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Structural evolution of synthetic alkali-activated CaO-MgO-Na$_2$O-Al$_2$O$_3$-SiO$_2$

materials is influenced by Mg content

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Appendix A

Table S1: Bulk oxide composition of each powder formulation as determined by X-ray fluorescence analysis. An error of approximately 1 wt. % is expected.

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<th>Sample</th>
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<th>Al$_2$O$_3$</th>
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</table>
Appendix B: BSE images and SEM-EDX data for additional samples not shown in main text

**Figure S1:** ESEM back-scattered electron (BSE) image and elemental maps of alkali-activated sample B cured for 180 days

**Figure S2:** ESEM back-scattered electron (BSE) image and elemental maps of alkali-activated sample C cured for 180 days

**Figure S3:** ESEM back-scattered electron (BSE) image and elemental maps of alkali-activated sample E cured for 180 days
Figure S4: ESEM back-scattered electron (BSE) image and elemental maps of alkali-activated sample F cured for 180 days.

Figure S5: ESEM back-scattered electron (BSE) image and elemental maps of alkali-activated sample G cured for 180 days.

Figure S6: ESEM back-scattered electron (BSE) image and elemental maps of alkali-activated sample H cured for 180 days.
Figure S7: ESEM back-scattered electron (BSE) image and elemental maps of alkali-activated sample I cured for 180 days

Figure S8: ESEM back-scattered electron (BSE) image and elemental maps of alkali-activated sample J cured for 180 days

Figure S9: ESEM back-scattered electron (BSE) image and elemental maps of alkali-activated sample K cured for 180 days
Figure S10: Projection of alkali-activated material chemistry onto the ternary CaO – Al₂O₃ – SiO₂ system (neglecting Na₂O and MgO content) showing elemental composition of AAMs cured for 3, 28 and 180 days for samples A, B and C (Ca/(Al+Si) = 0.67 and Al/Si = 0.05) as marked, as determined by ESEM-EDX analysis. A random selection of points evenly distributed across a representative 500 µm × 500 µm section of the sample were used for analysis. Approximate regions of C-S-H and C-(N)-A-S-H determined from [1] and [2].
Figure S11: Projection of alkali-activated material chemistry onto the ternary CaO – Al₂O₃ – SiO₂ system (neglecting Na₂O and MgO content) showing elemental composition of AAMs cured for 3, 28 and 180 days for samples D, E and F (Ca/(Al+Si) = 0.67 and Al/Si = 0.15) as marked, as determined by ESEM-EDX analysis. A random selection of points evenly distributed across a representative 500 µm × 500 µm section of the sample were used for analysis. Approximate regions of C-S-H and C-(N)-A-S-H determined from [1] and [2].
**Figure S12:** Projection of alkali-activated material chemistry onto the ternary CaO – Al₂O₃ – SiO₂ system (neglecting Na₂O and MgO content) showing elemental composition of AAMs cured for 3, 28 and 180 days for samples G, H and I (Ca/(Al+Si) = 1.00 and Al/Si = 0.05) as marked, as determined by ESEM-EDX analysis. A random selection of points evenly distributed across a representative 500 µm × 500 µm section of the sample were used for analysis. Approximate regions of C-S-H and C-(N)-A-S-H determined from [1] and [2].
Figure S13: Projection of alkali-activated material chemistry onto the ternary CaO – Al₂O₃ – SiO₂ system (neglecting Na₂O and MgO content) showing elemental composition of AAMs cured for 3, 28 and 180 days for samples G, H and I (Ca/(Al+Si) = 1.00 and Al/Si = 0.15) as marked, as determined by ESEM-EDX analysis. A random selection of points evenly distributed across a representative 500 µm × 500 µm section of the sample were used for analysis. Approximate regions of C-S-H and C-(N)-A-S-H determined from [1] and [2].
Figure S14: Projection of alkali-activated material chemistry onto the ternary MgO – Al₂O₃ – SiO₂ system (neglecting CaO and Na₂O content) showing elemental composition of AAMs cured for 3, 28 and 180 days for samples A, B and C (Ca/(Al+Si) = 0.67 and Al/Si = 0.05) as marked, as determined by ESEM-EDX analysis. A random selection of points evenly distributed across a representative 500 µm × 500 µm section of the sample were used for analysis.
Figure S15: Projection of alkali-activated material chemistry onto the ternary MgO – Al₂O₃ – SiO₂ system (neglecting CaO and Na₂O content showing elemental composition of AAMs cured for 3, 28 and 180 days for samples D, E and F (Ca/(Al+Si) = 0.67 and Al/Si = 0.15) as marked, as determined by ESEM-EDX analysis. A random selection of points evenly distributed across a representative 500 µm × 500 µm section of the sample were used for analysis.
Figure S16: Projection of alkali-activated material chemistry onto the MgO – Al₂O₃ – SiO₂ system (neglecting CaO and Na₂O content) showing elemental composition of AAMs cured for 3, 28 and 180 days for samples G, H and I (Ca/(Al+Si) = 1.00 and Al/Si = 0.05) as marked, as determined by ESEM-EDX analysis. A random selection of points evenly distributed across a representative 500 µm × 500 µm section of the sample were used for analysis.
Figure S17: Projection of alkali-activated material chemistry onto the ternary MgO – Al₂O₃ – SiO₂ system (neglecting CaO and Na₂O content) showing elemental composition of AAMs cured for 3, 28 and 180 days for samples G, H and I (Ca/(Al+Si) = 1.00 and Al/Si = 0.15) as marked, as determined by ESEM-EDX analysis. A random selection of points evenly distributed across a representative 500 µm × 500 µm section of the sample were used for analysis.
Figure S18: Projection of alkali-activated material chemistry onto the ternary Na$_2$O – Al$_2$O$_3$ – SiO$_2$ system (neglecting CaO and MgO content) showing elemental composition of AAMs cured for 3, 28 and 180 days for samples A, B and C (Ca/(Al+Si) = 0.67 and Al/Si = 0.05) as marked, as determined by ESEM-EDX analysis. A random selection of points evenly distributed across a representative 500 µm × 500 µm section of the sample were used for analysis.
Figure S19: Projection of alkali-activated material chemistry onto the ternary Na₂O – Al₂O₃ – SiO₂ system (neglecting CaO and MgO content) showing elemental composition of AAMs cured for 3, 28 and 180 days for samples D, E and F (Ca/(Al+Si) = 0.67 and Al/Si = 0.15) as marked, as determined by ESEM-EDX analysis. A random selection of points evenly distributed across a representative 500 µm × 500 µm section of the sample were used for analysis.
**Figure S20:** Projection of alkali-activated material chemistry onto the ternary Na₂O – Al₂O₃ – SiO₂ system (neglecting CaO and MgO content) showing elemental composition of AAMs cured for 3, 28 and 180 days for samples G, H and I (Ca/(Al+Si) = 1.00 and Al/Si = 0.05) as marked, as determined by ESEM-EDX analysis. A random selection of points evenly distributed across a representative 500 µm × 500 µm section of the sample were used for analysis.
Figure S21: Projection of alkali-activated material chemistry onto the ternary Na$_2$O – Al$_2$O$_3$ – SiO$_2$ system (neglecting CaO and MgO content) showing elemental composition of AAMs cured for 3, 28 and 180 days for samples J, K and L (Ca/(Al+Si) = 1.00 and Al/Si = 0.15) as marked, as determined by ESEM-EDX analysis. A random selection of points evenly distributed across a representative 500 µm × 500 µm section of the sample were used for analysis.
**Figure S22**: Summary of bulk atomic ratios Ca/Si versus Si/Al (60 measurements per sample) for the alkali-activated material for samples A – L cured for 3, 28 and 180 days as indicated.
Figure S23: Summary of bulk atomic ratios Mg/Si versus Si/Al (60 measurements per sample) for the alkali-activated material for samples A – L cured for 3, 28 and 180 days as indicated
Appendix C: Attenuated total reflectance Fourier transform infrared spectroscopy.

ATR-FTIR spectra collected for precursor powders are presented in Figure S24. A broad, intense band is observed at 894 cm\(^{-1}\) and a shoulder can also be observed at 995 cm\(^{-1}\) in the spectra of all precursors. These bands are attributed to stretching vibrations of Si-O-T bonds (T = Si or Al) due to a highly depolymerised silica network and consistent with that observed in GGBFS [3-6]. A small band at approximately 465 cm\(^{-1}\) is also observed in the spectra of all precursors and is attributed to symmetrical bending of Si-O-T bonds, respectively [7].

The spectra of all precursors exhibit bands at approximately 1460 cm\(^{-1}\) and 1415 cm\(^{-1}\) which are attributed to asymmetric stretching of O-C-O bonds in CO\(_3^{2−}\) present in different polymorphs of CaCO\(_3\) (vaterite and calcite, respectively) which has formed as a consequence of reaction of free lime with CO\(_2\) during calcination [3, 6, 8]. A shoulder at 850 cm\(^{-1}\) is also observed in the spectra of the precursor for all samples and is likely due to the presence of HCO\(_3^−\) formed via reaction of adsorbed water and CO\(_2\) [9].

The sharp band at 875 cm\(^{-1}\) in the spectra of all precursors is attributed to asymmetric stretching of AlO\(_4^−\) groups in Al-O-Si bonds within the polymerised aluminosilicate phase [3, 4]. A small bands at 713 cm\(^{-1}\) is also observed in the precursor for all samples and is associated with bending vibrations of internal oxygen bridges Si-O-Al are [10] as well as pseudo-lattice vibrations occurring within 3- and 4-unit aluminosilicate rings comprised of TO\(_4\) tetrahedra [10-14]. A small bands observed at 508 cm\(^{-1}\) in the spectra of all precursors is attributed to O-Si-O bending vibrations [15] and 5 membered single rings and 6 membered double rings comprising of TO\(_4\) tetrahedral units [10].

The vibration modes present in the ATR-FTIR spectra of the precursor for all samples are consistent with calcium, silicon and aluminium bonding environments commonly observed in GGBFS [3, 9], calcium aluminosilicate glasses [4, 13] and Mg-free synthetic calcium aluminosilicate powders synthesised using the same method [6]. These modes are also consistent with a heterogeneous
mixture of a depolymerised calcium silicate phase and a polymerised aluminosilicate phase within the amorphous phase identified by XRD [6, 16].

**Figure S24:** ATR-FTIR spectra of the precursor powder and alkali-activated material for samples A – L cured for 3, 28 and 180 days as indicated
References


