

1 Interplay between silicate and hydroxide ions during
2 geopolymerization

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11

12 **Abstract**

13 Two set of activating solutions were prepared with increasing sodium hydroxide content, either
14 containing or not silicates. Their alkalinities, here defined as the ability of solutions to resist
15 changes in pH, were determined and compared by measuring Hammet acidity functions that can
16 be assimilated to extended pH values. Such Hammet functions in sodium silicate solutions are
17 reported for the first time. The impact of both the alkalinity and the initial Hammett function on
18 the reactivity of metakaolin (MK)-based pastes was assessed using Isothermal Conduction micro-
19 Calorimetry (ICC). It was concluded that the reactivity of MK mixed with sodium hydroxide
20 solution related directly to the Hammett function values whereas in sodium silicate mixes, the
21 alkalinity value was a more pertinent parameter. A mechanism was deduced to clarify the role of
22 hydroxide ions during the geopolymerization, highlighting at the same time the role of silicate
23 species as hydroxide reservoir to nurture the dissolution process.

24

25 **1. Introduction**

26 Geopolymers refer to alumino-silicate binders obtained by reaction of a powdered alumino-
27 silicate source, such as dehydroxylated kaolin (metakaolin, MK), with an alkali hydroxide or
28 alkali silicate solution, as described by Davidovits¹. Schematically, the geopolymerization
29 process can be described by three simplified steps²⁻⁵. First, MK dissolution in the activating
30 solution provides aluminate and silicate species to the reacting medium. These species then
31 rearrange in solution, to finally polycondense, yielding the 3D network of the hardened
32 geopolymer.

33 Carrying out a detailed mechanistic study of these three steps is a hard task. They occur
34 concurrently and furthermore, no realistic reaction equations can be written to describe any of
35 these steps. However, since most of the expected reaction steps are exothermic, the use of
36 Isothermal Conduction Calorimetry (ICC) was previously reported⁶⁻¹¹ as being an efficient tool
37 for studying the whole geopolymerization process. Indeed, heat flow and heat profiles recorded
38 during geopolymerization provide qualitative and quantitative information. As an example, the
39 global geopolymerization extent at a given time has been calculated as the ratio of the cumulated
40 heat $Q(t)$ release to the theoretical total heat at completion, Q_{\max} ^{6,9,10}. Hence, in alkali hydroxide
41 activating solutions free from silicates, Zhang *et al.*⁹ reported an increase of the aforementioned
42 geopolymerization extent with increasing hydroxide ions content.

43 The relationship between activating solution composition and geopolymerization has been the
44 subject of an extensive body of literature. Indeed, such a topic is a key issue for the use of
45 geopolymers and their industrial development. For examples, Rahier *et al.*¹² reported that the
46 activating solution modulus, defined as the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio, and the amount of water,
47 defined as the $\text{H}_2\text{O}/\text{Na}_2\text{O}$ molar ratio, are driving parameters to tune geopolymers stoichiometry

48 and consistency respectively. At a Na/Al molar ratio equal to one, the optimal geopolymer
49 stoichiometry can thus be reached by choosing the appropriate $\text{SiO}_2/\text{Na}_2\text{O}$ modulus of the
50 activating solution. Later, Duxson *et al.*¹³ observed an increase in the proportion of unreacted
51 metakaolin and a decrease in the geopolymers density when increasing the silicate content of
52 activating solutions as a consequence of the resulting simultaneous increase of the $\text{SiO}_2/\text{Al}_2\text{O}_3$
53 and $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratios. Such a result was further rationalized by using Density Functional
54 Theory (DFT)-based Coarse-Grain Monte-Carlo simulations¹⁴. Similarly, Zhang *et al.*¹⁰ reported
55 that an increase in the activating solution modulus, defined as the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio, leads to
56 a decrease in the geopolymerization extent, evaluated by isothermal calorimetry.

57 The use of ²⁹Si Nuclear Magnetic Resonance (NMR) clearly exhibited that silicates connectivity
58 in activating solutions increases when increasing the modulus of the solutions¹⁵⁻¹⁷. Duxson *et al.*¹³
59 postulated that the higher the silicates connectivity, the lower the silicates species lability.
60 According to these authors, highly connected silicate species would thus hardly rearrange and
61 densify before gelation, leading to the formation of a gel of lesser density and thinner pore size
62 distribution, around metakaolin grains.

63
64 In most of the aforementioned studies, the activating solutions compositions are described in
65 terms of silicate content, $\text{SiO}_2/\text{Na}_2\text{O}$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ molar ratios. The influence of the free
66 hydroxide ions content on the geopolymerization reaction is thus not explicit. Although it had
67 already been mentioned by Xu and Van Deventer¹⁸ and Zhang *et al.*⁹, to the best of our
68 knowledge, only one scientific paper has been dedicated to that topic. Indeed, by increasing the
69 alkali hydroxide content of activating solutions and using fly ash as an aluminosilicate source,
70 Phair and Van Deventer¹⁹ reported that a higher activating solution pH leads to a higher

71 polycondensation extent. However, pH reported values seem to be approximate as they are given
72 only in full pH units¹⁹. In any case, these three studies^{9,18,19} clearly highlight the importance of
73 hydroxide ions in the geopolymerization process.

74 An effect of solution pH on aluminosilicates dissolution was indeed evidenced by Xu and Van
75 Deventer¹⁸ when studying in diluted suspensions the dissolution of 15 aluminosilicates minerals.
76 They concluded that the extent of dissolution increases for increasing alkali hydroxide solution
77 concentrations. Complementarily, Duxson *et al.*² (and references therein) and Granizo *et al.*²⁰
78 amongst others also pinpointed that the dissolution kinetics of aluminosilicate sources was highly
79 dependent on the initial pH of the solution.

80 However, all the previously mentioned experiments^{2,18,20} were carried out using solutions free
81 from silicates and using high liquid to solid ratio. As such, the role of silicate species and their
82 interplay with hydroxide ions on the dissolution step during geopolymerization have never been
83 investigated. This literature gap may have resulted from the difficulty to assess by standard pH-
84 metry pH values of solutions containing extremely high amounts of alkali metal ions.

85
86 In consequence, the present study firstly aims at quantifying the hydroxide content and the
87 alkalinity of two sets of activating solutions. Two sets of solutions of increasing sodium
88 hydroxide content were considered: the first one with a fixed silicate content and the second one
89 devoid of silicate species. Each time, Hammet acidity functions of studied solutions were
90 measured instead of pH, as described in the theoretical part. The corresponding alkalinity²¹,
91 defined here as the ability of a solution to resist to changes in pH, was evaluated for the two sets
92 of solutions. Then, the geopolymers reactivity observed by mixing metakaolin into these
93 solutions was evaluated by using Isothermal Conduction Calorimetry (ICC). Finally, these new

94 data led us to discuss the role of silicate species and their interplay with hydroxide ions during
95 geopolymerization.

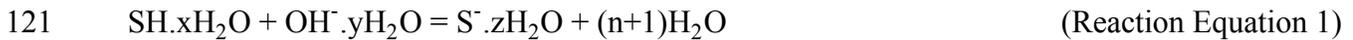
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97 **2. Theoretical basis.**

98 In activating solutions used for geopolymers elaboration, molality of alkali metal ions can range
99 between 1 mol / kg of water to 15 mol / kg of water. The use of a glass electrode sensitive to
100 oxonium ions H_3O^+ to assess pH values is then questionable in such media. First, a high sodium
101 concentration in basic solutions often leads to an alkaline error, since the alkali ion concentration
102 can be typically orders of magnitudes larger than the oxonium ions one. As an example, the alkali
103 ion concentration is 10^{14} times higher than the oxonium one in a sodium silicate solution
104 containing 10 mol / kg of sodium ions at $\text{pH} \approx 13$. Then, water activity in the studied solution can
105 be far below the value of 0.9 expected in a 3 mol / kg potassium chloride electrode filling
106 solution. As a consequence, the ionic flow from the electrode to the studied medium could be
107 strongly impacted, leading to false measurements. Finally, in the specific case of silicate-
108 containing activating solutions, silicate species can interact or even deteriorate the glass electrode
109 surface, leading to additional errors.

110 Consequently, in this work, the measurement of Hammet acidity functions²²⁻²⁴ was chosen
111 instead of standard pH-metry to quantify the amount of hydroxide ions in activating solutions.
112 Such a function represents the hydroxide ions ability to deprotonate a weak acid, noted SH in
113 reaction equation 1, added in small amounts in the aqueous medium. It is obviously equivalent to
114 pH in dilute systems. Upon introduction in the studied medium, again in small amounts, the
115 weak acid SH plays the role of an acid-base indicator whose ionization ratio is measured
116 quantitatively thanks to the intensity shift of its UV-visible spectrum induced by its deprotonation
117 . This concept was initially introduced to measure acidity of extremely acidic solution and later
118 adapted to basic solutions, either in aqueous alkali hydroxide solutions or in non-aqueous
119 solvents²⁵⁻³⁰.

120



122

123 In reaction equation 1, the coefficient $n = (x + y - z)$ accounts for the difference in hydration
124 degrees between reactants and products, according to the model used by Edward²⁹. The
125 corresponding equilibrium constant K is then written as:

126
$$K = \frac{a_{\text{S}^-} \cdot a_{\text{H}_2\text{O}}^{(n+1)}}{a_{\text{SH}} \cdot a_{\text{OH}^-}} = \frac{K_a}{K_w} \quad (\text{Equation 1})$$

127 with a_i the activity of the species i .

128 As reaction equation 1 represents an acid-base reaction between the two couples SH/S⁻ and
129 OH⁻/H₂O, the constant K can also be written as the ratio of the associated ionization constants: K_a
130 for the acid ionization constant of SH and K_w for the one of water (tabulated by Bandura and
131 Lvov³¹ and taken as 10^{-14} at 25°C),

132 Hammett²³ defined the acidity function H_- according to equation 2. Rearranging equation 1 also
133 provides equation 3, another definition of the acidity function:

134
$$H_- = pK_a + \log \frac{[\text{S}^-]}{[\text{SH}]} \quad (\text{Equation 2})$$

135
$$H_- = pK_w + \log a_{\text{OH}^-} - (n + 1) \cdot \log a_{\text{H}_2\text{O}} + \log \frac{\gamma_{\text{SH}}}{\gamma_{\text{S}^-}} \quad (\text{Equation 3})$$

136 With:

137 pK_x the cologarithm of constant K_x ,

138 $\frac{[\text{S}^-]}{[\text{SH}]}$ the ionization ratio,

139 $[i]$ the concentration of species i in mol / kg of water,

140 and γ_i its activity coefficient defined such as $a_i = \gamma_i \cdot [i] / [i]^\circ$ where $[i]^\circ$ is the standard state

141 concentration of species i conventionally set equal to 1 mol / kg.

142 The experimental determination of activity coefficients being complex, equation 3 is mainly of
143 theoretical interest, except in the rare cases when good approximations of activity coefficients^{24,29}
144 are possible. Nevertheless, equation 3 clearly states that the function H takes into account not
145 only the hydroxide ions activity but also their environment through the parameter n and the
146 variables a_{H_2O} and γ_{SH}/γ_{S^-} , respectively related to the ions hydration, the free water content and the
147 ionic force of the solution. In consequence, the acidity function is an appropriate tool to represent
148 the ability of hydroxide ions to react in a solution.

149 If both S^- and SH forms absorb UV-visible light at different wavelengths, the $[S^-]/[SH]$
150 ionization ratio can be measured by using spectrophotometry. From Beer-Lambert's law, the
151 ionization ratio can be obtained from absorbance measurements for a constant indicator
152 concentration according to (eq. 4).

$$153 \quad \frac{[S^-]}{[SH]} = \frac{A - A_{SH}}{A_{S^-} - A} \quad (\text{Equation 4})$$

154 With

155 A_{SH} the absorbance of a solution where the indicator is fully protonated,

156 A_{S^-} the absorbance of a solution where the indicator is fully deprotonated,

157 A the absorbance of any basic solution with intermediate concentration.

158 A set of three solutions is thus needed to determine an ionization ratio.

159

160 **3. Experimental section.**

161 **3.1. Activating solutions elaboration**

162 Sodium hydroxide solutions were elaborated with an increasing molality ranging from $3.17 \cdot 10^{-2}$
 163 to $1.40 \cdot 10^1$ mol / kg by dissolving sodium hydroxide pellets (AR grade, VWR) in ultrapure water
 164 (18.2 MΩ). A set of alkali silicate solutions was then elaborated by diluting in water a
 165 commercial alkali silicate solution (Betol[®] 52T, Wöllner: 30.2% w/w SiO₂, 14.7% w/w Na₂O and
 166 55.1% w/w H₂O) and by adding sodium hydroxide pellets in order to reach increasing sodium
 167 ions molality, ranging from 5.46 to $1.40 \cdot 10^1$ mol/kg. All solutions were stirred for at least 4 h
 168 and cooled down to 25°C prior to any use. Solutions compositions are reported in Tables 1 and 2.

169
 170 **Table 1.** Composition in molality, water activity and acidity function values of sodium hydroxide
 171 solutions together with the molar ratios of the corresponding geopolymers prepared with
 172 metakaolin. Acidity functions were taken from literature when indicated (^a Rochester³²,
 173 ^b Schwarzenbach²⁵).

	Solutions			Geopolymers	
	[NaOH] (mol/kg)	a _{H2O} (± 0.008)	H.	Na/Al	$\frac{\text{SiO}_2}{\text{Na}_2\text{O}}$
Na1	$3.17 \cdot 10^{-2}$	1.000	12.51 ± 0.06	$3.28 \cdot 10^{-3}$	733
Na2	$1.00 \cdot 10^{-1}$	1.000	12.99 ± 0.06	$1.04 \cdot 10^{-2}$	232
Na3	$3.17 \cdot 10^{-1}$	-	13.42 ± 0.08	$3.28 \cdot 10^{-2}$	73.2
Na4	1.00	0.987	14.01 ^a	$1.04 \cdot 10^{-1}$	23.2
Na5	2.00	0.956	14.42 ^a	$2.07 \cdot 10^{-1}$	11.6
Na6	3.01	0.917	14.72 ^a	$3.11 \cdot 10^{-1}$	7.73
Na7	5.00	0.812	15.19 ^a	$5.18 \cdot 10^{-1}$	4.64
Na8	7.00	0.692	15.62 ^a	$7.25 \cdot 10^{-1}$	3.32
Na9	9.66	0.520	16.06 ^a	1.00	2.41
Na10	$1.20 \cdot 10^1$	-	16.47 ^b	1.24	1.94
Na11	$1.40 \cdot 10^1$	0.275	16.87 ^b	1.45	1.66

174
 175
 176

177 **Table 2.** Molality, molar ratio, water activity and acidity function values of sodium silicate
 178 solutions. When indicated, the composition of the corresponding geopolymers prepared with
 179 metakaolin is also given.

	Solutions						Geopolymers	
	[NaOH] _{added} (mol/kg)	[Na] _{total} (mol/kg)	[Si] (mol/kg)	$\frac{\text{SiO}_2}{\text{Na}_2\text{O}}$	$a_{\text{H}_2\text{O}}$ (± 0.008)	H.	Na/Al	$\frac{\text{SiO}_2}{\text{Na}_2\text{O}}$
NaS1	0	5.46	5.79	2.12	0.965	-	0.57	6.36
NaS2	$5.26 \cdot 10^{-1}$	6.01	5.80	1.93	0.952	10.82 ± 1.98	0.62	5.79
NaS3	1.54	7.01	5.80	1.65	0.928	11.64 ± 0.35	0.73	4.97
NaS4	2.54	8.02	5.79	1.45	0.903	12.19 ± 0.14	0.83	4.34
NaS5	3.53	9.00	5.80	1.29	-	12.52 ± 0.10	-	-
NaS6	4.20	9.68	5.80	1.20	0.837	12.74 ± 0.10	1.00	3.60
NaS7	5.02	10.5	5.80	1.10	-	13.10 ± 0.11	-	-
NaS8	5.52	11.0	5.80	1.05	0.767	13.25 ± 0.12	1.14	3.16
NaS9	6.54	12.0	5.80	$9.66 \cdot 10^{-1}$	0.711	13.59 ± 0.20	1.24	2.68
NaS10	7.54	13.0	5.79	$8.91 \cdot 10^{-1}$	0.649	14.12 ± 0.53	1.34	2.32
NaS11	8.54	14.0	5.80	$8.27 \cdot 10^{-1}$	-	-	-	-

180

181

182

183 3.2. Geopolymers preparation

184 Prior to the cure and any measurements, geopolymer pastes were prepared by mixing 32.05 g of
 185 metakaolin (MK, Metakaolin Argical M1000 from Imerys, characteristics in Table 3) with the
 186 appropriate weight of activating solution to obtain a constant (initial water)/MK weight ratio of
 187 0.78. Elaborated geopolymers formulations are reported in Tables 1 and 2.

188

189 **Table 3.** Physical and chemical characterization of Metakaolin by XRF, laser granulometry and
 190 N₂ adsorption-desorption (with BET method) as provided by the supplier.

Oxides	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	TiO ₂	K ₂ O
Composition %w/w	54.40	38.40	0.10	1.27	1.60	0.62
Granulometry (μm)	d ₁₀	1.8	d ₅₀	10.3	d ₉₀	48.2
surface area (m ² /g)	18					

191

192

193 **3.3. Acidity function measurements**

194 Thiazole Yellow G (TYG, also known as Titan Yellow, Sigma-Aldrich) was used in the present
195 study as the weak acid UV-visible-sensitive indicator, chosen to be compatible with the expected
196 acidity function range of the studied solutions. Absorptions of activating solutions containing
197 TYG were measured in the spectral range 300 to 600 nm, with a resolution of 1 nm, in 10-mm
198 quartz cells at 25°C. Absorbance spectra were recorded on a dual-beam spectrophotometer
199 (Genesys 10S UV-Visible, ThermoFischer Scientific), with a xenon flash lamp. Indicator-free
200 activating solutions were used as backgrounds so that only the indicator would contribute to the
201 recorded spectra. For the whole set of solutions, absorbance of indicator-free solutions was
202 checked to be close to zero for wavelength ranging from 400 to 500 nm.

203 The absorbance at 480 nm has been checked to be proportional to TYG concentration up to
204 approximately $5 \cdot 10^{-4}$ mol / kg in sodium hydroxide solution, defining the range of validity of the
205 Beer-Lambert law (details are available in supplementary information). Accordingly, the working
206 concentration of TYG in all activating solutions was set to $5 \cdot 10^{-5}$ mol / kg. In sodium hydroxide
207 solutions, absorption bands centered at 405 and 475 nm have been observed respectively for the
208 SH form and S⁻ form, with an isobestic point at 433 nm. In sodium silicate solution with
209 increasing amounts of sodium hydroxide, absorption bands were centered at 390 and 480 nm,
210 with an isobestic point at 438 nm. Previous observations from Allain and Xue³³ in sodium
211 hydroxide solutions support the existence of a simple acid-base equilibrium for TYG as described
212 in Reaction Equation 1. Allain and Xue also reported that TYG has a good chemical resistance to
213 hydroxide ions, and a large dynamic spectral range. In addition, the similar position of the S⁻
214 form absorption band in both media corroborates the absence of any drastic conformation

215 modification, at least for the deprotonated form. This meant that silicates did not interact to any
216 significant level with the indicator and that the latter was only involved in a simple acid-base
217 equilibrium. Acidity functions were thus calculated from absorbance at 480 nm.

218 The pK_a of TYG has been measured in sodium hydroxide solution following Safavi and
219 Abdollahi's procedure³⁴. The pK_a value of 12.92 ± 0.01 at 25°C measured in this work is
220 consistent with the 12.92 value reported by Safavi and Abdollahi. TYG was thus considered as a
221 suitable weak acid indicator for acidity function measurements in study alkali silicate activating
222 solutions.

223 Finally, the working range of TYG was established (see Sup. Inf.) to be comprised between 11.9
224 and 13.9, corresponding to an H . range equal to approximately $pK_a \pm 1$, which is consistent with
225 the dynamic spectral range found by Safavi and Abdollahi³⁴ and Allain and Xue³³.

226

227 **3.4. Water activity measurements**

228 Water activity was measured in all considered activating solutions in presence of 5.10^{-5} mol/L of
229 TYG. Measurements were done at $25 \pm 2^\circ\text{C}$ with a Hygropalm HP23-AW-A analyzer equipped
230 with a HC2-AW water activity probe (Rotronic) and calibrated in temperature and humidity with
231 Rotronic certified humidity standards at 50% RH and 80% RH. After an equilibration time of
232 5 min, water activity was measured with a precision of ± 0.008 . Water activity measurement
233 relies on Equilibrium Relative Humidity measurement (ERH, in %), when the atmosphere in the
234 sample holder is at equilibrium with the solution ($a_{H_2O} = \text{ERH}/100$).

235

236 **3.5. ²⁹Si Nuclear Magnetic Resonance.**

237 ^{29}Si NMR measurements were performed on silicate activating solutions to investigate the silicate
238 connectivity. Spectra were recorded at a Larmor frequency of 99.36 MHz (at $25 \pm 2^\circ\text{C}$) in
239 zirconia rotors using a Bruker Avance spectrometer and a 7-mm commercial Bruker MAS probe
240 but without spinning. 1600 transients were acquired using a single 90° pulse of $6.4 \mu\text{s}$ and a
241 recycle time of 10 s. The recycle time was verified to be long enough by increasing it ten folds
242 and confirming that intensities did not vary. Spectra were referenced externally to
243 tetramethylsilane (TMS). The proportions of the different types of silicon centers were obtained
244 by the integrated intensities of their resonances using the software Dmfit developed by D.
245 Massiot *et al.*³⁵. The different silicon centers were designated according to Engelhardt's
246 nomenclature¹⁵. Each center is designated as Q since silicon atoms are quadri-coordinated to
247 oxygen. A superscript Q^n ($0 \leq n \leq 4$) indicates the number of siloxo bonds (Si-O-Si), without
248 considering the protonation degree of non-bridging oxygens. For example Q^0 designates a single
249 silicate, Q^1 a silicate with one neighbor silicate (end-chain or in a dimer) and so on. When
250 present, subscript c indicates that silicates are part of a three-membered ring. These Q^2
251 resonances are detected at slightly different frequencies compared to the ones of Q^2 groups in
252 chains or larger rings due to their more constraint geometry.

253

254 **3.6. Isothermal Conduction Calorimetry**

255 Approximately 5 g of each elaborated geopolymer has been then introduced in a sealed ampoule
256 to assess its reactivity by using Isothermal Conduction Calorimetry at 25°C on a TAM Air
257 microcalorimeter. Water was used as the reference, to compensate for possible external
258 temperature disturbances. Due to the external mixing procedure, a parasitic heat flow signal
259 associated to the introduction of sample interfered with the initial reaction signal. The

260 equilibration time of this interference amounted to about 1.5 h, measured on an inert sample
261 (available in supplementary information). Normalized heat flow release during
262 geopolymerization, expressed in mW/g of paste, was recorded as a function of time during 90 h.
263 Cumulative heat releases were obtained by integrating heat flow profiles after the end of the
264 introduction peak here defined as when the heat flow drops to a value of 8 mW / g to minimize
265 the contribution of the introduction peak.

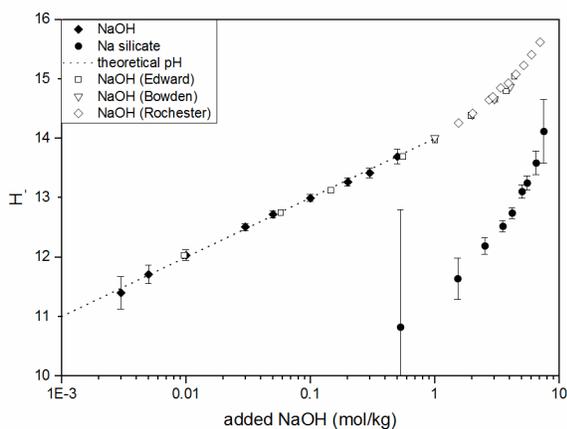
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268 4. Results

269 **4.1. Acidity function H and alkalinity evaluation.**

270 Acidity function values were measured for the first time in sodium silicate solutions and
271 compared to the ones of pure sodium hydroxide solutions. Results are plotted as a function of
272 added sodium hydroxide molality in Figure 1.



273
274 **Figure 1.** Comparison of H . acidity function scales of pure sodium hydroxide (◆) or sodium
275 silicate solutions (●) (with $[Si] = 5.8 \text{ mol / kg}$) as a function of added sodium hydroxide
276 molality. Literature data from Edward²⁹ (□), Bowden³⁰ (▽) and Rochester³² (◇) were used for
277 highly concentrated sodium hydroxide solutions. The dash line represents calculated theoretical
278 pH which is equivalent to H . in dilute solutions ($< 1 \text{ mol / kg}$).

279
280 In a sodium hydroxide solution free from silicate, an addition of approximately 0.97 mol / kg
281 sodium hydroxide is needed to raise the H . value from 12.00 to 14.01 (value from Bowden³⁰).
282 Within this concentration range and in the specific case of pure sodium hydroxide solutions, H . is
283 fairly equivalent to theoretical pH calculated by $pK_w + \log [OH]$ (with a mean deviation of 0.03)
284 and our measured values were consistent with previously reported data²⁹. Above 1 mol / kg , H .

285 values are out of the working range of TYG, and cannot be measured with this indicator. For
286 sodium hydroxide addition higher than 1 mol / kg, the deviation of the H . function from the
287 linearity is illustrated by plotting data from the literature^{29,30,32}. Such a deviation is mainly due to
288 a sharp decrease in water activity as mentioned by Edward²⁹, which was measured for reference
289 and reported in Tables 1 and 2.

290 In a silicate-containing solution, an addition of approximately 4.0 mol / kg sodium hydroxide was
291 needed to raise the H . value from 12.19 to 13.59. For higher sodium hydroxide additions, the
292 resulting H . function values were higher than the 13.9 threshold value of TYG working range.

293 This set of data remarkably highlights the alkalinity difference between sodium hydroxide and
294 sodium silicate solutions. Alkalinity is here defined as the ability of a solution to resist changes in
295 pH in a given pH range. Using this working definition, the alkalinity of both sets of studied
296 solutions was calculated as the amount of hydroxide ions that has to be added to the solution to
297 raise the H . value by one unit, within a H . range from 12 to 14. For H . values ranging from 12 to
298 14, the alkalinity values were found to be 0.48 mole added hydroxide per H . unit for a silicate-
299 free solution and 2.86 for a solution containing 5.80 mol/kg of silicate,. Within the same acidity
300 function range, the alkalinity of the silicate-containing solution is thus more than 5 times higher
301 than the one of the silicate-free solution.

302

303 **4.2. Silicate connectivity**

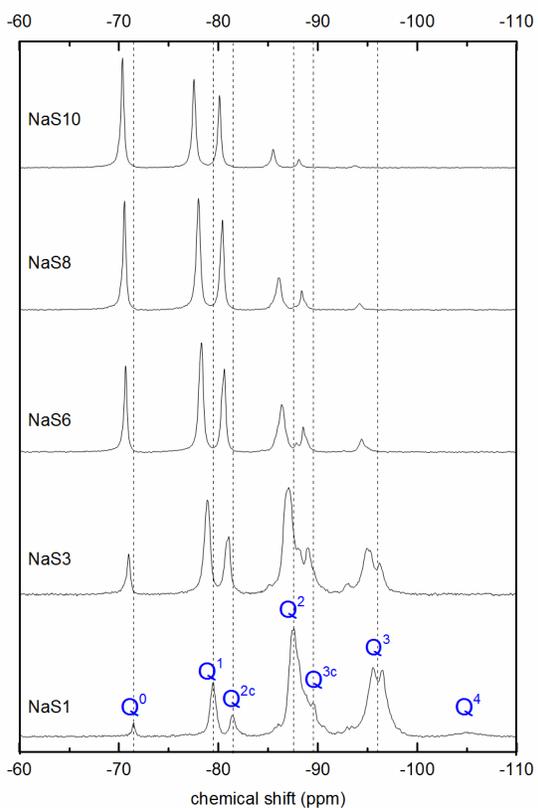
304 Liquid state ²⁹Si NMR spectra of some sodium silicate solutions investigated herein are reported
305 on Figure 2. Several types of silicate species were present. The most deshielded are Q^0 silicates (δ
306 = -71.45 ppm in NaS1) and then Q^1 (δ = -79.45 ppm in NaS1), Q^2_c (δ = -81.36 ppm in NaS1) Q^2
307 (δ = -87.47 ppm in NaS1), Q^3_c (δ = -89.55 ppm in NaS1), Q^3 (δ = -95.52 ppm in NaS1). A Q^4 (δ =

308 -105.4 ppm) resonance was only observed in NaS1. For indication, the ^{29}Si resonances are known
309 to shift to higher frequencies (higher deshielding) when increasing the alkali hydroxide content.
310 This well-known fact is due both to the deprotonation of silanol groups (Si-OH) and to the
311 formation of ion pairs (Si-O⁻ +Na) according to Kinrade and Swaddle¹⁷. As expected, when the
312 alkali hydroxide content is increased, the peak intensities decreased for highly connected silicates
313 and increases for poorly connected silicates, reflecting the general decondensation of silica
314 oligomers with pH. Poorly resolved Q^2 and Q^3_c contributions were decomposed by fitting spectra
315 with gausso-lorentzian lineshapes using the freeware Dmfit³⁵. The average connectivity of Si
316 centers was calculated from the spectral decomposition of ^{29}Si NMR measurements:

$$c = \frac{\sum_n n \cdot Q^n}{\sum_n Q^n}$$

317 with Q^n the proportion of each silicate population (%).

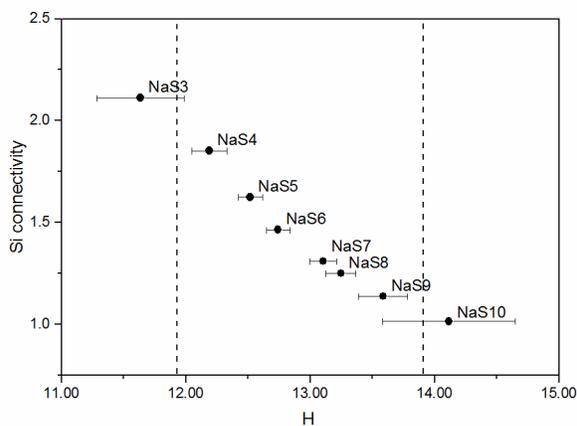
318



319
 320 **Figure 2.** Liquid state ^{29}Si NMR spectra of some sodium silicate solutions investigated herein
 321 with varying sodium hydroxide contents. Peaks are named after Engelhardt notation¹⁵.

322
 323 On Figure 3, the average silicate connectivity is plotted as a function of acidity function values in
 324 silicate solutions. In the working range of TYG (dash lines), the average connectivity decreases
 325 for increasing H . values. For sodium hydroxide additions from 2.54 to 6.54 mol/kg and
 326 corresponding H . values ranging from 12.19 to 13.59 respectively, the silicate connectivity is
 327 divided by almost 2. It demonstrates the decondensation of silicates species when sodium
 328 hydroxide is added to solutions, as already reported by many authors.¹⁵⁻¹⁷ Decondensation
 329 consists in the hydrolysis of siloxo bonds Si-O-Si. Such an effect, highlighted by Svensson *et*

330 *al.*¹⁶, can be seen as the transfer of hydroxide ions from the solution onto silicates in the form of
 331 Si-OH groups. This leads to the consumption of initially added hydroxide ions, as illustrated by
 332 Reaction Equation 2:

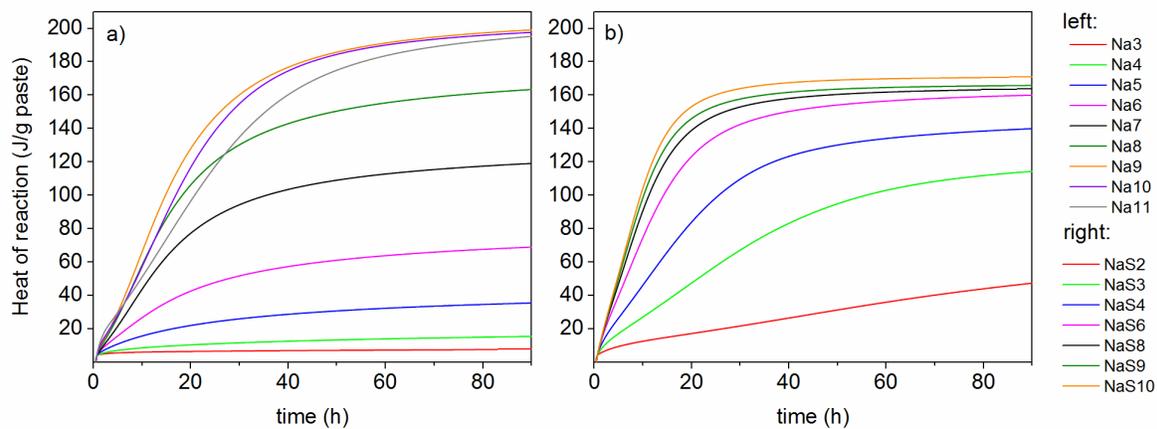


334
 335 **Figure 3.** Evolution of the average connectivity of silicate oligomers in sodium silicate activating
 336 solutions as a function of their acidity function *H*. along the working range of the indicator TYG.
 337 Consequently, it was apparent that the low *H*. values in silicate solutions (<14) despite their high
 338 sodium hydroxide contents, up to 7.5 mol/kg, were due to the presence of silicate species in
 339 solutions and to the associated reaction described above. The presence of silicate was thus
 340 responsible for the alkalinity measured in silicate-containing solutions.

341
 342 **4.3. Isothermal Conduction Calorimetry measurements**

343 Metakaolin-based pastes were then prepared with the solutions under investigation. For all the
 344 studied compositions, cumulative heat profiles could be described as a succession of two stages⁶⁻
 345 ¹¹ (Figure 4). The sharp heat release at the early beginning of the reaction can be ascribed mainly
 346 to the metakaolin dissolution. But this contribution often overlapped second stage of the

347 geopolymerization, namely the alumino-silicate polycondensation. After a variable duration, the
348 heat release stabilized as the reaction slowed down. The heat value at the plateau (Figure 4 and 5)
349 could then be assumed to be approximately proportional to the extent of geopolymerization.^{6,9,10}

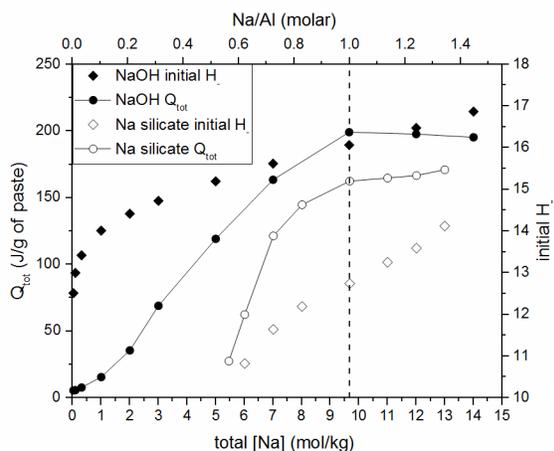


350
351 **Figure 4.** Total heat release of geopolymer pastes prepared from a) sodium hydroxide solutions
352 and b) sodium silicate solutions, with varying NaOH content, measured by ICC.

353

354 **5. Discussion**

355 The final heat value was plotted as a function of total sodium ions content. In the same figure, the
 356 initial H . values of the activating solutions were plotted on the right axis (Figure 5).



357
 358
 359 **Figure 5.** Comparison of the final heat released at 90 h of MK-based geopolymers measured by
 360 Isothermal Conduction Calorimetry (●) with the initial H . function (◆) in either pure sodium
 361 hydroxide solutions (solid symbols) or sodium silicate solutions (empty symbols) as a function of
 362 total sodium molality.

363 For both sets of experiments, i. e. with or without silicate in the activating solution, increasing the
 364 total sodium ions molality by adding sodium hydroxide up to 9.66 mol / kg led to an increase in
 365 the heat of geopolymerization. Above this 9.66 mol / kg value, the heat released during
 366 geopolymerization remained constant. It has to be noted that this molality value corresponded to
 367 a Na/Al ratio equal to 1, described in literature³⁶ as the optimal geopolymer stoichiometry due to
 368 the charge balance between Na^+ ions and AlO_4^- units. At this point, the initial H . values of
 369 activating solutions amount to 12.7 and 16.1 respectively in silicate-containing and silicate-free
 370 activating solution. At this 9.66 mol / kg sodium molality, (Na/Al = 1), the H . value in the

371 silicate-containing solution was thus more than 3 units lower than in the silicate-free one. Despite
372 this huge difference, and for the same total sodium ions concentration, geopolymerization extents
373 were rather close in both systems.

374
375 While, it was predictable that the composition of the reactants with respects of the stoichiometry
376 of the final geopolymer product ($\text{Na}/\text{Al} = 1$) piloted the possibility or not to reach completion,
377 and that this explains the dependence on the sodium content of the activating solution, it
378 remained surprising at first glance that the silicate containing activating solutions, despite their
379 much lower initial H . values, led to large geopolymerization extent. Indeed, Xu and Van
380 Deventer¹⁸ have demonstrated among others that increasing the pH value of the dissolution media
381 enhances alumino-silicate minerals dissolution and one might expect consequently a much lower
382 extent of reaction for metakaolin in silicate solutions than in pure NaOH ones. The benefits in
383 adding silicate species in activating solutions to enhance the geopolymerization process have
384 been previously mainly attributed to their role on condensation reactions, since silicate species
385 are available from the beginning of geopolymerization according to Duxson *et al.*¹³. Moreover,
386 Phair and Van Deventer¹⁹ have shown that increasing the alkali content leads to less condensed
387 and more labile silicate species. A more porous and less dense geopolymer would thus be yielded
388 at lower modulus $\text{SiO}_2/\text{Na}_2\text{O}$ ^{13,19}.

389 However, the data presented here suggest another important role for the silicate species. When
390 using a silicate-free solution as the activating solution, hydroxide ions are consumed by
391 metakaolin dissolution, as described by Reaction Equation 3 as already reported by Xu and Van
392 Deventer¹⁸. Due to the low alkalinity of sodium hydroxide solutions, meaning, as defined in the

393 introduction, that they do not oppose pH changes, the pH necessarily drops during reaction and,
394 to insure that all metakaolin is dissolved, a high initial H . value was necessary.

395



397

398 At the opposite, when a silicate-containing solution was used to activate metakaolin and for a
399 same Na/Al ratio (typically 1), the H . initial values were lower but a similar level of
400 geopolymerization was reached. Obviously, the lower acidity function H . values were
401 compensated by the strong alkalinity resulting from the presence of silicate species. While
402 hydroxide ions are also consumed by the metakaolin dissolution which releases aluminate and
403 silicate species in solution, following Equation 3, the hydroxide are removed from solution but
404 the concomitant release of silicate and aluminate species in solution favors condensation of pre-
405 existing alumino-silicate species, thus releasing further hydroxide ions or water molecules in
406 solution (Reaction Equations 4 and 5). Those freshly released hydroxide ions are then available to
407 react in turn at the metakaolin surface, releasing more and more silicate and aluminate species
408 which can feed the condensation. As a result, a chain reaction can be established thanks to this
409 circular mechanism that nurtures the dissolution process. This phenomenon is enhanced in
410 silicate-containing solutions due to their alkalinity. In other terms, the initial silicate in solution
411 act as a reservoir of hydroxide compensating the effect of the H . values which are initially lower
412 than in silicate-free solutions but remain probably somewhat constant during the dissolution.



415 It is understood, as shown in Reaction Equation 5, that condensation can also possibly release
416 water molecules. Nevertheless, it has been shown that $\text{Si}(\text{OH})_2\text{O}_2^{2-}$ and $\text{Si}(\text{OH})_3\text{O}^-$ are the
417 predominant forms of silicate monomers in activating solutions for geopolymers with respective
418 pK_a 's of 12.6 and 15.7³⁷. Besides, silicates pK_a 's decrease with their connectivity³⁷. In
419 consequence, the level of silicate deprotonation should thus be significant in the present
420 activating solutions. The release of hydroxide ions rather than water molecules would thus be
421 favored.

422 **5. Conclusion**

423 Comparing initial H . values at identical Na content in sodium hydroxide and sodium silicate
424 allowed assessing for the first time the role of activating solution alkalinity in the
425 geopolymerization process, where the alkalinity is defined as the ability of activating solutions to
426 resist to H . changes. As a consequence, the role of silicate species in the geopolymerization
427 process is indirectly highlighted, since the presence of silicate species is responsible for
428 activating solutions alkalinity.

429 The basicity of geopolymer activating solutions was investigated by UV-Visible spectroscopy
430 using Thiazole Yellow G as a weakly acidic indicator to calculate their Hammett acidity function
431 H .. Sodium silicate and sodium hydroxide solutions alkalinity has thus been measured by using
432 this methodology. The present results on sodium hydroxide solutions were consistent with
433 previous results from Safavi³⁴, validating the implemented methodology. For the first time to our
434 knowledge, this technique was applied to alkali silicate solutions. Quantitative data on the
435 basicity of geopolymer activating solutions were obtained, without using pH-metry. Thiazole
436 Yellow G was an appropriate indicator to measure H . functions comprised in the range 11.9 -
437 13.9, which is ideally suitable for concentrated alkali silicate activating solutions.

438 The variation of acidity function was found low in silicate-based solutions when compared to
439 silicate-free solutions, for similar sodium hydroxide additions. This alkalinity difference, defined
440 as the ability of studied solutions to resist changes in pH, is due to the condensation and
441 decondensation of silicate species in the medium, as evidenced by using liquid state ^{29}Si NMR.

442
443 The reactivity of metakaolin-based geopolymers elaborated with previously investigated
444 activating solutions was studied by using Isothermal Conduction Calorimetry. Taking into
445 account initial H . values and corresponding alkalinity of activating solutions allow to precise the
446 respective role of hydroxide ions and silicate species in the geopolymerization process. After
447 metakaolin dissolution initiation by hydroxide ions, the “hydroxide reservoir” on silicates can
448 gradually release hydroxide ions into the solution during the subsequent condensation of
449 alumino-silicate species. Those freshly released hydroxide ions would then be able to dissolve at
450 their turn additional amounts of metakaolin. This would generate a chain reaction and a self-
451 sustained circular mechanism. This high alkalinity explain why silicate solutions of low initial H .
452 values lead to a similar extent of geopolymerisation compared to a silicate-free solution
453 presenting drastically higher H . values. The fact that silicate solutions allow the reaction to take
454 place at lower hydroxide concentrations is probably crucial in directing the reaction path towards
455 geopolymers rather than zeolites.

456 Experimental work has to be enriched to further validate this proposition, especially by
457 measuring acidity functions during the course of geopolymerization. It must be understood
458 however that only discontinuous measurements would be possible with this technique, after
459 extracting the solution from the geopolymer paste at different times, since translucent media are
460 required for absorption based methods.

461

462 **6. Conflicts of interest**

463

464 There are no conflicts to declare

465 **7. Reference section**

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