

Hydrothermal synthesis of crystalline calcium silicate hydrate phases from combustion waste feedstocks

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On my honor as a University Student, I have neither given nor received unauthorized aid on this assignment as defined by the Honor Guidelines for Thesis-Related Assignments

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Abstract

A variety of combustion waste feedstocks rich in either calcia (CaO) or silica (SiO₂) were combined and tested in a hydrothermal synthesis experiment to investigate the precipitation of crystalline calcium silicate hydrate (CCSH) phases or Al-substituted CCSH phases. Three binary mixes were tested at three different time steps with two different mix conditions. The results show that after 7 days, the samples with a higher pH generated more hydrate phases. Many of the samples also formed calcium silicate hydroxide hydrate phases, which can be a precursor to CCSH formation.

Introduction

Concrete is the second most consumed material in the world, surpassed only by water. Nearly all this concrete is made from Ordinary Portland Cement (OPC). OPC is consumed at such high rates that the production of OPC is responsible for nearly 10% of all anthropogenic CO₂ emissions and are only projected to rise as the world continues to develop [1]. This figure is highly concerning, as climate scientists have agreed that a dramatic reduction in CO₂ emissions is necessary to preserve a livable environment on Earth [2]. OPC has been instrumental in developing the world, but it is time to focus on lowering the carbon footprint of the construction industry, beginning with cement production. Industry leaders have committed to lowering emissions, but decarbonizing OPC is not the only solution.

Pseudowollastonite (pwol) based cements are a new class of cements that strengthen through mineral carbonation, in which the introduction of CO₂ to the system promotes the formation of calcium carbonates [2]. Mineral carbonation can be used to both strengthen pwol cements through carbonate formation and sequester atmospheric CO₂. The carbonation of calcium silicate cement can also precipitate crystalline calcium silicate hydrate (CCSH) phases, lauded for their high strength and resistance to acid attack [2]. The prior work on calcium silicate cements has focused on pwol as a model calcium silicate because of its congruent dissolution in water, where calcium and silicon ions dissolve at the same rate. However, the synthesis of pwol is still an energetically intensive process as it is a high-temperature polymorph of wollastonite (CaSiO₃) [3]. The study of pwol-based cements has led to identification of CCSH phases and a better understanding of the chemical mechanisms governing CCSH formation.

Three possible reaction mechanisms from pwol to CCSH phases are shown in Figure 1. Each of the formation routes occur when carbon dioxide dissolves the pwol, leading to Ca²⁺ and SiO₂ in solution with Na⁺ ions from a NaOH buffer solution to increase pH. These ions in solution form carbonates. From these carbonate phases, it is possible CCSH phases can nucleate on carbonates, carbonates can convert to CCSH phases, or that CCSH and carbonate phases form independently. The mechanism for CCSH formation is not fully understood, but prior work has shown that pH and impurity ions have a major influence of CCSH phases [2].

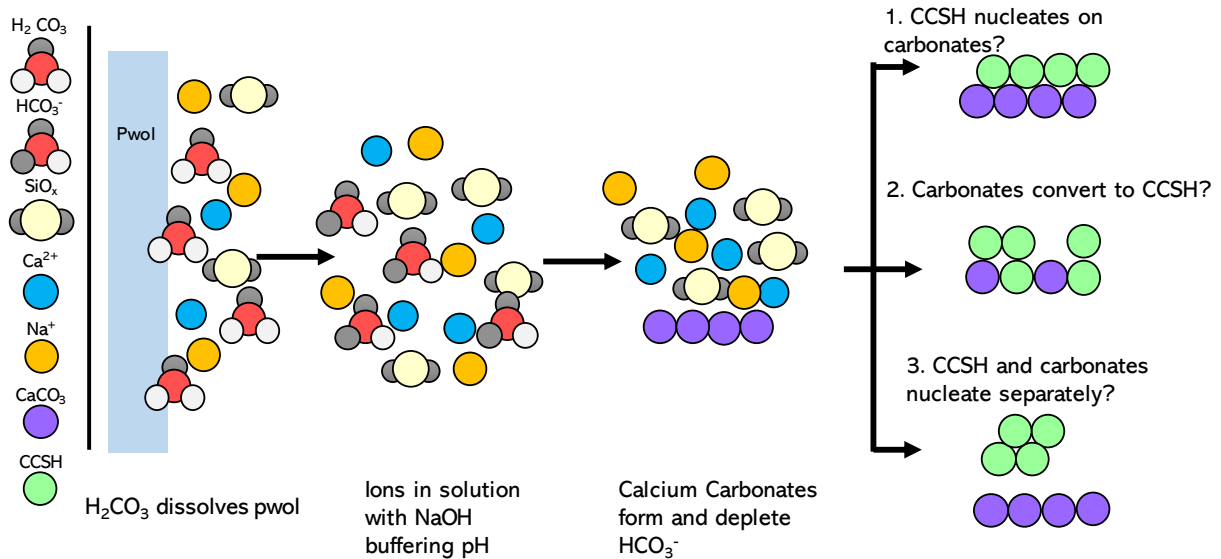


Figure 1: Curing mechanism of pseudowollastonite (pwol) carbonation and three possible routes for formation of CESH phases. Carbonates increase the compressive strength of CCS concrete by reducing density and can act as nucleation sites for desirable CESH phases [5].

Tobermorites are a family of CESHs that are often credited for the high strength and longevity of Roman concrete. Tobermorites have layered structures, where calcium oxide layers and interlayers of Ca^{2+} and water are separated by silica chains, as seen in Figure 2. The tobermorite family is extensive, with variation in the amount of water or amount of Ca^{2+} in the interlayers and the orientation of the silica tetrahedra [5].

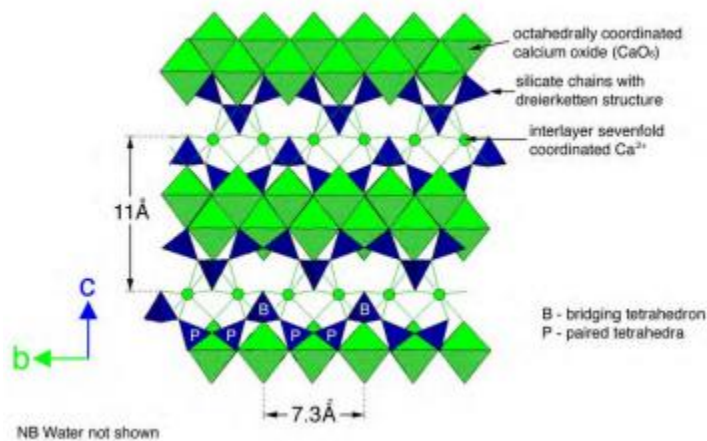


Figure 2: Structure of tobermorite 11Å along (210) [5]

Al-tobermorite can form in the presence of aluminum ions, where the Al^{3+} ion substitutes for the Si^{4+} , often at bridging sites between tetrahedra, as shown in Figure 3. This substitution carries a charge that can be compensated by cation exchange, such as with Na^+ . Al-tobermorite

with Na^+ as the stabilizer has been found to form faster than pure tobermorite [5]. Prior work has shown that the molar ratio of calcium to the sum of silicon and aluminum ($\text{Ca} : (\text{Si} + \text{Al})$) is an important factor in tobermorite formation [4]. In Al-tobermorite, Al^{3+} substitutes for Si^{4+} . This exchange stabilizes the crystal and decreases the formation time [5].

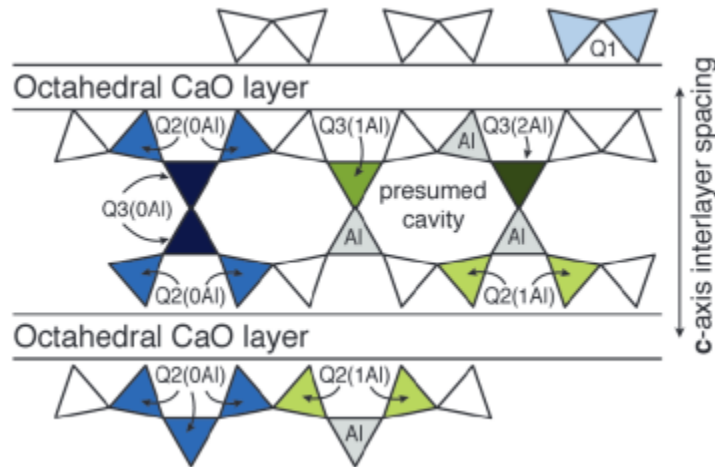


Figure 3: Location of Al substitution in Al-tobermorite, with $Q-X-(YAl)$ showing that there are X tetrahedral bonds and Y of the XZ bonds are aluminum tetrahedra [5]

Because synthesizing pwol is such an energetically expensive process and there is evidence that impurity ions can promote CCSH formation, there is high motivation to find a different feedstock material. There are many waste feedstock materials from energy production that are rich in calcium or silica, such as slags, fly ashes, and silica fumes. These waste materials are a byproduct of fossil fuel combustion and therefore have no associated carbon footprint [6]. This negative carbon cost and the high contents of calcium and silicon within many waste streams has motivated research into the addition of waste materials as additives to OPC formation [6] as well as bypassing cement and creating construction material solely from waste feedstocks [7].

Hypothesis

If waste materials that are rich in CaO and SiO_2 and contain Al_2O_3 are combined to form a mix with a $\text{Ca}:\text{Si}$ ratio of 5:6 and reacted in a batch experiment with a source of sodium, then CCSH phases including Al-tobermorite will be formed, because a higher concentration of impurity ions will promote the cation exchange necessary to form these phases.

Methods

Three calcia-containing feedstocks were utilized, identified as Code L, Slag 4 Greig (S4G), and slag cement. Additionally, three silica-containing waste feedstocks were utilized, identified as Wacker silica fume (SF), Panadyne silica fume, and Class F fly ash. The waste feedstocks characterized with x-ray fluorescence (XRF, Epsilon3x) to determine chemical composition as shown in Table 1 (XRF). The waste feeds were then mixed with 50:50 lithium

metaborate, lithium tetraborate at 50 mg waste to 100 mg borate. The mixture was then heated in a platinum crucible to 1000 °C for 30 min, then air quenched to form a glass. The glass was crushed, then digested in 10 mL of 1M hydrofluoric acid and nitric acid for 24 hours. The digestions were diluted 100 times and analyzed via inductively coupled plasma optical emissions spectroscopy ICP-OES (Thermo Fisher iCAP 6200), Figures 4-7. Additionally, X-ray diffraction (XRD) was used to determine structure using a Panalytical Empyrean x-ray diffractometer with the following parameters: Cu K α -radiation ($\lambda = 1.5405 \text{ \AA}$), current = 40 mA, tension = 45 kV, measurement range = 4.8–60°2 θ , time per step = 60 s, and step size = 0.0143°2 θ . The sample was spun during analysis to maximize signal and the scans were repeated 3 times and summed.

Table 1: Composition of waste feedstocks as determined by XRF analysis (weight%)					
Ca-sources					
Code L		Slag 4 greig		Slag Cement	
CaO	69.41%	CaO	28.35%	CaO	32.31%
SiO ₂	2.35%	SiO ₂	15.11%	SiO ₂	22.47%
Al ₂ O ₃	1.26%	Al ₂ O ₃	4.89%	Al ₂ O ₃	5.14%
Cl	0.57%	MgO	2.24%	MgO	6.12%
K ₂ O	0.57%	SO ₃	4.72%	SO ₃	1.93%
SO ₃	4.88%	K ₂ O	0.37%	K ₂ O	0.39%
Fe ₂ O ₃	1.32%	TiO ₂	0.72%	TiO ₂	0.31%
		MnO	1.15%	MnO	0.33%
		Fe ₂ O ₃	1.69%	Fe ₂ O ₃	0.54%
		SrO	0.10%	Cr ₂ O ₃ ,SrO, Y ₂ O ₃ ,ZrO ₂	trace
		Y ₂ O ₃ ,ZrO ₂ ,BaO	trace		
Si-sources					
Wacker Silica Fume		Class F Fly Ash		Panadyne Silica Fume	
SiO ₂	98.880%	SiO ₂	96.419%	SiO ₂	72.712%
CaO	0.069%	CaO	1.001%	CaO	0.259%
Al ₂ O ₃	0.603%	MgO	0.397%	Al ₂ O ₃	0.504%
P ₂ O ₅	0.228%	P ₂ O ₅	0.321%	MgO	0.219%
Cl	trace	K ₂ O	0.915%	P ₂ O ₅	0.249%
		Fe ₂ O ₃	0.172%	SO ₃	0.611%
		ZnO	0.164%	Fe ₂ O ₃	1.213%
		Cl,MnO,CuO,SrO	trace	K ₂ O	0.398%
				MnO,Cl,ZnO, As ₂ O ₃ ,NiO,CuO	trace

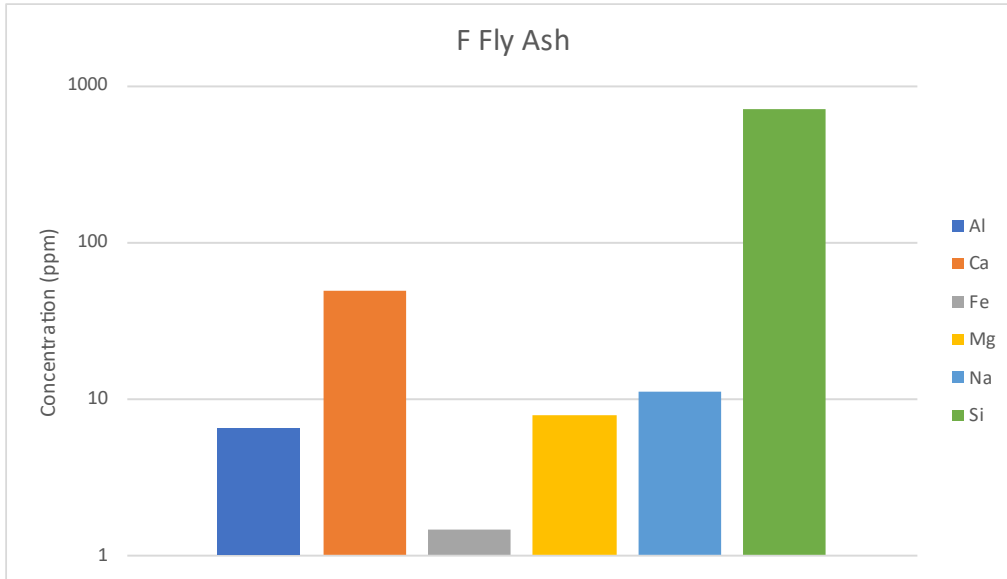


Figure 4: ICP-OES results of Class F fly ash borate flux measuring the concentration of aluminum, calcium, iron, magnesium, sodium, and silicon.

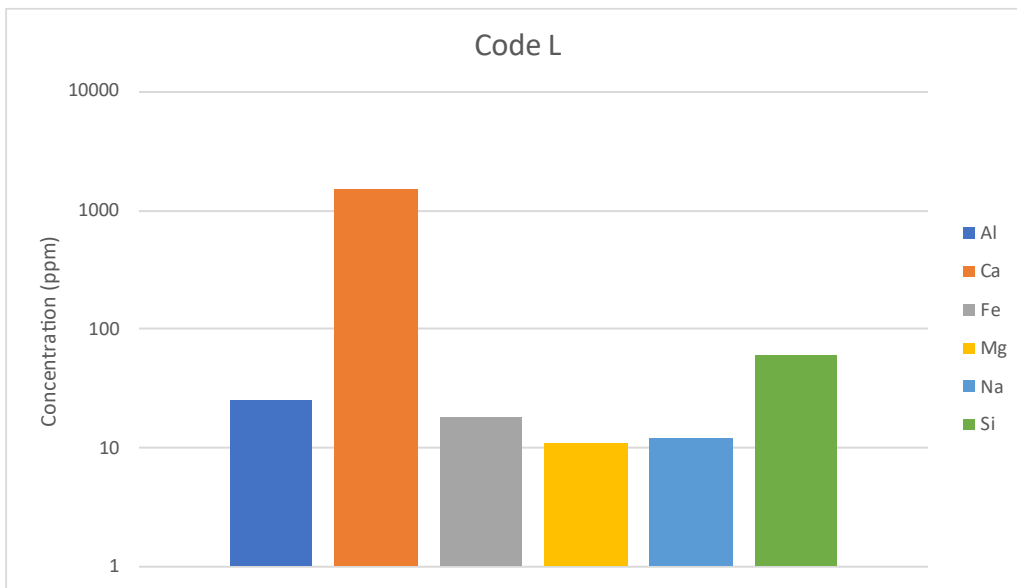


Figure 5: ICP-OES results of Code borate flux measuring the concentration of aluminum, calcium, iron, magnesium, sodium, and silicon

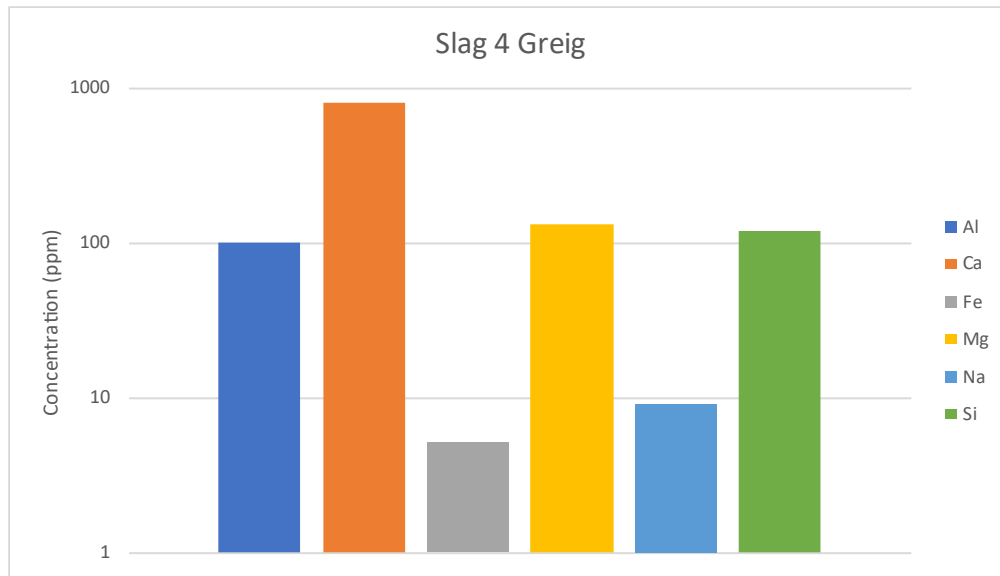


Figure 6: ICP-OES results of Slag 4 Greig borate flux measuring the concentration of aluminum, calcium, iron, magnesium, sodium, and silicon

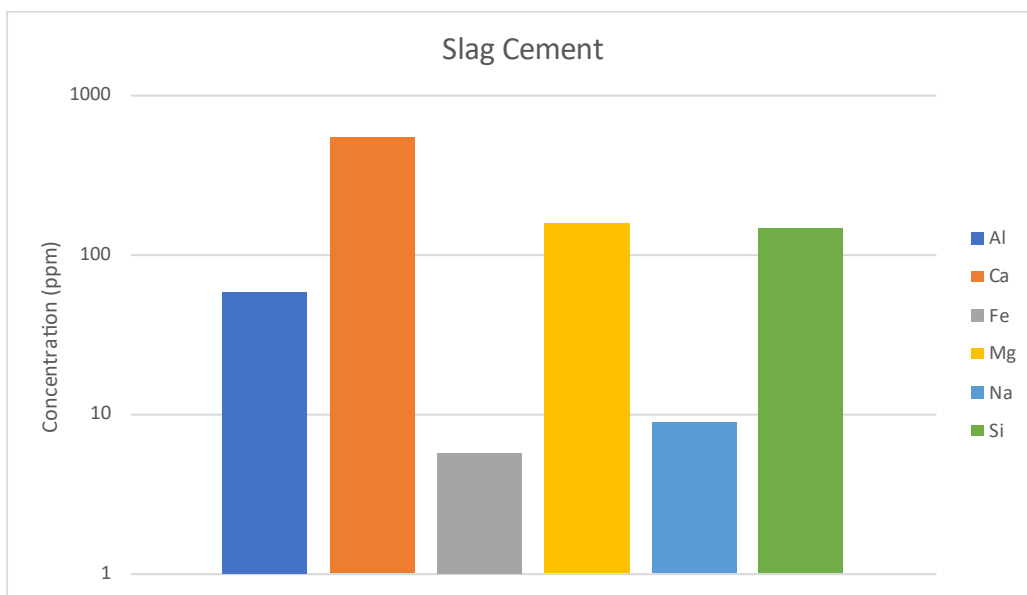


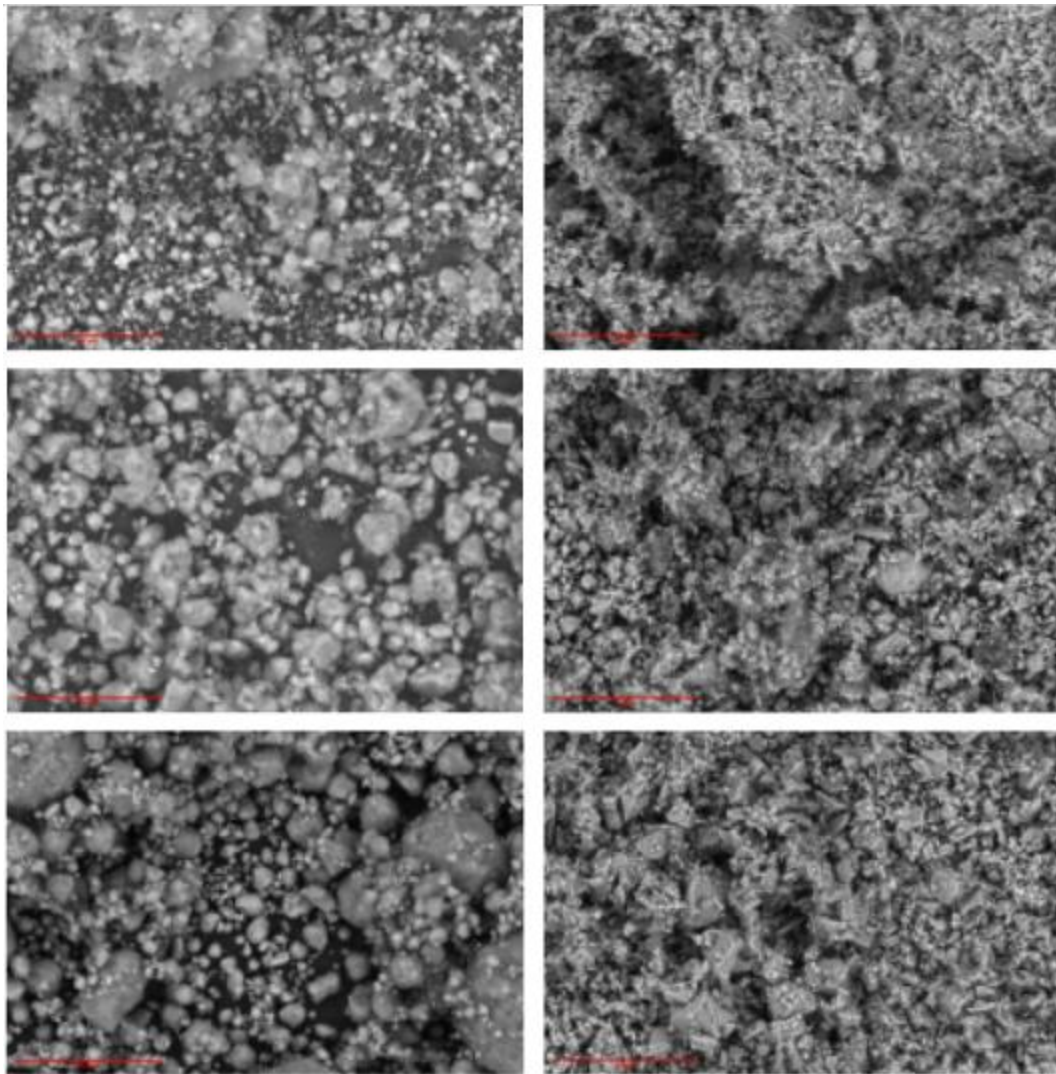
Figure 7: ICP-OES results of slag cement in borate flux measuring the concentration of aluminum, calcium, iron, magnesium, sodium, and silicon

Each of the six waste feedstocks was ball-milled for 24 hours and sieved to 90 μm . Scanning electron microscopy (SEM, FEI Quanta 650 Field Emission SEM) images of the ball-milled and sieved samples at 400x magnification are shown in Figure 8, show that there is still a difference in particle size. The particle size was determined using the ImageJ Fiji software to analyze micrographs. First, the scale was set within the program to correlate the length in pixels to the actual length. Then, a grid was overlaid on the image and each particle at an intersection

point of the grid was measured along two major axes if possible. These measurements were exported, and particle size was computed according to the formula:

$$A = \pi ab \quad (1)$$

Where a and b represent the length of the major axes and the particle is approximated as an ellipse. Particles at grid points that could not be quantified were skipped, and the average particle size and standard deviation can be seen in Table 2. The Class F fly ash had the largest average particle size at $1575 \mu\text{m}^2$, which is less than 20% of the maximum size allowed through the sieve, $8100 \mu\text{m}^2$.



*Figure 8: SEM micrographs of ball-milled and sieved waste feedstocks at 400x magnification. Scale bar = $90 \mu\text{m}$
Top row: Wacker SF, Code L; Middle row: Class F fly ash, Slag 4 Greig; Bottom row: Panadyne SF, slag cement*

waste feedstock	average particle size (μm^2)	standard deviation (μm^2)
Wacker silica fume	505.3	1246
Class F fly ash	1575	1373
Panadyne silica fume	1371	2431
Code L	50.40	67.89
Slag 4 Greig	154.6	199.8
Slag Cement	146.4	181.0

The six powders were separated into three binary mixes, each combining a silica source and a calcia source. For each mix design, two different mix conditions were used, a 2-gram sample with 20 mL of 0.1 M NaOH matching previous work done with pure feedstocks (2g samples) and a sample matching the mass ratios used by Guillot et al.: 1.046 grams of powder, 20 mL DI water, and 0.954 g Na_2CO_3 (G samples). Previous work has shown that a Ca:Si ratio of 5:6 promoted tobermorite formation [5]. A system of equations was used to determine the amount of each powder to use based on the chemical composition as determined by the XRF data. One equation was the sum of the powder masses, and the other equation was used to achieve the desired Ca:Si ratio, as each waste feedstock contains both CaO and SiO_2 . The mix designs are summarized in Table 3.

condition	mix 1		mix 2		mix 3	
2 g	Code L	1.0641 g	Slag 4 greig	1.6336 g	Slag Cement	1.5829 g
	Wacker SF	0.9359 g	Class F FA	0.3664 g	Panadyne SF	0.4171 g
Guillot	Code L	0.5565 g	Slag 4 greig	0.8544 g	Slag Cement	0.8279 g
	Wacker SF	0.4895 g	Class F FA	0.1916 g	Panadyne SF	0.2181 g

The powders were combined according to the mix design summarized in Table 2 in a 25 mL borosilicate test tube. The powders were then vortexed for 20 seconds each. Then, 20 mL of NaOH was added to the 2g samples and 20 mL of DI water and 0.954 g Na_2CO_3 were added to the G samples. The test tubes were vortexed for another 20 seconds before being placed in a test tube rack and sealed in a pressure vessel with 1.5 L of water and heated to 150°C for 1 day, 3 days, or 7 days. The vessel was naturally cooled to room temperature. The supernatant was collected and stored for ICP-OES analysis. The remaining solids were acidified with 0.1 M acetic acid, filtered, and dried at 90°C overnight. The powders were then stored for XRD analysis.

After exposure, filtration, and drying, all powders were characterized with XRD. The data were analyzed with HighScore Plus (version 4.9) using the International Centre for Diffraction Data (ICDD) databases to identify phases. The supernatant was collected from all samples except for the 7-day 2g samples, as there was no supernatant to collect. For each supernatant, 5 mL was acidified with 5 mL of a 1 M HF and HNO_3 solution. The digested

samples were diluted 100x and the calcium, iron, magnesium, sodium, and silicon concentrations were measured using ICP-OES.

Results

After 7 days of exposure, the G mass condition of each mix formed more hydrate phases than the corresponding 2g sample, as shown in Table 4. The mix 3 2g condition was the only 7-day sample that formed no identifiable hydrate phases. Figure 9 shows the XRD patterns of the 1-day samples compared to the constituent waste feedstock patterns. Figures 10-15 show the XRD patterns of each sample and the locations of major peaks of all identified samples in the 7-day sample, organized by mix number and mass condition. The ICP-OES results of the supernatants are shown in Figures 16-18, organized by time step. There was no supernatant remaining in the 7-day 2g samples as all the liquid had reacted.

Table 4: Summary of hydrate phase formation in 7-day samples						
phase	mix 1 2g	mix 1 G	mix 2 2g	mix 2 G	mix 3 2g	mix 3 G
crystalline calcium silicate hydrate	X	X		X		
Al-substituted CASH				X		X
calcium silicate hydroxide hydrate	X		X			
sodium aluminum silicate hydrate		X				
sodium aluminum silicate hydroxide hydrate		X		X		
sodium calcium aluminum silicate hydrate		X				
sodium calcium aluminum silicate hydroxide hydrate		X	X	X		
sodium aluminum silicon oxide hydrate				X		X

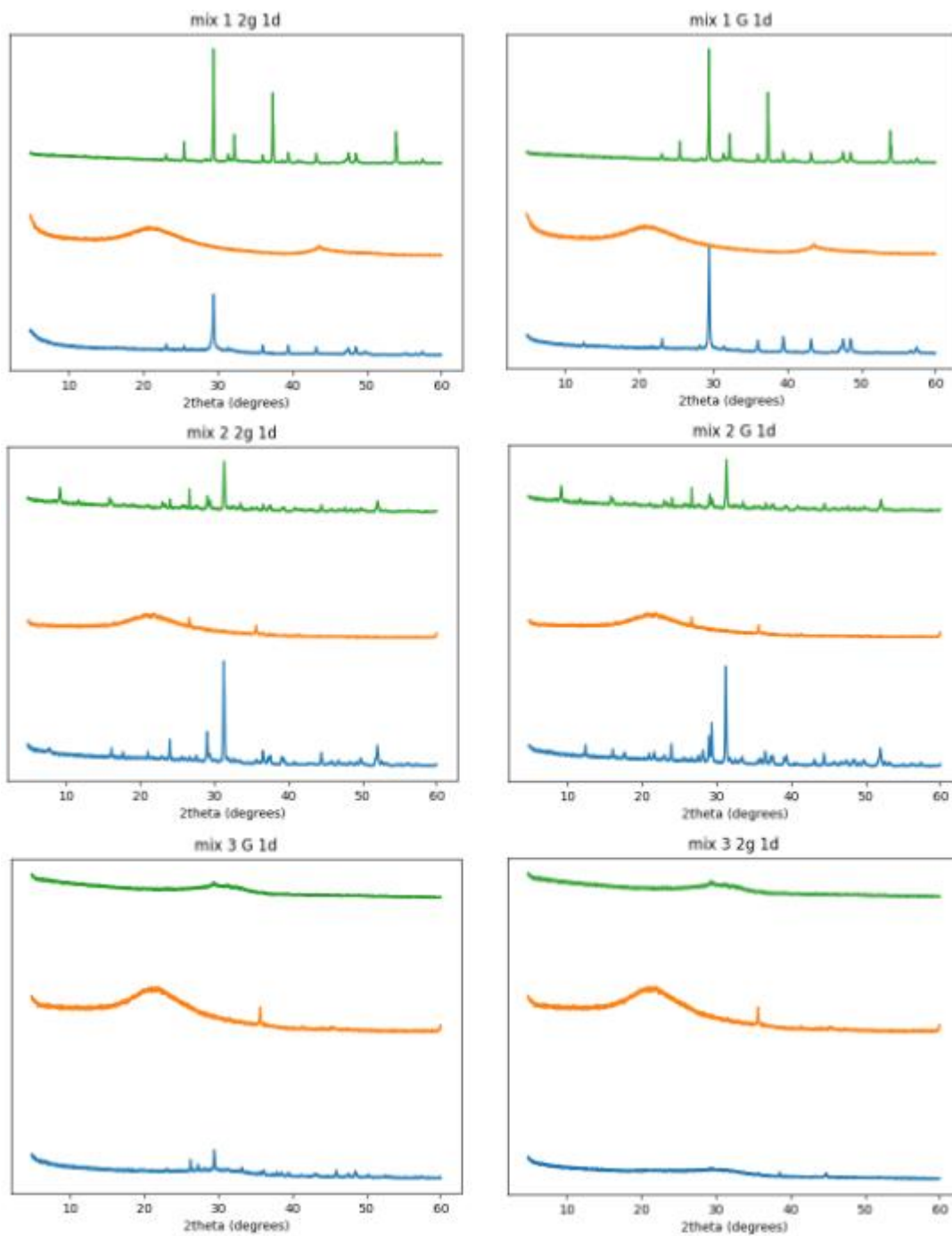


Figure 9: XRD patterns of each 1-day sample (blue) with the constituent waste feedstocks (silica source shown in orange, calcia source in green)

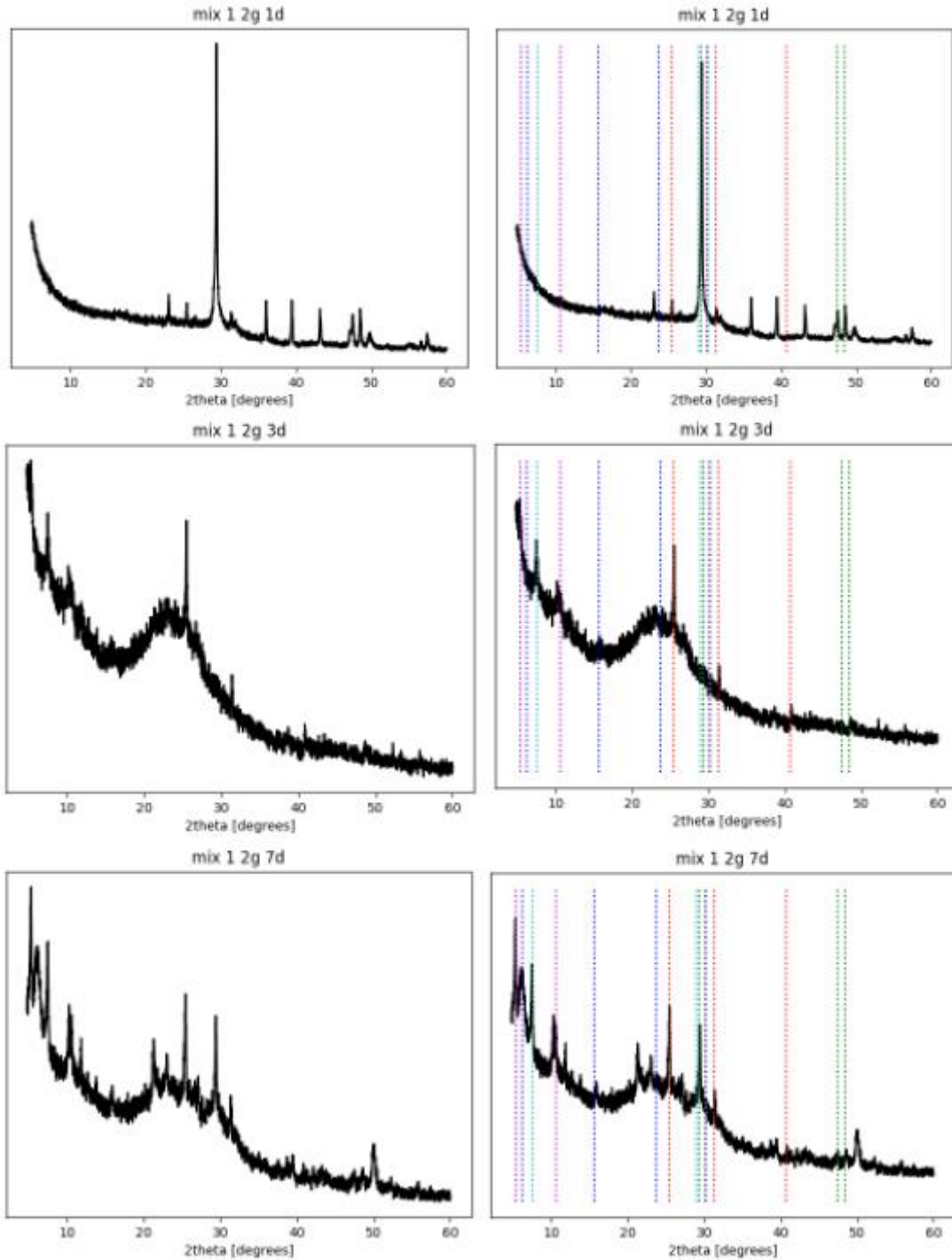


Figure 10: XRD patterns of mix 1 2g samples at each time step with representative peaks of identified phases in the 7-day sample.

Legend (line color : compound name : ICDD reference number)
 red : calcium sulfate : 01-072-0916
 green: calcium carbonate : 01-078-4615
 blue: calcium silicate hydrate : 01-076-0618
 cyan: calcium silicate hydroxide hydrate : 00-067-0046
 magenta: disodium dodecanedioate tetrahydrate : 00-063-1317

Table 5: crystalline phases formed in mix 1 2g 7d sample		
ICDD reference code	compound name	chemical formula
01-072-0916	calcium sulfate	Ca(SO ₄)
01-078-4615	calcium carbonate	Ca(CO ₃)
01-076-0618	calcium silicate hydrate	Ca _{0.731} Si ₆ O _{12.731} (H ₂ O) _{0.894}
00-067-0046	calcium silicate hydroxide hydrate	approx: Ca ₄ (Si ₂ O ₅ (OH ₂))(OH) ₄ · 5H ₂ O struct: (Ca _{4.02} Na _{0.01})(Si ₂ O _{5.07} (OH) _{1.93} ((OH) _{3.16} F _{0.84})) · 5H ₂ O
00-063-1317	disodium dodecanedioate tetrahydrate	Na ₂ ((O ₂ C) ₂ C ₁₀ H ₂₀) · 4H ₂ O

The results of XRD analysis of mix 1 2g samples are summarized in Figure 10 and Table 5. One CCSH phase was formed in the 2g sample after 7 days of exposure, in addition to calcium sulfate and calcium carbonate. A calcium silicate hydroxide hydrate phase and a hydrate phase without calcium or silicon were also formed. The results of mix 1 G samples are summarized in Figure 11 and Table 6. After 7 days of exposure, one CCSH phase, one sodium-stabilized aluminum substituted CCSH phase, and one sodium calcium aluminum silicate hydroxide hydrate phase were formed. In addition, two sodium aluminum silicate hydrate phases, one sodium aluminum silicate hydroxide hydrate, and aragonite were formed. Additionally, there is amorphous content in the 3- and 7-day samples of both the 2g and G conditions. This amorphous content is attributed to calcium silicate hydrate gel.

Table 6: crystalline phases formed in mix 1 G 7d sample		
ICDD reference code	compound name	chemical formula
01-080-0699	sodium aluminum silicate hydrate	Na _{3.552} (Al _{3.6} Si _{12.4} O ₃₂)(H ₂ O) _{10.656}
01-076-6569	sodium aluminum silicate hydrate	Na _{0.9} ((Al _{0.9} Si ₂)O ₆)(H ₂ O)
01-081-9793	calcium silicate hydrate	Ca ₁₂ (S ₈ O ₂₈)(H ₂ O) ₁₃
00-025-0781	sodium aluminum silicate hydroxide hydrate	approx: NaAl ₄ (Si, Al) ₈ O ₂₀ (OH) ₄ · 2H ₂ O
01-084-0174	sodium calcium aluminum silicate hydrate	Na _{0.384} Ca _{2.186} H _{1.94} (Si _{28.044} Al _{7.956} O ₇₂)(H ₂ O) _{1.28}
01-085-6708	aragonite (calcium carbonate)	CaCO ₃
00-060-0320	sodium calcium aluminum silicate hydroxide hydrate	approx: (Ca, Na) _{0.3} Al ₂ (Si, Al) ₄ O ₁₀ · xH ₂ O

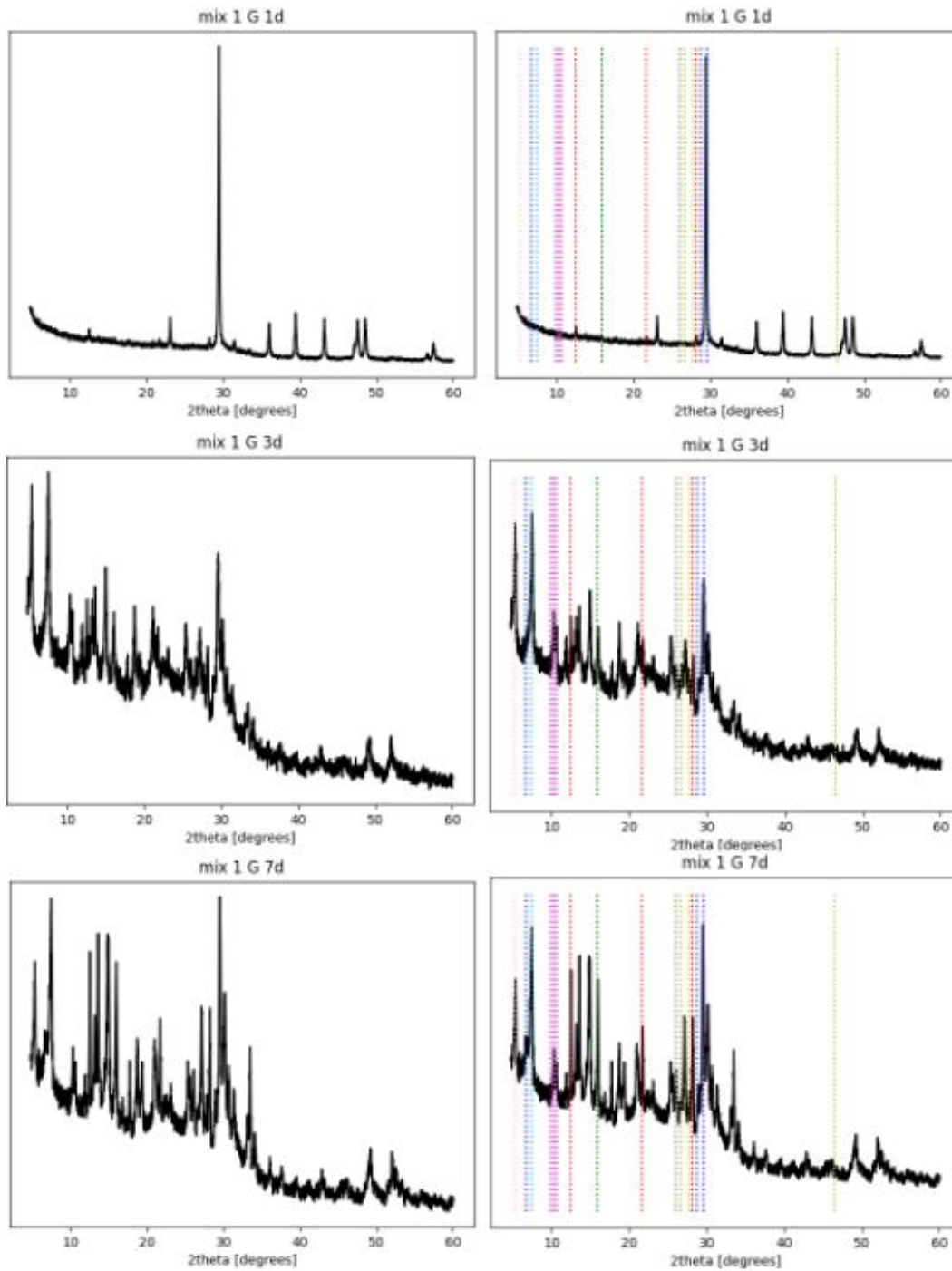


Figure 11: XRD patterns of mix 1 G samples at each time step with representative peaks of identified phases in the 7-day sample.

Legend (line color : compound name : ICDD reference number)

red : sodium aluminum silicate hydrate : 01-080-0699

green: sodium aluminum silicate hydrate : 01-076-6569

blue: calcium silicate hydrate : 01-081-9793

cyan: sodium aluminum silicate hydroxide hydrate : 00-25-0781

magenta: sodium calcium aluminum silicate hydrate : 01-084-0174

yellow : aragonite (calcium carbonate) : 01-085-6708

pink : sodium calcium aluminum silicate hydroxide hydrate : 00-060-0320

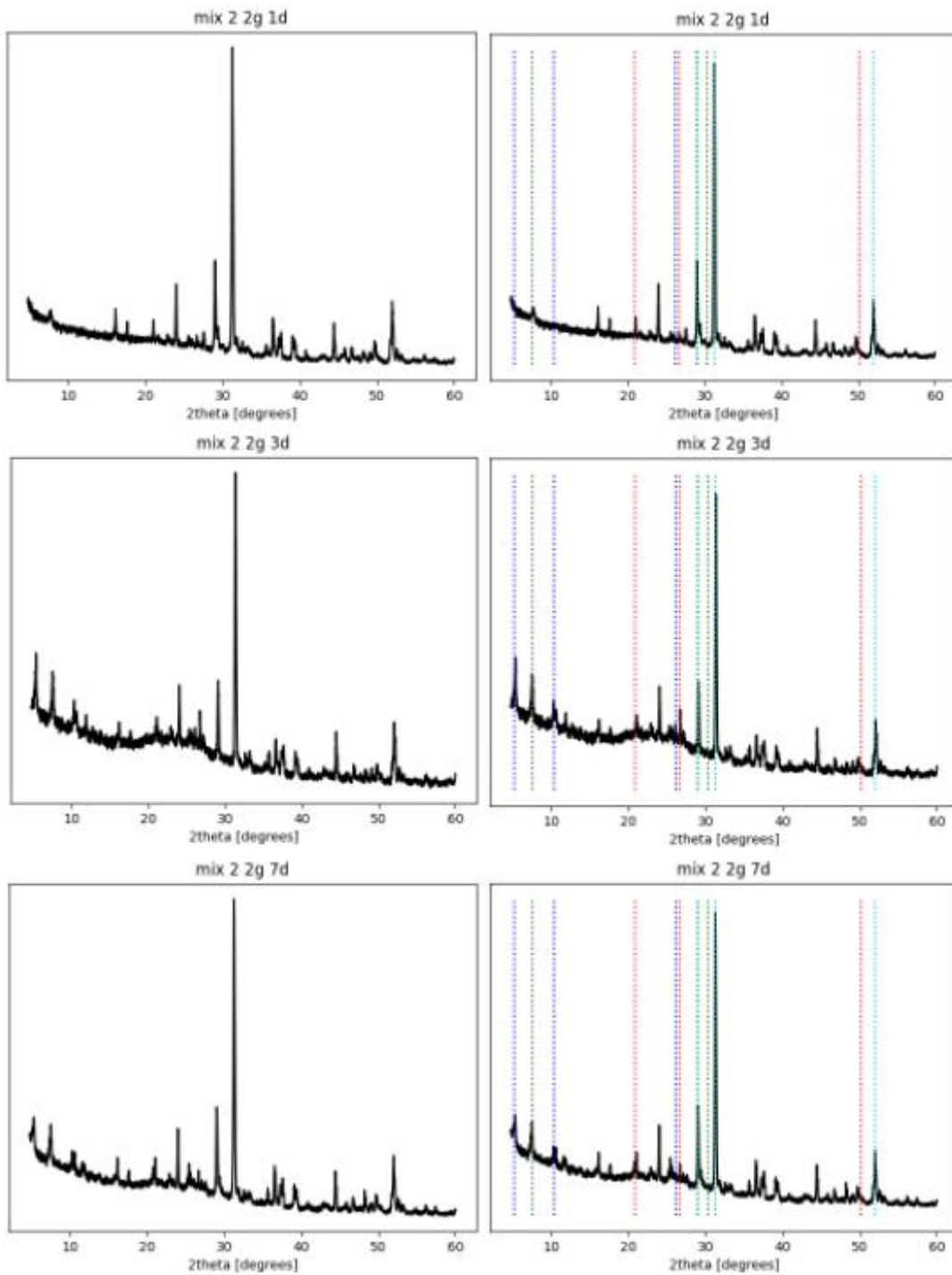


Figure 12: XRD patterns of mix 2 2g samples at each time step with representative peaks of identified phases in the 7-day sample.

Legend (line color : compound name : ICDD reference number)

red : silicon oxide : 01-085-0797

green: calcium silicate hydroxide hydrate : 00-067-0046

blue: sodium calcium aluminum silicate hydroxide hydrate : 00-060-0320

cyan: gehlenite (calcium aluminum silicon oxide) : 04-015-7930

ICDD reference code	compound name	chemical formula
01-085-0797	silicon oxide	SiO ₂
00-067-0046	Calcium Silicate Hydroxide Hydrate	approx: Ca ₄ (Si ₂ O ₅ (OH ₂))(OH) ₄ · 5H ₂ O struct: (Ca _{4.02} Na _{0.01})(Si ₂ O _{5.07} (OH) _{1.93} ((OH) _{3.16} F _{0.84}) · 5H ₂ O
00-060-0320	sodium calcium aluminum silicate hydroxide hydrate	approx: (Ca, Na) _{0.3} Al ₂ (Si, Al) ₄ O ₁₀ · xH ₂ O
04-015-7930	calcium aluminum silicon oxide (gehlenite)	Ca ₂ Al ₂ SiO ₇

The results of the mix 2 2g 7-day experiment are summarized in Figure 12 and Table 7. After 7 days of exposure, two calcium silicate hydroxide hydrate phases were formed, one of these phases also contained sodium and aluminum. Additionally, two oxides were formed in this sample, silicon oxide and gehlenite, a calcium aluminum silicon oxide. The results of the mix 2 G 7-day sample are shown in Figure 13 and Table 8. This sample formed metaheulandite, a calcium aluminum silicate hydrate phase and a sodium calcium aluminum silicate hydroxide hydrate phase. Additionally, there were three hydrate phases that did not contain calcium: Garronite-Na (sodium aluminum silicon oxide hydrate), rectorite (sodium aluminum silicate hydroxide hydrate), and natrolite (sodium aluminum silicon oxide hydrate). Additionally, a silicate and oxide were formed in this sample, alumoakermanite (sodium calcium magnesium aluminum iron silicate) and hydrogen aluminum silicon oxide. Additionally, there is amorphous content in the 2g 3- and 7-day samples and the 7-day G sample, this is attributed to CSH gel.

ICDD reference code	compound name	chemical formula
00-060-0320	sodium calcium aluminum silicate hydroxide hydrate	approx: (Ca, Na) _{0.3} Al ₂ (Si, Al) ₄ O ₁₀ · xH ₂ O
01-080-5267	alumoakermanite (sodium calcium magnesium aluminum iron silicate)	(Ca _{0.76} Na _{0.24}) ₂ (Al _{0.5} Fe _{0.3} Mg _{0.2})(Si ₂ O ₇)
04-023-2956	Garronite-Na (sodium aluminum silicon oxide hydrate)	Na ₃ Al ₃ Si ₅ O ₁₆ (H ₂ O) _{3.6}
00-025-0781	rectorite (sodium aluminum silicate hydroxide hydrate)	approx: NaAl ₄ (Si, Al) ₈ O ₂₀ (OH) ₄ · 2H ₂ O
04-016-8866	hydrogen aluminum silicon oxide	H _{0.17} Al _{0.17} Si _{0.83} O ₂
00-019-0209	metaheulandite (calcium aluminum silicate hydrate)	Ca(Al ₂ Si ₇ O ₁₈) ₁ · 7H ₂ O
04-010-2945	natrolite (sodium aluminum silicon oxide hydrate)	Na ₄ Al ₄ Si ₆ O ₂₀ (H ₂ O) ₄

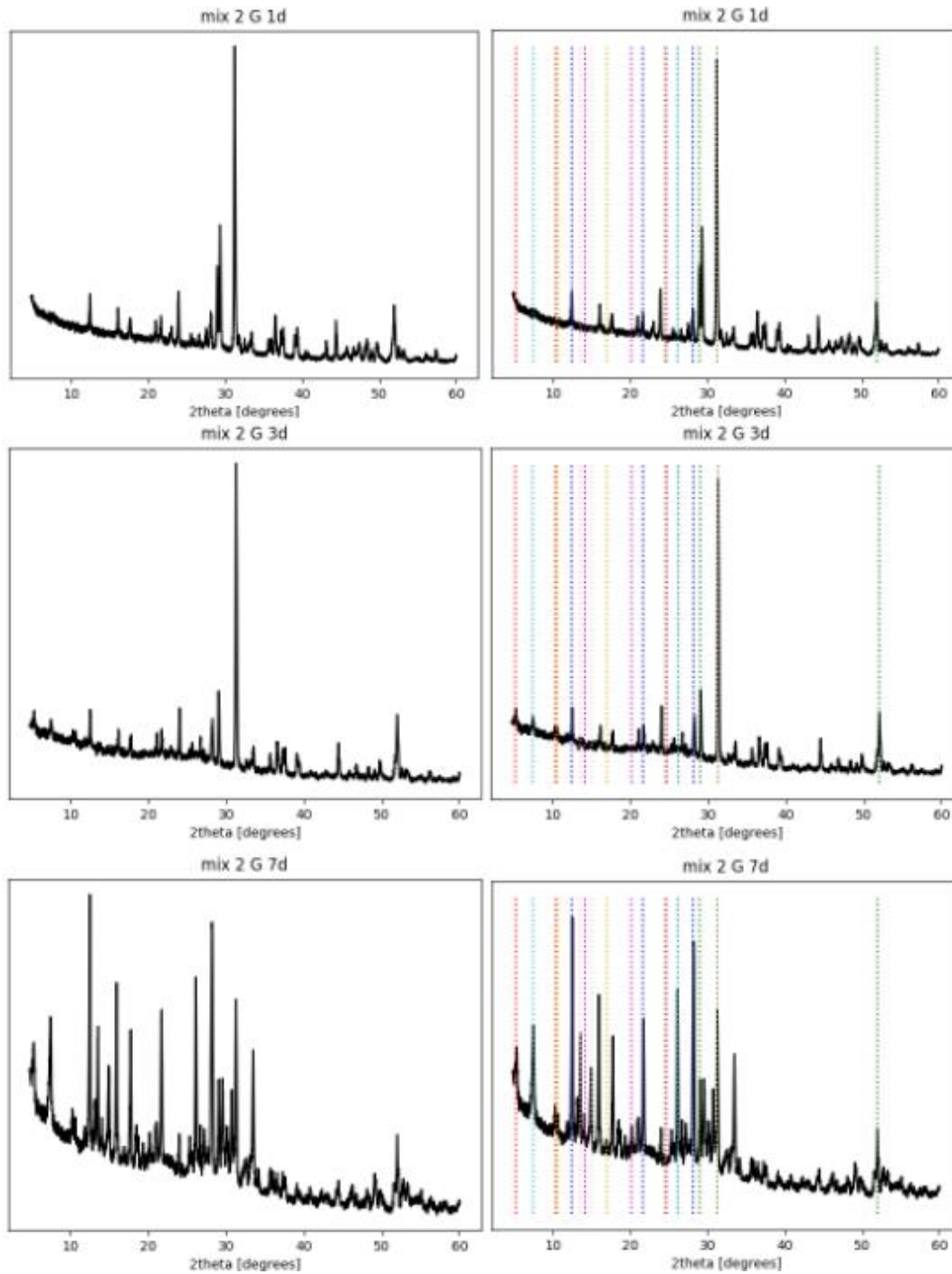


Figure 13: XRD patterns of mix 2 G samples at each time step with representative peaks of identified phases in the 7-day sample.

Legend (line color : compound name : ICDD reference number)
 red : sodium calcium aluminum silicate hydroxide hydrate : 00-060-0320
 green: alumoakermanite (sodium calcium magnesium aluminum iron silicate) : 01-080-5267
 blue: Garronite-Na (sodium aluminum silicon oxide hydrate): 04-023-2956
 cyan: rectorite (sodium aluminum silicate hydroxide hydrate : 00-025-0781
 magenta: hydrogen aluminum silicon oxide : 04-016-8866
 yellow : metaheulandite (calcium aluminum silicate hydrate) : 00-019-0209
 pink : natrolite (sodium aluminum silicon oxide hydrate : 04-010-2945

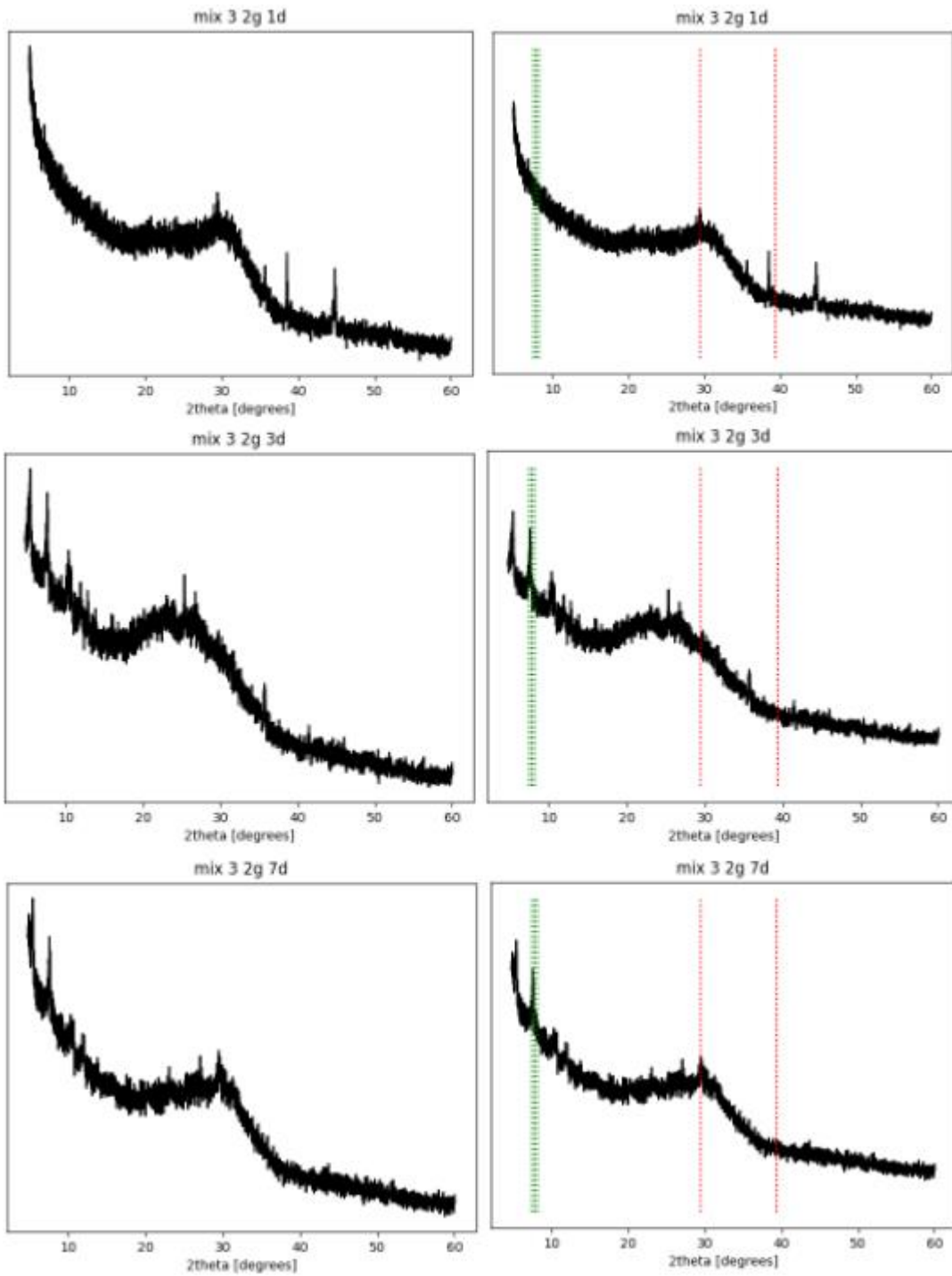


Figure 14: XRD patterns of mix 3 2g samples at each time step with representative peaks of identified phases in the 7 day sample.

Legend (line color : compound name : ICDD reference number)
 red : calcite (calcium carbonate) : 00-005-0586
 green: boggsite (calcium aluminum silicate) : 01-073-7700

ICDD reference code	compound name	chemical formula
00-005-0586	calcite (calcium carbonate)	CaCO ₃
01-073-7700	boggsite (calcium aluminum silicate)	Ca _{7.77} (Al _{16.96} Si _{79.04} O ₁₉₂)

The mix 3 2g samples show a large amount of amorphous content (Figure 14). Table 9 summarizes the crystalline phases identified, calcite (calcium carbonate) and boggsite (calcium aluminum silicate). However, the mix 3 2g samples are largely CSH gel. The mix 3 G samples also have a large amount of CSH gel, but HighScore analysis shows the formation of two calcium aluminum silicate hydrate phases: gmelinite-Ca and wairakite (Figure 15 and Table 10). Additionally, stellerite (calcium silicon oxide) and Garronite-Na (sodium aluminum silicon oxide hydrate) were formed in the mix 3 2g 7d sample. In addition to these crystalline phases, the G samples also show a large amount of amorphous CSH gel.

ICDD reference code	compound name	chemical formula
01-076-0169	gmelinite-Ca (calcium aluminum silicate hydrate)	Ca(Al ₂ Si ₄ O ₁₂)(H ₂ O) ₆
01-086-2797	stellerite (calcium silicon oxide)	Ca _{6.9} Si _{171.95} O _{145.5}
00-042-1451	wairakite (calcium aluminum silicate hydrate)	CaAl ₂ Si ₄ O ₁₂ · 2H ₂ O
04-023-2956	Garronite-Na (sodium aluminum silicon oxide hydrate)	Na ₃ Al ₃ Si ₅ O ₁₆ (H ₂ O) _{3.6}

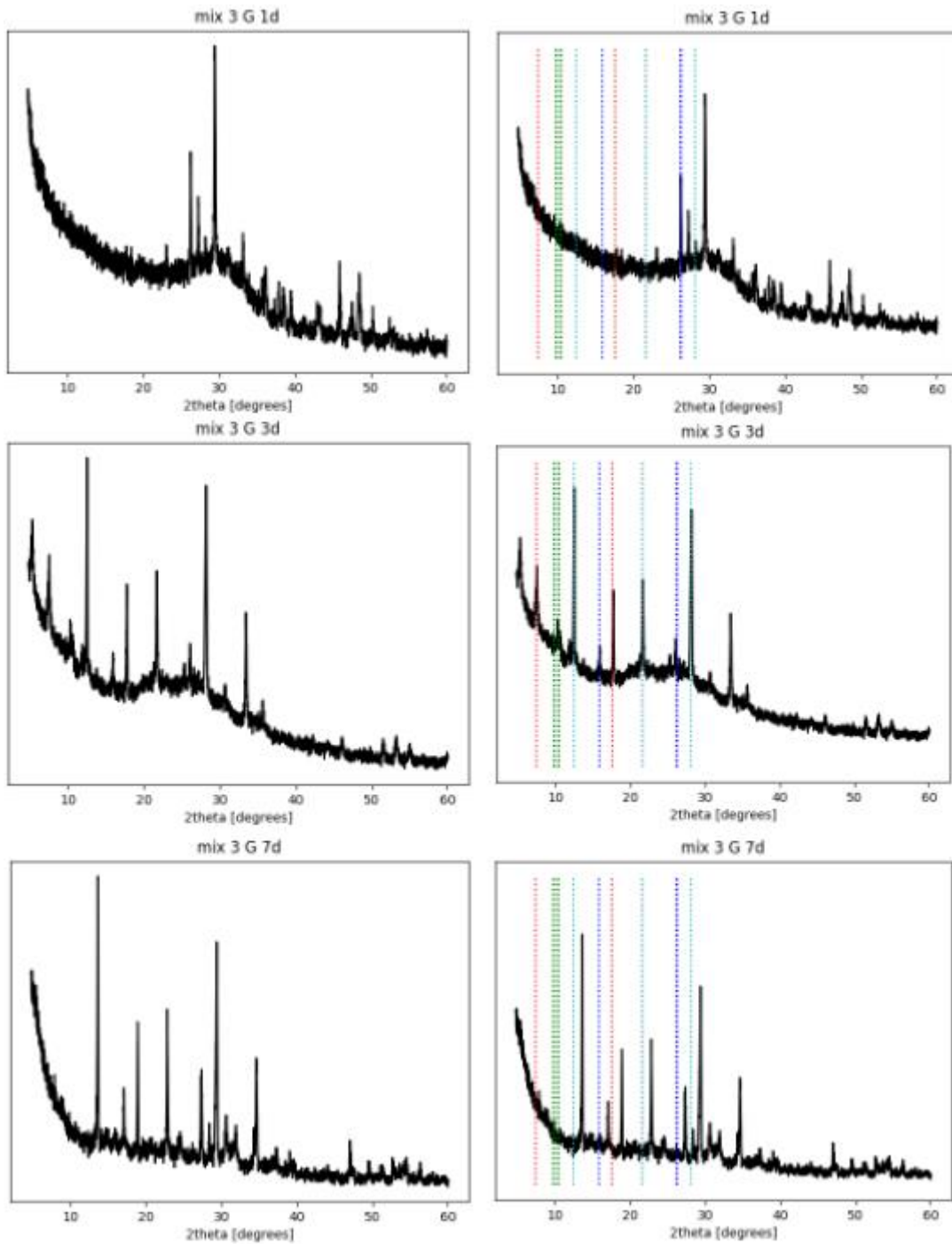


Figure 15: XRD patterns of mix 3 G samples at each time step with representative peaks of identified phases in the 7 day sample.

Legend (line color : compound name : ICDD reference number)
 red : gmelinite-Ca (calcium aluminum silicate hydrate) : 01-076-0169
 green: stellerite (calcium silicon oxide) : 01-086-2797
 blue: wairakite (calcium aluminum silicate hydrate) : 00-042-1451
 cyan: Garronite-Na (sodium aluminum silicon oxide hydrate): 04-023-2956

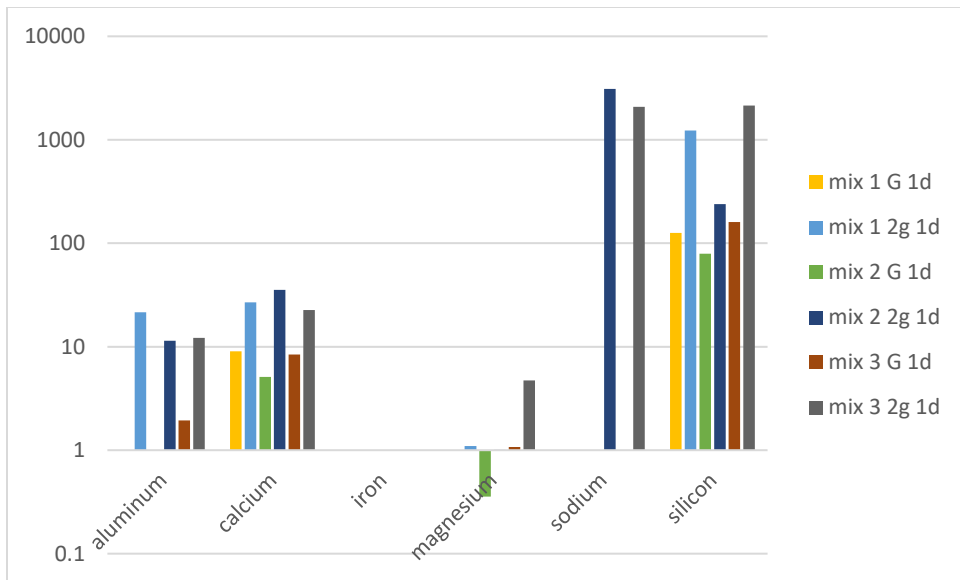


Figure 16: ICP-OES results of supernatants remaining after 1 day of exposure. Note: sodium oversaturated for many samples. Iron and magnesium were not present for all samples. Also note that these results are approximate, based on the average of three repeats.

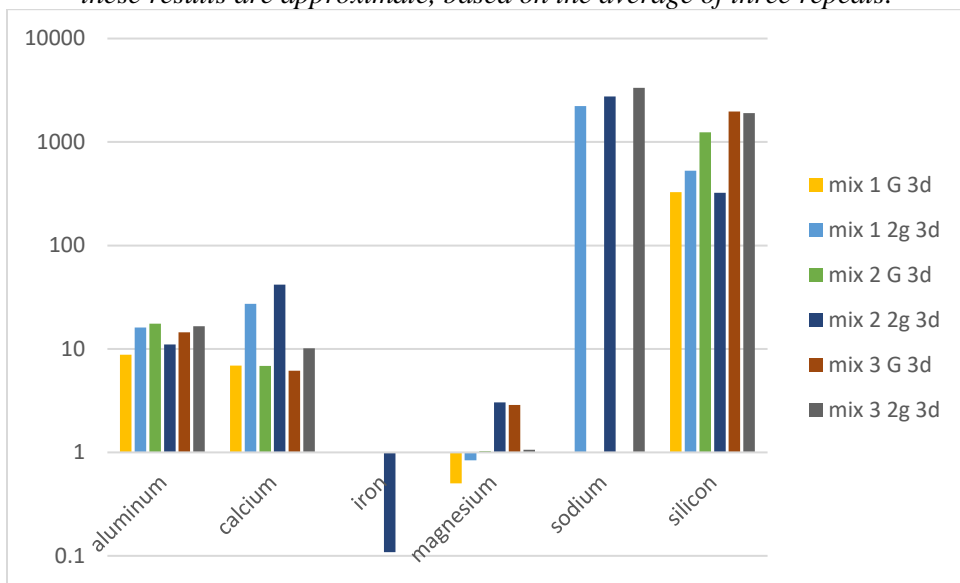


Figure 17: ICP-OES results of supernatants remaining after 3 days of exposure. Note: sodium oversaturated for many samples. Iron and magnesium were not present for all samples. Also note that these results are approximate, based on the average of three repeats.

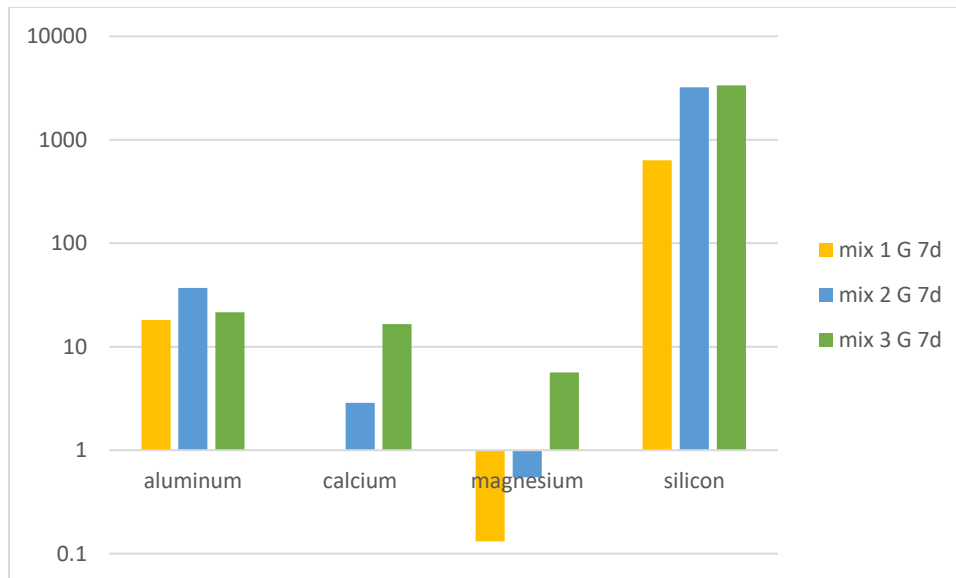


Figure 18: ICP-OES results of supernatants remaining after 7 days of exposure. Note: sodium oversaturated for many samples. Iron and magnesium were not present for all samples. Also note that these results are approximate, based on the average of three repeats.

Discussion

These experiments were performed to better understand the mechanisms behind CCSH formation in the presence of impurity ions under a Ca:Si ratio of approximately 5:6. There are 3 major observations from the data: the G samples outperformed the 2g samples after 7 days of exposure, many of the experiments formed calcium silicate hydroxide hydrates, and mixes 1 and 2 outperformed mix 3. The first observation can be explained by the higher pH of the G samples as compared to the 2g samples. Yang et al. also found that alkaline environments promoted the formation of CCSH phases, as hydroxide ions promote the breaking of amorphous SiO_2 bonds. This leads to the formation of SiO_4 tetrahedra, a building block of CCSH phases [8]. The second observation also supports the work done by Yang et al., as they found that calcium silicate hydroxide hydrate phases formed as a precursor to tobermorite. Their results indicate that raising the synthesis temperature to 260°C could promote the formation of tobermorite over calcium silicate hydroxide hydrates [8]. The final observation is that mixes 1 and 2 outperformed mix 3. The XRD patterns of mix 3 (Figures 14 and 15) show amorphous reactant products. This is likely an amorphous calcium silicate hydrate (CSH) gel. The work done by Yang et. al cited CSH gel formation as the first step in crystal evolution of calcium silicates under hydrothermal synthesis [8]. As shown in Figure 9, slag cement was the only calcia-source that was amorphous. Additionally, as shown in Figure 7 and Table 1, slag cement had a higher concentration of aluminum, magnesium, and silicon than the other calcia sources. These differences might have contributed the lack of crystalline hydrate formation in both mass conditions of mix 3.

Conclusion

With the goal of studying the formation of crystalline calcium silicate hydrate phases, six different waste feedstocks were characterized and combined into three binary mixes consisting of a calcia source and a silica source with an approximate Ca:Si ratio of 5:6 and combined with a

source of sodium and water and reacted under pressure at 150°C for 1, 3, or 7 days. There were two mass conditions with different sources of sodium as a crystal stabilizer. These different conditions had a different total mass of powder as well. The remaining supernatant was collected for ICP analysis to measure the species that remained in the unreacted liquid. The powders were acidified and dried and characterized using XRD for phase identification. After 7 days of exposure, four of the six samples had formed at least one CESH or aluminum substituted CESH phase. Three of the four samples that formed a CESH phase were the G mass condition, meaning that every 7-day G sample formed a CESH or Al-substituted CESH. In comparing these results to the work done on calcium silicon slag and silica fume by Yang et al., it is postulated that raising the synthesis temperature could promote more CESH formation.

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