Mineralization Dynamics of Metakaolin-based Alkali-Activated Cements

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Abstract

This paper investigates the early-age dynamics of mineral formation in metakaolin-based alkali-activated cements. The effects of silica availability and alkali content on mineral formation were investigated *via* X-ray diffraction and solid-state ²⁹Si magic-angle spinning nuclear magnetic resonance at 2, 7, 14, and 28 days. Silica availability was controlled by using either liquid- (immediate) or solid-based (gradual) sodium silicate supplements. Mineral (zeolitic) and amorphous microstructural characteristics were correlated with observed changes in bulk physical properties, namely shrinkage, density, and porosity. Results demonstrate that, while alkali content controls the mineralization in immediately available silica systems, alkali content controls the silica availability in gradually available silica systems. Immediate silica availability generally leads to a more favorable mineral formation as demonstrated by correlated improvements in bulk physical properties.

Keywords: D. Alkali-Activated Cement, D. Metakaolin, B. X-Ray Diffraction, C. Stability, Nuclear Magnetic Resonance (Nominated Keyword)

1. Introduction

The long-term durability of alkali-activated cements (AACs) depends on the stability of the aluminosilicate system, which is comprised of aluminosilicate minerals, mainly zeolites, and an amorphous phase that largely resembles a gel precursor to zeolite formation. It is well known that zeolites are thermodynamically metastable and can restructure into higher-stability zeolites over time. Similarly, the amorphous phase, which is less thermodynamically stable, has exhibited a potential to order into zeolitic minerals [1].

The formation and composition of amorphous phases, which is influenced by soluble silica, alkali content, and both curing time and temperature, dictate both the type and rate of potential zeolite formation [2] and influence the development of nano- and microstructures and influence both short-term material properties (e.g., compressive strength, porosity) and long-term durability [3]–[6] of AACs. Previous studies found that increasing soluble silica

contents in alkali-activating solutions affect short- and long-term mineral dynamics by retarding zeolite formation [4]. In addition, the presence of soluble silica species has been shown to impact reaction kinetics of aluminosilicate precursors (e.g., metakaolin) that form amorphous phases [7]. For example, AACs with initially higher amorphous contents have exhibited greater increases in compressive strength over time, due to a thermodynamic restructuring into more ordered crystalline phases [3], [5].

Most previous studies have utilized pure liquid sodium silicate (NaSi) solutions to provide immediately available silica during alkali activation, while other researchers have investigated the utilization of recycled waste glass to produce NaSi solutions [8], [9], [10]. Studies implementing waste-glass-derived liquid NaSi solutions in fly ash- and slag-based AAC materials found no significant microstructural changes between such systems and those using industrially produced NaSi solutions [11], [12]. In 2015, Bobirica, et al., [13] studied ground waste glass as a solid NaSi supplement to fly ash- and fly ash/slag-based AACs. In this study, samples that included both liquid and solid NaSi supplements demonstrated improved mechanical properties compared to those that were solely glass-supplemented. While these studies demonstrate the impact of liquid versus solid NaSi supplements on bulk material properties, no studies have mechanistically investigated the effect of silica availability and alkali content on the mineralization dynamics of AACs.

1.2 Scope of work

The purpose of this study was to isolate and investigate the effects of time-dependent silica dissolution on early-age mineral formation and stabilization in MK-based AACs. In this work, two MK-based systems were investigated, namely (1) a system activated with a conventional sodium hydroxide (NaOH) and liquid sodium silicate (NaSi) solution (rapid silica dissolution) and (2) a system activated with NaOH and a NaSi solution with additions of solid waste glass (slow silica dissolution). The effect of Na:Si ratio on the time-dependent mineralization dynamics at the nanoscale was explored in both systems using X-ray diffraction (XRD) and solid-state ²⁹Si magic angle spinning nuclear magnetic resonance (MAS-NMR). In addition, observable mineral dynamics were correlated with macroscale changes in bulk material properties, namely shrinkage, density, and permeable porosity.

2. Materials and Experimental Methods

2.1 Materials

Metakaolin (MK) (MetaMax) was supplied by BASF Chemical Corporation (Georgia USA). **Table 1** shows the chemical composition of MK, which was obtained *via* inductively coupled optical emission spectrometry (ICP-OES)

using a modified technique developed by [14]. Five mL of a 7:3 mixture of hydrochloric acid and hydrofluoric acid is combined with 2 mL of nitric acid and placed in the digestion tubes and heated to 95°C in a digestion block (HotBlock by Environmental Express) for approximately two hours. Samples were then cooled and brought up to 50 mL with a 1.5% by weight boric acid solution. The samples were then reheated to 95°C for about 15 minutes and cooled for analysis. The samples were diluted 10x and analyzed with an ARL 3410+ ICP-OES. A blank and three standards, which were made by accurately diluting certified standards, were used for calibration. The raw MK was supplemented either with a reagent-grade sodium silicate (NaSi) solution supplied by Sigma Aldrich or waste soda-lime glass. The chemical composition of the NaSi solution was determined to have a Na:Si weight modulus of 2.5, as obtained *via* ICP-OES. Clear waste soda-lime glass was collected from a recycling waste stream at the University of Colorado Boulder, soaked in a diluted nitric acid bath (5% acid by volume) for 12 hours, and washed thoroughly with Alkanox cleaning agent to remove any acidity and residue. Glass was subsequently ground in mill capsules with clean and well-packed yttrium-stabilized zirconium grinding beads (American Elements) at a rate of 0.2 g/min using a McCrone micronizing mill. A No. 325 sieve was used to ensure a sub-45 µm particle size. The chemical composition of the waste glass was measured with the same protocol as MK and is also shown in **Table 1**. Reagent-grade NaOH pellets with >97% chemical purity (No. S5881) were supplied by Sigma-Aldrich.

Table 1. Chemical composition of MK and waste glass in weight percent.

(wt.%)	SiO ₂	Al ₂ O ₃	CaO	SO ₄	Fe ₂ O ₃	K ₂ O	Na ₂ O	P ₂ O ₅
MK	54%	47%	0.1%	0.3%	0.4%	0.1%	0.3%	0.1%
Glass	80%	1.6%	12%	0.6%	0.1%	0.7%	13%	-

2.2 Experimental methods

2.2.1 AAC sample preparation

In this study, two classes of AACs were prepared with liquid-based NaSi (N) and solid-based, waste-glass-supplemented, NaSi (G) solutions with varying molar concentrations – high (H), medium (M), and low (L) – according to the prescribed mix-design parameters shown in **Table 2**. In these specific mixture formulations, liquid-to-solid (L:S) ratios were 1.5 ml/g for G- samples and 2.25 ml/g for N- samples to ensure complete reaction during mixing. Constant Si:Al ratio of 2.0 for all samples permitted explicit investigation of the effect of Na:Si ratio on the mineralogical evolution in these two AAC systems.

NaOH solutions of different molar concentrations were prepared for each sample to obtain the specified Na:Si ratios, as seen in **Table 1**, by dissolving NaOH pellets in deionized water under continuous agitation using a

magnetic stir bar. Dissolution was performed in a temperature-controlled cold room (4°C) to minimize evaporation due to the exothermic nature of NaOH hydration. Once the NaOH solutions were prepared, the corresponding amount of NaSi solution was added and the new solution was left to equilibrate for approximately two hours in the cold room prior to mixing with N- samples. For the glass-based samples, waste glass was added as a solid silica supplement directly to the MK to prevent any glass dissolution prior to sample preparation.

Solids were mixed with their respective alkali-activating solutions to produce MK-based AACs that were silica-supplemented with glass (G- samples) or liquid NaSi solutions (N- samples). All materials were mixed at room temperature using a Waring PDM112 mixer. The mixing procedure consisted of one minute of initial mechanical mixing, followed by one minute of hand mixing to ensure no material was unmixed on the sides of the vessel. Hand mixing was followed by three minutes of additional mechanical mixing to ensure homogeneity.

Table 2. Sample classifications and mixture proportions for MK-based alkali-activated cements. Na:Si ratios were varied by controlling the amount of NaOH used in preparation of the alkali-activating solution.

Mixes	Constituent Materials					
	Solids		Alkali-Activating solution		Important Parameters	
	MK (g)	SiO ₂ Glass (g)	NaSi (ml)	NaOH (M)	Si:Al	Na:Si
NH	60	-	90	17	2.0	1.0
NM	60	-	90	6	2.0	0.6
NL	60	-	90	1	2.0	0.5
GH	60	42.3	-	8	2.0	0.9
GM	60	42.3	-	4	2.0	0.5
GL	60	42.3	-	2	2.0	0.3

Paste samples were cast in flat disk molds (diameter 5.2 cm) for X-ray diffraction (XRD) and solid-state magic-angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy and cylindrical molds (diameter 2.7 cm, height 10 cm) for density, shrinkage, and permeable porosity testing. Samples were then cured inside hermetically sealed plastic containers that maintained a 100% constant relative humidity condition. The constant-humidity chamber was prepared according to ASTM E104 by placing a supersaturated salt solution of sodium phosphate (Sigma Aldrich) inside the plastic containers. The containers were placed inside a Quincy forced-air laboratory oven set to 60°C. The temperature and humidity in each chamber was recorded using an EL-USB-2-LCD temperature and humidity data logger from Lascar Electronics, respectively. Samples were allowed to cure for 2, 7, 14, and 28 days. The containers were opened for 24 hours prior to the day of testing to allow samples to dry at 60°C. Samples were subsequently submerged in acetone (ACS-certified, 0.2 % H₂O, Fisher Scientific) for 15 minutes to halt hydration

and then submerged in anhydrous ethanol (200 proof, 0% H₂O, Decon Labs) for 15 minutes to halt alkali activation prior to experimental testing [11].

2.2.2 X-Ray Diffraction (XRD)

To determine mineralogy, flat disk samples were first crushed into a powder with a mortar and pestle. The powder was then prepared for analysis using a modified method based on [15]. First, the powder was homogenized and split into a representative aliquot. 1000±0.5 mg of the powdered sample was mixed with 250±0.5 mg of corundum (American Elements) as an internal standard and added to a mill capsule containing clean, well-packed yttrium-stabilized zirconium grinding beads. The mixture was subsequently ground using a McCrone micronizing mill with 4 mL ethanol for 5 minutes, generating particle sizes with 95% below 30 µm, measured *via* Malvern Mastersizer 3000 laser diffraction system. A slurry of the mixture was created by adding approximately 25 mL of ethanol and then dried overnight at 60 °C in a laboratory oven. The sample was then placed into a plastic scintillation vial with three Delrin balls. 500 µL of Vertrel cleaning agent (Miller-Stephenson) was added to the sample to generate aggregates with random particle orientation. The scintillation vial was then mixed for ten minutes in a SK-L330 Pro mechanical shaker. Finally, the samples were sieved through a 250 µm mesh and packed into XRD analysis plates.

A Siemens D500 X-ray diffractometer was used to acquire diffraction patterns for all samples. Samples were analyzed from 5 to 65 degrees 2θ using Cu Kα X-ray radiation with a step size of 0.02 degrees and a dwell time of 2 seconds per step. Mineralogy was identified using Jade software (MDI, version 9) and the International Centre for Diffraction Data (ICDD) 2003 database. Corundum was used to normalize peak heights between samples and to align diffraction patterns.

2.2.3 Solid-state ²⁹Si Magic Angle Spin-Nuclear Magnetic Resonance (²⁹Si MAS-NMR)

Solid-state ²⁹Si MAS-NMR spectra were acquired using a Varian INOVA 400 spectrometer (magnetic field 9.39 T; operating frequency of 12.1 KHz for ²⁹Si). ²⁹Si chemical shifts were determined using the absolute spectrometer frequency, calibrated such that the NMR signal from DSS (trimethylsilyl propane sulfonic acid, sodium salt) appeared at 0.0 ppm. Calibrated chemical shifts were referenced to TMS within 1 ppm, resulting in a 5-6 ppm shift upfield to the aluminosilicate NMR signal reference as reported by Klinowski, et al. [16]. The accuracy of DSS or TMS referencing was verified *via* MAS ¹H NMR of DSS by setting the proton to 0.0 ppm and using absolute referencing for the ²⁹Si spectra. Thus, peak shifts using DSS and TMS as standards were verified and found to only differ by -1.5ppm. For the acquisition of ²⁹Si spectra, samples were packed into 4 mm zirconia rotors sealed at either

end with Teflon end plugs, and spun at 12.2 kHz in a Varian probe equipped with a 4mm MAS spinning module designed and manufactured by Revolution NMR, LLC (Fort Collins, CO). The spectra were acquired over 1024 scans using a pulse recycle delay of 5 s, a pulse width of 4.5 μ s and an acquisition time of 20 ms. Each spectrum took on average approximately 90 minutes to acquire. Deconvolution of NMR data was performed using NUTS[®] software developed by Acorn NMR, Inc. All specimens were fully dehydrated to ensure that the presence of well-resolved peaks in the spectra presented here indicate ordered silicon environments and not the presence of free soluble silicon components in the pore solution.

2.2.4 Dimensional shrinkage and density

Dimensional shrinkage was calculated as the percent difference in average diameter of samples prior to bulk permeable porosity tests and initial diameter of the cylindrical molds. The diameters and heights of cylindrical samples were measured using calipers. Using the measured volume and weights of samples from the bulk permeable porosity the density for each sample was calculated.

2.2.5 Bulk permeable porosity

Permeable porosities were measured using a vacuum-method (ASTM C1202). This method was selected due to its proven higher efficiency when compared to other laboratory methods of calculating permeable porosity [17]. The standard was modified by utilizing anhydrous ethanol in lieu of water to prevent any further alkali-activation or reaction with water. Cylinder samples were first demolded after the 24-hour drying time. A Milwaukee 6-in diameter angle grinder (9000 rpm) with a 3M polishing disc was used to grind the bottom and tops of cylinder samples. Sample volumes were calculated by measuring the diameters and heights using calipers. Additionally, samples were subjected to a vacuum of 508 mm-Hg for 24 hours. The saturated surface dry (SSD) weight was recorded using a Mettler Toledo PL 1502E scale after ethanol-vacuum immersion. Samples were then dried at 60°C for 24 hours and their oven-dry (OD) weights were recorded. Permeable porosity was calculated as the difference in SSD mass and OD mass normalized by the density of ethanol (0.803 g/cm³) all divided by the total sample volume.

3. Experimental Results and Discussion

3.1 Time-dependent mineralogy

Mineralogical data were acquired *via* XRD for all AAC pastes at four different curing ages. **Table 3** describes the main aluminosilicate minerals identified in at least one sample with their respective unit geometries, volumes, and

densities, as determined by each reference standard. XRD patterns shown in **Figure 1** and **Figure 2** explicitly show the presence or absence of those minerals in each N- and G- sample, respectively, at 2, 7, 14, and 28 days.

Table 3. Summary of aluminosilicate minerals of interest found *via* XRD with their corresponding symbols. Mineral shapes, unit volumes, and densities have been obtained using the Jade5 zeolite database reference standard. Symbols correspond to peak identification in **Figure 1** and **Figure 2**.

Mineral Name	Stoichiometry	Si:Al	Symbol	Shape	Unit Volume ($\text{\AA}^3$)	Density (g/cm^3)	Reference
Zeolite ZSM-3	$\text{Na}_{1.88}\text{Al}_2\text{Si}_{2.77}\text{O}_{9.48}$	1.39	⊖	Hexagonal	13,671	2.60	[18]
Zeolite A ^(a)	$\text{Na}_2\text{Al}_2\text{Si}_{1.71}\text{P}_{0.48}\text{O}_{8.6}-4.32\text{H}_2\text{O}$	~ 1.0	*	Cubic	1,843	2.16	[19]
Zeolite Na-P	$\text{Na}_{3.6}\text{Al}_{3.6}\text{O}_3\text{Si}_{12.4}\text{O}_{32}-14\text{H}_2\text{O}$	3.44	o	Tetragonal	1,009	2.13	[20]
Sodalite	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2(\text{H}_2\text{O})_2$	1.00	▼	Cubic	703	2.46	[21]
Phillipsite-K	$(\text{K},\text{Na})_2(\text{Si},\text{Al})_8\text{O}_{16}-4\text{H}_2\text{O}$	1.00	□	Monoclinic	1,017	2.22	[22]
Zeolite P1	$\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}(\text{H}_2\text{O})_{12}$	1.67	†	Tetragonal	1,013	2.21	[23]
Faujasite-Na	$\text{Na}_{1.84}\text{Al}_2\text{Si}_4\text{O}_{11.92}-7\text{H}_2\text{O}$	2.00	+	Cubic	15,550	2.02	[24]
Zeolite 5A ^(b)	$\text{NaCaAl}_3\text{Si}_3\text{O}_{12.28}\text{I}_{2.8}$	1.00	‡	Cubic	1,856	3.24	[25]

^(a) XRD pattern corresponds to Zeolite A with partial replacement of Si-O bonds with P-O bonds, no significant framework change is reported in [19]. ^(b) XRD pattern corresponds to Zeolite 5A subjected to iodide absorption; no significant framework changes are reported in [25].

In general, the N- samples exhibit lower mineral diversity and broader peak patterns, indicating a higher disordered mineral structure and/or smaller effective particle size in comparison to the G- samples. In addition, high alkali content promoted early formation of zeolite mineral phases in both N- and G- systems. For example, Faujasite-Na is formed after 2 days in NH samples (**Figure 1a**), while NL samples (**Figure 1c**) exhibit Faujasite-Na formation after 14 days. Sodium carbonate (natrite, Na_2CO_3) was only present in the diffraction patterns of N- samples, suggesting that the sodium in N- samples is more readily available to react with ambient carbon dioxide.

Figure 1. XRD spectra of NH (a), NM (b), and NL(c) samples at 2, 7, 14, and 28 days. Vertical grey lines correspond to the corundum internal standard. Mineral symbols are defined in **Table 3**.

Figure 2. XRD spectra of GH (a), GM (b), and GL (c) samples at 2, 7, 14, and 28 days. Vertical grey lines correspond to the corundum internal standard. Mineral symbols are defined in **Table 3**.

3.1.1 Time-dependent mineralogy of N- samples

The observed mineral formation process for the NH samples was: Zeolite ZSM-3 + Faujasite-Na $\rightarrow$ Zeolite ZSM-3 + Faujasite-Na + Zeolite Na-P $\rightarrow$ Zeolite ZSM-3 + Faujasite-Na + Zeolite Na-P + Zeolite P1 (**Figure 1a**). The observed mineral formation process for the NM samples was: Phillipsite-K $\rightarrow$ Faujasite-Na + Phillipsite-K + Zeolite P1 (**Figure 1b**). Phillipsite-K is formed at 14 days, increasing in pattern intensity from day 14 to day 28. At 28 days, Phillipsite-K and Zeolite P1 are present. Both minerals have similar unit densities and volumes. NL samples exhibited sparse mineral formation. The observed mineral formation process of the NL samples was: Faujasite-Na $\rightarrow$ amorphous aluminosilicate (**Figure 1c**). The unexpected disappearance of Faujasite-Na at 28 days might be due to a complete amorphization of the mineral at high Si:Na ratios, as previously reported in literature [26].

Immediate silica availability coupled with a high sodium-alkali content yield early zeolite mineral formation. NH samples exhibit early Faujasite-Na formation from an early age of 2 days through 28 days. Decreased sodium-alkali content reduces mineral formation and retards Faujasite-Na formation, as seen in NM (**Figure 1b**) and NL (**Figure 1c**) samples. Faujasite-Na formation might be a result from the mineral stabilization of Zeolite ZSM-3, as previously discussed in literature [18]. Zeolite ZSM-3, a low Si:Al mineral phase, was observed at 2 days in NH samples. The formation of this zeolite may be the result of stabilization of an aluminum-rich gel, as described by Fernandez-Jimenez and Palomo [27]. Such aluminum-rich phases were expected to develop first, given aluminum's higher affinity for dissolution compared to that of silicon [7]. While Zeolite ZSM-3, a synthetic and relatively unstable zeolite, has been reported to convert to Phillipsite (a more stable phase) [23], no Phillipsite was observed in the NH samples under experimental conditions. Instead, Faujasite-Na is observed to form from Zeolite ZSM-3. Previous literature has characterized this mineral stabilization pathway as a loss in the regularity in the cubo-octahedral layer of Zeolite ZSM-3, resulting in the formation of Faujasite-Na [18]. Thus, Zeolite ZSM-3 may give rise to Faujasite-Na, a more stable, yet less dense, mineral [24].

High mineralization rates may degrade the bulk material properties of AACs, as is evident in the NM samples from 14 to 28 days. All N- samples illustrate that, at early ages (2-14 days), increases in alkali content from low (-L) to medium (-M) correspond to relatively little change in overall crystallinity. At later ages (28 days), however, the proportions of crystalline-to-amorphous intensities (C:A Ratio) in both NL and NM samples differ. More specifically, NL samples exhibit the lowest C:A Ratio of all N- samples at 28 days, while NM samples exhibit the

highest C:A Ratio of all N- samples. As a result, NM samples have the highest change in C:A Ratio from 14 to 28 days, indicating a rapid crystallization of the sample during that time period. As discussed in Section 3.3, this abrupt change in crystallinity is critical for understanding and, ultimately, controlling bulk material properties of AACs.

3.1.2 Time-dependent mineralogy of G- samples

The observed mineral formation process for the GH samples was: Zeolite A + Zeolite 5A $\rightarrow$ Zeolite A + Sodalite + Zeolite 5A $\rightarrow$ Zeolite A + Sodalite + Zeolite 5A + Phillipsite-K $\rightarrow$ Zeolite A + Zeolite P1 + Sodalite + Zeolite 5A (**Figure 2a**). G- samples exhibited rapid crystallization as evident by consistently high C:A Ratios obtained in these samples in comparison to the N- samples. For example, at 7 days, sodalite was formed in GH samples. At 28 days, Zeolite P1 was also present, while Phillipsite-K was only observed at 14 days. The observed mineral formation process for the GM samples was: Zeolite A + Zeolite 5A $\rightarrow$ Zeolite A + Faujasite-Na + Zeolite 5A $\rightarrow$ Zeolite A + Faujasite-Na + Zeolite P + Zeolite 5A (**Figure 2b**). The intensity of the diffraction pattern for Zeolite A, an aluminum-rich mineral, increases from day 2 to 14, while, at 28 days, the pattern yields to the formation of geometrically distinct Zeolite P. Faujasite-Na is present in GM samples at both 14 and 28 days. While GL samples exhibit sparse mineral formation, the following mineral formation process was observed: Zeolite A $\rightarrow$ Zeolite A + Zeolite 5A, (**Figure 2c**).

The results suggest that the gradual incorporation of silica into AAC frameworks (due to slow glass dissolution over time) with high alkali content allows for the transformation of the cubic unit cell of Zeolite A into a monoclinic (Phillipsite-K) and later tetrahedral (Zeolite P1) unit cells with successively decreasing dimensions. GH samples at 14 days demonstrate changes in diffraction patterns attributed to decreased Zeolite A and formation of Phillipsite-K. By 28 days, the diffraction pattern of Zeolite A is further reduced and, while Phillipsite-K is no longer observed, Zeolite Na-P1 is present. These results may be indicative of successive solid-solid mineral transformations as suggested by Ostwald's law of successive reactions [28]. The potentially deleterious effect of such solid-solid transformation on bulk porosity is presented in Section 3.3.

The data demonstrate that gradual silica availability (G- samples) and alkali content affects the typology of silicon-rich minerals and leads to increases in the Si:Al ratio of stabilized minerals over time. In general, incorporation of silicon into silicon-rich minerals can lead to unit cell contractions and higher densities of precursor minerals and amorphous gels. For example, in the GM samples, zeolites that formed from day 7 to day 28 exhibited increases in Si:Al ratio. Zeolite A (Si:Al 1) was present on day 2, while Faujasite-Na (Si:Al 2) and Zeolite Na-P

(Si:Al 3.44) are formed by day 28. Increases in Si:Al ratios of zeolites result in mineral phases with higher unit densities and lower unit volumes at later ages compared to those at early ages. Silica availability might reach an optimal level at medium alkali levels. GM samples form silicon-rich Faujasite-Na and Zeolite P. Increasing alkali content hampers the formation of silicon-rich minerals and, instead, forms flexible framework Zeolite Na-P1. Therefore, alkali content, in addition to silica availability, affects mineral variety and typology in gradually available silica systems.

3.1.3 Comparative XRD analysis of N- and G- samples

Figure 3 summarizes the primary short-term mineral formation, transformation, and stabilization processes for each sample investigated herein. Evidence suggests that the N- samples demonstrate early formation of silicon-rich minerals, while G-samples tend to mineralize faster than N-samples, with most minerals possessing low-silicon contents.

The previously proposed theory of nanocrystalline coexistence within the amorphous phase of AACs [29] can be further supported by the herein observed time-dependent increase in crystallinity in all samples. In the N- samples, pattern intensities increase with time. Aging allows for the gradual stabilization of the aluminosilicate framework *via* thermodynamically favored crystalline mineral formation, as suggested by the observed increase in C:A Ratios, presented in the **Supplementary Material**. The observed time-dependent increase in crystallinity might be due to nucleation and growth of nanocrystals larger than 8 nm, which would make them X-ray visible [30]. As explained by Provis, et al., [33] the presence of zeolite nucleation sites dictates the mineralogy present in the microstructure of AACs. Immediate silica availability *via* liquid NaSi solutions result in low mineral formations due to an increased number of silica-competing zeolite nucleation sites. However, alkali hydroxide-activated cements (AACs without liquid NaSi solutions) produce fewer zeolite nuclei, allowing larger crystal development. These crystals which are unable to pack densely within the binder phase result in a more porous material [29]. In this study, gradually available silica systems (G- samples), examples of alkali hydroxide-activated cements, expectedly exhibit higher degrees of crystallization (higher C:A Ratios), compared to the N- samples. Unexpectedly, however, at medium alkali levels (GM samples), the gradual availability of silica forms silicon-rich Zeolite-P (Si:Al ratio of 3.44), a zeolite otherwise only present in NH samples. Also unexpectedly, Faujasite-Na in GM samples is formed earlier, at 14 days, than in NM samples. Therefore, the gradually available silica at this medium alkali content enhances the formation of silicon-rich zeolites. This behavior is unlike the alkali hydroxide-activated cement systems described in

[33] as gradually available silica may reduce the silica competition between zeolite nucleation sites, resulting in silicon-rich mineral formation.

Both gradual (G-) and immediate (N-) silica availability at medium and high sodium-alkali contents ($\text{Na:Si} > 0.5$) promote different formation patterns of gismondine-type framework zeolites, Zeolite P and Zeolite Na-P1, at later ages. XRD patterns at 28 days demonstrate that Zeolite Na-P1 is evident in the GM samples, while Zeolite Na-P is present in NM samples. At these same ages, both Zeolite Na-P1 and Zeolite P are present in NH samples, and only Zeolite Na-P1 is present in GH samples. Investigating the effect of alkali content on the formation of these zeolites in N- samples demonstrate that, as the alkali content decreases, only Zeolite Na-P1 is formed. The opposite trend is observed in G- samples, where high alkali contents form Zeolite Na-P1 and medium alkali contents form Zeolite P. Important differences exist between these minerals. For example, Zeolite P1 is flexible and can be readily distorted, while Zeolite Na-P has a higher silica content and the highest possible gismondine-type symmetry [20], [23]. Therefore, as alkali content decreases in immediately available (N-) silica systems, favorable formation of flexible gismondine-type framework zeolites occurs, while, in contrast, as alkali content decreases in gradually available (G-) silica systems, favorable formation of silicon-rich gismondine-type framework zeolites occurs. As discussed in Section 3.3, different zeolite formation and stabilization pathways induce observable macrostructural changes to bulk physical properties.

Figure 3. Mineral dynamics as silica availability and alkali content vary over time based on observed XRD data for all samples. Quantity of minerals depicted is derived from relative intensity of XRD mineral patterns observed for each sample as time progressed.

3.2 Solid-state ^{29}Si MAS-NMR

3.2.1 MAS-NMR of metakaolin and ground waste glass

The atomic silicon coordination of both raw metakaolin and ground waste glass, which were acquired via ^{29}Si solid-state MAS-NMR, is shown in **Figure 4**. Expectedly, the NMR spectrum for metakaolin is broad (band width: 100 ppm), indicating a highly disordered environment (**Figure 4a**). The main metakaolin peak at -104 ppm corresponds to a predominate $\text{Q}^4(1\text{Al})$ coordination. A secondary peak is observed at -91 ppm, which corresponds to $\text{Q}^4(3\text{Al})$ atomic coordination. The presence of $\text{Q}^4(3\text{Al})$ corresponds to nanostructures with high silicon contents, which, due to silicon's slower rate dissolution compared to aluminum, can decrease the dissolution and precipitation kinetics of the aluminosilicate material. The NMR signal for ground waste glass (**Figure 4b**) was also characterized using a

reference for alkali silicon glasses from the NMR handbook [31]. The main peak at -92 ppm is attributable to Q^2 coordination, while the secondary peak at -101 ppm is attributable to Q^3 coordination.

Figure 4. ^{29}Si solid-state MAS NMR spectra of both (a) metakaolin and (b) ground waste glass, showing deconvoluted components below each spectrum. The main metakaolin peak at -104 ppm corresponds to a predominate $Q^4(1\text{Al})$ coordination. The main glass peak at -92 ppm is attributable to Q^2 coordination in an aluminosilicate system.

3.2.2 ^{29}Si MAS-NMR of N- and G- samples

Deconvolution of NMR spectra was carried out for all N- and G- samples using a modified methodology presented by Duxson, et al. [32], to account for both disordered (amorphous) and ordered (mineral) silicon sites. Following their aluminosilicate gel NMR-fitting methodology, broad Gaussian curves with fixed linewidths of 4-9 ppm were fitted for all silicon-aluminum disordered sites with variable intensities ($Q^4(n\text{Al})$). Fitted curves with linewidths less than 4 ppm were deemed to have ordered silicon sites. Aluminosilicate amorphous material is characterized by a complete distribution of $Q^4(n\text{Al})$, where n varies from 0-4 [33]. Disordered peak positions were allowed to vary within the ranges for each $Q^4(n\text{Al})$ coordination, as determined by [16] in a seminal study of aluminosilicate structures. After disordered silicon sites were fitted, clear ordered silicon sites were fitted with line widths less than 3-4 ppm and a variable intensity to provide an appropriately summed curve fit. Calculation of internal Si:Al ratios could not be compared with known chemical composition of each sample due to mineral formation affecting the

silicon and aluminum contents of the amorphous material. The Si:Al ratio of the amorphous phase was estimated using the following equation [33]:

$$Si/Al = \frac{\sum_{n=0}^4 I_{Si(nAl)}}{\sum_{n=0}^4 \frac{n}{4} I_{Si(nAl)}} \quad \text{Eq. 1}$$

where $I_{Si(nAl)}$ is the intensity of each peak in the deconvoluted disordered ^{29}Si spectra for $n = 0, 1 \dots 4$. While Si:Al ratio is only appropriate to describe the amorphous material content, it is known that mineral formation or creation of large quantities of Si(0Al) will affect this ratio.

Both MK and glass precursors are consumed as a function of time and alkali content as evidenced by decreasing silicon coordination sites within the amorphous phase. The percentages of silicon coordination sites present in the amorphous phases of N- and G- samples at 7, 14, and 28 days are shown in **Figure 5**. The data show that increased alkali content enhances dissolution of both MK and glass. Increased alkali content allows for a lower resonance intensity at -100 ppm, which is attributed to the main resonance of unreacted MK, as seen in **Figure 4**. N- samples experience a decrease in the $Q^4(1Al)$ component (~100 ppm) of the spectra as alkali content increases, implying that the signal resulting from MK has been largely diminished (**Figure 5**). The lower intensity of the $Q^4(1Al)$ component could be a result of unreacted MK being almost completely consumed during the synthesis or disruption of the network from dissolution processes [34]. Increase in C:A ratios, with alkali content further verify that both unreacted and amorphous material are utilized for zeolite formation. Time is suspected to gradually dissolve the MK precursor as $Q^4(1Al)$ sites are diminished from days 7 to 14 in NM and NL samples. This behavior is not observed in NH samples potentially due to a high C:A ratio, see **Supplementary Material**, and early-age mineralization, minimizing the observed decrease in $Q^4(1Al)$ sites (**Figure 5**). G-samples exhibit the similar trend increasing $Q^4(1Al)$ and C:A ratios as alkali content increase. Similar to the lower resonance intensity at -100ppm of MK, G-samples experience an additional, but delayed, decrease in the resonance intensity at -92ppm, attributed to $Q^4(3Al)$ sites of the AAC and Q^2 sites of glass, see **Figure 4**. As seen in **Figure 5**, GM and GL samples reduce the resonances at -92 ppm at later ages of 14 and 28 days. The lower intensity of the region could be a result from a gradual dissolution process of glass at later ages due to lower alkali contents. Lower alkali contents are suspected to achieve lower pH levels in the synthesis of AAC pastes, which would decrease the dissolution process of the glass. Thus, the glass dissolution of GM and GL samples is controlled by a temperature dissolution of silica. This behavior

is not observed in GH samples potentially due to a high C:A ratio, see **Supplementary Material**, and early-age mineralization, minimizing the observed decrease in $Q^4(3Al)$ sites, see **Figure 5**.

Reductions in aluminum-rich atomic sites, namely $Q^4(4Al)$ and $Q^4(3Al)$, and simultaneous increases in available silica coincided with formation of silicon-rich minerals in AAC samples (i.e., Faujasite-Na). Comparison of the NMR $Q^4(nAl)$ sites at 7 and 14 days (see **Figure 5**) demonstrate the shift of the N- samples toward aluminum-rich amorphous phases ($Q^4(4Al)$) with increases in alkali content. The G- samples also exhibit the same trend, but generally exhibit higher percentages of $Q^4(4Al)$ than the N- samples. This finding is consistent with the observed reduction of silicon-rich minerals in these samples *via* XRD (see **Figure 3**). At low alkali levels (e.g., GL), however, this trend is not observed, because the mineralization of these samples is very low, as evidenced by the low C:A Ratios of the XRD patterns. The GM samples, however, form silicon-rich Faujasite-Na and Zeolite P at later ages. Together, these results suggest that the creation of silicon-rich minerals is dependent not necessarily on a high Si:Al ratio, but rather on the availability of silica in conjunction with aluminum-rich atomic sites in the amorphous phase.

Figure 5. Fraction of silicon sites present in the amorphous phase as $Q^4(4Al)$, $Q^4(3Al)$, $Q^4(2Al)$, and $Q^4(1Al)$ for all samples as time varies: 7, 14 and 28 days. NH at 28 days is not presented as no amorphous phase was appropriately fitted according to described methodology.

3.2.3 Disordered and Ordered ^{29}Si atomic site distribution in *N* samples

The presence of ordered silicon sites is indicated for all *N*- samples in **Table 5**, along with the corresponding total deconvolution for all Si(*n*Al) sites. ^{29}Si spectra of *N*- samples were, to a large degree, characteristically disordered. The increases of ordered silicon sites as both time and alkali content increase are consistent with observed XRD data for these samples (see **Figure 3**). Deshielding of the silicon NMR signal is observed at high alkali contents from 7 days with more increases of $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$ sites than medium and low alkali content samples ($\text{NH} > \text{NM} > \text{NL}$). Similarly, ordered silicon sites follow a similar trend with ordered $\text{Q}^4(4\text{Al})$ being the only ordered atomic arrangement in the NH sample. This opposite trend is supported by low alkali samples, which have a higher proportion of shielded silicon sites, $\text{Q}^4(2\text{Al})$, $\text{Q}^4(1\text{Al})$, and $\text{Q}^4(0\text{Al})$ ($\text{NL} > \text{NM} > \text{NH}$), as shown in **Figure 5**.

Table 5. ^{29}Si NMR signal deconvolution for AAC samples at different curing ages. Q_n represents non-tetra-coordinated units.

	Age	Q_n	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)	Si:Al
NH	7 Day	18%	37% ^(a)	38%	0%	6%	1%	1.30
	14 Day	2% ^(a)	39% ^(a)	31% ^(a)	21%	7%	0%	1.47
	28 Day	29% ^(a)	28% ^(b)	13% ^(b)	15% ^(b)	10% ^(b)	5% ^(b)	1.49
NM	7 Day	5%	24%	31% ^(c)	23%	14%	3%	1.52
	14 Day	1%	16%	44% ^(c)	30%	7%	2%	1.51
	28 Day	2%	1% ^(a)	40% ^(a)	43% ^(a)	13% ^(a)	2%	1.79
NL	7 Day	1%	8%	22%	27%	28%	14%	2.18
	14 Day	-	20%	38%	24%	14%	3%	1.55
	28 Day	-	12%	2%	32%	25%	29%	2.81
GH	7 Day	8%	24% ^(a)	59% ^(a)	0%	5%	4%	1.36
	14 Day	9%	25% ^(a)	55% ^(a)	6%	3%	2%	1.73
	28 Day	-	52% ^(a)	26%	15%	5%	2%	1.39
GM	7 Day	9% ^(a)	21%	58% ^(a)	10%	0%	2%	1.32
	14 Day	5% ^(a)	14%	52% ^(a)	17%	7%	4%	1.57
	28 Day	11% ^(a)	17%	43% ^(a)	19%	7%	3%	1.54
GL	7 Day	-	16%	32% ^(a)	14%	16%	22%	1.86
	14 Day	-	10%	37% ^(a)	22%	17%	13%	1.83
	28 Day	-	24% ^(a)	38% ^(a)	0%	20%	18%	1.93

^a Silicon ordered coordination present. ^b Silicon ordered signal fitted with fixed linewidth (2.5 ppm) and ppm shifts.

^c Peaks of high intensity, yet broad linewidth (8 ppm), relating to ordered silicon coordination.

As time progresses, higher silicon magnetic shielding is observed in disordered atomic arrangements of NH and NM samples. While both samples decrease in $\text{Q}^4(4\text{Al})$ content, higher alkali samples experience shifts to lower

resonance frequencies ($Q^4(2,1Al)$) to a greater degree than medium alkali samples ($Q^4(3,2Al)$). As a result there is a greater proportion of Si-O-Si bonds in the amorphous content of the NH at 14 days. The increase of silicon in an aluminosilicate framework decreases its thermodynamic stability, which leads to an increased propensity to form zeolites of higher thermodynamic stability [28]. This propensity is affirmed by the observed increase in C:A Ratios and the formation of silicon-rich minerals, such as Faujasite-Na, as previously discussed.

Limitations of NMR deconvolution of aluminosilicate gels are evident in samples that have varying degrees of mineralization. For example, NMR spectra of medium alkali content samples demonstrate a high intensity, yet broad, peak at $Q^4(3Al)$ (8 ppm line width), suggesting a disordered environment. Such a large line width cannot be confidently deconvoluted using a Gaussian distribution and be classified as a completely disordered atomic environment. While the Duxson, et al., [32] NMR deconvolution methodology might seem applicable, XRD data reveals the presence of Phillipsite-K. Due to probable eclipse of ordered signals within disordered signals, this seemingly amorphous system is, in actuality, a composite system of both mineral and amorphous content. Therefore, the results from this study affirm that this methodology is currently limited only to systems of gel aluminosilicates with no significant mineral formation. Further evidence is provided by NL samples, whose respective disordered sites shift toward higher silicon contents. This shift occurs in tandem with the development of silicon-rich minerals (Faujasite-Na) at 14 days as identified by XRD. However, the highly disordered arrangement of NL samples has not allowed for the clear distinction of an ordered peak within the NMR spectra.

The NH signal corresponded to a highly ordered system (2.5 ppm line width), which limited the analysis of an amorphous phase. Deshielding of silicon's magnetic resonances is observable in NH samples as seen by an increase in $Q^4(4Al)$ sites and Q_n sites (see **Table 5**). Q_n sites correspond to silicon monomers, dimers, and trimers [35]. The occurrence of this deshielding is most significant in NH samples and thus, it is potentially attributable to high alkali content present in the system. As discussed in Duxson, et al., [32] this deshielding might be due to the effects of high alkali content or the high energy penalty associated with the possible formation of Al-O-Al bonds.

3.2.4 Disordered and Ordered ^{29}Si atomic sites distribution in G- samples

The presence of ordered silicon sites is indicated for all G- samples are also shown in **Table 5**. As previously discussed, in gradually available silica systems, the formation of silicon-rich minerals is largely determined by alkali content, as was evidenced by the silicon-rich minerals only observed in the GM samples. Between 14 and 28 days, GM samples formed silicon-rich Zeolite P and Faujasite-Na at high crystallization rates, as determined by the abrupt

changes in C:A Ratios in that timeframe, which was accompanied by minimal changes to the distribution of $Q^4(nAl)$ sites in the amorphous phase between 14 and 28 days (see **Figure 5**). This result is expected, given that the creation of Faujasite-Na and other silica rich minerals partly consumes $Q^4(4Al)$ and $Q^4(3Al)$ sites of the amorphous phase, as previously discussed. This behavior is also observed in GH samples, which exhibited a decrease in silicon rich atomic sites, namely $Q^4(2Al)$, as the amorphous and mineral phase is consumed in the formation of Zeolite P1, another silicon-rich mineral, at 28 days. This result is important as higher alkali contents (Na:Si ~ 1.0) demonstrate a highly dynamic amorphous and crystalline phase than lower alkali contents (Na:Si ~ 0.5) in samples with gradual silica availability. As alkali content decreases, the silicon content of the ordered and disordered sites increase from 14 to 28 days. For example, GH samples have a higher content of $Q^4(4Al)$ sites, while GM and GL retain a higher content of $Q^4(3Al)$ sites (see **Figure 5** and **Table 5**). As a result, gradually available silica spares the solid-solid transformation of the amorphous phase into crystalline zeolites.

As previously discussed, the GM samples were the only samples to form Faujasite-Na and also the only G-samples to exhibit an ordered Q_n formation. The highly deshielded Q_n sites are potentially associated with the formation of silicon-rich zeolites, such as Faujasite-Na, as also seen in the NH samples and, to a lesser extent, the NM samples. This trend is however not observed in NL samples at 14 days, which could be due to an eclipsing of the major disordered silicon sites over those ordered or complete amorphization of Faujasite-Na minerals.

3.3 Bulk physical properties

3.3.1 Density and dimensional shrinkage

The densities and dimensional shrinkages of the N- and G- samples are shown below in **Table 6**. High density and shrinkage values were achieved either *via* formation of Faujasite-Na at steady rates or formation of a prominent amorphous phase. NH samples, for example, which demonstrate early formation of Faujasite-Na (see **Figure 3**) and with a gradual increase in C:A Ratio from 7 to 28 days, also exhibited the highest density of all samples. In contrast, NL samples, which demonstrated no mineral formation at 28 days and low C:A ratios, exhibited the second-highest density and the highest shrinkage at 28 days, which can be attributed to its prominent amorphous phase. ^{29}Si NMR analysis proves that NL samples have a silicon-rich amorphous phase ($Q^4(0Al)$, $Q^4(1Al)$), which also exhibits a high density value, see **Figure 5**. Silicon-rich phases have a greater water content, which would allow greater shrinkage of the samples and densification [36].

Low density and shrinkage values were achieved *via* rapid and increased formation of minerals. The rapid crystallization of NM samples from 14 to 28 days, as indicated by an increase in C:A Ratio exhibit the lowest dimensional shrinkage (2%) and a low density. In general, G- samples exhibit high CA Ratios, indicating high degrees of mineralization. Analysis of the ^{29}Si NMR spectra of GL samples reveals that these samples also have a greater content of silicon-rich amorphous phase ($\text{Q}^4(0\text{Al})$, $\text{Q}^4(1\text{Al})$), than their G- sample counterparts. As a result, GL samples exhibit greater shrinkage than GM and GH samples. However, the shrinkage values are very low compared to N-samples, most probably due to the high crystallization (high C:A Ratios) observed in the G- samples.

Table 6. Density at 28 days and dimensional shrinkage of AAC samples at 7, 14, and 28 days.

N/A denotes that no data was able to be collected for this sample due to incomplete curing.

Sample	Density (g/cm^3)	Shrinkage		
		7 Days	14 Days	28 Days
NH	1.62	11%	4%	15%
NM	0.77	N/A	2%	2%
NL	1.18	16%	11%	16%
GH	0.72	1%	1%	1%
GM	0.74	1%	1%	3%
GL	0.59	4%	2%	3%

3.3.2 Bulk permeable porosity

Figure 6 shows the permeable porosities obtained at 14 and 28 days for all samples. NH samples exhibited the lowest porosity, while GH exhibits the highest porosity of all samples investigated herein. In general, immediate silica availability allows for the retardation of the rate of mineral formation and, thus, achieves favorably lower permeable porosities over time in the range of 21%-62%. Gradual silica availability, however, promotes higher crystallization and corresponding increases in permeable porosity, as evidenced by the G- samples.

As discussed, gradual silica availability allows for solid-solid transformations of zeolite minerals, which can lead to higher permeable porosity. For example, in the GH samples, the probable transformation of the cubic unit cell of Zeolite A into a monoclinic (Phillipsite-K) and, later, a tetrahedral (Zeolite P1) unit cell in the GH samples (see **Figure 3**) correlates to a 6% increase in permeable porosity. While the mechanism of such solid-solid transformation has not been explicitly studied herein, the observed changes are in agreement with Ostwald's law of successive reactions [28]. The increased porosity of GH samples is expected from the abrupt change in C:A Ratio observed from 14 and 28 days.

Mineralization rate and mineral typology suggest a possible direct influence on the bulk permeable porosities of the AACs investigated herein. The presence of Phillipsite-K and Zeolite P1 (gismondine-type frameworks) in the GH and NM samples coincides with increases in permeable porosity. In addition, the formation of Faujasite-Na and high amorphous contents are known to decrease porosity in AACs [1]. Expectedly, the GM samples experience a slight decrease in porosity that can be attributed to late-age Faujasite-Na formation. The early formation of Faujasite-Na, however, coincides with decrease permeable porosity, as observed for NH, NM, NL and GM samples.

Data from the NH and NH samples provide evidence that bulk physical properties can be affected by mineral formation and stabilization pathways. Crystallization rates of AAC paste are important for bulk properties. The NH samples exhibit a much more gradual increase in relative C:A phase intensities, yielding a decrease in permeable porosity. Thus, the high alkali content in NH samples allows for higher crystal phase diffraction intensities in proportion to their bulk amorphous signal at an early age, with not much change at later days. Contrastingly, NM samples exhibit a change of 0.30 from 14 to 28 days, which relates to a 9% increase in permeable porosity. The steady crystallization behavior most exhibited by NH samples may be critical to minimizing permeable porosity development.

As expected, high shrinkage correlates to a dense material due to a tightening of the matrix, which allows for reduction in porosity. As observed in the data, **Table 6** and **Figure 6**, NH and NL samples have both the highest shrinkage and density, which correlate to both decreases in porosity from 14 to 28 days. The shrinkage in both samples can be due to loss of water from a silicon rich amorphous phase composed of $Q^4(0Al)$ and $Q^4(1Al)$, as evident in the NL sample (**Figure 5**). ^{29}Si NMR deconvolution analysis did not discern a distinct amorphous phase in the NH samples at 28 days, yet presence of Q^n sites might be indicative of highly deshielded silicon sites in the amorphous phase. Furthermore, the presence of an amorphous phase can be deduced due to a high shrinkage value as observed in the NL samples.

Figure 6. Bulk permeable porosities of G- and N- samples at 14 and 28 days.

4. Conclusions

This study isolated and investigated the effects of time-dependent silica dissolution on early-age mineral formation and stabilization in MK-based AACs. The effects of immediate and gradual silica availability and alkali content (Na:Si ratio) on the mineralization dynamics at the nanoscale was explored using XRD and solid-state ^{29}Si MAS-NMR and correlated with macroscale changes in bulk physical properties.

The results demonstrate that mineral formation and stabilization pathways in MK-based AACs is dependent not only on Si:Al ratio, but also on both silica availability and alkali content. The time-dependent XRD patterns and NMR spectra, in concert with characterization of bulk physical properties, show that these mineralization and stabilization pathways can have adverse effects on bulk physical properties. For example, the early formation and growth of silicon-rich minerals or the existence of a predominant silicon-rich amorphous phase coincided with reductions in bulk permeable porosity. However, late-age crystallization (amorphous-to-crystalline) and solid-solid (crystalline-to-crystalline) mineralogical transformations, which were observed, both led to increases in porosity. These results demonstrate the importance of understanding and, ultimately, controlling the mineral formation and stabilization dynamics in MK-based AAC systems.

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6. References

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