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1 **The Role of Zinc in Metakaolin-Based Geopolymers**

2 Lei Wang^{1,2,3}, Daniel A. Geddes¹, Brant Walkley^{1,4}, John L. Provis¹, Viktor Mechtcherine³,
3 Daniel C.W. Tsang^{2,*}

4

5 ¹ Department of Materials Science and Engineering, The University of Sheffield, Sir Robert Hadfield
6 Building, Mappin St, Sheffield S1 3JD, United Kingdom.

7 ² Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom,
8 Kowloon, Hong Kong, China.

9 ³ Institute of Construction Materials, Technische Universität Dresden, 01062 Dresden, Germany.

10 ⁴ Department of Chemical and Biological Engineering, The University of Sheffield, Sir Robert Hadfield
11 Building, Mappin St, Sheffield S1 3JD, United Kingdom.

12 * Corresponding author: dan.tsang@polyu.edu.hk

13

14 **Abstract**

15 Geopolymers are low-calcium, sustainable cementitious materials. The role of Zn, a known
16 retardant used in Portland cement, in geopolymer systems is not well understood. This study
17 scrutinises the effect of Zn on metakaolin-based geopolymer reaction mechanisms and kinetics,
18 and investigates the incorporation mechanism of Zn in geopolymer gels. Isothermal
19 calorimetry and X-ray diffraction analyses show that substitution of ZnO (20 mol.% c.f.
20 metakaolin) significantly hinders reaction, likely due to preferential formation of a Na/K-Zn
21 containing phase. Solid-state nuclear magnetic resonance spectroscopy shows that Zn²⁺
22 partially substitutes for Na⁺/K⁺ in charge-balancing sites within the geopolymer gel. Setting
23 time and leaching tests show that the retarding effect of Zn on reaction kinetics is significantly
24 greater in Na-activated geopolymers compared with K-activated geopolymers, whereas Na-
25 activated geopolymers exhibit superior fixation capacity to Zn. A lab-scale experiment

26 demonstrates that metakaolin-based geopolymers are promising candidates for the
27 stabilisation/solidification of Zn-rich hazardous waste.

28

29 **Keywords:** geopolymer; alkali-activation; reaction kinetics; retarding mechanism; hazardous
30 waste immobilisation.

31

32 **Highlights:**

- 33 • High-dosage of ZnO significantly hindered the geopolymer reaction process.
- 34 • Crystalline ZnO consumed in alkali-activation reaction to form new amorphous material.
- 35 • Zn^{2+} partially replaced Na^+/K^+ in charge-balancing sites within geopolymer gel framework.
- 36 • Retarding effect of Zn on reaction kinetics was significantly greater in Na-activated
37 geopolymers compared with K-activated geopolymers.
- 38 • Na-activated geopolymer performed with superior efficiency in Zn-immobilisation.

39

40 **1. Introduction**

41 Geopolymers are alternative cementitious materials comprised of a three-dimensionally cross-
42 linked, highly polymerised, and non-crystalline alkali aluminosilicate network [1].
43 Geopolymers are produced via reaction of aluminosilicate precursors, such as metakaolin
44 (MK), blast furnace slag, and pulverised fuel ash, with alkaline solutions, typically alkali
45 silicate or alkali hydroxide [2]. Geopolymer cements offer up to 80% reduction of CO₂
46 emissions compared to Portland cement (PC) by avoidance of CO₂ release from limestone
47 calcination and the need for high temperature (1400 °C) treatment during cement clinker
48 production [3,4]. As a consequence, geopolymers are low-carbon, sustainable cementitious
49 materials and viable substitutions for PC in certain applications. The nanostructure of
50 geopolymer cements is different from that of PC, primarily due to the low-Ca content of

51 geopolymer systems [5]. Calcium silicate hydrate (C-S-H) gel is the main hydration product of
52 PC and exhibits a tobermorite-like structure, whereas the sodium/potassium aluminosilicate
53 hydrate ((N/K)-A-S-H) gel formed in geopolymer cements exhibits a fully polymerised and
54 disordered structure [2]. When properly formulated, geopolymer cements exhibit superior
55 performance to PC in many applications, including fire-resistant composites, acid-resistant
56 concrete, and hazardous and radioactive waste immobilisation [6-9].

57

58 Cement-based stabilisation/solidification (S/S) is a widely accepted and reliable technology for
59 soil remediation and hazardous waste treatment via chemical fixation and physical
60 encapsulation of toxic or hazardous components [10-12]. Cementation of toxic or hazardous
61 wastes offers advantages over other solidification approaches, such as low cost, ease of use,
62 rapid waste processing, and high durability [13]. Furthermore, S/S products can be recycled
63 and used as sustainable and value-added construction materials [14,15]. However, in PC-based
64 S/S system, many toxic or hazardous elements can delay hydration and compromise the
65 physicochemical properties of S/S products. Zinc (Zn) is particularly problematic, and is a well-
66 known retarder in PC systems [16,17]. Previous research showed that the presence of 0.2 wt%
67 ZnO in PC paste prolongs the initial and final setting times by 4 times and 3.5 times,
68 respectively [18]. Zn in cement clinker should therefore be below a threshold of 0.7 wt%;
69 higher content of Zn can significantly delay, and even halt, PC hydration [19,20]. Such adverse
70 effects limit the application of PC for S/S of Zn-rich industrial waste [21]. The retarding
71 mechanism has been attributed to the formation of $\text{Ca}(\text{Zn}(\text{OH})_3)_2 \cdot 2\text{H}_2\text{O}$ which surrounds
72 clinker particles [18], hindering the further dissolution and reaction, and depletes soluble
73 calcium [22], limiting nucleation and growth of C-S-H gel or calcium aluminium silicate
74 hydrate (C-A-S-H) gels. In both cases, the retarding mechanism results from the interaction of
75 Ca and Zn in the cement system. Low-Ca or Ca-free geopolymer cements are have therefore

76 gained significant interest for S/S of Zn-contaminated waste.

77

78 Although there remains an absence in the literature of a complete mechanistic understanding
79 of the interaction of Zn and geopolymer cement systems, recent findings [22] have shown that
80 the presence of low-dosage ZnO of up to 1 wt% has a negligible inhibitory effect on the
81 reaction process of low-Ca alkali-activated materials. Furthermore, MK-based geopolymers
82 have the potential to adsorb Zn ions due to the porous and amorphous nature of MK [23],
83 further reducing any inhibitory effect on reaction kinetics. However, many industrial processes
84 produce Zn-rich by-products or wastes via different physicochemical processes (e.g.
85 coagulation/precipitation and sedimentation). As a result, highly concentrated Zn is observed
86 in mine tailings, smelter waste, and industrial sludge [24-26]. In particular, electroplating
87 sludge contains approximately 46.6 wt% ZnO, and is therefore a severe threat to human health
88 and to ecosystem. Therefore, to develop appropriate S/S technologies for the safe treatment of
89 Zn-rich waste, the inhibitory effect of high amounts of Zn on the reaction mechanisms and
90 kinetics in geopolymer systems must be investigated.

91

92 Ion retention, dictated by the incorporation mechanisms and mass transport processes, is the
93 primary indicator of S/S efficiency when encapsulating toxic waste. Recent work has shown
94 that the fully polymerised alkali aluminosilicate framework structure in geopolymer cements
95 is beneficial for encapsulation of toxic elements within the structure [27], and that the negative
96 charge due to Al(III) in fourfold coordination in (N,K)-A-S-H gels can be charge-balanced by
97 alkaline earth cations Ca^{2+} and Sr^{2+} [28]. However, there remains an absence from the literature
98 of a detailed understanding of the effect of high amounts of Zn on the reaction mechanisms
99 and kinetics in the MK-based geopolymer cements.

100

101 To provide insight into the effect of Zn on the reaction mechanisms, kinetics and Zn-
102 incorporation mechanisms of geopolymer cements, and to offer engineering solutions for the
103 application of geopolymer-based S/S for Zn-rich waste, this study aims to: (i) elucidate the role
104 of Zn in the reaction processes occurring during the formation of different (N,K)-A-S-H gels,
105 including any inhibitory effects; (ii) assess the incorporation mechanisms of Zn in different
106 geopolymer cement systems with varying alkalinity; (iii) evaluate the efficiency of geopolymer
107 for S/S of Zn-rich sludge in terms of setting time, compressive strength, and leachability.

108

109 **2. Materials and Methods**

110 **2.1 Materials**

111 In this study, MK was used as a precursor, and sodium or potassium silicate solutions were
112 used as activators. High purity MK was purchased from BASF, Germany, with a $\text{SiO}_2/\text{Al}_2\text{O}_3$
113 ratio of 2.0 and a particle size d_{50} of 25 μm . The activating solutions were made of either
114 sodium or potassium silicate (PQ Silicates, UK) mixed with reagent grade MOH (M
115 representing either Na or K; Fisher, UK). Zn-rich industrial sludge (46.6 wt% ZnO), used for
116 geopolymer-based S/S, was collected from an electroplating factory in Zhejiang Province,
117 China. The chemical composition and XRD patterns of this sludge are illustrated in Table S1
118 and Figure S1 (Supplementary Information), respectively. The dewatered sludge cake
119 contained 57.2 wt% remaining water and yielded a 24.7 wt% loss on ignition. The sludge was
120 freeze-dried and crushed into particles with diameters less than 0.3 mm before use.
121 Additionally, high purity ZnO/Zn(OH)₂ was used to evaluate the role of Zn on the reaction
122 mechanisms, kinetics and incorporation processes in geopolymer cements. ZnO/Zn(OH)₂ was
123 synthesised from zinc nitrate hexahydrate (98% purity, Fisher) and sodium hydroxide ($\geq 99\%$
124 purity, Fisher) via a hydrothermal synthesis method, as described previously [29]. At
125 atmospheric pressure and room temperature, almost all of the formed $\varepsilon\text{-Zn(OH)}_2$ was

126 transformed into ZnO. Thus, ZnO powder ($\geq 95\%$) is a predominant component in the final
127 products, with trace amounts of Zn(OH)_2 [29]. The XRD pattern of the synthesised ZnO is
128 illustrated in Figure S1.

129

130 ***2.2 Sample Preparation***

131 Sodium silicate or potassium silicate were designed with a $\text{SiO}_2/\text{M}_2\text{O}$ molar ratio of 0.5, 1.0,
132 and 1.5, and a $\text{H}_2\text{O}/\text{M}_2\text{O}$ molar ratio of 13. In Zn-free geopolymer (control) system, $\text{Al}_2\text{O}_3/\text{M}_2\text{O}$
133 ratio was 1. In the Zn-substituted geopolymer system, $\text{Al}_2\text{O}_3/\text{M}_2\text{O}$ ratio was 0.8 and $\text{ZnO}/\text{M}_2\text{O}$
134 ratio was 0.2. For geopolymer samples with Zn-sludge addition, geopolymer paste/sludge
135 ratios were designed at 1:1, 1:2 and 1:4 by weight, and extra water (50% of dry sludge) was
136 added to achieve favourable flowability. The mixture design of geopolymer samples with and
137 without ZnO/Zn-rich sludge is illustrated in Table 1. For sample preparation, MK precursor
138 powder was mixed into the activating solution by a high-speed stirrer for 5 min. ZnO or sludge
139 powder was gradually added into the mixture and stirred for another 5 min. The fresh pastes
140 were transferred into sealed containers and steel moulds ($2 \times 2 \times 2 \text{ cm}^3$). Sealed samples and
141 demoulded samples (after 3-day casting) were cured at $20 \text{ }^\circ\text{C}$ for 7 days and 28 days,
142 respectively. All the experiments on the cement pastes and sludge S/S blocks were performed
143 in triplicate and quadruple, respectively.

144

145 **Table 1.** Mixture design (molar ratios) of geopolymer samples with or without Zn.

	SiO ₂ /M ₂ O	SiO ₂	Na ₂ O	K ₂ O	H ₂ O	MK	ZnO	Sludge*
S/N 0.5	0.5	0.5	1	0	13	1	0	0
S/N 1.0	1.0	1	1	0	13	1	0	0
S/N 1.5	1.5	1.5	1	0	13	1	0	0
S/K 0.5	0.5	0.5	0	1	13	1	0	0
S/K 1.0	1.0	1	0	1	13	1	0	0
S/K 1.5	1.5	1.5	0	1	13	1	0	0
S/N 0.5-Z	0.5	0.5	1	0	13	0.8	0.2	0
S/N 1.0-Z	1.0	1	1	0	13	0.8	0.2	0
S/N 1.5-Z	1.5	1.5	1	0	13	0.8	0.2	0
S/K 0.5-Z	0.5	0.5	0	1	13	0.8	0.2	0
S/K 1.0-Z	1.0	1	0	1	13	0.8	0.2	0
S/K 1.5-Z	1.5	1.5	0	1	13	0.8	0.2	0
N-S1	1.0	1	1	0	13	1	0	1:1
N-S2	1.0	1	1	0	13	1	0	1:2
N-S4	1.0	1	1	0	13	1	0	1:4
K-S1	1.0	1	0	1	13	1	0	1:1
K-S2	1.0	1	0	1	13	1	0	1:2
K-S4	1.0	1	0	1	13	1	0	1:4

146 M₂O: Na₂O or K₂O; MK: metakaolin

147 *binder-to-sludge mass ratio

148

149 **2.3 Characterisation and Analyses**

150 The initial and final setting times of the geopolymer samples with or without ZnO/sludge were
 151 examined by a Vicat apparatus [30]. The uniaxial compressive strength of the sludge-based
 152 blocks was tested using a universal testing machine at a loading rate of 0.3 MPa s⁻¹ [31]. The
 153 kinetics of the reaction of Zn-incorporated geopolymer samples were assessed using an
 154 isothermal calorimeter (TAM Air instrument) at 20 ± 0.02 °C. The leachability of Zn/sludge-
 155 incorporated samples was tested according to the Toxicity Characteristic Leaching Procedure
 156 (TCLP) [32]. The leaching concentrations of toxic elements were detected by means of
 157 inductively coupled plasma atomic emission spectrometry (ICP-AES, Spectro Arcos).

158

159 Chemical components of the geopolymer samples were analysed by thermogravimetric

160 analysis coupled with mass spectrometry (TGA-MS, Perkin Elmer TGA 4000 coupled to MS)
161 at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from $30\text{ }^{\circ}\text{C}$ to $1000\text{ }^{\circ}\text{C}$ with nitrogen as the purging gas. All
162 samples were held at $30\text{ }^{\circ}\text{C}$ for 20 min before the heating process. Water vapour, carbon
163 monoxide, nitrogen, oxygen, and carbon dioxide were analysed during the programmed heating
164 process. The surface morphology of the geopolymer samples was observed using by scanning
165 electron microscopy (SEM) with energy-dispersive X-ray (EDX) (QUANTA FEG 250).
166 Elemental mapping was performed on the crushed samples. Back scattered electron (BSE)
167 imaging was conducted on the polished geopolymer samples. The mineralogy of the powdered
168 samples was scanned using X-ray diffraction (XRD) (Bruker D8) in the range 2θ of $5\text{-}70^{\circ}$ and
169 at a step size of 0.020° . A Cu anode was used as source and the Cu K- α wavelength was 1.5406
170 \AA . A 10 wt% MgO was incorporated as an internal standard to quantify the content of ZnO
171 engaging in reaction.

172

173 The local structure of geopolymer reaction products was evaluated using solid-state magic
174 angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The ^{29}Si and ^{27}Al
175 spectra were acquired using a 500 MHz ($B_0 = 11.7\text{ T}$) solid-state NMR spectrometer
176 (GEOL500), yielding a Larmor frequency of 99.362 MHz for ^{29}Si NMR and 130.318 for ^{27}Al .
177 The chemical shifts of ^{29}Si and ^{27}Al were referenced to external standards of tetramethylsilane
178 (TMS) and a 1.0 M aqueous solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, respectively. The ^{29}Si experiments were
179 conducted using a 7 mm standard bore, one pulse MAS probe head, a rotational rate of $\nu_R =$
180 4.5 kHz , and a recycle delay of 30 s, acquiring from 108 to 2,000 scans. ^{27}Al NMR experiments
181 were conducted using a 4 mm MAS probe, a rotational rate of $\nu_R = 10\text{ kHz}$, a recycle delay of
182 2 s with 1000 scans. Gaussian peak profiles were used for the fitting of ^{29}Si MAS NMR spectra.
183 A single Gaussian peak was used for representing different $Q^n(\text{mAl})$ species, and these peaks
184 were used to create a simulation of the ^{29}Si NMR spectra by using a least-squares fitting

185 method. Peak intensities are consistent with the structural constraints described by the
186 statistical thermodynamic model for (N,K)-A-S-H products [33]. The molar ratio of Si/Al in
187 (N,K)-A-S-H gel can be calculated based on Engelhardt's formula [34] (Eq. 1):

$$188 \frac{\text{Si}}{\text{Al}} = \frac{\sum_{m=1}^4 I_{AQ^4(mAl)}}{\sum_{m=1}^4 0.25 \times m \times I_{AQ^4(mAl)}} \quad (1)$$

189 Where $I_{AQ^4(mAl)}$ is the normalised relative integral areas of ^{29}Si MAS NMR fitting peaks of
190 each $Q^4(mAl)$ site in the geopolymer gel.

191

192 **3. Results and Discussion**

193 ***3.1 The Role of Zn in the Alkali-Activation Reaction***

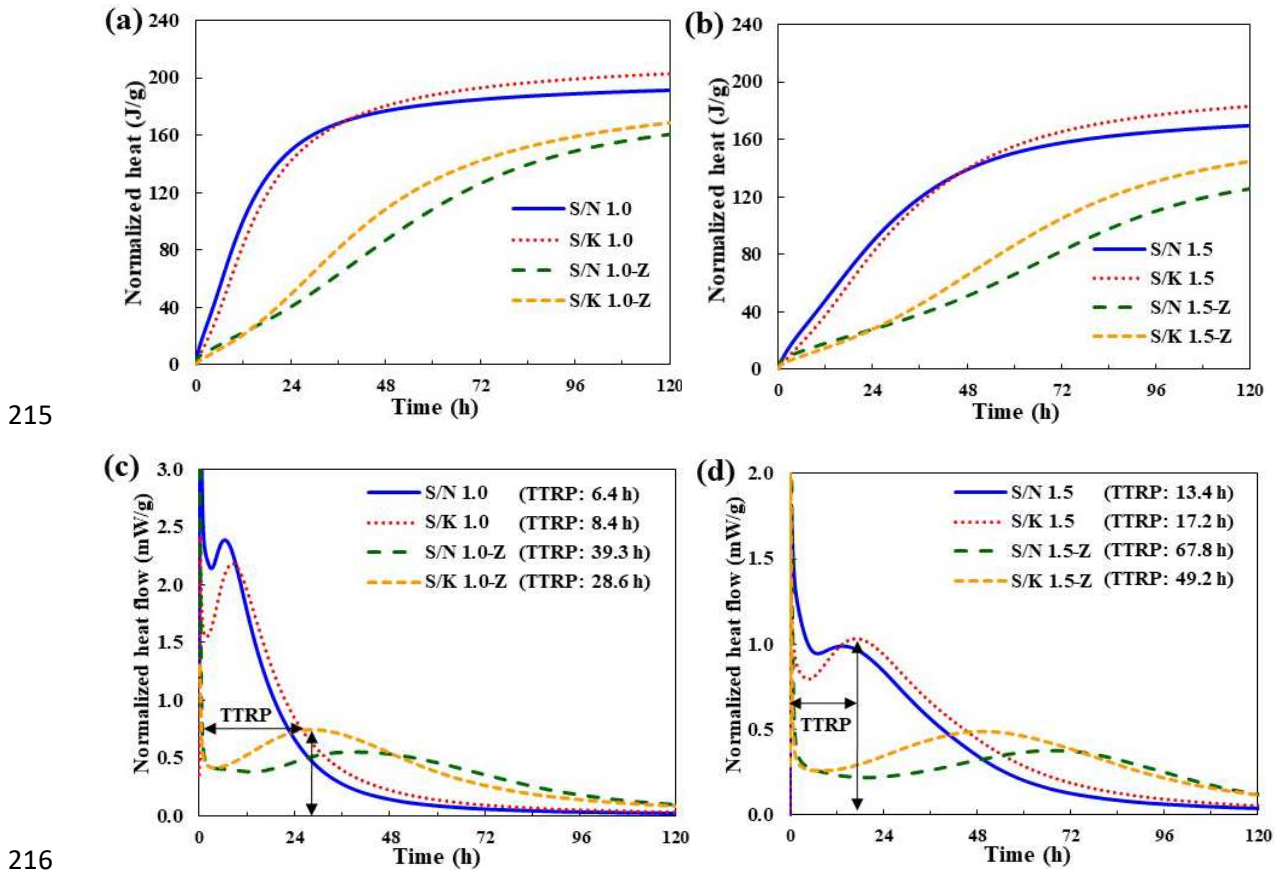
194 Figure 1 illustrates the heat evolution curves for the geopolymer pastes with and without ZnO.

195 As shown in Figure 1c, Na-activated geopolymer (S/N 1.0) samples presented a short dormant
196 period and the time to reach the reaction peak (TTRP) was 6.4 h. By comparison, the TTRP of
197 K-activated geopolymer (S/K 1.0) samples was longer. This indicated that the reaction in Na-
198 based geopolymer was relatively vigorous in the early stage. However, the cumulative heat
199 from S/K 1.0 surpassed S/N 1.0 samples after 37.8 h (Figure 1a). After substitution of ZnO,
200 the TTRPs were significantly prolonged and the cumulative heat was reduced. Interestingly,
201 TTRP in S/N 1.0-Z (39.3 h) was longer than that in S/K 1.0-Z samples (28.6 h), and cumulative
202 heat in S/N 1.0-Z samples was relatively low during the reaction over 120 h, which reflected
203 that Zn interacted with geopolymer chemically and had a more significant delay effect on the
204 Na-activated geopolymer.

205

206 From Figure 1b & d, in low-alkali geopolymer samples, i.e., $\text{SiO}_2/\text{M}_2\text{O}$ molar ratio of 1.5, the
207 TTRPs were longer and cumulative heats were lower than the values for high-alkali
208 geopolymer samples ($\text{SiO}_2/\text{M}_2\text{O}$ ratio of 1.0). This is ascribed to low concentrations of sodium
209 and potassium ions limiting nucleation and growth of the (N,K)-A-S-H gel [22]. It should be

210 noted that TTRPs in S/M 1.5-Z samples were much longer than that in S/M 1.0-Z samples.
 211 This revealed that while Zn exerted an inhibitory effect on both high- and low-alkali
 212 geopolymers, the effect was most pronounced in low-alkali geopolymers. The associated
 213 variations in setting time are discussed in Section 3.3.
 214



217 **Figure 1.** Isothermal calorimetry data of geopolymer pastes with and without ZnO: (a)
 218 cumulative heat of geopolymer pastes with SiO₂/M₂O ratio of 1.0; (b) cumulative heat of
 219 geopolymer pastes with SiO₂/M₂O ratio of 1.5; (c) heat flow corresponding to (a); (d) heat flow
 220 corresponding to (b). (TTRP: time to reach the reaction peak).

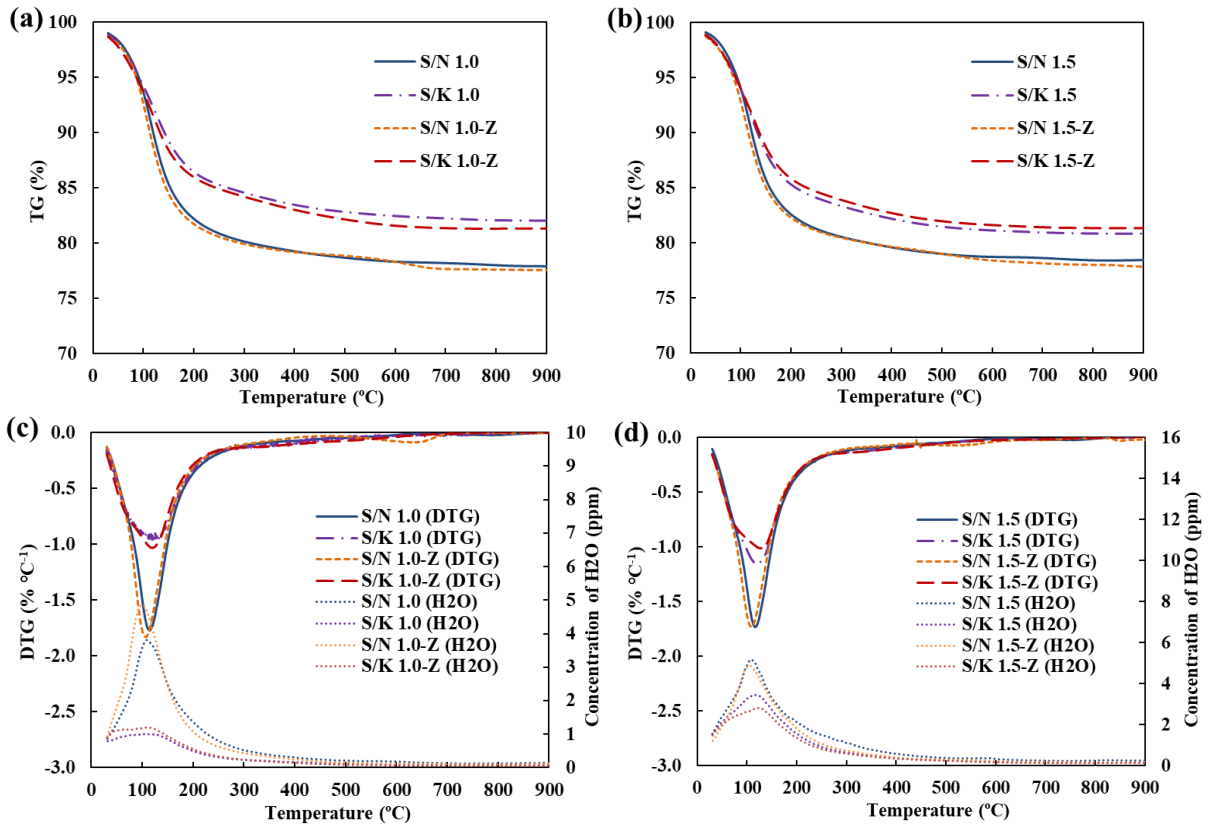
221
 222 Based on simulation results obtained using Visual MINTEQ software (Table S2), Zn(OH)₃⁻
 223 was the dominant dissolved species (13.3% to 80.5%) of Zn in S/N 1.0-Z samples at high
 224 alkaline levels (pH 13-14), although the solubility of ZnO was minimal (less than 0.355%).
 225 Similarly, the Zn(OH)₃⁻ was also the dominant dissolved species in the S/K 1.0-Z samples.
 226 Previous studies [22,35] reported that the existence of a metastable Ca-Zn phase

227 $(\text{Ca}(\text{Zn}(\text{OH})_3)_2 \cdot 2\text{H}_2\text{O})$ in the Zn-incorporated cement system poisoned the nucleation and
228 growth of C-S-H gel. Considering geopolymer systems contain high concentrations of OH^- ,
229 Na^+ and $\text{Zn}(\text{OH})_3^-$ (Table S2), there is a possibility that a Na/K-Zn phase (e.g.,
230 $(\text{Na}/\text{K})(\text{Zn}(\text{OH})_3)_2 \cdot n\text{H}_2\text{O}$) was generated in Zn-incorporated geopolymer systems. Therefore,
231 the ZnO retarding mechanism in geopolymer could be attributed to the preferential formation
232 of such a Na/K-Zn phase that may inhibit the nucleation and growth of (N,K)-A-S-H gel.

233

234 ***3.2 Efficacy of Zn on Reaction Products of Geopolymer***

235 TGA curves of 28-d cured geopolymer samples are shown in Figure 2. A remarkable mass loss
236 peak existed from 30 °C to 300 °C in the S/N 1.0 samples, which was associated with H_2O
237 release, as detected by MS analysis (Figure 2b). The water release resulted from the evaporation
238 of free water, physically adsorbed water, and chemically bound water from the geopolymer
239 gels [36,37]. The K-activated samples (S/K 1.0) showed similar mass loss peaks in the same
240 range. However, the total mass loss (18.0%) was smaller than the value in the S/N 1.0 samples
241 (22.4%) (Figure 2a). This phenomenon was in line with previous experimental findings [38,39],
242 where greater geopolymerisation with a Na-based activator led to a larger mass loss for Na-
243 based geopolymer. Herein, other potential reasons come to light. Because the ionic radius of K
244 (152 pm) is larger than that of Na (116 pm), the N-A-S-H gel with relatively small molar
245 volume may adsorb more water compared to K-A-S-H gel. Assuming per-unit of N-A-S-H-
246 and K-A-S-H-gel containing the same molar weight of bound water, due to the relatively large
247 molar mass of K, the mass fraction of H_2O in K-based systems is relatively low, resulting in
248 the lower mass loss.



249

250

251 **Figure 2.** TGA of 28-d cured geopolymer pastes with and without ZnO: (a) TG curves of
 252 samples with SiO₂/M₂O molar ratio of 1.0; (b) TG curves of samples with SiO₂/M₂O molar
 253 ratio of 1.5; (c) DTG and water release curves corresponding to (a); (d) DTG and water release
 254 curves corresponding to (b). Water release curves in c) and d) were obtained from mass
 255 spectrometry data.

256

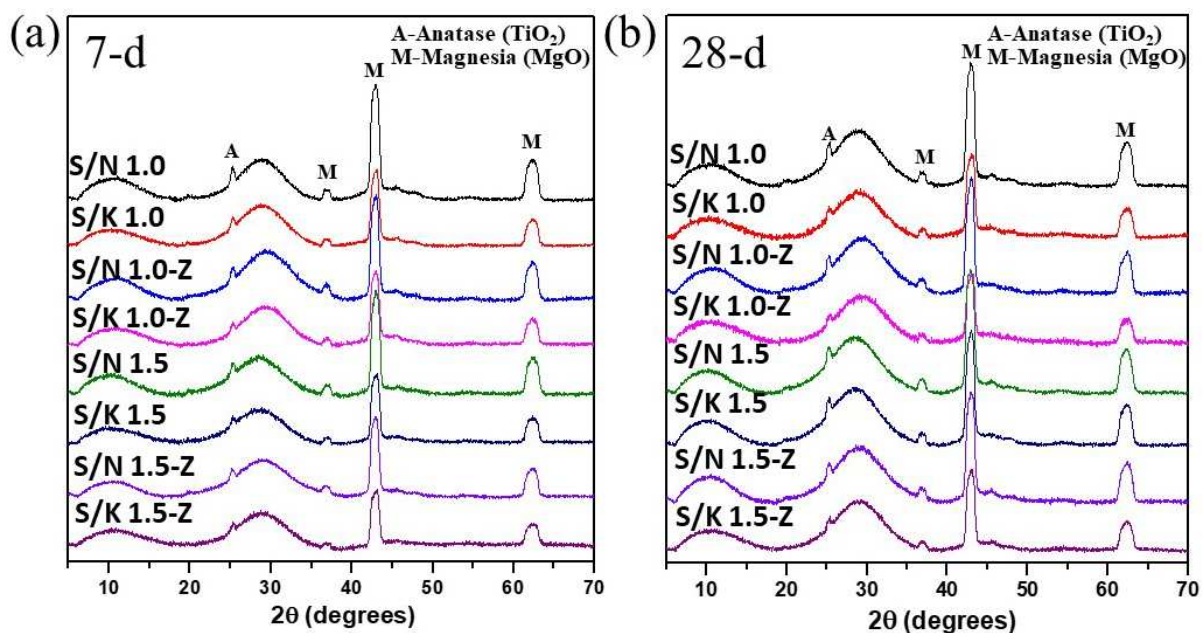
257 From Figure 2a & c, the partial substitution of ZnO had a negligible effect on mass loss or
 258 water release of Na/K-based geopolymer samples. Here it should be noted that the
 259 decomposition temperature of Zn(OH)₂ (125 °C) lies in the range of 30 °C to 300 °C [40,41].
 260 Thus, based on TGA results, it is difficult to determine the contents of geopolymer gels and
 261 zinc hydroxide in S/N 1.0-Z and S/K 1.0-Z samples. As shown in Figure 2b, low-alkali
 262 geopolymer samples with an S/M ratio of 1.5 showed a relatively low mass loss, suggesting a
 263 small amount of reaction products in low-alkali samples. In the low alkali geopolymer system,
 264 incorporating ZnO also had a negligible effect on the variability of mass loss according to the
 265 TGA data.

266

267 XRD analysis was used to investigate the reaction products of geopolymer samples both with
268 and without ZnO substitution. From Figure S1, there is a predominant, broad peak due to
269 diffuse scattering centred at approximately 22° in the raw metakaolin curve, consistent with
270 the amorphous nature of MK. Sharp peaks at 25.3° and 32.6° are attributed to a small amount
271 of anatase (TiO₂). After a 7-d reaction at 20 °C (Figure 3a), two broad peaks centred at 11°
272 and 29° appeared in the MK-based geopolymer samples, indicating the formation of
273 crystallographically disordered products [28]. Na-activated samples and K-activated samples
274 showed similar XRD patterns. MgO (analytical reagent) was added to the samples prior to
275 XRD analysis as an internal standard to quantify the degree of ZnO involved in the reaction.
276 However, after 7-d curing, the major ZnO peaks at 31.8°, 34.4°, and 36.3° had completely
277 disappeared in the S/N 1.0-Z and S/K 1.0-Z samples, while other crystalline peaks of TiO₂ and
278 MgO still existed. This demonstrated that all the ZnO (observable by XRD) had reacted and
279 formed amorphous components. In alkaline solution, zinc and silicate ions can form amorphous
280 zincate-silicate complexes [42], e.g., [(HO)₃ZnO(SiO₂)O(SiO₂)OH]⁶⁻ and
281 [(HO)₃ZnOSiO₂OH]⁴⁻. In this study, the inclusion of ZnO in the reaction mixture did not
282 change the line-shape of the XRD patterns of the geopolymer binders, suggesting that ZnO did
283 not alter the general structure of major reaction products.

284

285 The XRD patterns of low-alkali geopolymer samples (S/M of 1.5) were very similar to those
286 of S/M 1.0 geopolymer samples (Figure 3a). Similar to observations for the high-alkali
287 geopolymers, the substitution of ZnO in the low-alkali system did not change the lineshape of
288 the XRD patterns. After 28-d curing, the ZnO peak disappeared, and no new peak appeared in
289 both the S/M 1.0-Z and S/M 1.5-Z geopolymer systems (Figure 3b). Therefore, the XRD results
290 indicated that ZnO reacted during alkali-activation to form amorphous products; however,
291 ZnO did not change the general structure of the major reaction products.



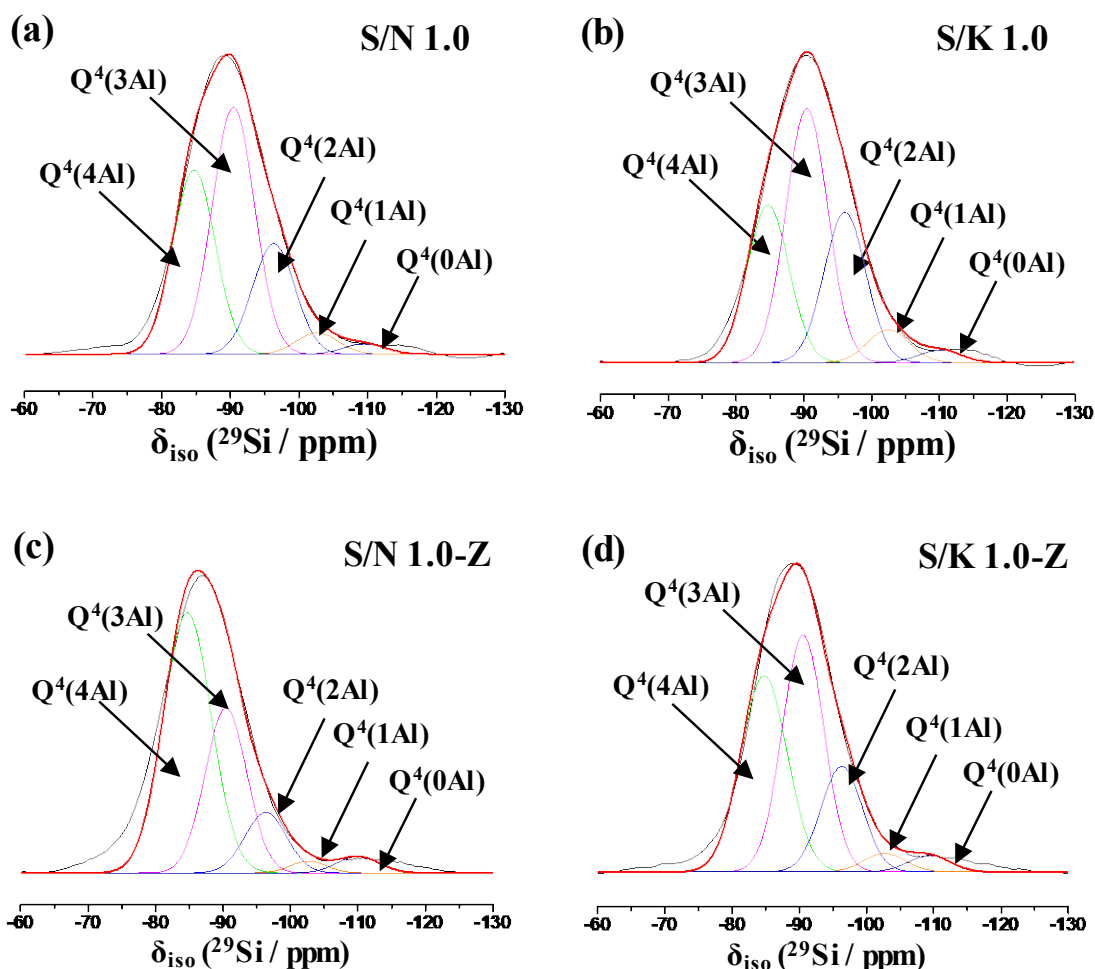
293

294 **Figure 3.** XRD data of geopolymer pastes with or without ZnO: (a) 7-d cured geopolymer
 295 pastes; (b) 28-d cured geopolymer pastes.

296

297 As illustrated in Figure S2a, the ^{29}Si MAS NMR spectra of MK showed a broad resonance
 298 arising from a distribution of isotropic chemical shifts, δ_{iso} , from -80 to -125 ppm, with the
 299 highest intensity at $\delta_{\text{iso}} = -108$ ppm. This suggests a wide distribution of silicon environments
 300 and a significant degree of disorder, consistent with the broad amorphous peak in XRD patterns
 301 and previous work in the literature [44]. Spectral fitting indicated that the resonances were
 302 attributed to $\text{Q}^4(0\text{Al})$, $\text{Q}^4(1\text{Al})$, $\text{Q}^4(2\text{Al})$, $\text{Q}^4(3\text{Al})$ and $\text{Q}^4(4\text{Al})$. Among them, $\text{Q}^4(0\text{Al})$ and
 303 $\text{Q}^4(1\text{Al})$ represented approximately 46% and 24%, respectively. It is noted that the large
 304 proportion of $\text{Q}^4(0\text{Al})$ was probably due to over-calcination of kaolinite, which may influence
 305 the geopolymerisation. The detailed parameters of fitting peaks in raw MK are shown in Table
 306 S3, and the full spectra of MK and geopolymers are illustrated in Figure S3. After 28-d curing,
 307 data for S/N 1.0 and S/K 1.0 samples exhibited a resonance from $\delta_{\text{iso}} = -75$ to -115 ppm (Figure
 308 4a & b), with the highest intensity at $\delta_{\text{iso}} = -89.5$ ppm and -90.5 ppm, respectively (Table S3).
 309 This suggests that the geopolymer gels were dominated by resonances of fully polymerised Q^4

310 species with high Al substitution, i.e., $Q^4(4Al)$ and $Q^4(3Al)$. The fitting and quantification
311 results from Figure 4 and Table 2 illustrate that the N-A-S-H gel in the S/N 1.0 samples was
312 composed of approximately 32% $Q^4(4Al)$, 43% $Q^4(3Al)$, 19% $Q^4(2Al)$, 4% $Q^4(2Al)$ and 2%
313 $Q^4(2Al)$, with a Si/Al molar ratio of 1.34. The detailed parameters of fitting peaks in
314 geopolymers are shown in Table S3. K-A-S-H gel in S/K 1.0 samples had similar distributions
315 of $Q^4(mAl)$ sites and the Si/Al molar ratio was 1.40. The Si/Al molar ratio was lower than the
316 value in the initial mixture, suggesting the preferential formation of Al-rich geopolymer gel.
317 After substitution of ZnO, the $Q^4(4Al)$ content was much larger than $Q^4(3Al)$ content in S/N
318 1.0-Z sample, and consequently it had a relatively low Si/Al molar ratio (1.21) (Table 2). This
319 is possibly due to the divalent charge Zn^{2+} cation substituting the monovalent charge Na^+ cation,
320 leading to an increase of charge-balancing capacity [28] (schematically illustrated in Figure 5).
321
322 By comparison, the substitution of ZnO only slightly decreased $Q^4(3Al)$ content and increased
323 $Q^4(4Al)$ content in K-activated system (Figure 4d). The magnitude of the reduction of Si/Al
324 molar ratio in K-activated system was relatively small compared to that of Na-activated system.
325 This discrepancy can be attributed to differences of ionic radii between Na^+ and K^+ . The ionic
326 radius of Zn^{2+} (88 pm) is closer to the radius of Na^+ (116 pm), compared to the value of K^+
327 (152 pm) [43]. Thus, Zn^{2+} can more easily substitute for Na^+ cation than K^+ cations. This
328 difference in Zn incorporation is likely to result in differences in Zn leachability in Zn-
329 incorporated samples (discussed in Section 3.3).



330

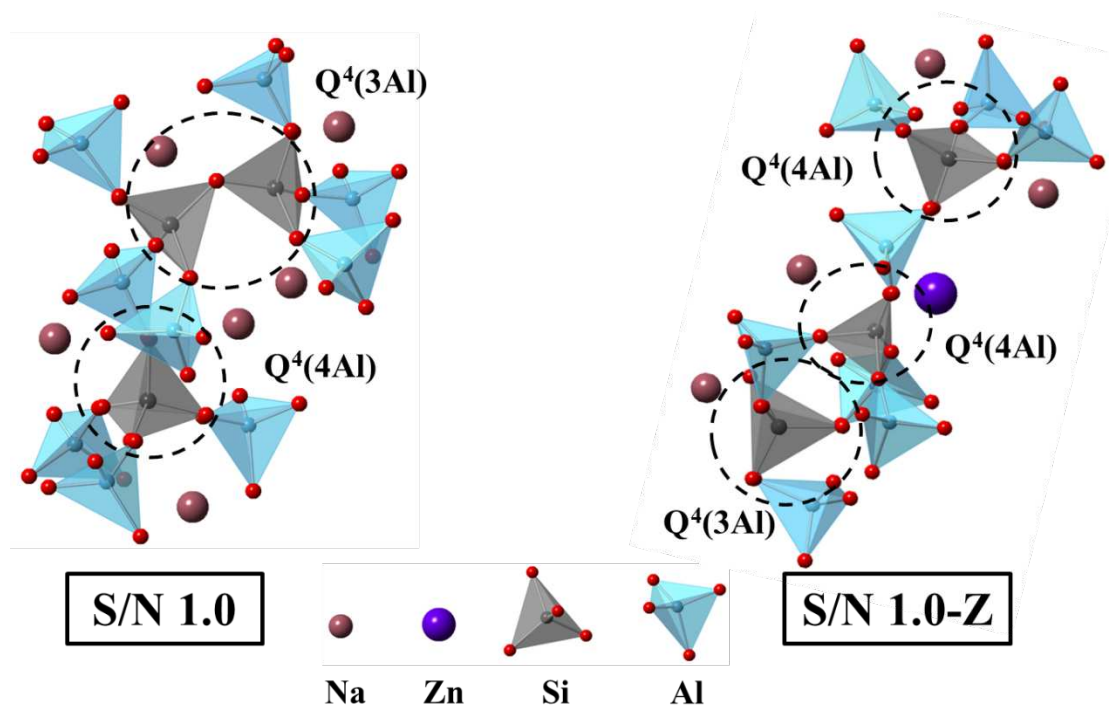
331 **Figure 4.** ^{29}Si MAS NMR spectra ($B_0 = 11.7$ T, $\nu_R = 4.5$ kHz) and associated fitting peaks for
 332 28-d cured geopolymer pastes: (a) Na-activated geopolymer; (b) K-activated geopolymer; (c)
 333 Na-activated geopolymer with ZnO; (d) K-activated geopolymer with ZnO.

334

335 **Table 2.** Relative integral areas for $Q^4(m\text{Al})$ sites within (N,K)-A-S-H gel.

	Relative integral area (%)*					Si/Al
	$Q^4(4\text{Al})$	$Q^4(3\text{Al})$	$Q^4(2\text{Al})$	$Q^4(1\text{Al})$	$Q^4(0\text{Al})$	
S/N 1.0	32	43	19	4	2	1.34
S/K 1.0	26	42	25	5	2	1.40
S/N 1.0-Z	54	30	11	2	3	1.21
S/K 1.0-Z	37	40	18	3	3	1.30

336 * The relative integrated intensity is obtained by simulating the ^{29}Si MAS NMR spectra and is
 337 normalised to the sum of all sites in geopolymers. Error in the relative integral area is
 338 approximately 1%.
 339



340

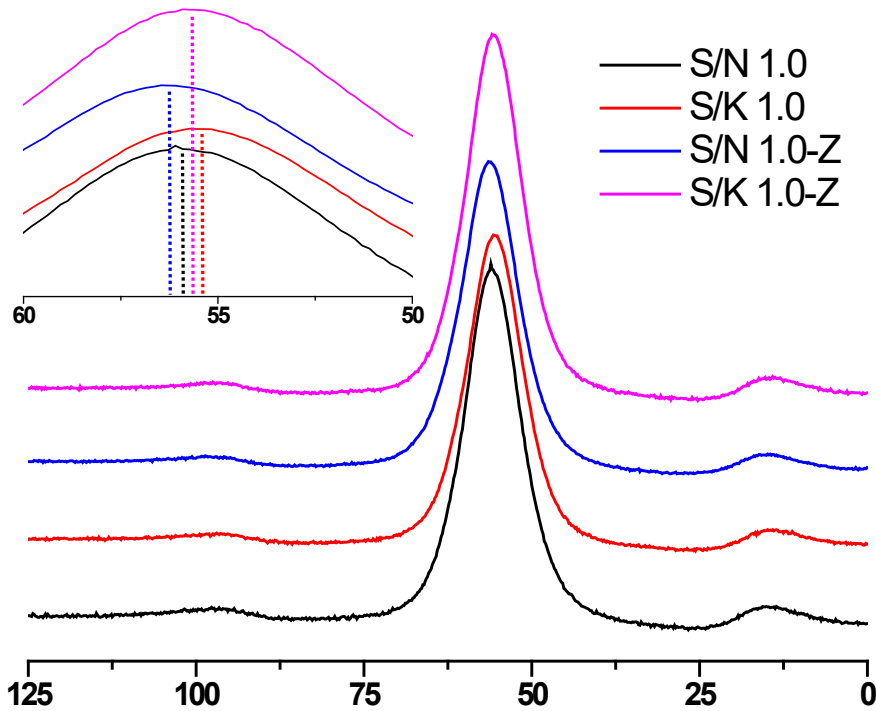
341 **Figure 5.** Schematic illustration of Na/Zn-A-S-H gels in S/N 1.0 and S/N 1.0-Z samples.

342

343 The ^{27}Al MAS NMR spectrum of MK (Figure S2) shows three broad resonances at $\delta_{\text{iso}} = 60$
 344 ppm, 27 ppm, and -2 ppm, respectively, due to Al in tetrahedral, pentahedral, and octahedral
 345 coordination [44]. After 28-d curing, the data for geopolymer samples exhibited a high intensity
 346 resonance due to tetrahedral Al at $\delta_{\text{obs}} = 56$ ppm (Figure 6). This signified that most Al in
 347 metakaolin took part in the reaction, consistent with observations from the ^{29}Si MAS NMR and
 348 XRD data. The resonance at $\delta_{\text{obs}} = 56$ ppm is ascribed to tetrahedral Al in a fully polymerised
 349 tetrahedral site (q^4) resulting from the substitution of Al^{3+} for Si^{4+} in the (N,K)-A-S-H
 350 framework [45], with the resultant negative charge balanced by alkali cations [46]. The
 351 incorporation of ZnO shifted the tetrahedral Al resonance to slightly higher δ_{obs} values, e.g.,
 352 0.37 ppm increment in the Na-activated samples, and 0.18 ppm increment in the K-activated
 353 samples. Such slight shifts may result from the partial substitution of Zn^{2+} for Na^+ and K^+ in
 354 charge balancing sites in the (N,K)-A-S-H gel. Zn^{2+} substitution had a negligible influence on
 355 the lineshape of the ^{27}Al MAS NMR spectra, indicating that it did not significantly change the
 356 nanostructure of the geopolymer gels, which is consistent with XRD results. It is noted that

357 ^{23}Na MAS NMR and ^{39}K MAS NMR may provide useful information about the (Na,Zn)-A-S-
358 H gel, Na-Z phase, (K,Zn)-A-S-H gel, and K-Z phase, which would be required for further
359 quantifying the structural change of products in future studies.

360



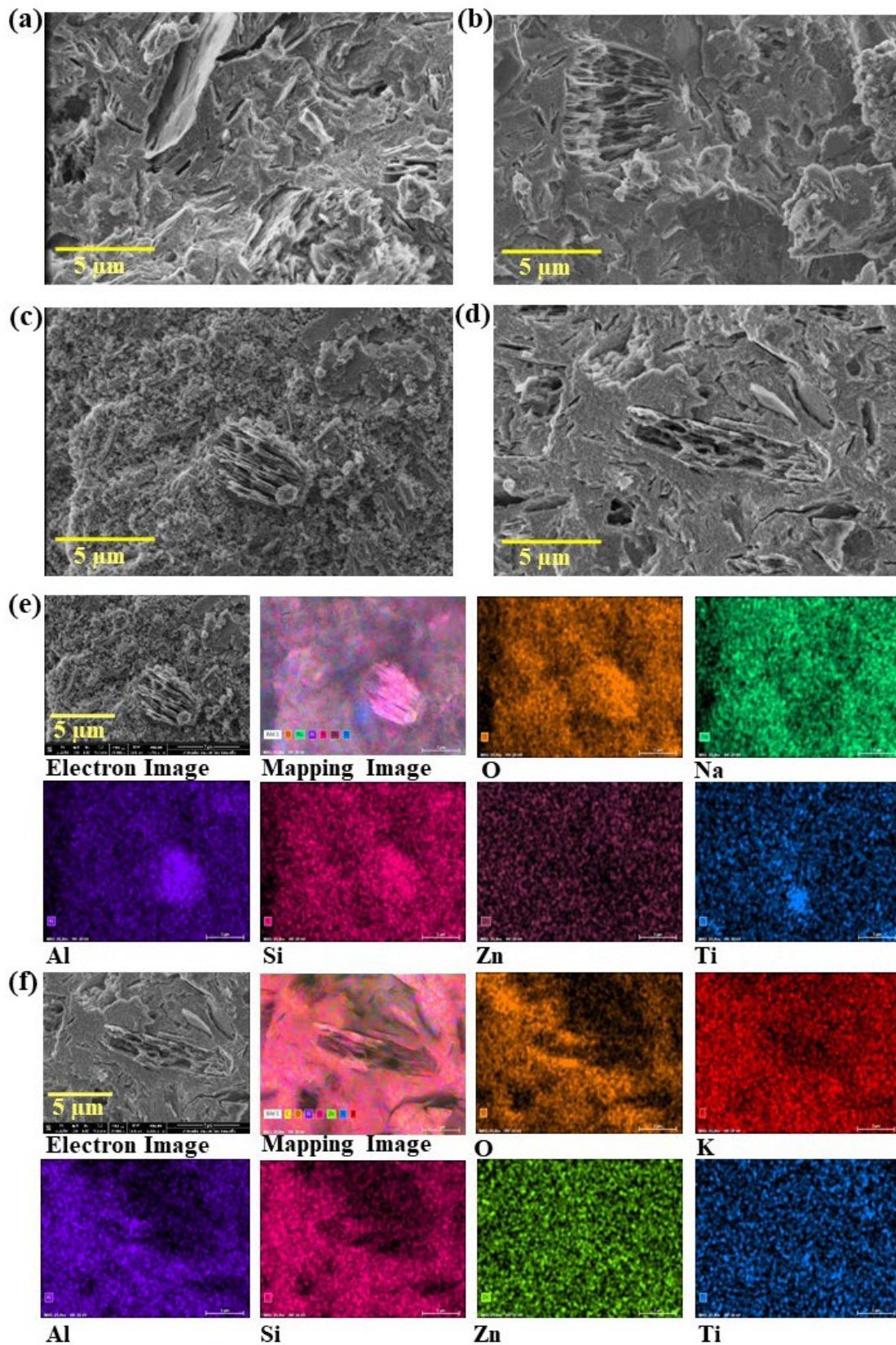
361

362 **Figure 6.** ^{27}Al MAS NMR spectra ($B_0 = 11.7$ T, $\nu_R = 10.0$ kHz) for 28-d cured geopolymer
363 pastes.

364

365 SEM image (Figure 7a) reveals some voids and microcracks on the fracture surface of S/N 1.0
366 samples, possibly due to the entrainment of air bubbles during the rapid geopolymerisation
367 when Na is the alkali source. By comparison and as shown in Figure 7b, S/K 1.0 samples
368 exhibited dense and flat surfaces with few voids, which is attributed to less rapid reaction
369 kinetics as revealed by isothermal calorimetry results. After ZnO substitution, many
370 agglomerates were observed on the matrix in S/N 1.0-Z samples (Figure 7c). Elemental
371 mapping (Figure 7e) verified that the porous blocks were composed of O, Al and Si, which
372 possibly resulted from the unreacted MK. Moreover, Zn was homogeneously distributed on

373 matrix. Theoretically, some zincate-silicate complexes can form in an alkaline solution [42];
374 however, the specific nature of the agglomerates in S/N 1.0 samples requires further
375 investigation. By comparison, there were no observable agglomerates in S/K 1.0-Z samples,
376 although the ZnO incorporation caused more voids (Figure 7d). The elemental mapping in
377 Figure 7f also indicated that Zn was homogeneously distributed in the geopolymer matrix in
378 the S/K 1.0-Z samples. The BSE images showed that the microstructure of S/N 1.0-Z samples
379 was much denser than that of S/K 1.0-Z samples (Figure S4). The different microstructures
380 observed in samples may influence the physicochemical properties of the geopolymer cements.
381 Therefore, the effects of Zn on setting time and ion retention of the geopolymer cements were
382 investigated.



383

384 **Figure 7.** SEM image with elemental mapping of 28-d cured geopolymers pastes: (a) SEM
 385 image of S/N 1.0; (b) SEM image of S/K 1.0; (c) SEM image of S/N 1.0-Z; (d) SEM image
 386 of S/K 1.0-Z; (e) element mapping of S/N 1.0-Z; (f) element mapping of S/K 1.0-Z.

387

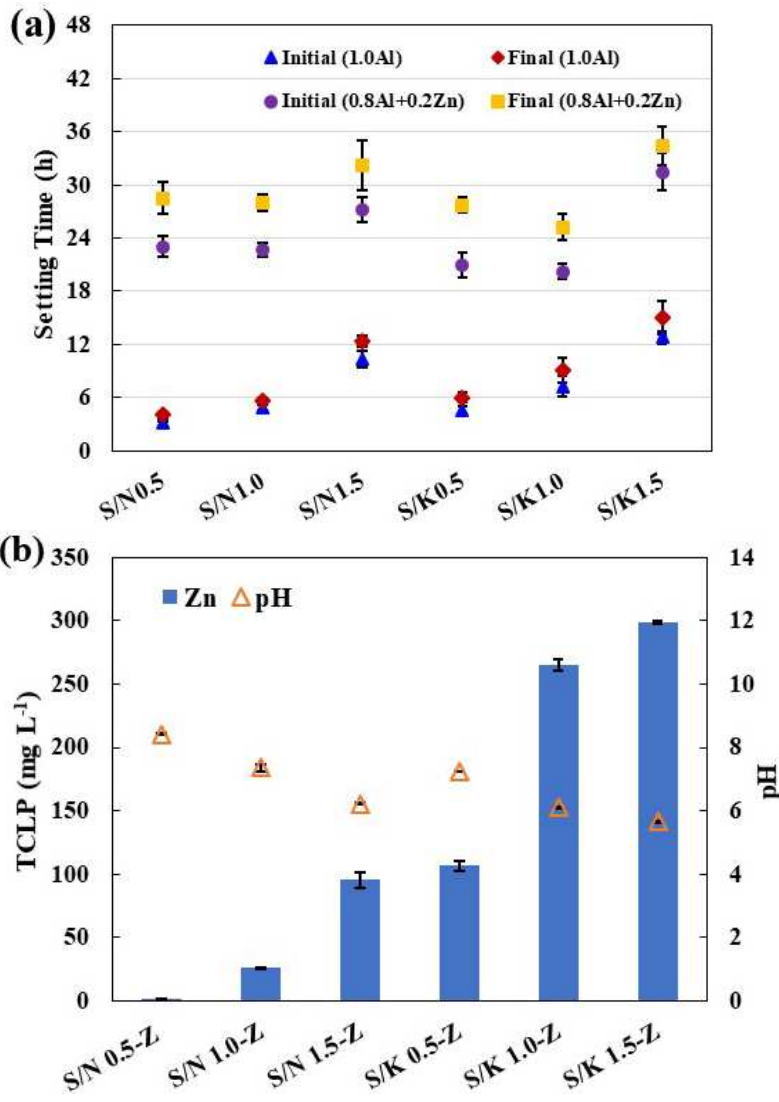
388 **3.3 Effects of Zn and Zn-rich Sludge on Physicochemical Properties of Geopolymer**

389 Figure 8a shows the setting time for the geopolymer pastes with and without ZnO. High-alkali
390 S/N 0.5 samples yielded the shortest initial setting time of 3.1 h and final setting time of 4.1 h.
391 The setting times increased along with the increase of Si/Na molar ratio, because Si and Al
392 cations dissolving in low-alkali samples gradually reached their critical limits of nucleation
393 and growth of the geopolymer gel. By comparison, K-activated geopolymer systems showed
394 the same trend, with the initial and final setting times being relatively long compared to samples
395 where Na is the alkali source, consistent with isothermal calorimetry results (Figure 1). The
396 substitution of ZnO (Al/Zn molar ratio of 4) significantly delayed both the initial and final
397 setting times in Na-activated geopolymer systems, especially for low-alkali samples. Zn also
398 had an inhibitory effect on the K-activated geopolymer systems; however, its magnitude was
399 relatively small in comparison with Na-activated geopolymer systems, consistent with
400 isothermal calorimetry results. The addition of additional ZnO in geopolymer systems also
401 caused a dramatic delay of initial and final setting times (Figure S5), likely due to the formation
402 of metastable Na/K-Zn phase as discussed in Section 3.1. This excludes the possibility of the
403 delayed setting time resulting from lower Al/Si content. Note that the addition of high-dosage
404 Zn would completely poison the reaction of PC and Ca-rich alkali-activated materials [36,47],
405 whereas Zn only retarded the reaction process of N/K-based geopolymer systems. This
406 indicates that N/K-activated geopolymers exhibit favourable compatibility with Zn during the
407 early stage of reaction, and K-activated geopolymer systems show greater compatibility with
408 Zn than Na-activated geopolymer systems.

409

410 Figure 8b illustrates the TCLP leaching concentrations of Zn and the corresponding pH values
411 of leachate from 28-d cured Zn-incorporated geopolymer samples. The S/N 0.5-Z samples
412 showed the lowest Zn leachability (1.4 mg L^{-1}), indicating strong incorporation of Zn in the

413 geopolymer gel. The Zn leachability significantly increased with increased of Si/Na molar ratio
414 (i.e. decreased alkali content). Interestingly, the Zn leachability of S/K 0.5-Z samples (106.6
415 mg L⁻¹) was 75 times higher than that of S/N 0.5-Z samples. This is likely due to the differences
416 in ionic radii of Na⁺ (116 pm) and K⁺ (152 pm), with Zn²⁺ (ionic radius of 88 pm) more easily
417 substituted for Na⁺ than K⁺. This is consistent with the findings from ²⁹Si MAS NMR data
418 (Figure 4) discussed above. The relatively dense structure of S/N 1.0-Z sample (Figure S4)
419 may also be favourable for the Zn immobilisation. Additionally, the lower pH value exhibited
420 by the solution for S/K 0.5-Z samples (~7.5) compared with S/N 0.5-Z samples (~8.5) will also
421 contribute to the higher leachability of Zn from S/K 0.5-Z samples, due to the greater solubility
422 of Zn²⁺ at lower pH [48]. The TCLP results demonstrate that Na-activated geopolymer cements
423 exhibit excellent immobilisation of Zn, with the use of high-alkali activators enhancing the
424 effectiveness of S/S.



425

426

427 **Figure 8.** Setting time and leachability of geopolymer pastes cured for 28 days: (a) setting time
 428 of geopolymer pastes with or without ZnO (20 mol.%) replacement; (b) Zn concentration and
 429 pH in leachate from ZnO-incorporated geopolymer pastes.

430

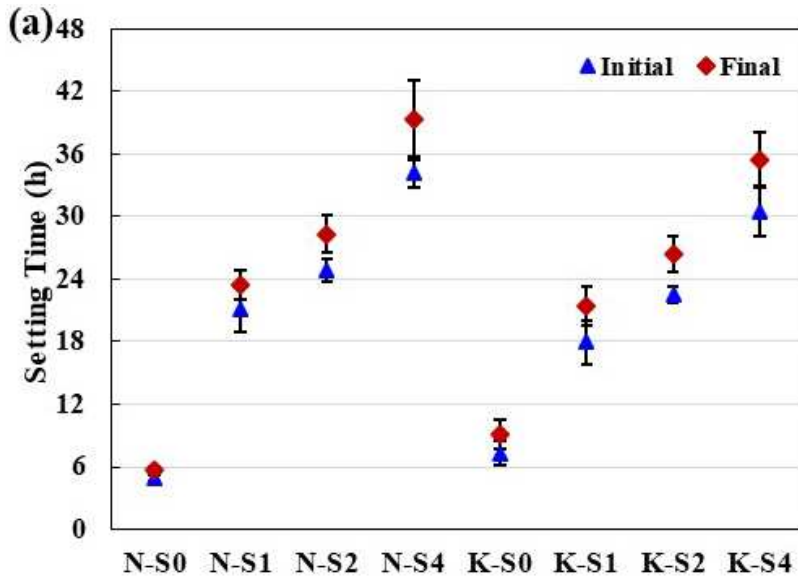
431 The effects of Zn-rich electroplating sludge on the physicochemical properties of geopolymer
 432 were evaluated in terms of setting time, TCLP leachability, and compressive strength. As
 433 shown in Figure 9a, the addition of 50% sludge (N-S1 sample) postponed the final setting time
 434 from 5.6 h to 23.4 h. The setting time was prolonged with increasing dosages of sludge.
 435 Although the final setting time of N-S4 samples reached 39.3 h, the setting and hardening
 436 process still occurred in approximately 80% sludge-incorporated samples. Zn-rich sludge
 437 addition showed a relatively small inhibitory effect on the K-activated geopolymer when

438 compared to Na-activated geopolymer samples, consistent with the effect of pure ZnO (Figure
439 9a).

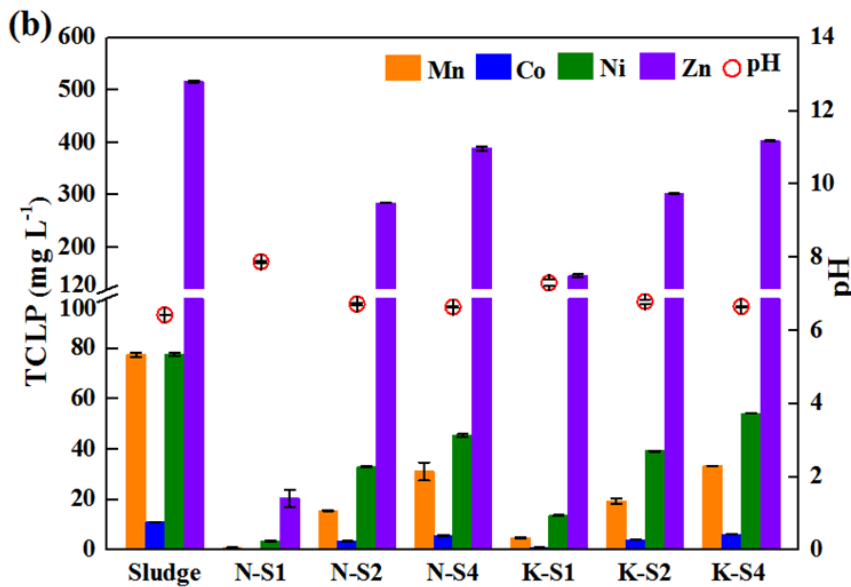
440

441 From Figure 9b, the TCLP leachate for electroplating sludge contained 516.7 mg L⁻¹ of Zn,
442 77.7 mg L⁻¹ of Ni, 77.5 mg L⁻¹ of Mn and 11.2 mg L⁻¹ of Co. The Zn leachability exceeded the
443 TCLP limit (250 mg L⁻¹) of landfill disposal criteria [49]. After the S/S process, the respective
444 leachability of the various toxic elements from N-S1 samples (with 50% sludge) was reduced
445 by 95.4% to 98.7%. However, Zn leachability dramatically increased to 285.5 mg L⁻¹ when the
446 mass ratio of sludge/Na-geopolymer was 2. This indicated that high sludge dosages (66.6 wt%)
447 exceeded the critical point required for a stable (Na,Zn)-A-S-H gel and resulted in extremely
448 high Zn leachability. Note that the leachability of other potentially toxic elements also
449 increased with the increase in sludge dosage. Similar performance results imply that these
450 divalent cations (Mn²⁺, Co²⁺, Ni²⁺) also might substitute monovalent charge Na⁺ cation in
451 charge balancing sites in the geopolymer gel. The Zn leachability of the K-S1 sample was 7.1
452 times higher than the value of N-S1 sample, consistent with the effect of pure ZnO (Figure 7a).
453 From Figure S6, after 28-d curing, all the sludge-incorporated samples solidified with at least
454 some degree of compressive strength (> 0.15 MPa). There was a negative correlation between
455 compressive strength and leachability. These data show that Na-activated geopolymers are
456 excellent candidates for the S/S of Zn-rich electroplating sludge. For practical S/S application,
457 the dosage of sludge should be well controlled to avoid exceeding the critical point required
458 for a stable (Na,Zn)-A-S-H gel.

459



460



461

462 **Figure 9.** Setting time and leachability of geopolymer with various amounts of industrial
 463 sludge ($\text{SiO}_2/\text{M}_2\text{O}$ molar ratio of 1.0): (a) setting time of sludge-added geopolymer samples;
 464 (b) element concentrations and pH in leachate from sludge-added geopolymer samples. (N/K-
 465 Sx: sodium/potassium silicate-activated geopolymer/sludge mass ratio of 1/x).

466

467 4. Conclusions

468 This study investigated the role of Zn on the reaction kinetics, phase assemblage and
 469 nanostructure of metakaolin-based geopolymer cements, and evaluated the feasibility of using
 470 metakaolin-based geopolymer cements for the S/S treatment of Zn-rich industrial sludge.
 471 Experimental results showed that ZnO substitution significantly inhibited the alkali-activation
 472 reaction and prolonged setting time, especially for low-alkali geopolymers, probably due to the

473 formation of metastable “Na/K-Zn” phase materials. ZnO substitution had a slight inhibitory
474 effect on the alkali-activation reaction in K-activated geopolymer systems compared to Na-
475 activated geopolymer systems. XRD results showed that upon alkali-activation ZnO reacted
476 completely after 7 days curing, and formed amorphous products; however, ZnO did not
477 significantly change the nanostructure of the primary reaction product ((N,K)-A-S-H gel), as
478 evidenced by ^{27}Al MAS NMR results. ^{29}Si MAS NMR spectra illustrated that after substitution
479 of ZnO, the content of $\text{Q}^4(4\text{Al})$ sites increased while $\text{Q}^4(3\text{Al})$ decreased, resulting in a decrease
480 of Si/Al ratio in the (N,K)-A-S-H gel. This indicated that Zn^{2+} partially substituted for Na^+/K^+
481 cations in charge balancing sites within the (Na,K)-A-S-H gel. This partial substitution of Zn^{2+}
482 for Na^+/K^+ occurred to a greater extent in Na-activated geopolymer gel than in K-activated
483 geopolymer gel, which might be due to discrepancy in the ionic radii of Na^+ and K^+ . As a result,
484 the TCLP leachability of Zn from Na-activated samples was relatively low. The S/S
485 experiments verified that K-activated geopolymer reaction kinetics were less inhibited by
486 addition of Zn-rich sludge, however Na-activated geopolymer samples exhibited greater
487 immobilisation capacity for Zn. In practical applications, alkali dosage, sludge content, and
488 other conditions should be optimised to achieve excellent and robust S/S performance.
489 Together, these findings reveal the reaction inhibiting and incorporation mechanisms of Zn in
490 geopolymer systems and suggest a sustainable and efficient geopolymer binder for S/S of Zn-
491 rich sludge.

492

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501

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