

Effects of Sodium Ions on Synthesized Alkali Silica Reaction Gels

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Abstract

The alkali-silica reaction (ASR), leading to serious structural degradation, is the chemical reaction between reactive silica presenting in aggregates and hydroxyl ions from cement paste or pore solution. Although the chemical mechanism of ASR attack has been well studied for years, the mechanism of micro scale ASR gel formation leading to macro scale expansion is still under debate.

The present study aims to illustrate the performance of ASR gel by investigating the interaction between ASR gel and sodium ion from solution. In this study, ASR gels with different calcium silica (Ca/Si) ratios (0.1, 0.5, 1) are synthesized by mixing reagent $\text{Ca}(\text{OH})_2$ with silica fume in a sodium hydroxide solution for seven days. Afterwards, the synthesized ASR gel is immersed in sodium hydroxide solutions with different concentrations (0.1mol/L, 0.5mol/L, 1.0mol/L) for seven days. Chemical composition, structure and water content of the ASR gel before and after alkali exposure are studied by XRD, XRF and TGA.

The results confirm that an ASR gel with a targeted Ca/Si ratio can be synthesized. In addition, XRD and TGA results show that part of the calcium in the ASR gel is exchanged by sodium, leading to a structural modification. In general, this study will give further comprehension of ASR gel performance under alkaline environment, and provide detailed data to investigate the interaction between ASR gel and calcium ions in an alkaline solution in the future.

Originality

Considering the importance of interaction between ASR gel and the alkalis-calcium system on explaining ASR expansion, the effect of alkalis on ASR gel is studied in the first place. The originality of this study lies both on the chosen Ca/Si ratio for ASR gel synthesis and exposing ASR gel to alkalis hydroxide solution after the gel is synthesized.

Firstly, in order to reasonably simplify real ASR happening in the interface of aggregates and paste, ASR gel is artificially synthesized with different Ca/Si ratios, which are used to represent the most common ASR gels, whereby the high calcium content gel mainly represents the situation close to the cement paste, while the one with low calcium content represents the situation close to the aggregate surface.

Secondly, in order to simulate the situation that the ASR gel diffusing into cement paste after its formation close to the surface of aggregates, the ASR gel is reacting in a controlled model system with a certain liquid solid ratio to achieve proper sodium silica ratio and Ca/Si ratio throughout alkali exposure process.

Keywords: ASR gel, cement paste, alkalis

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1. Introduction

The alkali-silica reaction (ASR), which was firstly reported by T.E. Stanton in 1940 (Stanton 1940), is the chemical reaction between reactive silica in aggregates and hydroxyl ions from pore solution of cement paste. A macro scale expansion caused by ASR can lead to structural degradation of concrete.

The expansion due to ASR in concrete is a two-step process. First of all, reactive silica from aggregates reacts with alkalis and hydroxyl ions from pore solution of cement paste to form alkali silicate hydrates (A-S-H) gel, which can convert to calcium silicate hydrates (C-S-H) gels by combining with calcium ions in solution. The nomination of C-S-H gel is mainly about the main oxides it contains, it does not necessarily give any implication about the possible composition and structure of the gel. This C-S-H gel is normally called ASR gel due to its close relationship with ASR expansion. In this study, the synthetic C-S-H gel equals the synthetic ASR gel. Secondly, the formation of C-S-H gels results in macro scale expansion and structural degradation. Within the second step, the mechanism of swelling and expansion is still controversial, though several explanations and models have been proposed for decades (Powers and Steinour 1955, Glasser 1979, Chatterji 1989, Wang and Gillott 1991, Prezzi, J.M. Monteiro et al. 1997, Ichikawa and Miura 2007).

As the trigger of ASR, siloxane bond (Si-O-Si linkage) of reactive silica is firstly attacked by hydroxyl ions to form silanol bond (Si-O-H linkage), leading to the formation of dissolving silicates which are negatively charged at high pH. The dissolution rate depends on the pH solution (Iler 1979) that the higher pH is in the solution, the faster and the more silica dissolves (Gaboriaud, Nonat et al. 1999). The negatively charged dissolving silicates are counter balanced mainly by alkalis (Na^+/K^+), leading to the formation of A-S-H gel. By combining with calcium ions in solution, A-S-H gels were converted into calcium alkali silicate hydrates (C-A-S-H) gel (Bulteel, Garcia-Diaz et al. 2002). Due to the similarity between the synthesis process and the ASR process in concrete, the synthetic gel has been reasonably chosen as a simplified model of the ASR gel which formed during ASR process and leading to ASR expansion. Hence the chemical and physical properties of the synthetic gel are thought to be comparable with the “real” ASR gel in concrete. As the one of the main factors deciding ASR expansion, the behaviors of ASR gel under different calcium and alkali conditions are investigated to achieve more evidence to explain how the swelling in micro scale leads to expansion in macro scale. These behaviors depend on the composition and structure of the gel, which have a close relationship with the calcium and alkali environment in pore solution, which can change the composition and structure of the gel in return: the gel and the solution are in a dynamic equilibrium. In other words, ASR expansion has a close relationship with calcium and alkali concentration in pore solution. However, research aiming at studying the performance of C-S-H gels in alkaline solution which is related to ASR is scarce.

In order to study the behavior of C-S-H gels linked to ASR in alkali solutions with different concentrations, the gels were made artificially with a modeled system by mixing silica fume, sodium hydroxide solution with different calcium hydroxide additions. Afterwards, the synthetic gels were exposed in alkaline solutions with different concentrations to study their behavior after alkaline exposure.

2. Materials and methods

2.1 Materials

The reactive silica used in this study was Elekem Microsilica Grade 940U, the composition of which is given in Tab.1 and the XRD pattern of silica fume is shown in Fig.1. The NaOH solutions used in the experiment were made by dissolving pellets of NaOH in the distilled and CO_2 -free water which was also used throughout this study. Pellets of NaOH and powder-like $\text{Ca}(\text{OH})_2$ were both the level for chemical analysis.

Tab.1 Chemical composition of silica fume / %

Compositions	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	SO ₃
Content	94.2	0.6	1.0	0.5	0.7	1.0	1.1	0.3

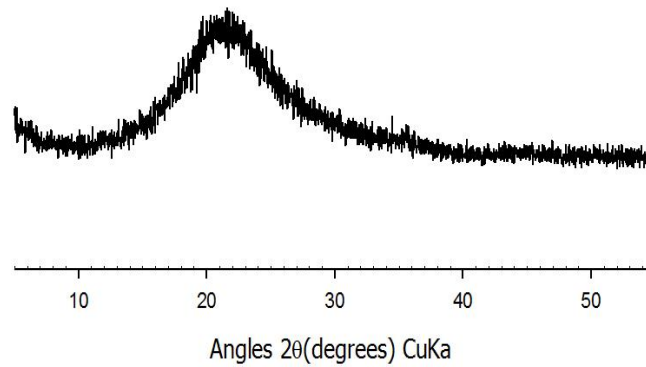


Fig.1 XRD pattern of silica fume.

2.2 Sample preparation

The sampling of this study consisted of two parts, gel synthesis and alkali hydroxide solution exposure. The mix design of gel synthesis is shown in Tab.2. The alkaline solution exposure is given in section 2.4.

Tab.2 The mix of synthetic gels

Samples	Targeted Ca/Si	Na/Si
MS01	0.1	0.19
MS05	0.5	0.28
MS10	1.0	0.39

2.3 Gel synthesis

C-S-H gels with targeted Ca/Si ratio were synthesized by adding a certain amount of 1 mol/L NaOH solution into the mixture of silica fume and calcium hydroxide with different Ca/Si ratios. This approach was used for many researchers to make ASR gel artificially. The slurry was sealed in a polypropylene bottle filled with argon gas to avoid carbonation and mixed by a rotary mixer at a speed of 60 rpm at room temperature. Liquid and solid ratio in this step was set as 3 to simulate partial silica dissolution which is the usual case of ASR in reality (Leemann, Le Saout et al. 2011) and to obtain appropriate workability as well. After the desired storage period, the slurry was filtered through a vacuum funnel and washed to remove excess NaOH. In order to stop reactions, the residue was immersed into isopropanol for 6 hours before it was dried at room temperature in a vacuum desiccator with silica gel for 24 hours.

2.4 Alkali hydroxide solution exposure

Synthetic C-S-H gels were immersed in NaOH solutions with concentrations of 0.1, 0.5 or 1.0mol/L, the samples were labeled according to certain rules e.g. MS0101 which means that a synthetic gel of MS01 was immersed in NaOH solution with a concentration of 0.1mol/L. Afterwards the samples were sealed and mixed in the same way as that in the first step for 7 days. After filtration and drying, the samples were sent for further tests.

2.5 Measurements

The powder X-Ray Diffraction (XRD) measurements were carried out by using a Thermo Scientific ARL X'tra Diffractometer equipped with a Peltier cooled detector.

The X-Ray Fluorescence (XRF) used in this study is EDAX Eagle III laboratory X-ray Fluorescence with polychromatic incident X-ray beam. All the samples were measured under vacuum condition.

The thermo gravimetric analysis/differential thermal analysis (TGA/DTA) data were collected with NETZSCH STA 449 F3 Jupiter thermal analyzer. The samples were heated up from room temperature to 1000 °C at a speed of 10 K/min under N₂ atmosphere to avoid any contamination.

3. Results and discussion

3.1 TGA results

TGA results for the synthetic gels and the gels after alkaline exposure with Ca/Si ratios of 0.1, 0.5 and 1.0 are presented in Tab.3. In order to exclude the impact of evaporation from trace free water and avoid underestimating of bound water, the initial weight was taken at 80 °C.

Tab.3 Mass loss determined by TGA

Samples	Mass loss below 400 °C / %	Total mass loss /%
MS01	7.32	8.87
MS05	8.72	10.14

MS10	10.43	11.53
MS0101	7.34	9.37
MS0105	8.80	12.02
MS0110	13.06	17.53
MS0501	14.23	17.19
MS0505	14.09	17.14
MS0510	14.66	17.97
MS1001	13.61	19.71
MS1005	13.47	20.61
MS1010	16.49	21.65

The results showed that the total loss increases with increasing Ca/Si ratio, consistent with the results from Leemann (Leemann, Le Saout et al. 2011). This is mainly due to the further hydration of silica fume by adding calcium so that more C-S-H gels and A-S-H gels were formed. Further measurements are necessary to verify which one contributed to most of the mass loss. The alkaline exposure enabled more C-S-H gel formations, and the increased alkaline concentration intensified this effect as expected.

3.2 XRD results

The silica fume used in this study is amorphous which is indicated by the XRD pattern given in Fig.1 with a broad peak centered around $22^\circ(2\theta)$. This means the silica fume used in this study is vulnerable to alkaline exposure.

The XRD pattern of the synthetic ASR gel samples are shown in Fig.2. The broad reflections from C-S-H gels (Kim, Foley et al. 2013) were observed from patterns for MS05 and MS10. It needs to be noted that the broad reflections for C-S-H formation in MS01 cannot be fully confirmed is mainly due to overlaps between broad reflections from C-S-H and peaks from other phases (Bellmann, Damidot et al. 2010). Nevertheless, this is in agreement with the result from Hou (Hou, Kirkpatrick et al. 2005) and enough for us to conclude that the gel synthesis in such a simulated system is successful. Besides, the XRD pattern illustrates phase changes as addition of portlandite increases. The more portlandite was added at the beginning, the less silica fume was observed from the pattern. The broad reflection from silica fume centered at $22^\circ(2\theta)$ disappears when the Ca/Si ratio equal 1. Additionally, residual portlandite can be clearly observed from the pattern of the same sample indicating the presence of excess portlandite which leads to fully consumption of silica fume. Actually for MS05, peaks from portlandite can be found at the same time as the presence of silica fume. This is consistent with the result of Leemann (Leemann, Le Saout et al. 2011) that more portlandite addition results in more silica consumption and more C-S-H gel formation. According to Leemann, residual portlandite was observed when Ca/Si ratio was 0.4. The peaks from calcite for MS10, as the product of carbonation, are observed at around $23^\circ(2\theta)$, $36^\circ(2\theta)$, $39^\circ(2\theta)$, $43^\circ(2\theta)$, and $49^\circ(2\theta)$, though the strongest characteristic peak occurring at $29^\circ(2\theta)$ overlaps with reflections from other phases. Most of the carbonation observed in Fig.2 happened when samples were transferred from the storage containers to the XRD chamber and during the measurements. The peaks for calcite are more obvious as Ca/Si ratio equals to 1. This indicates that the more portlandite is left in the samples, the more carbonation happens. TGA confirmed the absence of portlandite and carbonation for MS01, and the presence of slight carbonation for MS10 (not present).

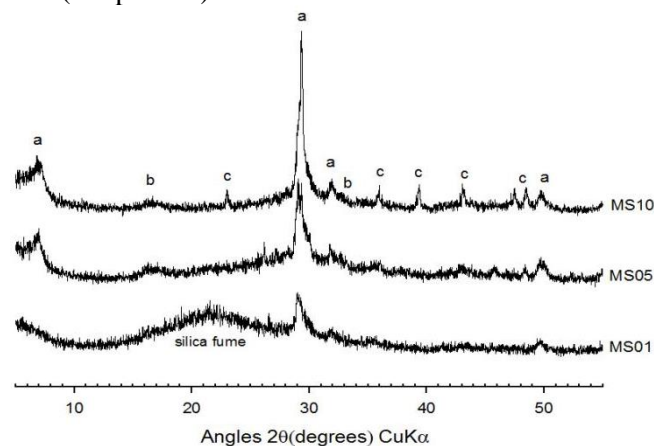


Fig.2 XRD pattern of synthetic C-S-H gels with different calcium hydroxide addition (a, C-S-H; b, calcium hydroxide; c, calcite)

The XRD patterns of the gels with different Ca/Si ratio after alkaline exposure are shown in Fig.3-5. The broad peak of silica fume (Fig.3-5) centered at 22° (2θ) disappears as alkaline concentration increases, indicating that silica fume present in the samples was consumed out after reacting with NaOH to produce A-S-H gels or C-S-H gels. The broad reflections of C-S-H gels become more and more obvious as the disappearance of the broad peak for silica fume. The peaks from $\text{Ca}(\text{OH})_2$ were observed both in XRD patterns before and after alkaline exposure (Figs.4 and.5), indicating the presence of excess $\text{Ca}(\text{OH})_2$ in the samples. This result alone cannot provide any evidence about if additional $\text{Ca}(\text{OH})_2$ has combined with newly formed A-S-H gels, other characterizations are needed. Besides, the presence of calcite are also confirmed by the peaks at around $23^\circ(2\theta)$, $36^\circ(2\theta)$, $39^\circ(2\theta)$, $43^\circ(2\theta)$, and $49^\circ(2\theta)$ from the XRD patterns before and after alkaline exposure.

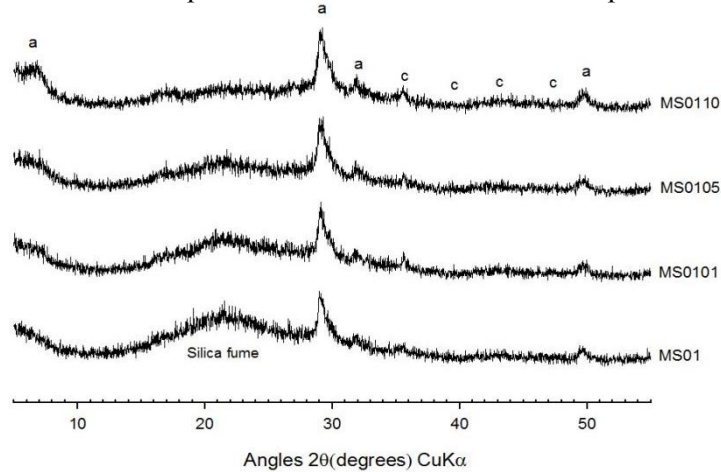


Fig.3 XRD pattern of synthetic gel after alkaline exposure with Ca/Si ratio of 0.1

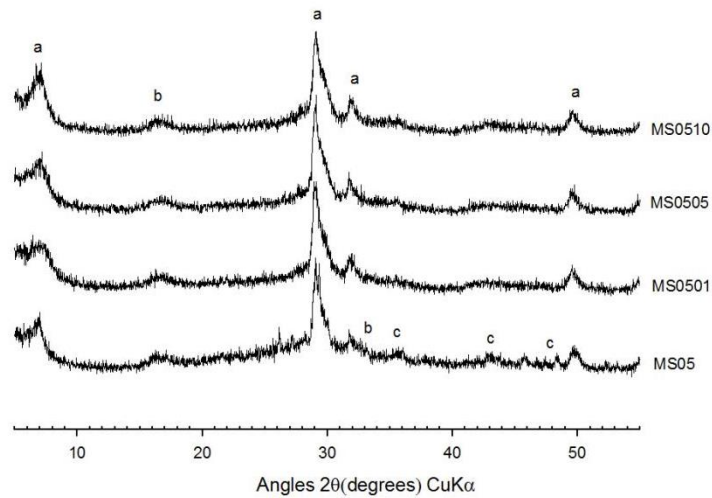


Fig.4 XRD pattern of synthetic gel after alkaline exposure with Ca/Si ratio of 0.5

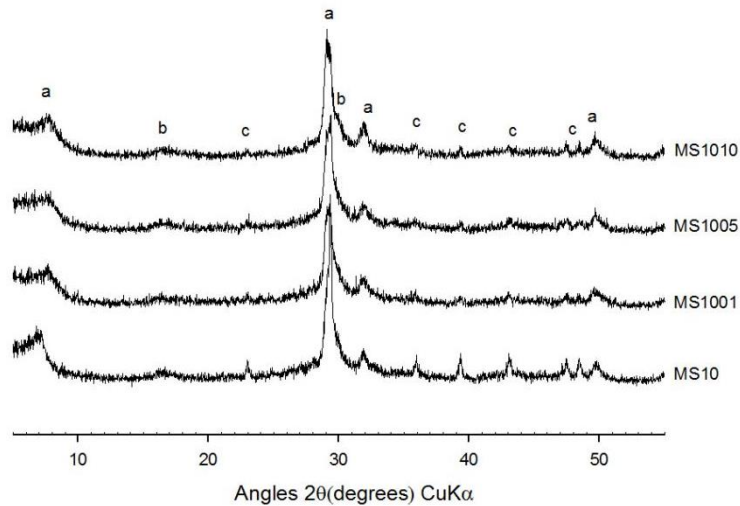


Fig.5 XRD pattern of synthetic gel after alkaline exposure with Ca/Si ratio of 1.0

3.3 XRF results

The XRF results focusing on Ca/Si ratio and Na/Si ratio of synthetic C-S-H gels before and after alkaline exposure are given in Fig.6 (a) and Fig.6 (b).

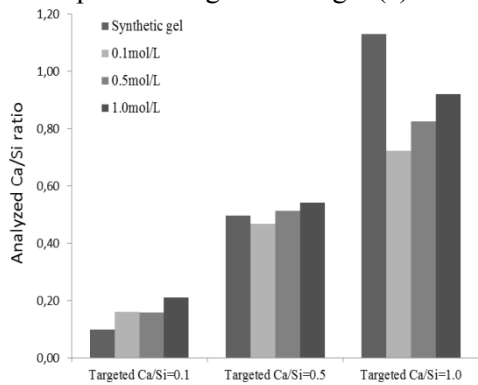


Fig.6 (a) Analyzed Ca/Si ratio of gels before and after alkaline exposure with different concentrations

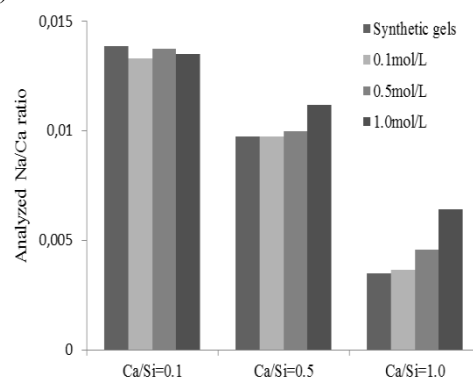


Fig.6 (b) Analyzed Na/Ca ratio of gels before and after alkaline exposure with different concentrations

Although some variations exist according to the results presented in Fig.6, the synthesis of C-S-H gels with targeted Ca/Si ratio is generally successful. The analyzed Ca/Si ratios are lower than the targeted Ca/Si ratio for MS01 and MS05, while MS10 has a greater analyzed Ca/Si ratio than the target. These variations are mainly due to the presence of excess $\text{Ca}(\text{OH})_2$, confirming the XRD results in the previous section. Considering the samples were washed with water several times during preparation, sodium present in residuals can be regarded as bound sodium. The washing can also result in the calcium leaching leading to the variations of Ca/Si ratio from the targeted ones. The amount of bound sodium increases with increasing targeted Ca/Si ratio. This is perhaps because more silica fume was attacked by OH^- with more $\text{Ca}(\text{OH})_2$ addition, leading to more sodium was bonded by C-S-H gels. This is consistent with the results from Hong and Glasser (Hong and Glasser 1999) where the alkali binding ability improves as the Ca/Si ratio increases.

As for the gels after alkaline exposure, the analyzed Ca/Si ratio of MS01 increases slightly after alkaline exposure, while the analyzed Ca/Si ratios of MS05 and MS10 after alkaline exposure drop dramatically. At the same time the analyzed Ca/Si ratio increases as alkaline concentration increases from 0.1 mol/L to 1 mol/L. This implies that this process of C-S-H gels exposed to alkaline treatment is not determined by one factor only. Two processes are happening for the synthetic C-S-H gel exposed to an alkaline solution: silica dissolution and ion exchange. After synthetic C-S-H gels were in contact with alkaline solutions, residual silica fume from the samples was dissolved by NaOH in solution lowering the silica content in the solid phase. At the same time, Na^+ exchanged with Ca^{2+} in C-S-H gels (Sugiyama 2008) leading to the decrease of the calcium content in samples and the increase of the sodium content as well. These two factors both contribute to the change of analyzed Ca/Si ratio and

Na/Ca ratio. When the C-S-H gel with Ca/Si ratio of 0.1 is immersed into an 0.1mol/L NaOH solution, silica dissolution is the main factor which contributes to the increase of analyzed Ca/Si ratio. This is perhaps due to the lack of calcium to be exchanged for C-S-H gels with Ca/Si ratio of 0.1 considering the slight decrease of analyzed the Na/Ca ratio. As the alkaline concentration increased to 1mol/L, more silica was dissolved due to the high pH. Meanwhile the Na/Ca ratio nearly remains constant. When the Ca/Si ratio of C-S-H gels is 0.5, the decrease of the Ca/Si ratio caused by ion exchange becomes strong enough to offset the increase caused by silica dissolution as alkaline concentration increases, which is verified by the increase of the Na/Ca ratio. This trend is more obvious for the C-S-H gels with a Ca/Si ratio of 1.0.

4. Conclusions

In this study, ASR is simulated in a modeled system consisting of silica fume that was dissolved by a NaOH solution with different Ca(OH)₂ additions. Due to the low liquid solid ratio during synthesis, silica fume is partly dissolved until the initial Ca/Si ratio of the mix equals to 0.5. The presence of additional Ca(OH)₂ in samples increases the risk of carbonation.

The alkaline exposure enables further hydration of residual silica fume present in synthetic gels. Silica dissolution and ion exchange both determine the composition of gels, which has a close relationship with ASR expansion.

Acknowledgements

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