Temperature and activator effect on early-age reaction kinetics of alkali-activated slag binders

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Abstract

The early-age reaction kinetics of alkali-activated ground granulated blast-furnace slag (GGBFS) binders as determined by in-situ isothermal calorimetry are discussed in this paper. Particular attention is paid to the effects of activator type (sodium hydroxide and sodium silicate) and concentration, as well as curing temperature (23 °C and 50 °C). The mechanical strength development, microstructure, and product phase composition are also discussed to provide context for the phenomena observed in the kinetics results. It is shown for both activators that elevated temperature curing greatly accelerates hydration, resulting in more rapid product formation and strength development. High-molarity sodium hydroxide activators are shown to accelerate early hydration at ambient temperature, but tend to present a barrier to advanced hydration thereby limiting the later-age strength. Elevated temperature curing is shown to remove this barrier to advanced hydration by improving solubility and diffusivity. Hydration of sodium silicate-activated

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slag is comparatively slow, resulting in the delayed formation of very dense products with higher mechanical strength. Increasing sodium oxide tends to accelerate hydration, resulting in improved early- and later-age strength, while increasing the silica tends to retard the reaction, resulting in slower, more complete hydration as well as improved mechanical strength.

Keywords: Alkali activation, Ground granulated blast-furnace slag, Reaction kinetics, In-situ calorimetry

1. Introduction

Alkali-activated industrial byproducts, and in particular ground granulated blast-furnace slag (GGBFS, hereafter *slag*), have received much attention in recent literature as potential sustainable alternatives to portland cement binders for concrete. The production of portland cement is one of the world's leading sources of carbon dioxide emissions and is a major barrier to the production of sustainable concrete mixtures. The partial replacement of portland cement with beneficiated industrial byproducts like fly ashes and slag has long been employed with noteworthy improvements to the rheology, strength, durability, and heat of hydration [1–7]. Despite its benefits when used in conjunction with portland cement, slag shows only latent hydraulic properties when used as the sole binder. While successful replacements of up to 70% of portland cement with slag have been routinely demonstrated, replacement is often limited to about 40 % in North America [7].

In pure water, slag rapidly develops a glassy shell on the grain surface, acting as a barrier to advanced hydration. When used in conjunction with portland cement, the high alkalinity of the pore solution breaks down this

18 barrier, promoting further hydration. When slag is used as the sole binder, an
19 alkaline activating agent like sodium hydroxide or sodium silicate is necessary
20 to promote advanced hydration [8–11]. The resulting binders are predomi-
21 nately composed of sodium and calcium aluminosilicate hydrates (C-A-S-H
22 and N-A-S-H), as well as some hydrotalcite-like products [12–15]. A cornu-
23 copia of studies in the past decades have shown alkali-activated slag binders
24 and concretes to be strong, durable, and environmentally-friendly, with 10–
25 50% lower associated CO₂ emissions than comparable portland cement for-
26 mulations [16, 17].

27 The behavior of alkali-activated aluminosilicates is highly dependent on
28 the type and concentration of the alkaline activator and on the curing tem-
29 perature [18–21]. Elevated-temperature curing greatly accelerates the forma-
30 tion of the microstructure and the development of mechanical strength [22–
31 26]. Sodium silicate-activated slag systems tend to gain strength much more
32 slowly than sodium hydroxide-activated slag, but with significant improve-
33 ments in later-age strength [13, 15, 21, 27, 28]. Increased mechanical strength
34 is attributed to increased silica or sodium oxide in sodium silicate-activated
35 slag. Meanwhile, sodium hydroxide-activated slag sets and gains strength
36 very rapidly [12, 20]. This early product formation, however, is accompanied
37 by the formation of a dense reaction ring surrounding incompletely-reacted
38 slag grains and limiting continued diffusion and product formation [15, 28].
39 As such, increased concentration of the sodium hydroxide activator often
40 does not improve mechanical strength.

41 Several studies have reported in detail on the composition of the hydra-
42 tion products in alkali-activated slag cured at both ambient and elevated

43 temperatures. These studies have concluded that the product phases are
44 generally C-S-H, C-A-S-H, and N-A-S-H, the crystallinity of which increases
45 with age [13, 29–31]. Several of these studies have suggested that the com-
46 position of the product phases is similar at both ambient and elevated curing
47 temperatures [29, 30].

48 A few early kinetics studies compared the hydration of sodium silicate-
49 activated slag with that of portland cement, concluding that both systems
50 underwent the same basic stages of hydration, viz. wetting, induction, ac-
51 celeration, deceleration, and steady-state, but that the mechanisms of hy-
52 dration during these stages were distinct [32–34]. The wetting period in
53 sodium-silicate activated slag is marked by the rapid early formation of C-
54 A-S-H and N-A-S-H gels, and the acceleration period is marked by the later
55 diffusion-limited reaction of larger slag grains [32, 34]. Krizan and Zivanovic
56 [35] showed the effect of silica on the kinetics of sodium silicate-activated slag,
57 citing an increase in both the magnitude of the initial heat evolution peak
58 and in the duration of the acceleration period. In addition, Haha et al. [36]
59 discussed the effect of activator type on the hydration kinetics of activated
60 slag, concluding that the high initial rate of reaction in sodium hydroxide-
61 activated slag limited the later-age decrease in coarse porosity, and therefore
62 limited the later-age strength as compared to sodium silicate-activated slag.
63 Much more recently, Gebregziabihier et al. [28] discussed the specific effects
64 of the molarity of sodium hydroxide activators and the silica modulus (rela-
65 tive concentration of silica to sodium oxide) of sodium silicate activators on
66 the hydration kinetics of alkali-activated slag binders cured at ambient tem-
67 perature. That study showed spontaneous hydration in sodium hydroxide-

68 activated slag, with significant product formation and microstructural devel-
69 opment within the first few hours. Increased activator molarity showed a
70 pronounced accelerating effect on the reaction, but did not significantly alter
71 the later-age strength or microstructure [28, 36]. Sodium silicate-activated
72 slag, on the other hand, reacted in a slower and more controlled manner.
73 Silica was shown to have a retarding effect on the reaction, allowing for the
74 formation of denser products with higher later-age strength [28]. These ob-
75 servations were consistent with those of Krizan and Zivanovic [35].

76 Despite the availability of several studies on the reaction kinetics of
77 alkali-activated slag, several important questions remain unanswered. First,
78 it has been well established that curing at elevated temperatures results
79 in much more rapid strength and microstructural development in alkali-
80 activated binders. However, these effect have not been quantitatively evalu-
81 ated by means of kinetic studies. Additionally, while the effects of activator
82 type and concentration on the hydration kinetics have been discussed to some
83 extent, these discussions have neglected the effect of sodium oxide concen-
84 tration of sodium silicate activators, focusing instead on the effect of silica in
85 those systems. The present study seeks to address these gaps in knowledge
86 in order to further the understanding of how the activator and temperature
87 affects the rate and degree of hydration in alkali-activated slag binders.

88 **2. Materials and methods**

89 *2.1. Materials*

90 The raw binder is an ASTM C 989-compliant grade-100 ground gran-
91 ulated blast-furnace slag (slag) sourced from a reputable commercial sup-

plier. The oxide composition as determined by X-ray fluorescent spectroscopy (XRF) is 39.8% CaO, 36% SiO₂, 10.5% Al₂O₃, 7.93% MgO, 2.11% SO₃, and less than 1% of Fe₂O₃, Na₂O, and K₂O. The Blaine surface area is 340m²/kg and the loss on ignition is 3%. The particle size distribution as determined by laser diffraction particle size analysis indicates a median particle size of 7.5 microns, with 80% of particle smaller than 10 microns. The X-ray diffraction analysis of the unreacted binder shows a diffuse diffraction pattern typical of an amorphous glassy material.

The alkaline activating agents are aqueous solutions of sodium hydroxide (NaOH) and sodium silicate (SS) (Na₂O + $m \cdot \text{SiO}_2$, where m is the silica modulus). The former are prepared by dissolving reagent-grade sodium hydroxide pellets in deionized water and allowing sufficient time for heat dissipation. The latter are prepared by diluting a pre-mixed reagent-grade sodium metasilicate solution ($m = 2.5$) with deionized water. The silica modulus m is altered using additions of sodium hydroxide, forming what is actually a compound solution of sodium hydroxide and sodium silicate. The sodium oxide equivalent is determined according to stoichiometry. The mixture details are presented in Table 1. The mass ratio of solution to binder (s/b) is 0.40 throughout.

2.2. Experimental methods

The methods and procedures related to this work are described exhaustively by Deir et al. [15] and Gebregziabihier et al. [28]; they are discussed only briefly here. Paste mixtures were mixed in a standard laboratory mixer in accordance with the specifications of ASTM C305. Fresh pastes were cast into the appropriate molds, consolidated on a vibrating table, sealed

Table 1: Activator compositions

Sodium hydroxide		
ID	Molarity (M)	
5M	5	
8M	8	
12M	12	
Sodium silicate		
ID	<i>m</i>	%Na ₂ O
S1	1.5	2.5
S2	1.5	5.0
S3	1.5	7.0
S4	2.5	2.5

117 in plastic, and placed in the specified curing environment. Specimens were
 118 either cylindrical, measuring 25 mm in diameter and 50 mm in length, or
 119 cubic, measuring 50 mm in each dimension. Cylindrical specimens were used
 120 for SEM analyses, and cubic specimens were used for strength evaluation.
 121 Specimens were either moist-cured at ambient temperature or heat-cured at
 122 elevated temperature. The former was at 23 ± 2 °C and in excess of 95 %RH
 123 and the latter at 50 ± 0.1 °C. Moist-cured specimens were demolded after 24
 124 hours when possible; a few slowly-setting mixtures were demolded after 72
 125 hours. Heat-cured specimens remained sealed within the molds to prevent
 126 moisture loss during curing.

127 Compressive strength of paste cubes was determined in accordance with
 128 the specifications of ASTM C109 after demolding and 7, 14, 28, and 56 d

curing for moist-cured specimens and after 24 and 48 h curing for heat-cured specimens. Microstructural features were observed by backscattered scanning electron microscopy of epoxy-impregnated, polished, and sputter-coated segments sawn from cured cylindrical paste specimens. Specimens were sputter-coated with gold and palladium. Carbon tape was used to maintain conductivity through the sample holder. The elemental composition of the pastes was determined by electron dispersive X-ray spectroscopy (EDS) in conjunction with electron microscopy. More than one dozen representative points per sample were used for EDS analysis. The experimental parameters have been describe in great detail by Deir et al. [15] and Gebregziabiher et al. [28].

Reaction kinetics were studied using in-situ isothermal conduction calorimetry in accordance with the specifications of ASTM C1702 at 25 °C and 50 °C. Calorimetry is ordinarily performed using ex-situ mixing, where the sample is mixed in an ampoule and then inserted into the calorimeter. The ex-situ mixing and thermal instability resulting from the insertion of the fresh binder into the calorimeter prevent the measurement of heat evolution during the first 30-40 minutes of hydration. In portland cement-based binders, this time period only involves the initial dissolution of the cement. In alkali-activated systems, significant product formation also occurs during this time period. It is therefore necessary to accurately measure the heat evolution during the very-early stages of the alkali-activation reaction. In order to do so, in-situ mixing was used in this study; the binder and activator were stored separately in a special mixing ampoule within the calorimeter until thermal stability was reached. The activator was then injected into the binder and

154 mechanically mixed, allowing for the accurate measurement of very- early
155 heat evolution.

156 **3. Results**

157 *3.1. Mechanical strength*

158 The compressive strength development of alkali-activated slag binders
159 cured at ambient and elevated temperature is presented in Figure 1. NaOH-
160 activated slag develops strength rapidly at both ambient and elevated curing
161 temperatures, as shown in Figures 1a and 1b (respectively). At ambient
162 temperature, early strength development is dependent on activator molarity.
163 Later-age strength was independent of activator molarity. This suggests that
164 increased activator molarity, while improving early-age strength, either has a
165 limiting effect on later-age strength or simply results in the binder reaching
166 it's maximum strength earlier. This is mainly due to the formation of a reac-
167 tion ring on the surface of slag grains, especially with high-molarity activators
168 [28]. The strength of NaOH-activated slag after 24 and 48 hours heat curing
169 improved with increased activator molarity, suggesting that curing at ele-
170 vated temperature helps to overcome any later-age strength-limiting effects
171 due to high-molarity activators. Most of the strength development occurred
172 within 24 hours with little improvement thereafter, as has been reported by
173 several studies [15, 21, 28].

174 The later-age compressive strength of SS-activated slag, as shown in Fig-
175 ures 1c and 1d, was generally higher than that of NaOH-activated slag. De-
176 spite this, the early strength development at ambient temperature was decid-
177 edly more gradual. With low sodium oxide dosages and ambient-temperature

curing, specimens could only be demolded after 72 hours curing due to delayed setting and low early strength. Despite slow early strength gain in SS-activated slag, these mixtures reached equivalent strengths to NaOH-activated slag within a few days. Later-age strengths were much improved. Under ambient curing, the compressive strength improved as silica modulus increased. At elevated temperature, the strength improved as both silica modulus and sodium oxide dosage increased. Most of the strength development again occurred within 24 hours. The later-age strength of specimens cured at ambient temperature was similar to the strength of those cured at elevated temperature. With very high sodium oxide dosage (7%), a strength of nearly 150 MPa was achieved.

3.2. Reaction kinetics

The reaction kinetics of the various activated slag systems studied here are presented in the following manner: The heat flow at 25 °C and 50 °C are first shown in two subfigures. Inset figures are used to magnify the very-early-age heat flow. A third subfigure simultaneously shows the cumulative heat evolution at both temperatures. The calorimetric data presented here reflect the average curve from several replicate samples, which showed little variation.

The reaction kinetics in NaOH-activated slag systems are described by Figure 2. Two reaction peaks were identified at 25 °C, corresponding to the formation of C-S-H with various levels of aluminum, magnesium, and sodium substitution [12]. Almost no induction period was observed between these two early reaction peaks. At 12M, the magnitude of the first peak almost completely eclipses the second. Despite drastically different heat flow during

Figure 1: Compressive strength development of alkali-activated slag binder pastes cured at ambient and elevated temperature. Note differences in scale

203 the initial dissolution, the total heat evolved after 60 hours is about the same
204 at all activator molarities. This reasonably follows the similarities in later-
205 age compressive strength discussed in the previous section. Both are likely
206 a result of the product formation on the surface of slag grains, which limits
207 later-age hydration and strength gain.

208 The hydration of NaOH-activated slag was greatly accelerated at 50 °C.
209 Only one major heat evolution event was recorded at all activator molarities.
210 The most rapid parts of the reaction occurred within the first three hours,
211 and the bulk of the heat evolution had subsided within 8 hours. Increased
212 activator molarity resulted in increased heat flow during the lone hydration
213 event as well as increased cumulative heat flow after 60 hours. This is fur-
214 ther evidence that elevated temperatures provide the energy necessary to
215 overcome the barriers to continued later-age hydration that are presented by
216 high-molarity activators. The compressive strength results presented in the
217 previous section again echo this conclusion.

218 The reaction kinetics in SS-activated slag systems with varying silica mod-
219 ulus and constant sodium oxide concentration (2.5 % by mass of slag) are
220 described by Figure 3. At 25 °C, an early peak corresponding to initial dis-
221 solution and wetting of slag particles was followed by two additional heat
222 evolution events. The first corresponds to early product formation, pro-
223 moted by the high alkalinity of the activator solution. The second occurs as
224 the alkalis are depleted by the early product formation and the relative silica
225 concentration increases, promoting the dissociation of calcium [24, 37]. The
226 retarding effect of silica was indicated by the greatly delayed occurrence of
227 the later two reaction processes, which were consequently of longer duration

Figure 2: Heat flow and cumulative heat evolution in sodium hydroxide-activated slag binders at varying activator molarity

228 and lesser intensity. The bulk of the reaction processes were complete within
229 about 72 h at 25 °C. The cumulative heat evolved was greater with lower
230 silica modulus for the first 60 h, but thereafter identical. This is indicative of
231 slower hydration with increased silica, but with no penalty in the degree of
232 hydration at later age. These calorimetry data closely follow the compressive
233 strength data for those binders cured at ambient temperature. However, the
234 strengths at elevated temperature were improved with increased silica modu-
235 lus, but the heat evolution after about 60 hours is very much the same. The
236 reason for this remains unknown.

237 At 50 °C, the initial dissolution of SS-activated slag was replaced by a
238 short endothermic period lasting fewer than ten minutes. Two additional
239 reaction peaks were again observed. The increased temperature resulted in
240 more rapid hydration, as expected, accelerating the reaction by a factor of
241 three or more. With lower silica modulus ($m = 1.5$), the reaction peaks
242 occurred after about 15 minutes and six hours. The increased silica at $m =$
243 2.5 delays the occurrence of these peaks to 2 and 9 h (respectively). The
244 duration and intensity of both reaction events at 50 °C were affected by silica
245 modulus in the same manner as previously discussed for 25 °C. Similarly,
246 the cumulative heat evolved was greater with lower silica modulus for the
247 first 12 h; thereafter, higher silica modulus resulted in greater cumulative
248 heat evolved. This again indicates slower but more complete hydration with
249 increased silica.

250 The reaction kinetics in SS-activated slag with varying sodium oxide con-
251 centration and constant silica modulus ($m = 1.5$) are described by Figure 4.
252 At both 25 °C and 50 °C, increased sodium oxide concentration greatly ac-

253 celerated hydration. This caused the dissolution and primary reaction peaks
 254 observed at low sodium oxide concentration (2.5% by mass of slag, Figure
 255 3) to morph into a single high-intensity peak lasting for the first hour of the
 256 reaction. The observed effect is similar to that seen with increased activa-
 257 tor molarity in NaOH-activated slag. The accelerating effect of increased
 258 sodium oxide at 25 °C is so great that the induction period, which lasts
 259 nearly 24 hours at 2.5 % Na₂O, is reduced to just one or two hours at 5 %
 260 and 7 % Na₂O. At 50 °C, the induction period is essentially nonexistent at
 261 5 % and 7 % Na₂O. At both temperatures, the cumulative heat evolved after
 262 60 hours increased with increased sodium oxide concentration; this, combined
 263 with similar compressive strength trends, indicates more advanced hydration
 264 in SS-activated slag with higher sodium oxide dosages. As expected, the cu-
 265 mulative heat evolved was much greater at 50 °C than at 25 °C due to the
 266 strong accelerating effect of increased curing temperature.

267 *3.3. Microstructure*

268 The microstructure of NaOH-activated slag pastes with varying activator
 269 molarity is compared in Figure 5. In backscattered scanning electron micro-
 270 graphs, the brightest features are the densest and the darkest are the least
 271 dense. The microstructure of such pastes has been reported to include three
 272 main phases, viz. the main reaction product (ground mass gel), incompletely-
 273 reacted slag grains, and an inner product reaction ring surrounding the un-
 274 reacted slag grains [13, 15, 28, 38]. Together, the latter two are known as
 275 the phenograins. Unreacted slag grains are visible as large white masses of
 276 the order 10 microns in diameter; these are by far the densest features of the
 277 microstructure. The inner product (reaction ring) appears as a dark gray

Figure 3: Heat flow and cumulative heat evolution in sodium silicate-activated slag binders at varying silica modulus and constant sodium oxide concentration (2.5 % by mass of slag)

(a) Heat flow at 25 °C

(b) Heat flow at 50 °C

(c) Cumulative heat evolution

Figure 4: Heat flow and cumulative heat evolution in sodium silicate-activated slag binders with varying sodium oxide concentration and constant silica modulus ($m = 1.5$)

278 ring surrounding the unreacted slag grains, and the ground mass gel is the
279 lighter gray matrix that makes up the bulk of the micrograph. Although
280 early-age micrographs are not presented, these phases were apparent after
281 as few as six hours curing at 23 ± 2 °C. The presence of the inner product
282 reaction ring is indicative of the diffusion-controlled reaction process where
283 the formation of the reaction ring hinders continued diffusion [15, 28].

284 Few differences were identified between the microstructure of NaOH-
285 activated slag cured at 23 °C and 50 °C. The inner product reaction ring
286 was observed at both curing temperatures, but the transition from ground
287 mass gel through the inner product ring to the unreacted slag grains was
288 more gradual at elevated temperature. The reaction rings appeared darker
289 and more defined at ambient temperature, and were therefore likely less
290 dense. This provides some context for the compressive strength results re-
291 ported above. The diffusion-limiting effect of high-molarity activators was
292 not observed at 50 °C, which is likely due to the formation of a denser and
293 therefore stronger inner product at elevated temperature. In addition, more
294 abundant nucleation sites and a reduced number of pores were visible in
295 pastes cured at 50 °C, indicating increased product formation at elevated
296 temperature. Some microcracking of pastes cured at elevated temperature
297 was also observed, particularly with low-molarity activators. Since crack-
298 ing generally occurs due to tensile stresses from the removal of water from
299 the hydrated paste, and since lower-molarity activators necessarily include
300 more abundant free water, increased prevalence of cracking at low molarity
301 is logical.

302 The microstructure of SS-activated slag with varying silica modulus is

Figure 5: Micrographs showing the effect of curing temperature and sodium oxide concentration on the microstructure of sodium hydroxide-activated slag binders

303 compared in Figure 6. In general, the microstructural development was
304 slower in SS-activated slag than in NaOH-activated slag. Most of the fea-
305 tures were not visible until about 24 h at 25 °C. Where the microstructure of
306 NaOH-activated slag was shown to include three prominent phases, only two
307 were observed in SS-activated slag; no prominent reaction ring was observed
308 on the surface of the unreacted slag grains in SS-activated pastes. The lack
309 of such a barrier to continued later-age hydration is a likely explanation for
310 improved later-age strength development in SS-activated slag as compared to
311 NaOH-activated slag. Both the density and homogeneity of the ground mass
312 gel and the size of the unreacted slag grains increased with silica modulus.
313 This indicates that, while hydration was slower with higher silica modulus,
314 the product formed is of higher quality; the practical implication of this con-
315 clusion is that the binder will be of higher strength, as evidenced by the
316 compressive strength values stated previously. The microstructure of pastes
317 cured at 50 °C was more porous and visibly less refined as a result of the
318 accelerated product formation. This suggests that the accelerated reaction
319 results in the formation of products of lesser density and quality. Neverthe-
320 less, the mechanical strengths were similar at both curing temperatures.

321 The microstructure of SS-activated slag with varying sodium oxide con-
322 centration and constant silica modulus ($m = 1.5$) is compared in Figure 7.
323 The density, degree of refinement, and abundance of the ground mass gel
324 increased with sodium oxide concentration, and the physical size of the unre-
325 acted slag grains was reduced. However, the prevalence of microcracking also
326 increased with sodium oxide concentration, which likely follows the enhanced
327 brittleness of these very-high-strength pastes.

Figure 6: Micrographs showing the effect of curing temperature and silica modulus on the microstructure of sodium silicate-activated slag binders

Figure 7: Micrographs showing the effect of sodium oxide concentration on the microstructure of sodium silicate-activated slag binders cured for 48 hours at 50 °C

3.4. Composition

The atomic composition of alkali-activated slag binders was evaluated by EDS in conjunction with microstructural analysis using SEM. At least one dozen representative points were analyzed for each sample. The elemental compositions are presented in Table 2 and in Figures 8 and 9. The compositions are given as the ratios of atom percentages as calculated by the EDS instrument software. The error bars in Figures 8 and 9 represent the average atom percentage error as given by the same. The percent composition of Na, Mg, Al, and Ca are given relative to Si. For reference, the abundance of Si (in atom %) is also given in Table 2. Although it is not visible from microscopy due to the very small scale, the inclusion of large quantities of Mg and Al indicate the presence of hydrotalcite within the C-S-H product. This has been previously observed by several studies [12, 31].

The abundance of Si in the inner product and ground mass gel in NaOH-activated slag increased slightly but measurably with increased activator molarity. The abundance of Si also increased slightly but measurably with curing temperature. The abundance of Na (relative to Si) in both the inner product and ground mass gel in NaOH-activated slag increased with activator molarity at both curing temperatures (Figure 8). This of course results from the increased dosage of sodium in higher-molarity activators. There was little measurable difference in the abundance of sodium at elevated or ambient temperature. The abundance of Mg and Al (relative to Si) generally decreased as activator molarity increased, while the abundance of Ca followed the opposite trend. These changes with activator molarity were minor relative to the error of the analysis. However, the appearance of this

Table 2: Average atomic ratios for reaction products in NaOH- and SS-activated GGBFS (IP = inner product, OP = outer product)

Activator	Location	Si (atom %)		Na/Si		Mg/Si		Al/Si		Ca/Si	
		25° C	50° C	25° C	50° C	25° C	50° C	25° C	50° C	25° C	50° C
5M NaOH	IP	8.3	8.9	0.15	0.14	0.35	0.42	0.38	0.27	1.36	1.21
5M NaOH	OP	8.5	8.3	0.24	0.32	0.38	0.46	0.36	0.30	1.22	1.15
8M NaOH	IP	8.8	9.0	0.40	0.31	0.31	0.44	0.48	0.25	1.63	1.33
8M NaOH	OP	8.6	8.9	0.77	0.56	0.25	0.39	0.39	0.25	1.34	1.18
12M NaOH	IP	9.2	9.6	0.51	0.79	0.24	0.31	0.36	0.21	1.81	1.41
12M NaOH	OP	8.8	9.3	0.98	1.25	0.13	0.21	0.33	0.19	1.43	1.32
SS $m = 1.5$	OP	8.5	10.1	0.17	0.09	0.14	0.31	0.13	0.24	1.01	1.09
SS $m = 2.5$	OP	9.8	15.3	0.14	0.07	0.36	0.17	0.24	0.21	0.82	1.10

353 general trend suggests the preferential formation of C-S-H with less inter-
354 mixed hydrotalcite [12, 31]. This was observed at both ambient and elevated
355 temperature, and in the inner product and ground mass gel. The effect
356 was strongest in the inner product at ambient temperature, but only by a
357 small margin. The abundance of Na is generally higher in the ground mass
358 gel, while the abundance of Ca is generally higher in the inner product. The
359 abundance of Mg and Al are about the same in the inner product and ground
360 mass gel.

361 In contrast to the results presented for NaOH-activated slag, the compo-
362 sition of SS-activated slag (relative to Si) was essentially unchanged, at least
363 within the margin or error of the EDS analysis. The abundance of silica
364 increased with silica modulus, as was expected. The abundance of silica also
365 increased with temperature, which is likely due to the increased solubility
366 of amorphous silica from slag at elevated temperature. There was a marked
367 decrease in the abundance of Ca (relative to Si) as the silica modulus in-
368 creased at ambient temperature, but this effect was not observed at elevated
369 temperature. This indicates that an increase in silica modulus leads to the

Figure 8: Atomic ratios (Na, Mg, Al, and Ca relative to Si) in sodium hydroxide-activated slag binders cured for 28 days at 23 ° and 48 hours at 50 °C

370 formation of C-S-H of a lower Ca/Si ratio. The abundance of sodium was
 371 unchanged with silica modulus. This makes sense, since the dosage of sodium
 372 oxide in the activator was constant. Additionally, there was little measurable
 373 change in the abundance of Al or Mg (relative to Si).

374 4. Discussion

375 Thy hydration of sodium hydroxide-activated slag is marked by rapid
 376 product formation within thirty minutes of mixing. Increased early heat
 377 evolution at ambient temperature suggests more product formation during
 378 this period. Increase abundance of Ca and Si in the inner product suggests
 379 the formation of a denser inner product which limits later age hydration. This
 380 limits the later-age strength gain. Despite differences in early-age strength

Figure 9: Atomic ratios (Na, Mg, Al, and Ca relative to Si) in sodium silicate-activated slag binders cured for 28 days at 23 ° and 48 hours at 50 °C

and heat evolution, the later-age strength and cumulative heat evolved are similar across molarities. Curing at elevated temperature seems to overcome this barrier to continued hydration. At 50 °C, the strength, heat evolution, and product phase composition all vary with activator molarity. The practical implication is that, while there is a limit at ambient temperature beyond which increased activator molarity will not improve mechanical strength, this can be overcome by curing at elevated temperature. Increased activator molarity tends to decrease increase the abundance of Ca and Si, and decrease the abundance of Mg and Al, suggesting that less hydrotalcite and more C-S-H is formed at higher molarities.

In stark contrast to sodium hydroxide-activated slag, the hydration of sodium silicate-activated slag is slow and controlled. Hydration is marked by the gradual formation of very dense product phases. The result is greatly

394 improved mechanical strength which increases with both silica and sodium
395 oxide concentration. Hydration is greatly accelerated by additions of sodium
396 oxide and retarded by additions of silica. The reaction continues to progress
397 through 60 h, with induction periods as long as 24 h. With high sodium oxide
398 concentration, however, the bulk of the reaction processes may be completed
399 within 12 h (at ambient temperature) or 4 h (at elevated temperature). The
400 practical implication here is that both the setting time and strength of these
401 binders may be easily tuned by adjusting the sodium oxide and silica con-
402 centration of the activator. This makes these binders extremely versatile.
403 The increased abundance of Ca and Si at elevated temperature and with
404 higher silica modulus suggests more complete product formation under both
405 conditions, which is echoed by improved compressive strength.

406 5. Conclusions

407 The conclusions drawn from these information can be summarized as
408 follows:

- 409 • In general, hydration occurs much more rapidly in sodium hydroxide-
410 activated slag than in sodium silicate-activated slag. At ambient tem-
411 perature, the microstructure of sodium hydroxide-activated slag is clearly
412 distinguishable after as little as 6 hours compared to 24 hours for
413 sodium silicate-activated slag. The heat of hydration is much lower
414 in sodium silicate-activated slag.
- 415 • Increased activator molarity in sodium hydroxide-activated slag accel-
416 erates hydration. At ambient temperature, this rapid hydration results

in the formation of an inner product reaction ring, the density of which is dependent on activator molarity. High-molarity activators, while providing excellent early strength development, limit later-age product formation due to this high-density diffusion-limiting barrier. The result of this is that the strength at ambient temperature is not improved with increased activator molarity.

- Curing sodium hydroxide-activated slag at elevated temperature greatly accelerates product formation and strength gain. Additionally, the increased temperature is sufficient to overcome the barrier to advanced hydration presented by the dense inner product ring observed with high-molarity activators. This results in improved strength with higher activator molarity when cured at elevated temperature.
- Silica in the alkaline activating solution has a distinct retarding effect on the hydration of sodium silicate-activated slag, which limits the early-age strength but results in the formation of denser product phases with higher later-age strength.
- Sodium oxide greatly accelerates hydration in sodium silicate-activated slag, resulting in significant improvements in early product formation and strength development as well as later-age strength. Very high-strength binders can be created using sodium silicate activators with high sodium oxide content.
- Elevated temperature curing greatly accelerates product formation and strength gain in sodium silicate-activated slag. These products are generally of higher density but are present at lower volume fraction

441 within the microstructure. Additionally, elevated temperatures have a
442 tendency to result in increasingly prevalent microcracking.

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