{III}N_{II}K_{III}$	1	0.409	-1	0.282	1	0.239	
1		$C_{II}N_{III}K_{III}$	-1	0.141	1	0.818	1	0.239	
10		$C_{III}N_{III}K_{III}$	1	0.409	1	0.818	1	0.239	
15		Axial points	$C_LN_IK_I$	-1.682	0.050	0	0.550	0	0.150
6			$C_HN_IK_I$	1.682	0.500	0	0.550	0	0.150
4	$C_LN_HK_I$		0	0.275	-1.682	0.100	0	0.150	
7	$C_LN_HK_I$		0	0.275	1.682	1.000	0	0.150	
20	$C_LN_IK_L$		0	0.275	0	0.550	-1.682	0.000	
11	$C_LN_IK_H$		0	0.275	0	0.550	1.682	0.300	
3, 8, 12, 13, 14, 17	Center points	$C_LN_IK_I$ (1) to (6) respectively	0	0.275	0	0.550	0	0.150	

TABLE 3. Mixture proportions of the gels.

Run order	Label	Ca(OH) ₂ (gr/ 1000 gr)	NaOH (gr/ 1000 gr)	KOH (gr/ 1000 gr)	Silica powder (gr/ 1000 gr)	H ₂ O (gr/ 1000 gr)
1	C _{II} N _{IH} K _{IH}	60.0	182.7	76.9	348.4	331.9
2	C _{II} N _{II} K _{IH}	71.3	71.1	91.4	414.2	352.0
3, 8, 12, 13, 14, 17	C _I N _I K _I	122.7	127.4	50.7	365.9	333.4
4	C _I N _I K _I	142.7	21.9	58.9	425.6	350.9
5	C _{II} N _{II} K _{II}	78.8	78.6	25.7	457.9	359.0
6	C _{II} N _I K _I	198.0	113.0	45.0	324.8	319.2
7	C _I N _{II} K _I	107.6	206.9	44.4	320.9	320.1
9	C _{II} N _{II} K _{IH}	176.4	60.7	78.1	353.9	330.9
10	C _{II} N _{IH} K _{IH}	151.9	159.8	67.3	304.7	316.3
11	C _I N _I K _H	114.6	118.9	94.6	341.7	330.2
15	C _I N _I K _I	25.5	145.8	58.0	419.0	351.7
16	C _{II} N _{IH} K _{II}	163.4	171.9	18.4	327.7	318.6
18	C _{II} N _{IH} K _{II}	65.2	198.7	21.3	378.8	336.0
19	C _{II} N _{II} K _{II}	192.1	66.1	21.6	385.3	334.9
20	C _I N _I K _L	132.1	137.1	0.0	393.8	337.0

Table 4. The shorthand ANOVA and coefficients output of free swelling strain results.

Term	Coefficients	95% CI	P-Value
Constant	7.28	(0.22, 14.34)	0.0440
Ca/Si	-207.8	(-298.6, -117.1)	0.0000
Na/Si	11.05	(7.50, 14.59)	0.0000
K/Si	12.31	(1.67, 22.95)	0.0260
Ca/Si ²	823	(457, 1190)	0.0000
Ca/Si ³	-937	(-1377, -497)	0.0000

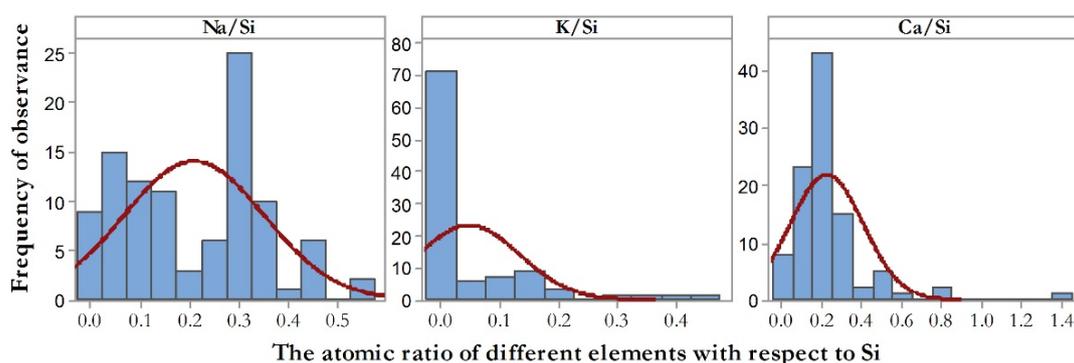


FIGURE 1: The distribution of the chemical composition of studied gels in the literature.

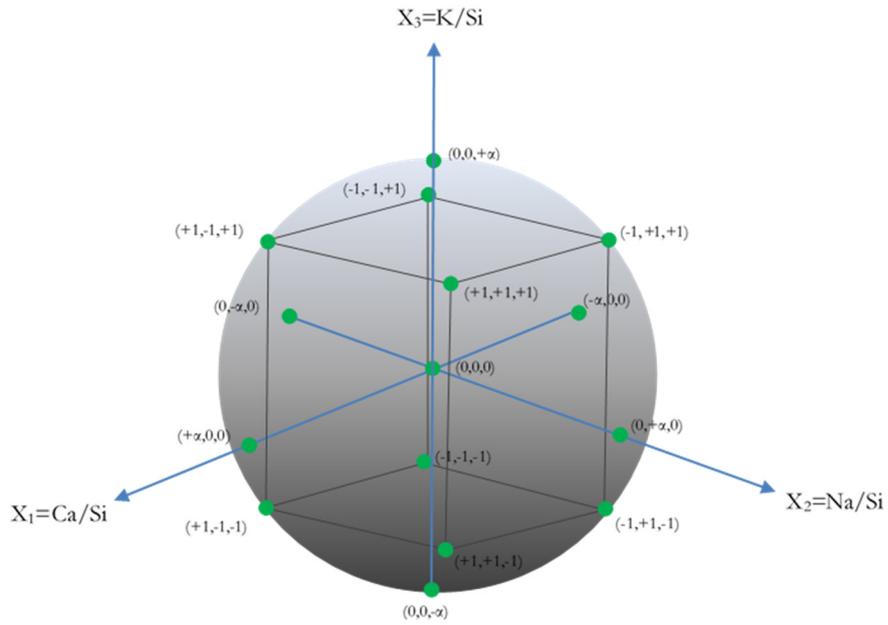


FIGURE 2: Graphical demonstration of RSM data point selection for 3 variables cases.

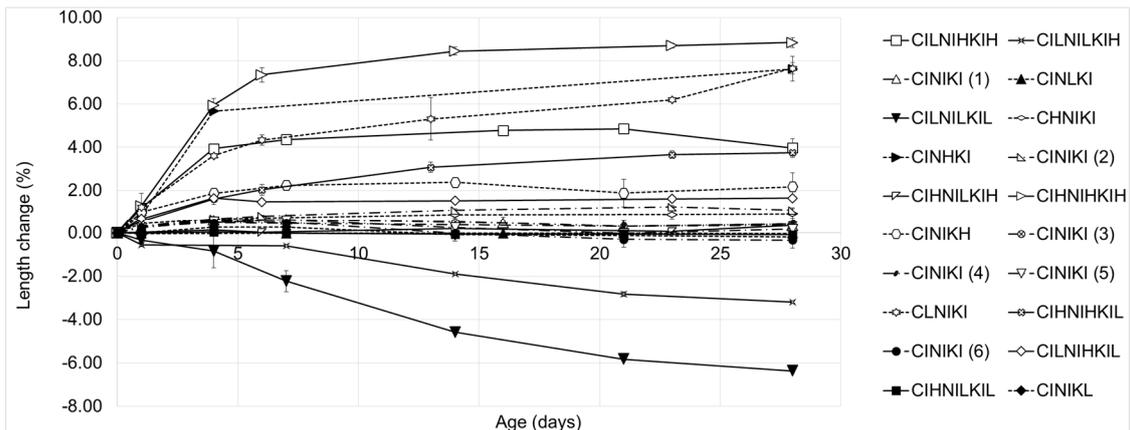


FIGURE 3: The free swelling strain (%) variations of ASR gel minibars up to 28 days (the error bars indicate two standard errors).

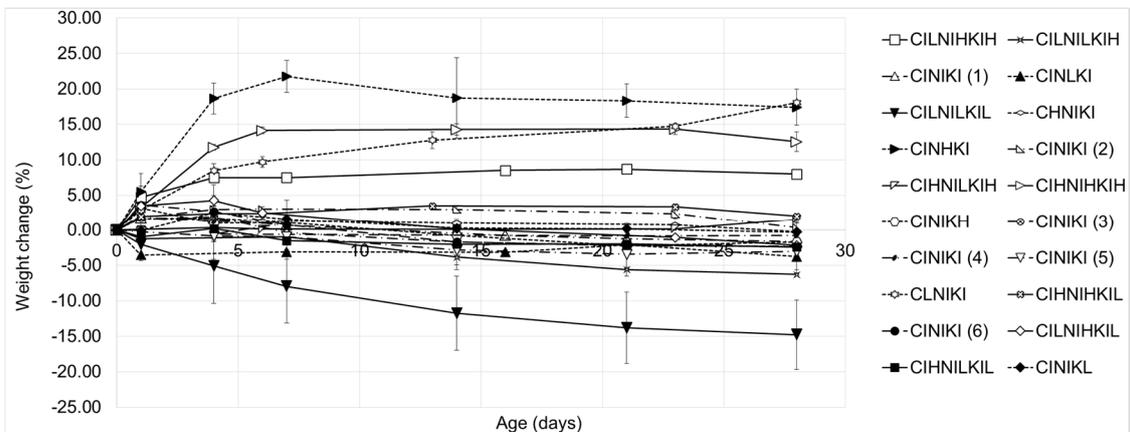


FIGURE 4: The weight change (%) variations of ASR gel minibars up to 28 days (the error bars indicate two standard errors).