

Phase Evolution and Property Development of Alkali-Silica Reaction Gel in Carbonation

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ABSTRACT

The formation and swelling of alkali-silica reaction (ASR) gels, products of the reaction between amorphous silica from aggregates and alkalis from cement capable of absorbing moisture, are considered the primary mechanism of ASR-induced deteriorations in concrete. To date, the ASR mitigation approaches mainly focus on the incorporation of supplementary cementitious materials and the use of lithium-based admixtures. These traditional approaches possess limitations in the extent of ASR suppression and might compromise concrete performance. Effective ASR mitigation under carbonation has been recently documented but the underlying mechanisms still remain unclear. To fill this knowledge gap, phase evolution and property development of ASR gels under carbonation are investigated in this study. A synthetic ASR gel with a calcium-to-silica ratio of 0.3 and an alkali-to-silica ratio of 1.0 was synthesized and conditioned under 20% CO₂ concentration, 75% relative humidity, and 25°C. The extent of carbonation and phase evolutions were characterized and quantified through X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). The modulus of elasticity and hardness of the carbonated ASR gels were measured using nanoindentation, and the moisture uptake capacity was evaluated using dynamic vapor sorption in stepwise relative humidity levels. The results indicate complete conversion of ASR gels into stable carbonates (nahcolite, vaterite, calcite and silica gel) with increased mechanical properties and suppressed hygroscopicity.

KEYWORDS: *Alkali-silica reaction, Mitigation, Carbonation, Phase conversion, Moisture absorption*

1. Introduction

Alkali-silica reaction (ASR) is one of the most deleterious reactions in concrete involving reactions of amorphous silica from reactive aggregates and alkalis from cement to form hygroscopic ASR gels that can absorb moisture, expand, and exert internal stresses to the surrounding concrete. Prior research showed ASR gel has a layered silicate structure with Q³ polymerization sites, which is responsible for the hygroscopic swelling behavior (Geng et al (2020)). The cracks caused by ASR render concrete more permeable by providing pathways for the ingress of external agents into concrete leading to a variety of secondary deteriorations. It was reported that the ASR-induced expansion in concrete can be decreased in the presence of CO₂ due to the carbonation of Ca(OH)₂ and densification of pore structure (Kihara (1997)), reduction of alkalinity in cement pore solution (Wang et al (2022)) and (Liu et al (2022)). A recent study on ASR gels showed the formation of calcite with enhanced modulus of elasticity (MOE) and hardness after 3 days under a CO₂ concentration of 3% (Narneni and Panesar (2021)). However, the interaction mechanisms between ASR gels and CO₂, and evolutions of phase, structure hygroscopic and mechanical properties of ASR gels under carbonation that can explain the ASR mitigation mechanism have not been explored.

The present study aims to fill this knowledge gap by elucidating the development of the phases, structure, and properties of a synthetic ASR gel during carbonation. The components, crystallization, and functional groups of the ASR gel before and after carbonation were characterized using thermogravimetric analysis (TGA), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The moisture

absorption and nano-mechanical properties of the raw and carbonated ASR gels were determined through the dynamic vapor sorption (DVS) and nanoindentation tests, respectively.

2. Materials and Methods

2.1 Materials and sample preparation

An ASR gel with a water-to-solid ratio of 0.5, and calcium-silica (Ca/Si) and alkali-silica ((Na+K)/Si) ratios of 0.3 and 1.0, respectively, based on hygroscopic and swelling behavior observed in the authors' previous work, was synthesized via a sol-gel method. The materials used for the synthesis of the ASR gel are reagent-grade calcium hydroxide (>95%), sodium hydroxide (>99%), potassium hydroxide (>97%), and colloidal nano-silica solution with a concentration of 50%, a particle size of 0.02 μm , and an average particle surface area of 180 m^2/g . The detailed synthesis procedure can be found in the authors' previous paper (Luo et al (2022)). The sample was sealed to allow the formation of ASR gel with eliminated interferences from external moisture, oxygen, and carbon dioxide. After 500 days, the ASR gel sample was crushed into powders and carbonated under a CO_2 concentration of 20%, relative humidity (RH) of 75% RH, and a temperature of 25°C for up to 3 days.

2.3 Experimental procedures

The phase evolution of the ASR gel during carbonation was evaluated through (i) XRD by scanning the powdered samples between 5° and 65° 2 θ at a 0.1° step size and step scanning time of 4 seconds using a benchtop XRD equipped with a Cu-K α X-ray source, and (ii) TGA by determining the mass loss of the samples from 30°C to 900°C at a heating rate of 15°C/min under an N_2 inert gas atmosphere. The development of functional groups in the raw and carbonated ASR gels was studied via FTIR spectroscopy by collecting 128 scans in an attenuated total reflection (ATR) mode at a resolution of 4 cm^{-1} .

The hygroscopicity of the raw and carbonated ASR gels was measured using DVS, where the mass changes of the samples were recorded under a constant temperature (25°C) and staged RH. A full desorption-absorption cycle consists of a drying process from 95% to 90% RH followed by a 10% RH decreasing step to 0 RH, and a reversed wetting process with the same steps. The mass equilibrium at each RH step was reached when the rate of mass change decreased to 0.0015 mg/min for 10 minutes. The changes in hardness and MOE of ASR gels were evaluated via nanoindentation. The raw and carbonated ASR gels were first dried under a vacuum pressure of 500 mTorr for 24 hours followed by 2-minute compaction into pellets with a diameter of 16 mm under a compaction pressure of 95 MPa to achieve improved particle packing, low surface irregularities, and eliminated preferential orientation of crystals (Hay et al (2022)). The samples were loaded to 2000 μN in 10 seconds, held for 180 seconds, and unloaded at the same rate under a Berkovich diamond tip. The reduced MOE was determined based on the slope of the unloading curve according to the Oliver-Pharr non-linear curve fit method and the hardness was calculated as the ratio of peak load and the projected area of indentation.

3. Results and discussions

3.1 Solid phase evolution

The TGA and differential thermogravimetric (DTG) curves (Figure 1a) show a large weight loss due to the evaporation of free and bound water indicating the high moisture absorption capacity of the raw ASR gel. The decompositions of sodium silicate hydrate (Na-kanemite) at around 230°C and tobermorite at around 275°C indicate the primary products in the ASR gel, which is similar to the real ASR gels collected from the existing ASR-impacted concrete structures and simulated concrete with reactive aggregates (Hou et al (2005)). After 1 day of carbonation, the weight loss of free and bound water disappeared, which indicates the suppressed ASR gel's hygroscopicity. No tobermorite and kanemite were observed with the detections of nahcolite (sodium bicarbonate) between 115° and 225°C, vaterite between 350 and 600°C, and calcite between 600° and 800°C. A small weight loss between 425° and 460°C after 1-day carbonation, suggesting the formation of a transient $\text{Ca}(\text{OH})_2$, which became undetectable after 3 days of carbonation as it was carbonated into vaterite.

The XRD pattern of raw ASR gel shows a semi-crystalline structure with distinct peaks at 29.4° , 31.9° and 49.9° 2θ indicating the presence of tobermorite, a C-S-H-like mineral with a layered silicate structure, while the broad peak between 25° and 35° 2θ signify the existence of amorphous Na- and K-kanemite (Figure 1b), which agrees with the results in Hou et al (2005) and our TGA results. After 1 day of carbonation, enhanced crystallinity of the ASR gel indicated by the replacement of semi-crystalline and broad peaks of tobermorite and kanemite with the sharp peaks of carbonates (nahcolite, vaterite, and calcite) was observed. In line with the findings from TGA, the enhanced nahcolite from 1 to 3 days indicate further carbonation in the sodium silicate phases whereas the contents of vaterite and calcite did not exhibit increases. The FTIR spectra of the raw ASR gel show the presence of Si-O-Si ($800\text{--}600\text{ cm}^{-1}$) and Si-O ($1100\text{--}900\text{ cm}^{-1}$) bonds (see Figure 1c). The Q^2 polymerization of tobermorite and kanemite is indicated by the bands at 900 cm^{-1} and 966 cm^{-1} . The Q^3 site in tobermorite and kanemite, a unique feature of ASR gels causing hygroscopic swelling, is signified by a peak at 1056 cm^{-1} . After 1 day of carbonation, Q^2 and Q^3 polymerization sites were replaced by Q^4 sites due to the formation of free silica triggered by the decalcification of ASR gel during carbonation. The bands at 876 cm^{-1} and 1425 cm^{-1} indicate the formation of C=O and CO_3^{2-} functional groups in calcite and vaterite, while the peaks at 695 cm^{-1} , 836 cm^{-1} , 1055 cm^{-1} , 1450 cm^{-1} and 1680 cm^{-1} indicate the formation of C-O and OH⁻ in nahcolite. The decreased HOH band in water detected from the raw ASR gel (1650 cm^{-1}) and the absence of the broad band for free and bound water (between 2500 and 3700 cm^{-1}) indicate the mitigated hygroscopicity in the carbonated ASR gel. In line with the XRD results, no significant change was observed in vaterite and calcite bands from 1 to 3 days of carbonation but the bands in nahcolite showed a slight increase.

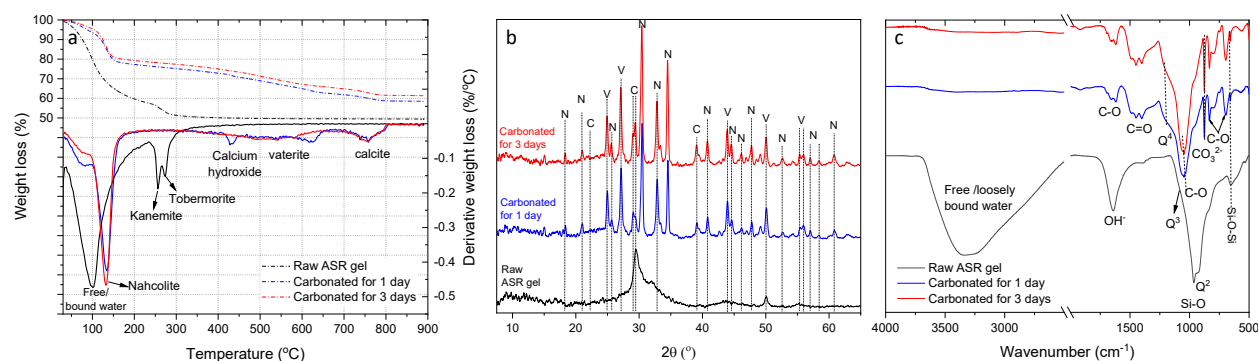


Figure 1. (a) TGA/DTG, (b) XRD, and (c) FTIR results of the raw and carbonated ASR gels (C-Calcite, N-Nahcolite and V-Vaterite).

3.2 Moisture sorption behavior

The raw ASR gel exhibited a total desorption of 146.2% and absorption of 145.9% in the drying and wetting cycles, respectively, between 95% and 0 RH (Figure 2a). A majority (83%) of total mass change was observed between 70% and 95% RH, indicating a high hygroscopicity of the ASR gel in a humid environment and the potential for deleterious swelling. After 3 days of carbonation, the ASR gel showed 26.7% and 9.5% reductions in the overall desorption and absorption, respectively. The non-swelling free silica gel formed during the decalcification of ASR gel, a known desiccant with abundant Q^4 silica polymerization and capable of imbibing moisture, might be the reason for the remarkable absorption of the carbonated ASR gel at the RH levels over 80%.

3.3 Mechanical properties

Based on nanoindentation, the raw ASR gel showed an average MOE and hardness of 1.16 GPa and 0.03 GPa (Figure 2b), respectively, which are lower than the previously reported values (Narneni and Panesar (2021)). This is most likely due to the lower Ca/Si ratio (0.409 vs. 0.3) adopted in this study, as well as the difference in sample synthesis and preparation (in-situ measurement vs. measurement on pellet samples). After carbonation, the MOE and hardness of the ASR gel increased by 79.3% and 267%, respectively, which indicates the conversion of ASR products into carbonates with enhanced crystallization is favorable to enhance the overall mechanical properties. It is worth noting that the uneven distribution of calcium-rich products (calcite and vaterite) during carbonation might be a reason for the increased standard error in the

MOE and hardness of the carbonated ASR gel. Further studies on the microstructure and molecular structure of carbonated ASR gels are necessary to get better into the evolution of mechanical properties.

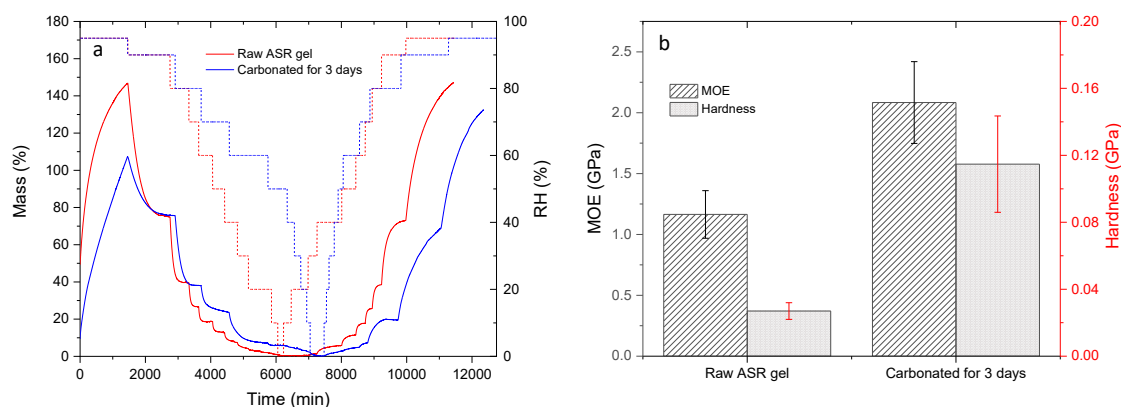


Figure 2. (a) DVS and (b) nanomechanical properties of the ASR gel before and after carbonation.

4. Conclusions

In this study, the carbonation behavior of a synthetic ASR gel under a CO₂ concentration of 20% for up to 3 days was investigated in terms of phase evolution and developments of hygroscopicity and mechanical properties. Before carbonation, the raw ASR gel consists of tobermorite and Na- and K-kanemite as the main components. During carbonation, conversions of tobermorite and kanemite into nahcolite, vaterite, and calcite were observed. As a result, the Q² and Q³ polymerization sites of ASR gel were converted into Q⁴ sites due to the formation of silica gel and C-O and C=O bonds in the formed carbonates. The overall reductions in moisture desorption and absorption of the ASR gel and increases in MOE and hardness indicate the suppressed hygroscopicity of ASR gels after carbonation along with improved stiffness and enhanced crystallinity.

Acknowledgments

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