Effect of Al on the formation and structure of alkali-silica reaction products

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ABSTRACT

The use of Al-rich supplementary cementitious materials can effectively reduce the expansion of concrete caused by alkali-silica reaction (ASR). However, the role of Al in mitigating the formation and structure of ASR products is only poorly understood, since direct investigation of the reaction in the micro-scale veins of aggregates is difficult. Recent successful synthesis of ASR products provides a unique opportunity to directly assess the role of Al in ASR. In this study, the effect of Al on the formation and structure of ASR products synthesized at 40 and 80 °C is investigated. It is found that the presence of Al in concentration lower than 0.1 mM neither prevents ASR nor alters the structure of the crystalline ASR products formed at 40 °C. However, formation of the crystalline ASR product at 80 °C is lowered at higher Al content due to the formation of a zeolitic precursor.

1. Introduction

Alkali-silica reaction (ASR) is one of the important concrete durability issues worldwide [1]. The reaction occurs between the reactive silica in concrete aggregates and alkali hydroxide together with calcium from the concrete pore solution, leading to the formation of ASR products with ensuing expansion and cracking of concrete. Numerous publications have shown that ASR expansion can significantly be reduced by adding supplementary cementitious materials (SCMs), such as silica fume, fly ash, granulated ground blast furnace slag and calcined clay during concrete production [2–11]. Moreover, many studies have also reported that Al-rich SCMs were more effective in mitigating ASR than the Si-rich SCMs [3,4,8,10,12]. Several mechanisms of using SCMs in mitigating ASR have been proposed such as reduction of pore solution alkalinity, increase of alkali binding, consumption of portlandite, and reduction of permeability [2,7]. However, the precise mechanisms are not yet fully understood, in particular the role of Al in mitigating ASR.

Many studies have reported that the main mechanism of SCMs in controlling ASR was the lowering of the pore solution pH [7,9,13–16], which was considered to be related to alkali fixation by calcium-silicate-hydrate (C-S-H) [13,17]. Hong and Glasser reported that incorporation of Al also increased the alkali fixation capacity of C-S-H [13]. However, other studies showed that the incorporation of Al did not significantly increase alkali fixation in C-S-H [18,19]. Chappex and Scrivener [19] concluded that the main reason for Al in mitigating ASR was due to Al absorption on the silica surface, which limited the dissolution of amorphous silica [20–23]. Alternatively, an initial formation of alumino-silicate on the silica surface and in the solution, and later a zeolite precipitation were also suggested to inhibit ASR, as it reduced the concentration of so-called “free” silica available for ASR [24]. Reduced ASR expansions were also observed in alkali-activated slag/fly ash mortars, where zeolites were formed at increased amounts of fly ash [25]. Moreover, some studies have also reported the presence of Al in ASR products based on scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM/EDS) analysis [2,26–31], while no Al or hardly detectable amounts in ASR products were reported by others [3,32–35]. Consequently, it remains unclear whether and how Al can affect the formation and structure of ASR products.

Understanding the mechanism of ASR and their mitigation mechanisms within concrete has been a challenge for many decades, since very small amounts of ASR products are formed within concrete aggregates in micro-scale. The small volume of the ASR products severely limits their chemical and physical characterizations by conventional laboratory techniques such as X-ray diffraction (XRD) analysis, Nuclear Magnetic Resonance (NMR), thermogravimetric analysis (TGA). Recently, two types of crystalline ASR products with different d-spacings at low 2θ angles have been synthesized in laboratory at different temperatures: 13.1 Å ASR products at 80 °C [36] and 10.8 Å ASR product at 40 °C [37]. The structures of the K(or Na)-13.1 Å ASR products observed at higher temperature were found to be very similar to the crystal structure of the natural mineral shlykovite (KCa[Si4O9(OH)]·3H2O) [36,38], which has a layered silicate structure with its SiO4 tetrahedron charge balanced...
by K\(^{+}\) (or Na\(^{+}\)) and Ca\(^{2+}\) in the main layer and by H\(^{+}\) in the interlayer. Both the 13.1 Å and 10.8 Å ASR products have a similar short-ordered silicate-sheet structure according to their comparable Raman spectra [37]. Further studies of concrete samples suggested that 13.1 Å ASR products (K-shlykovite and Na-shlykovite) are formed in concrete under accelerated ASR conditions between 60 and 80 °C [39], while the 10.8 Å ASR product is formed in concrete under accelerated test at 38 °C and in field concrete [40]. The successful synthesis of these ASR products provides a unique opportunity to directly assess the role of Al in ASR, since such an approach allows identifying the formation and structure of ASR products, performing thermodynamic calculations and investigating the impact of temperature on the mineralogy of the crystalline ASR products [36,37,41,42].

In this study, the effect of Al on the formation and structure of the 10.8 Å and 13.1 Å ASR products synthesized at 40 and 80 °C is investigated by adding different amounts of Al(OH)\(_3\) during the synthesis. The lower temperature corresponds to standard accelerated testing conditions at 38 °C and field concrete [40]; the higher temperature corresponds to standard accelerated testing conditions at 60 and 80 °C [39].

2. Experimental procedure

2.1. Sample preparation

The samples were prepared by mixing amorphous silica (SiO\(_2\), hydrophilic silica, surface area 200 m\(^2\)/g, from EVONIK industries) with freshly burnt CaO (obtained by burning calcium carbonate for 12 h at 1000 °C), analytical KOH pellet (>85% KOH basis), aluminum hydroxide (63–67 wt% Al\(_2\)O\(_3\), from Sigma-Aldrich, mainly gibbsite according to XRD analysis) and Milli-Q water (deionized water with a resistivity of 18.2 M\(\Omega\)cm at 25 °C) at designated portions as given in Table 1. The prepared samples have initial bulk Ca/Si molar ratio of 0.25, K/Si molar ratio of 0.5 and different Al/Si molar ratios from 0 to 0.3 with an increment of 0.05. All the samples have an initial OH\(^-\) ions concentration of 1 mol/L. The samples for the reaction at 40 °C were mixed in 100 mL hard polyethylene (PE-HD) bottles, stored at 40 °C in an oven and filtrated after 160 days. Three selected samples for the reaction at 80 °C were mixed in Teflon bottles and filtrated after 120 days. In both cases, the time is sufficient with respect to the formation of ASR products based on previous studies [36,37]. All the samples were filtrated with paper filter with mesh size of 0.2 μm. After filtration, half of each solid sample from 40 °C was rinsed first with approximately 50 mL of 1:1 water-ethanol solution and then with 50 mL 94% ethanol solution. Afterwards, they were dried in a desiccator with a relative humidity (RH) of 35%. The rest of the solid samples from 40 °C and 80 °C were vacuum dried at 0.01 mbar for 3 days. The obtained solutions were saved for pH measurements and composition analyses.

2.2. Analytical methods

The obtained solid samples from two different drying conditions (35%RH and vacuum) were analyzed with X-ray powder diffraction (XRD, PANalytical X’pert Pro) with CoKα radiation in a 0–0 configuration and a step size of 0.017° 20 between 5 and 90° 20 for 2.5 h. The vacuum-dried samples (10 to 30 mg) synthesized at 40 °C were analyzed with thermogravimetric analysis (TGA/DTA) with a Mettler Toledo TGA/SDTA 8513 using a heating rate of 20 °C/min from 30 to 980 °C as recommended in [43]. N\(_2\) was used as a purging gas with a rate of 30 to 50 mL/min.

The 27Al MAS NMR experiments were recorded on the vacuum-dried samples with a Bruker Avance III NMR spectrometer using a 2.5 mm CP/MAS probe at 104.3 MHz applying the following parameters: 25000 Hz sample rotation rate, 3072 scans, π/12 pulses of 1.0 μs, 1 s relaxation delays, no 1H decoupling. The chemical shifts of the 27Al MAS NMR spectra were referenced to an external sample of 1.1 M Al(NO\(_3\))\(_3\) in D\(_2\)O at 0.0 ppm.

The 29Si MAS NMR experiments were recorded on the same samples with the same instrument using a 7 mm CP/MAS probe at 79.5 MHz applying the same parameters used in the previous study [36]. The 29Si NMR chemical shifts were externally referenced to tetramethylsilane (TMS) at 0.0 ppm.

The morphology of the reaction products was investigated using a scanning electron microscope (SEM) FEI Quanta 650 with a Large Field Detector (LFD) on the powdered samples. Chemical analysis was performed with a Thermo Noran Ultra Dry 60 mm\(^2\) detector and Pathfinder X-Ray Microanalysis Software.

The pH was measured at room temperature around 23 °C immediately after filtration using small fraction of the filtrated solution with a Knick pH meter (pH-Meter 766) equipped with a Knick SE100 electrode. Another part of filtrated solution was diluted with MilliQ water in ratios of 1:10, 1:100 and 1:1000 and used for ionic chromatography (IC) analysis.

2.3. Thermodynamic modelling

Thermodynamic modelling was performed using the Gibbs free energy minimization software GEMS v3.6 [44,45]. It is a general-purpose geochemical modelling program which can be used to calculate the thermodynamic equilibrium and predict the composition of a system composed of aqueous, solid and gaseous phases at the temperature and pressure of interest by minimizing the Gibbs free energy of the system. In this study, the aqueous chemistry and solid phase assemblages are calculated using the PSI/Nagra general thermodynamic database [46] and the Cemdata18 database [47]. The activity coefficient (γ\(_i\)) of the relevant species were calculated using the extended Debye–Hückel equation with the common ion-size parameter q\(_i\) of 3.67 Å for KOH and 3.31 Å for NaOH solutions and the common third parameter b\(_y\) according to the equation: logγ\(_i\) = \(-A_yq_i^2/1+q_i^2)+b_yI\), where z\(_i\) is the charge of species i, I is the effective molal ionic strength, b\(_y\) is a semi-empirical parameter (~0.123 for KOH and ~0.098 for NaOH electrolyte at 25 °C), and A\(_y\) and b\(_y\) are P,T-dependent coefficients. For uncharged species, the above equation reduces to logγ\(_i\) = b\(_y\)I. This extended Debye-Hückel activity correction is applicable up to approx. 1 to 2 M ionic strength [48].

The CKASH from previous studies was used to predict the

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>SiO(_2)</th>
<th>CaO</th>
<th>KOH</th>
<th>Al(OH)(_3)</th>
<th>H(_2)O</th>
<th>Ca/Si</th>
<th>K/Si</th>
<th>Al/Si</th>
<th>Temperature °C</th>
</tr>
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<tbody>
<tr>
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<td>1.40</td>
<td>2.81</td>
<td>0.00</td>
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<td>0.25</td>
<td>0.5</td>
<td></td>
<td>40</td>
</tr>
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<td>2.81</td>
<td>0.39</td>
<td>50</td>
<td>0.25</td>
<td>0.5</td>
<td>0.05</td>
<td>40</td>
</tr>
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<td>6.01</td>
<td>1.40</td>
<td>2.81</td>
<td>0.78</td>
<td>50</td>
<td>0.25</td>
<td>0.5</td>
<td>0.1</td>
<td>40</td>
</tr>
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<td>1.40</td>
<td>2.81</td>
<td>1.18</td>
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<td>0.25</td>
<td>0.5</td>
<td>0.15</td>
<td>40</td>
</tr>
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<td>1.40</td>
<td>2.81</td>
<td>1.57</td>
<td>50</td>
<td>0.25</td>
<td>0.5</td>
<td>0.2</td>
<td>40</td>
</tr>
<tr>
<td>SKCA_0.25</td>
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<td>1.40</td>
<td>2.81</td>
<td>1.96</td>
<td>50</td>
<td>0.25</td>
<td>0.5</td>
<td>0.25</td>
<td>40</td>
</tr>
<tr>
<td>SKCA_0.3</td>
<td>6.01</td>
<td>1.40</td>
<td>2.81</td>
<td>2.35</td>
<td>50</td>
<td>0.25</td>
<td>0.5</td>
<td>0.3</td>
<td>40</td>
</tr>
</tbody>
</table>
precipitation of C-S-H [41,49]. To account for the possible formation of zeolites or zeolite precursors data for solid solution of phillipsite (K-end member: KAlSiO₃(OH)₂ and Ca-end member: Ca₀.₅Al₂Si₃O₁₀(H₂O)₃) were added to the database [50]. The thermodynamic data of these phases and the other phases used in this study is summarized in Appendix A, Table A1. Experimentally developed thermodynamic data for K-shlykovite synthesized at 80 °C from a previous study [41] and for 10.8 Å ASR synthesized at 40 °C from this study (see Appendix A, Table A1 and Table A2) are also incorporated in the GEMS codes to predict the formation of ASR products at a given temperature. It should be noted that based on the general PSI/Nagra thermodynamic database the aqueous silica concentrations increase strongly with pH; at pH values above 10, aqueous Si species are dominated by H₂SiO₄⁻ and at pH 12 and above by H₂SiO₄²⁻ and in particular at high Si concentration by Si₄O₁₄⁶⁻; no other polymeric Si-species are included in the PSI/Nagra thermodynamic database [46]. The behavior of such polynuclear complexes at high temperature and high ionic strength is not well-known, which may cause some deviations between the calculated and experimental results.

3. Results and discussions

3.1. Samples synthesised at 40 °C

3.1.1. XRD

The XRD patterns of the samples synthesised at 40 °C with initial Al/Si ratio from 0 to 0.3 are shown in Fig. 1 corresponding to the drying conditions at 35% RH (Fig. 1a) and under vacuum (Fig. 1b). For all samples, crystalline ASR product with the d-spacing of 10.8 Å at low 2θ (9.5°–20) is observed independent of the drying conditions. However, vacuum drying resulted in a shift of the second peak from 11.5° 2θ (d = 8.8 Å) to 13.5° 2θ (d = 7.6 Å) as seen from the Al-free samples. A previous study has demonstrated that such structural changes were reversible and were caused by absorption/desorption of water from the ASR product [37].

For all samples dried at 35% RH, the peak positions of the ASR product remain unchanged as shown in Fig. 1a, while its relative intensities are reduced in the presence of more Al due to the dilution effect by the presence of the increased amounts of gibbsite. For the vacuum-dried samples, an additional peak at 11.5° 2θ is observed at higher Al additions, as shown in Fig. 1b. The position of this peak matches very well with the second XRD peak (11.5° 2θ) of the samples dried at 35% RH. Clearly, the appearance of this peak is not attributed to the increase amounts of Al. Instead, it is due to rewetting of the samples during the measurement, as the samples were exposed to air with RH over 35%. These samples were continuously measured following the order of increasing their Al/Si ratios with each measurement lasting 2.5 h. Thus, more and more water are absorbed by the samples with increasing their Al/Si ratios before that they were measured. The disappearance of the peak at 13.5° 2θ for the samples with Al/Si ratios ≥0.25 suggests that the ASR product has completely transformed its structure from the vacuum-dried state to the ambient state after 12.5 h of exposure in air. Similar to the samples dried at 35% RH, dilution effect is also observed for the vacuum-dried samples with increasing the Al/Si ratio as seen directly from the intensity of the first XRD peak. Thus, the intensity of the second peak at 11.5° 2θ does not show systematic increase with increasing Al/Si ratio.

3.1.2. DTG

The DTG results of the vacuum-dried samples are shown in Fig. 2, where the data for the used Al(OH)₃ powder are also plotted for comparison. The results show that the first two DTG peaks at low temperature range (100–200 °C) related to the ASR product remain unchanged at initial Al/Si ratio from 0 to 0.2, while the intensity of the DTG peaks related to Al(OH)₃ increases. At high Al/Si ratio of 0.25 and 0.3, the intensity of the DTG peaks for Al(OH)₃ is further increased. However, the two peaks related to the ASR product become less distinguishable, which seems to be attributed to the presence of more C-S-H phase. XRD data in Fig. 1a clearly shows that the position of peaks related to ASR product remain unchanged, indicating that the changes in the observed DTG curves are not related to the change of ASR product with increasing the Al/Si ratio of the samples.

3.1.3. NMR

The ²⁷Al and ²⁹Si MAS NMR spectra of the vacuum-dried samples synthesised at 40 °C are shown in Fig. 3a and b, respectively. Similar ²⁷Al NMR spectra are observed for all samples as seen in Fig. 3a, where only the peak intensities are different between these samples. These spectra are similar to that of gibbsite reported in literature, which contains two typical overlapped non-equivalent Al atoms in octahedral environments at ca. 7 ppm and some edges of a second-order line shape for the other Al site at ca. −3 ppm [51,52]. This observation indicates that only gibbsite as Al-rich product is detectable in the samples. The results show neither detectable aluminum in calcium-aluminate-silicate-hydrate (C-A-S-H) which contains IV, V or VI-fold coordination of Al [53,54] nor Al-rich zeolite or its precursors, where resonances in the range of 50–80 ppm are expected [55,56]. The increased overall intensity of gibbsite with increased initial Al/Si is in line with the XRD results in Fig. 1 and the DTG results in Fig. 2. The results suggest that Al
Fig. 2. DTG results of the vacuum-dried samples synthesized at 40 °C with different initial Al/Si ratios. The DTG of the used gibbsite (Al(OH)₃) is also plotted for comparison. The Y-axis of DTG curves are shifted for better visualization for all samples except for the reference sample without Al. Thus, direct reading of the values from Y-axis is only meaningful for the reference sample. For the other samples, the offset should be considered.

Similarly, the samples with initial Al/Si ratio below 0.15 show comparable ²⁹Si NMR spectra as shown in Fig. 3b, where ASR product with several resolved resonances between −90 and −98 ppm are observed together with observation of some C-S-H phase with the main chemical shifts at −82 and −86 ppm from Q² sites. The detailed discussion of the ²⁹Si NMR spectra of the synthesized ASR product with its molecular structure is presented in [37]. A significantly different ²⁹Si NMR spectrum is seen for the sample with initial Al/Si ratio of 0.3. The spectrum indicates the presence of more C-S-H, as also indicated by the DTG results in Fig. 2. Moreover, the broad spectrum with a main peak at −90 ppm suggests also presence of amorphous ASR product [57]. Such signals from C-S-H and amorphous ASR product overlap with those of the Q³ species of the crystalline ASR product cause the change of the overall spectrum of this sample.

3.1.4. SEM/EDS

The morphologies and chemical compositions of the ASR product and gibbsite in the vacuum-dried SKCA_0.15 sample synthesized at 40 °C are shown in Fig. 4. The presence of Al in this sample does not seem to affect the typical plate-like morphology of the ASR product as shown in Fig. 4a. Trace of Al is only detectable in few areas (4 and 8 in Fig. 4b) of the ASR product, which is caused by contaminations of gibbsite in close contact. The presence of K, Ca and Si in locations 1, 2 and 3 of gibbsite is attributed to the contaminations by ASR products as indicated by the white arrows as shown in Fig. 4b, where ASR products are formed in the porosity of gibbsite crystals. Similar to this sample, the ASR product in most of the other samples can also be distinguished from the large gibbsite crystals, which enables their EDS analysis as summarized in Table 2. The results show absence or only trace amount of Al in these samples due to contaminations. However, significant amount of Al is present for the measured spots of the sample with initial Al/Si ratio of 0.3, since the ASR product is intermixed with the dominant gibbsite crystals and cannot be isolated for EDS analysis on the pure ASR product.

3.1.5. Aqueous chemistry and thermodynamic modelling

The measured aqueous concentrations and pH together with their predicted values using thermodynamic modelling and calculated phase assemblages are shown in Fig. 5. Overall, the measured aqueous concentrations and pH agree well with the predicted values as shown in Fig. 5a. All samples show high concentration of Si and K, while low concentration of Ca and Al. The elemental concentrations (except for Al) and the pH values remain nearly unchanged for the samples with different initial Al/Si ratios. However, some differences in the absolute values between the calculated and measured data were observed, in particular for Si and K concentrations. This can be related to the poor description of the aqueous polynuclear silica complexes at high Si concentrations and at high temperature as already observed in previous studies [41,42] and/or to an inadequate description of the uptake of K in C-S-H and the solubility of the 10.8 Å ASR product. The measured concentrations and pH values were used to calculate the saturation indices with respect to C-S-H, amorphous silica, gibbsite, phillipsite and 10.8 Å ASR products as shown in Table 3. As expected, the solutions are predicted to be oversaturated with respect to C-S-H while undersaturated with respect to the amorphous silica as shown in Table 3, which are in lines with the experimental observations (e.g. Fig. 3b) and phases predicted by thermodynamic modelling in Fig. 5b (absolute...
values) and Fig. 5c (normalized values). However, the solutions are predicted to be under-saturated with respect to the 10.8 Å ASR product due to the aforementioned poorly described aqueous polynuclear silica complexes, although the presence of the 10.8 Å ASR product is observed experimentally and it is predicted by thermodynamic modelling as shown in Fig. 5b and c. Moreover, the solutions are also predicted to be under-saturated with respect to gibbsite despite of its presence, which is likely related to the slow dissolution of gibbsite since gibbsite was added as a raw material rather than formed as a reaction product. This explains the measured relatively lower Al concentrations than the predicted ones in Fig. 5a, and thus slightly increased Al concentration with increasing the Al/Si ratio as shown in the same figure. The solution, however, were calculated to be oversaturated with respect to K-philipsite, a zeolite which has been observed to form at the interface between cement and clay minerals at 70 °C [58]. In fact, most of the K-zeolites are not expected to precipitate due to their slow formation kinetics at ambient temperature [59, 60]. No zeolitic phase is observed in our experiments at 40 °C thus the formation of phillipsite was suppressed in the calculations of the hydrate assemblage at 40 °C.

The predicted phases, C-S-H, gibbsite and 10.8 Å ASR product are in line with the experimental observations from XRD, DTG and NMR results. Thermodynamic modelling predicts no alteration of C-S-H and ASR product with increasing the amounts of aluminum. The observed higher amount of C-S-H for the samples with higher initial Al/Si ratio from DTG and 29Si NMR results is likely due to the kinetic hindrance of the formation of the 10.8 Å ASR product. Overall, both experimental results and thermodynamic modelling show that the addition of Al neither prohibits the formation of the 10.8 Å ASR product nor alters its molecular structure.

3.2. Samples synthesized at 80 °C

3.2.1. XRD

The XRD patterns of the vacuum-dried samples synthesized at 80 °C are shown in Fig. 6. A Previous study has shown that vacuum-drying does not change the structure of the crystalline ASR product formed at this temperature (i.e., K-shlykovite with a basal spacing of 13.1 Å) [36]. As expected, K-shlykovite is observed in the reference sample without Al. It is also seen in the sample with Al/Si ratio of 0.1 together with some gibbsite. However, no K-shlykovite is present in the sample with the highest Al/Si ratio of 0.3, while an amorphous phase and only trace amounts of gibbsite are present in this sample. For all samples, a minor peak at low 2θ angle (6.4° 2θ) is observed, which is due to the presence of the amorphous ASR product, ASR-P1 (K0.52Ca1.16Si4...)

Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ca/Si</th>
<th>K/Si</th>
<th>Al/Si</th>
<th>Measured products</th>
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<tr>
<td>SKCA_0</td>
<td>0.25±0.01</td>
<td>0.30±0.02</td>
<td>0.004±0.003</td>
<td>13.1 Å</td>
</tr>
<tr>
<td>SKCA_0.05</td>
<td>0.26±0.01</td>
<td>0.34±0.01</td>
<td>0.016±0.002</td>
<td>13.1 Å</td>
</tr>
<tr>
<td>SKCA_0.1</td>
<td>0.24±0.01</td>
<td>0.35±0.01</td>
<td>0.020±0.002</td>
<td>13.1 Å</td>
</tr>
<tr>
<td>SKCA_0.15</td>
<td>0.26±0.01</td>
<td>0.33±0.02</td>
<td>0.025±0.002</td>
<td>13.1 Å</td>
</tr>
<tr>
<td>SKCA_0.3</td>
<td>0.22±0.01</td>
<td>0.21±0.01</td>
<td>0.035±0.0005</td>
<td>10.8 Å + gibbsite</td>
</tr>
<tr>
<td>SKCA_0.2</td>
<td>0.25±0.01</td>
<td>0.37±0.01</td>
<td>0.010±0.002</td>
<td>10.8 Å</td>
</tr>
<tr>
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<td>0.28±0.02</td>
<td>0.36±0.02</td>
<td>0.009±0.009</td>
<td>10.8 Å</td>
</tr>
<tr>
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<td>0.22±0.01</td>
<td>0.21±0.01</td>
<td>0.015±0.0005</td>
<td>10.8 Å</td>
</tr>
</tbody>
</table>

a Not detectable.

In this sample, the 10.8 Å crystalline ASR product is intermixed with gibbsite, which cannot be isolated for SEM/EDS analysis, thus causing higher Al/Si ratio.

Fig. 4. (a) Morphology of the 10.8 Å ASR product. (b) SEM/EDS analysis of the vacuum-dried SKCA_0.15 sample synthesized at 40 °C with formation of the 10.8 Å ASR product and gibbsite. White arrows indicate the formation of the 10.8 Å ASR product in the porosity of gibbsite crystals.
O_8(OH)_{2.84} \cdot 1.5H_2O), identified in our previous study [36]. As shown in that study, the presence of the trace ASR-P1 in the samples at this initial Ca/Si ratio is attributable to a kinetic effect, which could be avoided by regularly shaking the sample during the synthesis. However, it can be stabilized at the slightly higher initial Ca/Si ratio of 0.3, where it is more stable than K-shlykovite as discussed in [41, 42].

3.2.2. NMR

The $^{27}$Al NMR spectra shown in Fig. 7a indicate that the amorphous product in the SKCA_0.3 sample seen from the XRD patterns is an amorphous aluminate-silicate product (or zeolite precursor) with typical resonances in the range of 50–80 ppm [55, 56]. Trace of such a zeolite precursor is also present in the SKCA_0.1 sample. In addition, gibbsite is also observed in these two samples with typical resonances at 7 ppm and 3 ppm [51, 52]. However its intensity is relatively lower for the SKCA_0.3 sample, which is consistent with the XRD results in Fig. 6. Neither zeolite precursor nor gibbsite are observed in the Al-free sample.

The formation of C-S-H and K-shlykovite in the SKCA_0 and SKCA_0.1 samples is also shown in the $^{29}$Si NMR spectra in Fig. 7b, whereas the zeolite precursor with the main chemical shift at ~90 ppm is observed in the SKCA_0.3 sample. Interestingly, this product show nearly identical $^{29}$Si NMR spectra with an previously synthesized Al-free amorphous ASR.
3.2.3. SEM/EDS

The morphologies of the K-shlykovite formed in the SKCA_0 sample and of the zeolite precursor formed in the SKCA_0.3 sample are shown in Fig. 8. The typical needle-like morphology is observed for the synthetic K-shlykovite as also reported in our previous study [36]. A somewhat different morphology of K-shlykovite can be observed in concrete aggregates although the Raman spectra are identical [39]. This could be attributed to the fact that the spatial restriction within concrete aggregates may affect the growth of K-shlykovite and thus its morphology. In the sample SKCA_0.3 where a zeolite precursor is observed, the SEM images in Fig. 8b,c show a nano-sized morphology of this product.

The EDS analysis of the corresponding samples is summarized in Table 2. Negligible amount of Al is detected in the reference sample SKCA_0 and only a trace amount of Al is measured for the SKCA_0.1 sample. A more significant amount of Al is incorporated into the nano-crystalline zeolite precursor in addition to Ca, K, and Si, where a Ca/Si ratio of 0.25, a K/Si ratio of 0.47 and an Al/Si ratio of 0.22 are observed indicating that the zeolite precursor not only contains Al but also significantly more K than the K-shlykovite.

3.2.4. Aqueous chemistry and thermodynamic modelling

The measured aqueous concentrations and pH together with their predicted values and phase assemblages for the samples synthesized at 80 °C are plotted in Fig. 9. Again, a similar trend is observed between the measured and calculated concentrations and pH values as shown in Fig. 9a. However, some differences of the absolute values of the aqueous concentrations were also observed, which could be again related to poorly described aqueous polynuclear silica complexes. For the Al-free sample and the sample with Al/Si ratio of 0.1, the calculated saturation indices in Table 3 indicate that the solutions are slightly undersaturated with respect to C-S-H as also predicted in phase assemblages in Fig. 9b (absolute values) and Fig. 9c (normalized values). However, the solutions are under-saturated with respect to K-shlykovite, which contradict the experimental observations probably due to the aforementioned poorly described aqueous polynuclear silica complexes. The Al-containing samples are over-saturated with respect to phillipsite and the SKCA_0.3 sample also with respect to gibbsite.

In contrast to the samples synthesized at 40 °C, where the K, Si, and Ca concentrations remain nearly unaffected by the Al content, the samples synthesized at 80 °C exhibit lower K, Si, and Ca concentrations, but higher pH values and Al concentrations at higher initial Al/Si ratios. The change of the solution chemistry for these samples is consistent with the alteration of phase assemblages shown in Fig. 9b and c. The modelling results show that C-S-H and phillipsite (K(Ca)AlSi_2O_5·3H_2O, a type of zeolite) are stabilized with increasing the initial Al/Si ratio while K-shlykovite is destabilized. Phillipsite is selected as a candidate zeolite in the prediction as it has similar chemical composition as the formed zeolite precursor and as its formation at below 100 °C has been observed experimentally [58]. Other types of K-containing zeolites including merlinoite and chabazite are also observed in cementitious system [50,59,61], however, their chemical compositions are significantly different from the zeolite precursor observed in this study. More other types of K-containing zeolites such as heulandite, clinoptilolite, stilbite, and mordenite are not selected as candidates since they favorably
Fig. 8. Morphologies of (a) the crystalline ASR product (i.e., K-shlykovite) and (b, c) the amorphous potassium aluminate-silicate formed at 80 °C in the SKCA_0 (a) and the SKCA_0.3 (b, c) samples.

Fig. 9. Thermodynamic modelling of (a) solution chemistry and (b) phase assemblages for the samples synthesized at 80 °C. (c) Normalized results from (b) to show the mass percentage of the phases in the resulting solids at equilibrium.
precipitate at higher temperatures [59,60]. The predicted aqueous results and phase assemblages are generally in line with the experimental observations. However, a crystalline zeolite rather than the amorphous zeolite precursor and gibbsite is predicted by thermodynamic modelling. Such discrepancies can be attributed to the slow kinetics of zeolite formation, which is expected to take much longer time and requires much higher reaction temperature.

3.3. Possible mechanisms of Al in mitigating ASR

Although many studies have shown a greater effectiveness of Al-rich SCMs than of Si-rich SCMs in mitigating ASR [3,4,8,10,12], only few studies have investigated the role of Al in ASR as reviewed in [62]. The following mechanisms have been proposed in literatures:

(i) enhanced alkali sorption in C-S-H;
(ii) formation of zeolite [24];
(iii) reduced dissolution rate of amorphous silica [20,21];

It is well known that Al can be incorporated into C-S-H structure [63–66]. Sun et al. [64] proposed that substitution of Si by Al in C-S-H structure provided a negative site that must be charge balanced by a net positive charge (e.g., Na\(^{+}\), K\(^{+}\), \(\text{CO}_3^{2-}\)), resulting in alkali binding; in fact, Hong and Glasser also pointed out that incorporation of Al in C-S-H may increase its alkali fixation capacity [13]. However, recent studies showed that the incorporation of Al did not increase the alkali fixation of the C-S-H in real cementitious materials significantly [18,19]. Thus, the first mechanism can be excluded.

Hünger [24] reported that there is an inverse relation between the silica releasing rate of aggregate and the amount of zeolite formed. Based on this observation, it was proposed that an initial formation of aluminosilicate on the silica surface and in the solution, and later a zeolite precipitation were expected to inhibit ASR, as it reduced the concentration of so-called “free” silica available for ASR. However, precipitation of zeolite in relation to ASR has so far only been reported in concrete under accelerated conditions at 80 \(^{\circ}\)C and exposed to 1 mol/L NaOH solution [24,25]. In fact in current study, only a zeolite precursor but not a crystalline zeolite is observed; and such poorly crystalline alkali aluminosilicates will be even more difficult to be observed in a concrete aggregate. On the other hand, crystalline zeolites are less likely to form in the presence of K than of Na at the same temperature [67] and the precipitation of K-rich crystalline zeolites seems to occur at higher temperature [59,60].

In this study, a complete mitigation of ASR occurs only in the sample with highest Al concentration in the equilibrium solution (26.8 mM). Such high Al concentration is considered irrelevant to cementitious materials, as most hydrated cements have maximum Al concentrations of their pore solutions below 0.1 mM even in presence of SCMs [68]. Within this range of Al concentration, alkali aluminosilicates may co-precipitate with K-shlykovite as observed from \(^{27}\)Al NMR spectra in Fig. 7a and also predicted by thermodynamic modelling in Fig. 9b and c.

At low temperature of 40 \(^{\circ}\)C, neither crystalline zeolite nor zeolite precursor is observed within the 160 days of the experiments. Thus, the role of Al in hydrated cements in mitigating the formation of ASR products in field concrete is expected to be limited. It is likely that the dominant role of Al in reducing the risk of ASR in field concrete is the absorption of Al on the silica surface, which slow down the dissolution of reactive silica in aggregates [20,21].

4. Conclusions

In this study, the effect of Al on the formation and structure of ASR products synthesized at 40 and 80 \(^{\circ}\)C is investigated by adding different amounts of Al(OH)\(_3\) during the synthesis. Two types of crystalline ASR products are formed: 10.8 Å ASR product at 40 \(^{\circ}\)C and K-shlykovite at 80 \(^{\circ}\)C.

At 40 \(^{\circ}\)C, both experimental studies and thermodynamic modelling show that the elemental concentrations and the pH values of the equilibrium solution remain nearly unchanged for the samples with different initial Al/Si ratios. In line with the aqueous results, characterization of the solid phases suggests that the formation and structure of 10.8 Å ASR product are not affected by introducing Al. The SEM/EDS analysis provides direct evidence that Al is not significantly incorporated into the 10.8 Å ASR product, but presents in its original form in gibbsite and physically mixed with the 10.8 Å ASR product.

At 80 \(^{\circ}\)C, the equilibrium solutions show lower K, Si, and Ca concentrations but higher pH values and Al concentrations at increasing the initial Al/Si ratio, as also predicted by thermodynamic modelling. The change of the solution chemistry at high Al concentration is due to the formation of a potassium aluminosilicate phase, which leads to the stabilization of C-S-H and the destabilization of K-shlykovite. The potassium aluminosilicate phase observed has been identified as an ill-crystalline zeolite precursor. At the highest initial Al/Si ratio of 0.3, no K-shlykovite is observed and the Al concentration of the equilibrium solution reaches up to 26.8 mM.

Overall, formation of a potassium aluminosilicate phase prevents to some extent the formation of ASR products at high temperatures. However, such an effect is not observed at lower temperature during the 160 days of experiments studied here, although it might form at longer times. Thus, it is likely that the dominant role of Al in reducing the risk of ASR in field concrete in the short term is the absorption of Al on the silica surface, which slows down the dissolution of the reactive silica in concrete aggregates, while in the long term the formation of zeolitic precursors could also contribute to the prevention of ASR.

CRediT authorship contribution statement

Zhenguo Shi: Conceptualization, Methodology, Investigation, Data analysis, Writing - original draft, Writing - review & editing. Bin Ma: Discussion, Writing - review & editing. Barbara Lothenbach: Conceptualization, Methodology, Discussion, Writing - review & editing.

Declaration of competing interest

The authors declared that they have no Conflicts of interest to this work.

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Appendix A

The standard thermodynamic properties at 25 °C (40 and 80 °C for ASR products) and 1 atm for the phases used in this study are summarized in Table A1. The solubility data for the 10.8 Å ASR product synthesized at 40 °C is obtained from dissolution experiments at the same temperature. The measured concentration and pH of the solution after dissolution is calculated:

\[
\gamma = \frac{\text{molal concentration}}{\text{mol/kg H}_2\text{O}}
\]

The activity coefficient \(\gamma\) is the molal concentration in mol/kg H\textsubscript{2}O. The activity coefficient \(\gamma\) of the relevant species were calculated using the extended Debye–Hückel equation as detailed in Section 2.3.

### Table A1

<table>
<thead>
<tr>
<th>Phases(^a)</th>
<th>(\log_{10} K_{50})</th>
<th>(\Delta G^\circ) [kJ/mol]</th>
<th>(\Delta H^\circ) [kJ/mol]</th>
<th>(S^\circ) [J/K/mol]</th>
<th>(C_p^\circ) [J/K/mol]</th>
<th>(V^\circ) [cm\textsuperscript{3}/mol]</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbsite: Al(OH)	extsubscript{3}</td>
<td>–1.12</td>
<td>–1151</td>
<td>–1289</td>
<td>70.1</td>
<td>93.1</td>
<td>32.0</td>
<td>[69]</td>
</tr>
<tr>
<td>Amorphous silica: SiO\textsubscript{2}</td>
<td>–2.714</td>
<td>–849</td>
<td>–903.3</td>
<td>41.3</td>
<td>44.5</td>
<td>29.0</td>
<td>[60]</td>
</tr>
<tr>
<td>C-K-A-S-H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSC\textsuperscript{2+}: (CaO)\textsubscript{1.25}·(SiO\textsubscript{2})\textsubscript{0.8}·(H\textsubscript{2}O)\textsubscript{3}</td>
<td>–11.6</td>
<td>–2465</td>
<td>–2721</td>
<td>167</td>
<td>237</td>
<td>80.6</td>
<td>[40]</td>
</tr>
<tr>
<td>TSC\textsuperscript{2+}: (CaO)\textsubscript{1.25}·(SiO\textsubscript{2})\textsubscript{0.25}·(H\textsubscript{2}O)\textsubscript{2.5}</td>
<td>–10.5</td>
<td>–2517</td>
<td>–2780</td>
<td>160</td>
<td>234</td>
<td>79.3</td>
<td>[40]</td>
</tr>
<tr>
<td>ToH\textsuperscript{2+}: (CaO)\textsubscript{0.125}(SiO\textsubscript{2})\textsubscript{0.75}·(H\textsubscript{2}O)\textsubscript{2.5}</td>
<td>–7.9</td>
<td>–2560</td>
<td>–2831</td>
<td>153</td>
<td>231</td>
<td>85</td>
<td>[40]</td>
</tr>
<tr>
<td>INFCA: (CaO)\textsubscript{0.5}(SiO\textsubscript{2})\textsubscript{0.4}·(H\textsubscript{2}O)\textsubscript{1.875}</td>
<td>–8.9</td>
<td>–2343</td>
<td>–2551</td>
<td>154</td>
<td>181</td>
<td>59.3</td>
<td>[40]</td>
</tr>
<tr>
<td>INFCA: (CaO)\textsubscript{0.5}(SiO\textsubscript{2})\textsubscript{0.4}·(H\textsubscript{2}O)\textsubscript{1.375}·(H\textsubscript{2}O)\textsubscript{0.875}</td>
<td>–11.2</td>
<td>–2468</td>
<td>–2652</td>
<td>212</td>
<td>165</td>
<td>77.5</td>
<td>[41]</td>
</tr>
<tr>
<td>Phillipsite (K)</td>
<td>–24.27</td>
<td>–4460</td>
<td>–4842</td>
<td>391</td>
<td>351</td>
<td>149</td>
<td>[50]</td>
</tr>
<tr>
<td>Phillipsite (Ca)</td>
<td>–21.99</td>
<td>–4441</td>
<td>–4824</td>
<td>342</td>
<td>321</td>
<td>151</td>
<td>[50]</td>
</tr>
<tr>
<td>K-shlykovite (K\textsubscript{2}Ca\textsubscript{8}Si\textsubscript{10}O\textsubscript{22}·2H\textsubscript{2}O)</td>
<td>–25.8 ± 2.0 (80 °C) (^{\text{b}})</td>
<td>–27.5 ± 0.9 (40 °C) (^{\text{b}})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>This study</td>
</tr>
</tbody>
</table>

\(\text{K-shlykovite} (\text{K}_2\text{Ca}_8\text{Si}_{10}\text{O}_{22}·2\text{H}_2\text{O})\) of the relevant species were calculated using the extended Debye–Hückel equation as detailed in Section 2.3.

\(\gamma\) is the activity coefficient of the species in mol/kg H\textsubscript{2}O.

The asterisks for the T2C\textsuperscript{*}, T5C\textsuperscript{*} and TobH\textsuperscript{*} end-members indicate that they have the same bulk chemistry but slightly modified thermodynamic properties relative to the T2C, TSC and ToH end-members of the downscaled GSH model as explained in \[46\].

\(^{a}\) All thermodynamic products refer to the reaction with respect to Al(OH)\textsubscript{4}−, Ca\textsuperscript{2+}, K\textsuperscript{+}, OH\textsuperscript{−}, SiO\textsubscript{2}\textsuperscript{2−} and H\textsubscript{2}O.

\(^{b}\) The solubility product of K-shlykovite refers to 80 °C: 

\[K_{50} (\text{K}_2\text{Ca}_8\text{Si}_{10}\text{O}_{22}·2\text{H}_2\text{O}) = \frac{[\text{K}^+]^{0.5}·[\text{Ca}^{2+}]^{0.5}·[\text{SiO}_2^{2-}]^{1.1·\text{H}_2\text{O}^{0.5}}{[\text{K}_2\text{Ca}_8\text{Si}_{10}\text{O}_{22}·2\text{H}_2\text{O}]^0}\]

### Table A2

The measured concentration and pH of the solution after dissolution.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Si</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Al</th>
<th>pH(^{\text{c}})</th>
<th>(\log_{10} K_{50}, 40^\circ\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.8 Å, 1</td>
<td>29.79</td>
<td>0.072</td>
<td>54.31</td>
<td>0.012</td>
<td>0.001</td>
<td>11.80</td>
<td>–28.6</td>
</tr>
<tr>
<td>10.8 Å, 2</td>
<td>18.93</td>
<td>0.084</td>
<td>54.32</td>
<td>0.082</td>
<td>0.000</td>
<td>10.77</td>
<td>–26.6</td>
</tr>
<tr>
<td>10.8 Å, 3</td>
<td>23.02</td>
<td>0.086</td>
<td>54.09</td>
<td>0.044</td>
<td>0.000</td>
<td>10.97</td>
<td>–26.9</td>
</tr>
<tr>
<td>10.8 Å, 4</td>
<td>29.93</td>
<td>0.078</td>
<td>51.04</td>
<td>0.022</td>
<td>0.001</td>
<td>11.57</td>
<td>–27.9</td>
</tr>
</tbody>
</table>

\(^{c}\) pH values measured at 23 °C.

\(^{\text{b}}\) The average value –27.5 ± 0.9 is used for thermodynamic calculations.

References


