

Carbonation of synthetic alkali-silica reaction gel

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INTRODUCTION

Alkali-silica reaction (ASR) is a deleterious mechanism in concrete which causes excessive cracking and loss of mechanical properties. Moisture from the atmosphere, alkali from the cement paste, and the reactive silicates from the coarse and fine aggregates are the primary reactants of ASR product. At early stages, the reaction product will be a gel which transforms to the crystalline structure after ageing [1]. Standard test methods to evaluate the ASR, such as ASTM C1293 [2] involves subjecting the concrete to elevated temperatures and evaluating the concrete performance and expansions. However, in the field conditions, ASR occurs at a slower rate compared to these standard tests. As the ASR in concrete progresses, the reaction kinetics will be modified by the external degradation mechanisms which also occur in the concrete simultaneously. Carbonation is a common degradation mechanism, which involves, shrinkage of concrete and corrosion of steel reinforcement. In carbonation of the ordinary portland cement (OPC) concrete, calcium hydroxide (portlandite) and C-S-H will be converted to calcium carbonate along with other products [3]. In addition to the hardened cement paste, the Ca, Na, and K oxides in the ASR gel may also have the potential to carbonate and change the reaction kinetics and its expansive nature. The present study investigates the ability of the synthetic ASR gel to carbonate in the presence of carbon dioxide through microscopic and analytical techniques. The study also examines the challenges of these techniques to investigate the carbonation of the ASR gel.

MATERIALS AND METHODS

The current study investigates the effect of the carbonation on the ASR gel using a synthetic gel. The synthetic gel mix design was shown in Table 1 adopted from [4]. The chosen mix has the highest free expansion of nearly 8.5% among mixes considered in the study [4]. Due to the relatively low levels of gel formation in laboratory mortars and concrete [4,5], synthetic gel offers a practical way to understand the behaviour of the gel in the presence of the carbonation.

The gel was prepared in accordance with the mixing guidelines of [4]. Two samples were made and kept in two different curing conditions. One sample was kept in seal curing for 6 days and labelled as “non-carbonated ASR gel”. Another sample was kept

in seal curing for 3 days followed by carbonation chamber (3% CO₂ concentration, 25 °C, and 50% RH) for 3 days and labelled as “carbonated ASR gel”.

The samples were examined under optical microscopy, thermogravimetric analysis (TGA), and X-ray diffraction (XRD). Different sample preparation methods were used for these examinations. Unaltered samples were kept as thin layers on glass plates to observe under the optical microscope. Samples were ground to pass a 63-micron sieve to use in TGA and XRD.

Table 1: Mix design of the synthetic ASR gel [4].

Constituents	Ca(OH) ₂	NaOH	KOH	Micro silica	H ₂ O
Weight (g)	151.9	159.8	67.3	304.7	316.3

RESULTS

Visual observations

After the curing period, the non-carbonated gel appeared to be a flexible paste that can be easily moulded. The carbonated gel appeared to be a brittle solid and easily crushed. These were the early indications of the carbonation effect on the synthetic ASR gel.

Optical microscopy

The samples were observed under cross polarization filters to observe the birefringent nature of the different phases of the samples. The non-carbonated sample is isotropic while the carbonated gel is birefringent under cross polarizers. The optical microscopy images of the carbonated gel particles are shown in Figure 1.

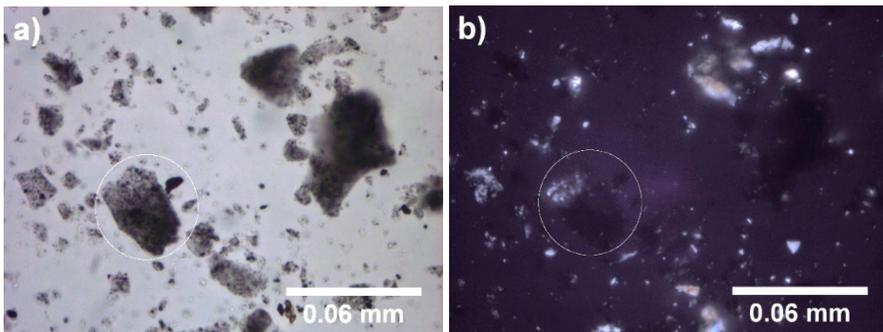


Figure 1: Carbonated synthetic ASR gel (a) without cross polarization filters (b) with cross polarization filters.

The non-carbonated ASR gel has oxides of silica, Ca, Na, and K. These constituents formed an amorphous gel. Portlandite, a raw material in the mix, is a birefringent mineral [6]. However, the non-carbonated gel is isotropic, light propagated through the non-carbonated gel is not visible from cross polarizers. The isotropic behaviour suggests the consumption of portlandite in the process of gel formation.

In the carbonated ASR gel, some of the phases of Ca, Na, and K react with CO₂ and form carbonates. Carbonation product of the Ca is calcite, a birefringent mineral which can be visible under cross polarizers as bright crystals.

In Figure 1a, the dried particles of carbonated gel can be observed in the order of 60 microns. In Figure 1b, the same particles show both isotropy and birefringence, implying the progressive conversion of Ca to calcite in carbonated ASR gel particle.

TGA

The samples were further investigated for TGA using a temperature range of 40 °C to 1000 °C. The non-carbonated sample was dried with isopropyl alcohol and later ground to pass a 63-micron sieve for TGA. The carbonated sample was easily ground to pass a 63-micron sieve without any need of drying.

The mass changes of the sample during heating are correlated with the changes in the composition of the sample. The primary product of cement paste carbonation, calcium carbonate will undergo thermal decomposition and forms calcium hydroxide and carbon dioxide. The temperature range of the calcium carbonate decomposition depends on the crystallinity of the calcium carbonate [7]. In the present study, the decomposition of calcium carbonate occurred at a temperature range of 650 °C to 850 °C and portlandite decomposed in the range of 380 °C to 530 °C.

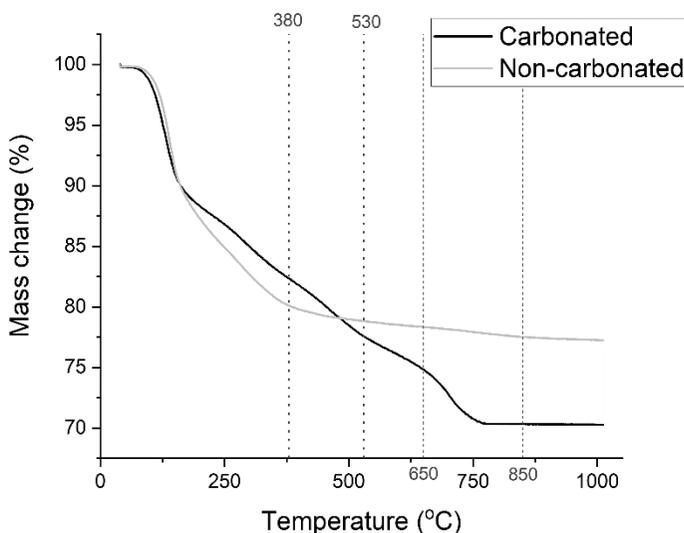


Figure 2: TGA of carbonated and non-carbonated synthetic ASR gels.

From Figure 2, the portlandite contents of the carbonated and the non-carbonated gels are 0.55% and 0.02% respectively. These small quantities of the portlandite cannot be used for either qualitative or quantitative comparison of the portlandite content in the

gels and can only suggest that the portlandite used in the mix was completely utilized in the formation of the synthetic ASR gel. This observation agrees with the previous study where the addition of 40% portlandite by mass resulted in only 0.3% portlandite in TGA [8]. These small quantities of portlandite also suggest that any formation of calcite can be primarily from the gel and not from the portlandite.

From Figure 2, the carbonated sample contained 3.37% of calcium carbonate while the non-carbonated sample contained 0.02% of calcium carbonate. This is an indication that the ASR gel at the early stage of its formation will undergo significant carbonation after exposure to carbon dioxide (3 days at 3% CO₂ concentration).

XRD

XRD of the samples is useful in identifying the crystal phases in the sample. Samples for XRD were prepared similarly to TGA samples. Diffraction patterns were obtained on carbonated and non-carbonated samples. Calcite has its major peak at the 2 θ angle of 29.5°. From Figure 3, while the calcite peaks can be identified, they are clouded by the amorphous peaks of the gel. The calcite peak in the carbonated sample is high in its intensity compared to the non-carbonated samples. The portlandite peaks in both samples are pronounced for small quantities of portlandite (<1% in TGA). Once the gel crystallizes, peaks can be identified more accurately.

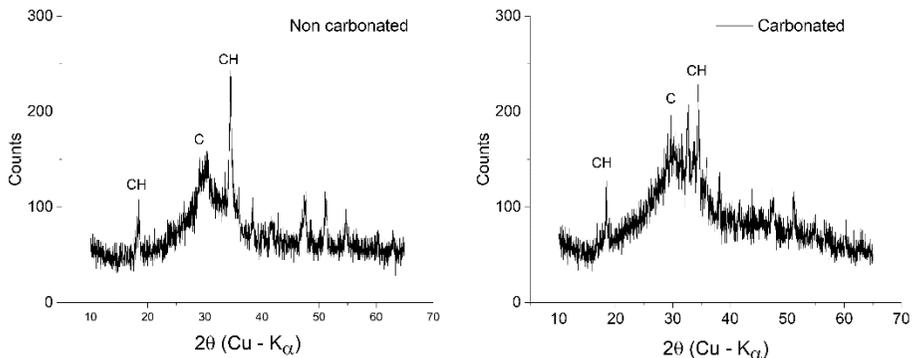


Figure 3: Powder XRD patterns of the non-carbonated (left) and carbonated (right) synthetic ASR gels (CH, portlandite; C, calcite).

DISCUSSION

Atmospheric carbonation of the mortar and concrete is a major deterioration mechanism. In OPC concrete elements (without any supplementary cementitious materials), the presence of Ca in portlandite and C-S-H makes the concrete vulnerable to carbonation. Similarly, ASR gel will also undergo carbonation due to the presence of alkali and Ca. This phenomenon can be observed from the results of the optical microscopy and the TGA shown in Figure 1 and Figure 2 respectively.

In the current study, portlandite, alkali, micro silica and water are used as raw materials. ASR gel is primarily a product of alkali, amorphous silica, and water. However, the Ca present in the pore solution of the hardened cement paste will increase the silicate dissolution [8] and viscosity of the gels [9], thus affecting the reaction rate and expansive stresses of the ASR gel. To accommodate this behaviour, the synthetic ASR gel studies employ various concentrations of the Ca in the gels [4], [8]. With very high quantities of Ca (in the order of 40% by mass of Ca [8] or Ca/Si molar ratio > 0.5 [10]), the gel composition resembles C-S-H. If the gel resembles C-S-H, it will be more prone to carbonation [3]. In the present study, only one composition of the gel mix was used from [4] due to its moderate Ca (15% by mass) content and high expansion to demonstrate its carbonation.

Optical microscopy is helpful in identifying the carbonation products through their birefringence while the ASR product is still in its gel form. As the ASR product crystallizes, differentiating the calcite and ASR crystals using their birefringence pattern will be challenging. TGA results from Figure 2 offer a quantitative estimation of the carbonation products. However, retrieving sufficient quantities of the ASR product from the concrete cracks can be challenging. In this regard, synthetic gel with similar chemical composition will be advantageous in understanding the carbon uptake of the gel.

Analysis of the carbonation of the ASR gel through XRD and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) will be challenging compared to the optical microscopy and TGA. In XRD, the amorphous peaks of the ASR gel could overlap with the crystalline peaks of the carbonation products as shown in Figure 3. As the ASR product crystallizes, the reduction of the amorphous peaks will enable the clear identification of the peaks of the carbonation products. However, similar to the TGA, obtaining sufficient quantities of the actual gel can be challenging. SEM-EDS will be inefficient in identifying low atomic number elements (carbon) with very low mass percentages ($< 1\%$).

Previous studies focused on the ASR product from the cracks of mortar and concrete [5,11]. The reactive aggregates in these studies are calcite based, so a conclusive argument cannot be made regarding the calcite found in the ASR gel to identify whether the calcite is from the ASR gel or from the surrounding reactive calcite aggregates. Previous studies of synthetic ASR gels involved preparation and processing in the sealed or nitrogen environments to avoid the carbonation [4,8]. The current study shows that the carbonation of the synthetic ASR gel is possible.

The setting and hardening nature of the synthetic ASR gel depends on the alkali to silica ratio of the mix. With decreasing alkali to silica ratio, the gel turns from being a viscous liquid to brittle solid [12]. However, for the same alkali to silica ratio, the non-carbonated ASR gel appears as a flexible paste while the carbonated ASR gel appeared as hardened and brittle in the present study. This behaviour suggests that carbonation is consuming the alkali and calcium in the gel and transforming the gel into hardened

brittle material. In the field concrete, this behaviour may change the expansive stresses of the gel and crack formation in the concrete.

This present study shows an interaction of ASR gel with the carbonation mechanism which is not considered in standard tests from ASTM, CSA, and RILEM. Further investigations of the effect of ASR-carbonation interaction on ASR product mineralogy, morphology, and mechanical properties are needed to understand its impact on the deterioration of concrete in field conditions.

CONCLUSIONS

ASR in concrete can be affected by external conditions. To understand this behaviour, synthetic ASR gel was prepared and subjected to carbonation (3 days at 3% CO₂ concentration). From the results, it is understood that ASR gel can undergo carbonation due to the Ca and alkali present in the gel. Visual observations, optical microscopy, and TGA provided information regarding the ability of the ASR gel to undergo carbonation. These tests on the carbonated synthetic ASR gel support the hypothesis that carbonation can affect morphology, reaction rate, and physical properties such as expansive stresses and hardness of the ASR gel in concrete. In addition, the challenges of the different techniques are also discussed. Further studies are needed to prove this behaviour in the ASR gel from concrete crack phases.

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