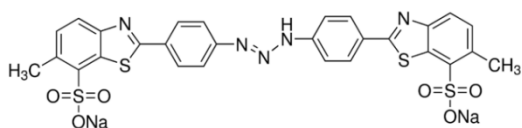


1 Supporting Information

2 Acidity functions measurements were performed in alkali hydroxide and alkali silicate
3 solutions by adding Thiazole Yellow G (TYG, figure 1) as a weak acid UV-Visible indicator.
4 First, the validity of the Beer-Lambert law was verified in sodium hydroxide solutions. TYG
5 solutions of concentrations increasing from 10^{-2} mmol/kg to 10 mmol/kg were prepared in
6 sodium hydroxide solutions (1 mmol/kg). Their absorbance spectra were recorded in the range
7 300-600 nm (a 1 mmol/kg sodium hydroxide solution was analyzed as the background). The
8 Beer-Lambert law was verified at 480 nm (figure 2) to ensure that the absorbance signal A is
9 only correlated to the concentration of TYG c according the relation $A = \epsilon \cdot \ell \cdot c$ (where ϵ is the
10 extinction coefficient at 480 nm and ℓ the path length of the beam light through the sample).
11 The absorbance at 480 nm was proportional to the TYG concentration up to a value of
12 $5 \cdot 10^{-1}$ mmol/kg, and beyond the spectrophotometer saturated. In the following, TYG was used
13 at a concentration of $5 \cdot 10^{-2}$ mmol/kg in order to determine acidity functions, in agreement
14 with the Beer-Lambert law.

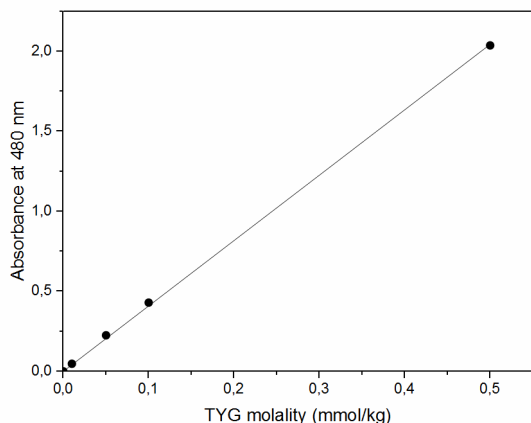
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17 **Figure 1:** chemical structure of Thiazole Yellow G



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21 **Figure 2:** Verification of the Beer-Lambert law on the indicator TYG in 1 mmol/kg sodium
22 hydroxide solutions. Correlation coefficient $R^2 = 0.9997$.



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25 The pK_a of TYG was then determined by using a set of sodium hydroxide solutions in the
26 range 0-0.7 mol/kg. On the set of corresponding absorption spectra (figure 3), an isobestic
27 point is present at 433 nm between absorption bands centered at 405 and 475 nm. These bands
28 correspond respectively to the protonated form of the indicator and its deprotonated form. The
29 evolution of the absorbance A at 480 nm was plotted as a function of the sodium hydroxide
30 concentration on figure 4. The absorbance was normalized by the absorbance at the isobestic
31 point to compensate possible fluctuations in the spectrophotometer (electronic and optical
32 systems), in the amount of indicator or in optical properties of solutions. The pK_a ($= -\log K_a$)
33 of TYG was then calculated by applying a least-squares fit of experimental points based on
34 the following eq. 1 from Safavi and Abdollahi¹:

$$35 \quad A = \frac{A_S \cdot K_a \cdot [OH^-] + A_{SH} \cdot K_w}{K_w + K_a \cdot [OH^-]} \quad \text{Equation 1}$$

36 With:

37 A_S , the absorbance of a solution where the indicator is fully deprotonated (most basic
38 solution),

39 A_{SH} , the absorbance of a solution where the indicator is fully protonated (least basic
40 solution),

41 K_a , the acidity constant of TYG,

42 K_w , the dissociation constant of water (10^{-14} at 25°).

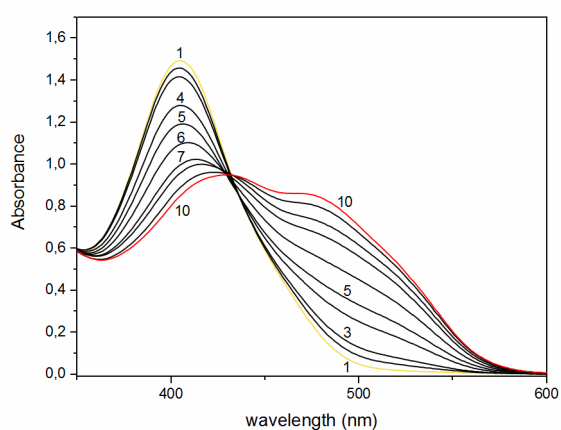
43 A_{S^-} and K_a were the fitting parameters (as A_{S^-} could not be clearly ascertained
44 experimentally contrary to A_{SH}) and it was found that $A_{S^-} = 0.9450$ and $K_a = 1.21 \cdot 10^{-13}$. The
45 pK_a value of TYG was thus found at 12.92 ± 0.01 at 25°C .

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49 **Figure 3:** Evolution of absorption spectra of TYG ($5 \cdot 10^{-5}$ mol/kg) with increasing sodium
50 hydroxide concentrations (in mol/kg): (1) 0.001 (2) 0.005 (3) 0.01 (4) 0.03 (5) 0.05 (6) 0.1 (7)
51 0.2 (8) 0.3 (9) 0.5 (10) 0.7 (11) 1. The yellow spectrum corresponds to the full protonation of
52 indicator and the red one corresponds to the full deprotonation of indicator.

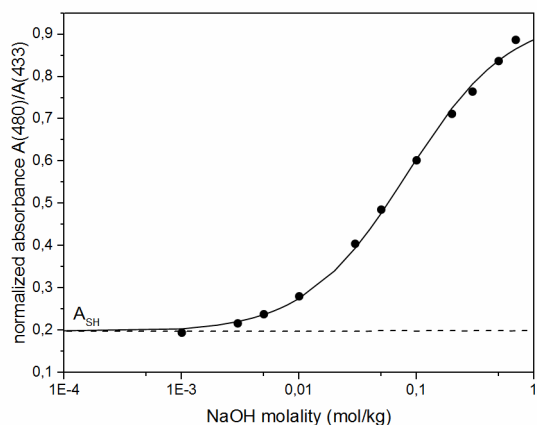


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56 **Figure 4:** Evolution of the absorbance at 480 nm normalized by the absorbance at the
57 isobestic point (433 nm) and the least-squares fit (solid line). The dash line represents the
58 limit A_{SH} of the absorbance of TYG in the least basic solution.



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62 Sodium silicate solutions were then prepared from a commercial solution and sodium
63 hydroxide solutions and analyzed by UV-Visible spectrophotometry. Absorption spectra are
64 presented on figure 5. An isobestic point is present at 438 nm between absorption bands
65 centered at 390 and 480 nm. Acidity functions were thus calculated from the absorbance at
66 480 nm, corresponding to the deprotonated form of the indicator. On figure 6, the absorbance
67 at 480 nm is represented by normalizing by the absorbance at the isobestic point (438 nm) and
68 relative to the highest absorbance measured at 480 nm. The absorbance at 480 nm evolves in
69 the form of an S-shaped curve indicating the presence of two plateaus. This confirmed that the
70 composition range of investigated solutions was wide enough to observe the gradual
71 deprotonation of TYG from the total protonation to the complete deprotonation of the
72 indicator. The lowest and highest absorbance values were thus taken respectively as A_{SH} and
73 A_S . to calculate acidity functions H . in silicate solutions according eq.2. The diagram on
74 figure 6 also highlights two zones on extrema within the absorbance variations are small;

75 acidity function measurements are thus less accurate in these zones. These extreme intervals
76 each correspond to about 10% of the total absorbance variation. From eq. 2, it can be
77 demonstrated that the intermediate interval (80%) is equivalent to acidity function variation of
78 $H_- = pK_a \pm 1$, by considering relative absorbance values ($A_{SH} = 0$, $A_{S^-} = 1$ and $A = 0.9$ or 0.1).
79 TYG can thus be used confidently used over about 2 H. function units, defining a working
80 range from 11.9 to 13.9.

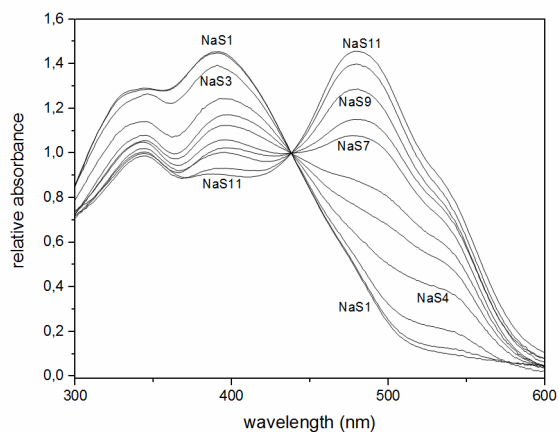
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$$H_- = pK_a + \log \frac{A - A_{SH}}{A_{S^-} - A} \quad \text{Equation 2}$$

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85 **Figure 5:** Evolution of absorption spectra of TYG (5.10^{-5} mol/kg) with increasing sodium
86 hydroxide concentrations in sodium silicate solutions at $[Si] = 5.79$ mol/kg.

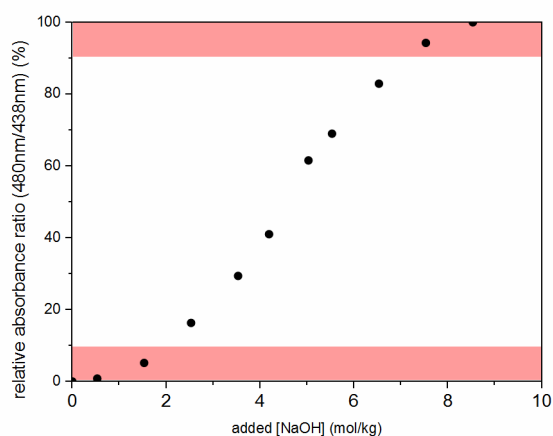


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90 **Figure 6:** Evolution of the absorbance at 480 nm (normalized by the absorbance at the
91 isobestic point and relative to the highest absorbance at 480 nm) of TYG in sodium silicate
92 solutions. The red zones indicate the limits of utilization of TYG, with insufficient variations
93 of the absorbance.

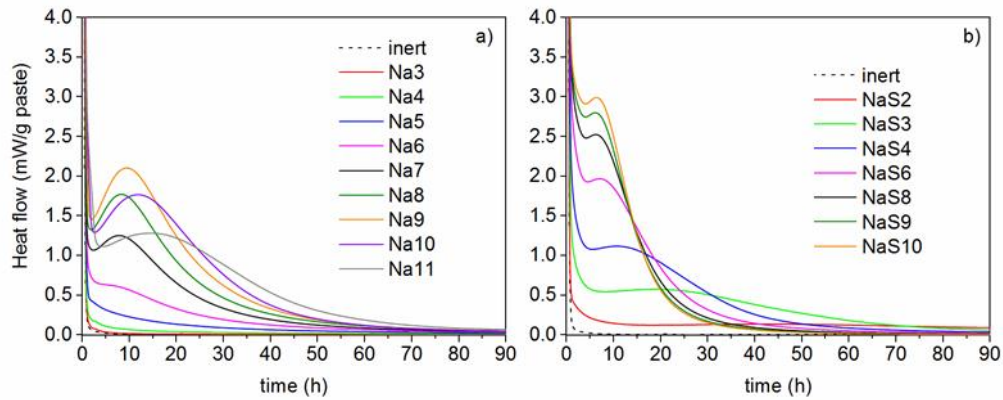


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96 Metakaolin-based pastes were then prepared with both silicate-free sodium hydroxide
97 solutions and sodium silicate solutions to analyze the reactivity of such mixes by Isothermal
98 Conduction Microcalorimetry. An external mixing procedure was used, inducing interference
99 on measured heat flows at the introduction of the sample. To determine the equilibration time
100 after which the reaction heat flows and heats released can be reasonably exploited, an inert
101 mixture was analyzed. It was composed of quartz and sodium silicate solution (composition
102 NaS6 with a weight ratio water/quartz = 0.78). The heat flow profile of this inert sample is
103 presented in figure 7. The heat flow at 1.5h was low enough to consider that the equilibration
104 time extends no longer than 1.5h after introduction of the sample. This corresponds to a heat
105 of 4 J/g of paste representing between 2 and 14 % of the final heat of samples. For indication,
106 heat flow profiles of the different pastes under investigation are also presented in figure 7.

107 **Figure 7:** Heat flow profiles of geopolymer pastes prepared from a) sodium hydroxide
108 solutions and b) sodium silicate solutions, with varying NaOH content, measured by ICC; c)
109 and d) are zooms of a) and b) at early age.

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112 References Section

113 (1) Safavi, A.; Abdollahi, H. Optical sensor for high pH values. *Anal. Chim. Acta* **1998**, *367* (1-
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