Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for:

Composition-solubility-structure relationships in calcium (alkali) aluminosilicate hydrate (C-(N,K-)A-S-H)

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Appendix S1. Structural constraints used to deconvolute the ^{29}Si MAS NMR spectra

The ^{29}Si MAS NMR spectra were deconvoluted using the structural constraints described here, for C-(N,K-)A-S-H nanostructures with nearest-neighbour Al-O-Al avoidance.[1] A ratio of $Q^2_p/Q^2_b = 2$ was specified for the non-cross-linked C-(N,K-)A-S-H components, which is required for consistency with 'dreierketten-type' (3*n*-1) chain structures.[2] Additional constraints were specified for the cross-linked C-(N,K-)A-S-H components,[3] which are:

i) $Q^2(1Al) \geq 2Q^3(1Al)$;

ii) $Q^2 + Q^2(1Al) \geq 2(Q^3 + 2Q^3(1Al))$;

iii) $Q^2_p{}^* \geq 0$;

iv) $Q^2(1Al)^* \geq 0$; and

v) $Q^2_p{}^*/Q^2_b = 2$

where $Q^2_p{}^* = Q^2_p - 2(Q^3 + Q^3(1Al))$ and $Q^2(1Al)^* = Q^2(1Al) - 2Q^3(1Al)$.

Mixed cross-linked/non-cross-linked C-(N,K-)A-S-H products were described using structural constraints for both of the structural types.

Appendix S2. Relevant thermodynamic data

Thermodynamic properties of the aqueous species and solid phases used to calculate effective saturation indices (SI^*) and $\log_{10}(K_s)$ values are shown in Tables S1-S3.

Table S1. Standard partial molal thermodynamic properties of the aqueous species used in the thermodynamic modelling calculations. The reference state is unit activity in a hypothetical one molal solution referenced to infinite dilution.

Species	**V° (cm^3/mol)**	**Δ_fH° (kJ/mol)**	**Δ_fG° (kJ/mol)**	**S° (J/mol.K)**	**Cp° (J/mol.K)**	**Reference**
Al^{3+}	-45.2	-530.6	-483.7	-325.1	-128.7	[4]
AlO^+ (+ H_2O = $Al(OH)_2^+$)	0.3	-713.6	-660.4	-113.0	-125.1	[4]
AlO_2^- (+ $2H_2O$ = $Al(OH)_4^-$)	9.5	-925.6	-827.5	-30.2	-49.0	[4]
$AlOOH^o$ (+ $2H_2O$ = $Al(OH)_3^o$)	13.0	-947.1	-864.3	20.9	-209.2	[4]
$AlOH^{2+}$	-2.7	-767.3	-692.6	-184.9	56.0	[4]
$AlHSiO_3^{2+}$ (+ H_2O = $AlSiO(OH)_3^{2+}$)	0	-1634.3	-1540.5	-25.0	-215.9	[5, 6]
$AlSiO_5^{3-}$ (+ $2H_2O$ = $AlSiO_3(OH)_4^{3-}$)	0	-2014.2	-1769.0	-66.3	-292.2	[5, 6]
Ca^{2+}	-18.4	-543.1	-552.8	-56.5	-30.9	[4]
$CaOH^+$	5.8	-751.6	-717.0	28.0	6.0	[4]
$Ca(HSiO_3)^+$ (+ H_2O = $CaSiO(OH)_3^+$)	-6.7	-1686.5	-1574.2	-8.3	137.8	[7]
$CaSiO_3^o$ (+ H_2O = $CaSiO_2(OH)_2^o$)	15.7	-1668.1	-1517.6	-136.7	88.9	[8]
K^+	9.0	-252.1	-282.5	101.0	8.4	[4]
KOH^o	15.0	-474.1	-437.1	108.4	-85.0	[4]
Na^+	-1.2	-240.3	-261.9	58.4	38.1	[4]
$NaOH^o$	3.5	-470.1	-418.1	44.8	-13.4	[4]
$HSiO_3^-$ (+ H_2O = $SiO(OH)_3^-$)	4.5	-1144.7	-1014.6	20.9	-87.2	[7]
SiO_2^o (+ $2H_2O$ = $Si(OH)_4^o$)	16.1	-887.9	-833.4	41.3	44.5	[9, 10]
$SiO_4O_{10}^{4-}$ (+ $2H_2O$ = $Si_4O_8(OH)_4^{4-}$)	0	-4082.7	-3600.8	-253.9	-1123.2	[5, 6]
SiO_3^{2-} (+ H_2O = $SiO_2(OH)_2^{2-}$)	34.1	-1098.7	-938.5	-80.2	119.8	[8]
OH^-	-4.7	-230.0	-157.3	-10.7	-136.3	[4]
H^+	0	0	0	0	0	[4]
H_2O^o	18.1	-285.9	-237.2	69.9	75.4	[11]
N_2^o	33.4	-10.4	18.2	95.8	234.2	[9]
O_2^o	30.5	-12.2	16.4	109.0	234.1	[9]

Table S2. Standard partial molar thermodynamic properties of the solid phases used in the thermodynamic modelling calculations. The reference state is 298.15 K and 1 bar.

Phase	**V°** **(cm^3/mol)**	**$\Delta_f H$°** **(kJ/mol)**	**$\Delta_f G$°** **(kJ/mol)**	**S°** **(J/mol.K)**	**Cp°** **(J/mol.K)**	**Reference**
$Al(OH)_3$ (microcrystalline), ½AH_3	32.0	-1265.3	-1148.4	140.0	93.1	[12]
Gibbsite, ½AH_3	32.0	-1288.7	-1151.0	70.1	93.1	[13]
Portlandite, CH	33.1	-984.7	-897.0	83.4	87.5	[14]
SiO_2 (amorphous)	29.0	-903.3	-848.9	41.3	44.5	[15]
Katoite, C_3AH_6	149.7	-5537.3	-5008.2	421.7	445.6	[12]
Si-hydrogarnet, $C_3AS_{0.84}H_{4.32}$	142.5	-5847.5	-5365.2	375.2	412.6	[16]
Strätlingite, C_2ASH_8	216.1	-6360.0	-5705.1	546.2	602.7	[8]
C-(N-)A-S-H solid solution, CNASH_ss						
5CA, $C_{1.25}A_{0.125}SH_{1.625}$	57.3	−2491	−2293	163	177	[17]
INFCA, $CA_{0.15625}S_{1.1875}H_{1.65625}$	59.3	−2551	−2343	154	181	[17]
5CNA, $C_{1.25}N_{0.25}A_{0.125}SH_{1.375}$	64.5	−2569	−2382	195	176	[17]
INFCNA, $CN_{0.34375}A_{0.15625}S_{1.1875}H_{1.3125}$	69.3	−2667	−2474	198	180	[17]
INFCN, $CN_{0.3125}S_{1.5}H_{1.1875}$	71.1	−2642	−2452	186	184	[17]
T2C*, $C_{1.5}SH_{2.5}$	80.6	−2721	−2465	167	237	[17]
T5C*, $C_{1.25}S_{1.25}H_{2.5}$	79.3	−2780	−2517	160	234	[17]
TobH*, $CS_{1.5}H_{2.5}$	85.0	−2831	−2560	153	231	[17]

Table S3. Dissolution reactions for the solid phases used in the thermodynamic modelling calculations (298.15 K, 1 bar).

Phase	Reaction	$\log_{10}(K_s)$	Reference
$Al(OH)_3$ (microcrystalline), ½AH_3	$Al(OH)_3 + OH^- \rightleftharpoons AlO_2^- + 2H_2O$	-0.67	12
Gibbsite, ½AH_3	$Al(OH)_3 + OH^- \rightleftharpoons AlO_2^- + 2H_2O$	-1.12	5, 6
Portlandite, CH	$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$	-5.20	5, 6
SiO_2 (amorphous)	$SiO_2\ (am) \rightleftharpoons SiO(OH)_3^- - OH^- - H_2O$	1.476	18
Katoite, C_3AH_6	$(CaO)_3(Al_2O_3)(H_2O)_6 \rightleftharpoons 3Ca^{2+} + 2AlO_2^- + 4H_2O + 4OH^-$	-20.50	12
Si-hydrogarnet, $C_3AS_{0.84}H_{4.32}$	$(CaO)_3(Al_2O_3)(SiO_2)_{0.84}(H_2O)_{4.32} \rightleftharpoons 3Ca^{2+} + 2AlO_2^- + 2.32H_2O + 3.16OH^- + 0.84HSiO_3^-$	-26.70	16
Strätlingite, C_2ASH_8	$(CaO)_2(Al_2O_3)(SiO_2)(H_2O)_8 \rightleftharpoons 2Ca^{2+} + 2AlO_2^- + HSiO_3^- + 7H_2O + OH^-$	-19.70	8
5CA, $C_{1.25}A_{0.125}SH_{1.625}$	$(CaO)_{1.25}(Al_2O_3)_{0.125}(SiO_2)_1(H_2O)_{1.625} \rightleftharpoons SiO_3^{2-} + 1.25Ca^{2+} + 0.25AlO_2^- + 0.25OH^- + 1.5H_2O$	-10.75	17
INFCA, $CA_{0.15625}S_{1.1875}H_{1.65625}$	$(CaO)_1(Al_2O_3)_{0.15625}(SiO_2)_{1.1875}(H_2O)_{1.65625} + 0.6875OH^- \rightleftharpoons 1.1875SiO_3^{2-} + Ca^{2+} + 0.3125AlO_2^- + 2H_2O$	-8.90	17
5CNA, $C_{1.25}N_{0.25}A_{0.125}SH_{1.375}$	$(CaO)_{1.25}(Na_2O)_{0.25}(Al_2O_3)_{0.125}(SiO_2)_1(H_2O)_{1.375} \rightleftharpoons SiO_3^{2-} + 1.25Ca^{2+} + 0.25AlO_2^- + 0.5Na^+ + 0.75OH^- + H_2O$	-10.4	17
INFCNA, $CN_{0.34375}A_{0.15625}S_{1.1875}H_{1.3125}$	$(CaO)_1(Na_2O)_{0.34375}(Al_2O_3)_{0.15625}(SiO_2)_{1.1875}(H_2O)_{1.3125} \rightleftharpoons 1.1875SiO_3^{2-} + Ca^{2+} + 0.3125AlO_2^- + 0.6875Na^+ + 1.3125H_2O$	-10.0	17
INFCN, $CN_{0.3125}S_{1.5}H_{1.1875}$	$(CaO)_1(Na_2O)_{0.3125}(SiO_2)_{1.5}(H_2O)_{1.1875} + 0.375OH^- \rightleftharpoons 1.5SiO_3^{2-} + Ca^{2+} + 0.625Na^+ + 1.375H_2O$	-10.7	17
T2C*, $C_{1.5}SH_{2.5}$	$(CaO)_{1.5}(SiO_2)_1(H_2O)_{2.5} \rightleftharpoons SiO_3^{2-} + 1.5Ca^{2+} + OH^- + 2H_2O$	-11.57	17
T5C*, $C_{1.25}S_{1.25}H_{2.5}$	$(CaO)_{1.25}(SiO_2)_{1.25}(H_2O)_{2.5} \rightleftharpoons 1.25SiO_3^{2-} + 1.25Ca^{2+} + 2.5H_2O$	-10.48	17
TobH*, $CS_{1.5}H_{2.5}$	$(CaO)_1(SiO_2)_{1.5}(H_2O)_{2.5} + OH^- \rightleftharpoons 1.5SiO_3^{2-} + Ca^{2+} + 3H_2O$	-7.91	17

Appendix S3. Solid phase assemblages determined from TGA, XRD and Rietveld analysis

Solid phase assemblages used in mass balances to determine chemical compositions for C-(N,K-)A-S-H products are shown in Tables S4-S5. Portlandite is the only secondary product that was used in mass balance calculations to determine C-(N,K-)A-S-H chemical compositions for the Ca/Si* = 0.8, 1.2 and 1.6 samples (with solid phase assemblages determined by TGA), as all the other secondary phases are present in small quantities in these specimen (≤2 wt.%).

Table S4. Solid phase assemblages of the C-(N,K-)S-H samples (Al/Si* = 0) synthesised at 50°C, as determined by TGA (italic font), and XRD and Rietveld analysis (normal font). The estimated absolute error is ±2 wt.% in the values determined by Rietveld analysis for the secondary products and ±4 wt.% in the values determined for portlandite by TGA.

Synthesis solution	**C-(N,K-)S-H (wt.%)**	**CH (wt.%)**	**C_3AH_6 (wt.%)**	**Calcite (wt.%)**	**Aragonite (wt.%)**	**Vaterite (wt.%)**	**Natrite (wt.%)**	**Thermonatrite (wt.%)**	**Trona (wt.%)**
Ca/Si* = 0.6									
Water	100	0	n/a [a,b]	0	0	0	n/a [a,c]	n/a [a,c]	n/a [a,c]
0.1 M NaOH	97.5	0	n/a [a,b]	0	2.5	0	0	0	0
0.1 M KOH	97.7	0	n/a [a,b]	0	2.3	0	n/a [a,c]	n/a [a,c]	n/a [a,c]
0.5 M NaOH/0.5 M KOH	96.3	0	n/a [a,b]	0	0	0	0	3.7	0
Ca/Si* = 0.8									
Water	*100*	*0*	*n/a* [a,b]	*0*	*0*	*0*	*n/a* [a,c]	*n/a* [a,c]	*n/a* [a,c]
0.1 M NaOH	*≥96*	*≤ 2* [d]	*n/a* [a,b]	*≤ 2* [e]	*≤ 2* [e]	*≤ 2* [e]	*0*	*0*	*0*
0.1 M KOH	*100*	*0*	*n/a* [a,b]	*0*	*0*	*0*	*n/a* [a,c]	*n/a* [a,c]	*n/a* [a,c]
0.5 M NaOH/0.5 M KOH	*≥71* [f]	*27* [f]	*n/a* [a,b]	*≤ 2* [e]	*≤ 2* [e]	*≤ 2* [e]	*0*	*0*	*0*
Ca/Si* = 1									
Water	100	0	n/a [a,b]	0	0	0	n/a [a,c]	n/a [a,c]	n/a [a,c]
0.1 M NaOH	100	0	n/a [a,b]	0	0	0	0	0	0
0.1 M KOH	99.2	0	n/a [a,b]	0	0.8	0	n/a [a,c]	n/a [a,c]	n/a [a,c]
0.5 M NaOH/0.5 M KOH	96.4	0	n/a [a,b]	0	0	0	3.2	0	0.3
Ca/Si* = 1.2									
Water	*100*	*0*	*n/a* [a,b]	*0*	*0*	*0*	*n/a* [a,c]	*n/a* [a,c]	*n/a* [a,c]
0.1 M NaOH	*100*	*0*	*n/a* [a,b]	*0*	*0*	*0*	*0*	*0*	*0*
0.1 M KOH	*100*	*0*	*n/a* [a,b]	*0*	*0*	*0*	*n/a* [a,c]	*n/a* [a,c]	*n/a* [a,c]
0.5 M NaOH/0.5 M KOH	*≥91*	*7*	*n/a* [a,b]	*≤ 2* [e]	*≤ 2* [e]	*≤ 2* [e]	*0*	*0*	*0*
Ca/Si* = 1.4									
Water	100	0	n/a [a,b]	0	0	0	n/a [a,c]	n/a [a,c]	n/a [a,c]
0.1 M NaOH	100	0	n/a [a,b]	0	0	0	0	0	0
0.1 M KOH	100	0	n/a [a,b]	0	0	0	n/a [a,c]	n/a [a,c]	n/a [a,c]
0.5 M NaOH/0.5 M KOH	85.3	12.6	n/a [a,b]	2.2	0	0	0	0	0

Table S4. Continued.

Synthesis solution	C-(N,K-)S-H (wt.%)	CH (wt.%)	C_3AH_6 (wt.%)	Calcite (wt.%)	Aragonite (wt.%)	Vaterite (wt.%)	Natrite (wt.%)	Thermonatrite (wt.%)	Trona (wt.%)
Ca/Si* = 1.6									
Water	*100*	*0*	*n/a* [a,b]	*0*	*0*	*0*	*n/a* [a,c]	*n/a* [a,c]	*n/a* [a,c]
0.1 M NaOH	*≥90*	*8*	*n/a* [a,b]	*≤ 2* [e]	*≤ 2* [e]	*≤ 2* [e]	*0*	*0*	*0*
0.1 M KOH	*≥89*	*9*	*n/a* [a,b]	*≤ 2* [e]	*≤ 2* [e]	*≤ 2* [e]	*n/a* [a,c]	*n/a* [a,c]	*n/a* [a,c]
0.5 M NaOH/0.5 M KOH	*82*	*18*	*n/a* [a,b]	*0*	*0*	*0*	*0*	*0*	*0*

[a] n/a = not applicable; no [b] Al or [c] Na was added during synthesis (<0.6 mM Na is present as an impurity in the 0.1 M KOH synthesis solution).

[d] a small amount of $Ca(OH)_2$ was detected in this sample by TGA (phase mass estimated to be ≤ 2 wt.% of the sample).

[e] a small amount of $CaCO_3$ was detected in this sample by TGA (total $CaCO_3$ mass estimated to be ≤ 2 wt.% of the sample).

[f] An additional major phase, possibly a zeolite, was formed in this sample in addition to C-(N,K-)S-H.

Table S5. Solid phase assemblages of the C-(N,K-)A-S-H samples (Al/Si* = 0.05) synthesised at 50°C, as determined by TGA (italic font), and XRD and Rietveld analysis (normal font). The estimated absolute error is ±2 wt.% in the values determined by Rietveld analysis for the secondary products and ±4 wt.% in the values determined for portlandite by TGA.

Synthesis solution	**C-(N,K-)A-S-H (wt.%)**	**CH (wt.%)**	**C_3AH_6 (wt.%)**	**Calcite (wt.%)**	**Aragonite (wt.%)**	**Vaterite (wt.%)**	**Natrite (wt.%)**	**Thermonatrite (wt.%)**	**Trona (wt.%)**
				Ca/Si* = 0.6					
Water	99.8	0	0	0	0	0.2	n/a [a]	n/a [a]	n/a [a]
0.1 M NaOH	100	0	0	0	0	0	0	0	0
0.1 M KOH	98.5	0	0	0	1.5	0	n/a [a]	n/a [a]	n/a [a]
0.5 M NaOH/0.5 M KOH [b]	98.0	0	0.3	0	0	0	1.7	0	0
				Ca/Si* = 0.8					
Water	*100*	*0*	*0*	*0*	*0*	*0*	*n/a* [a]	*n/a* [a]	*n/a* [a]
0.1 M NaOH	*≥98*	*0*	*0*	*≤ 2* [d]	*≤ 2* [d]	*≤ 2* [d]	*0*	*0*	*0*
0.1 M KOH	*100*	*0*	*0*	*0*	*0*	*0*	*n/a* [a]	*n/a* [a]	*n/a* [a]
0.5 M NaOH/0.5 M KOH	*100*	*0*	*0*	*0*	*0*	*0*	*0*	*0*	*0*
				Ca/Si* = 1					
Water	100	0	0	0	0	0	n/a [a]	n/a [a]	n/a [a]
0.1 M NaOH	98.1	0	0.6	0	1.2	0	0	0	0
0.1 M KOH	100	0	0	0	0	0	n/a [a]	n/a [a]	n/a [a]
0.5 M NaOH/0.5 M KOH [c]	89.8	0	0.6	0	0	0	0	9.6	0
				Ca/Si* = 1.2					
Water	*100*	*0*	*0*	*0*	*0*	*0*	*n/a* [a]	*n/a* [a]	*n/a* [a]
0.1 M NaOH	*100*	*0*	*0*	*0*	*0*	*0*	*0*	*0*	*0*
0.1 M KOH	*100*	*0*	*0*	*0*	*0*	*0*	*n/a* [a]	*n/a* [a]	*n/a* [a]
0.5 M NaOH/0.5 M KOH	*≥92*	*6*	*≤ 2* [e]	*0*	*0*	*0*	*0*	*0*	*0*
				Ca/Si* = 1.4					
Water	99.5	0	0	0.5	0	0	n/a [a]	n/a [a]	n/a [a]
0.1 M NaOH	99.3	0.7	0	0	0	0	0	0	0
0.1 M KOH	97.8	1.1	0	1.1	0	0	n/a [a]	n/a [a]	n/a [a]
0.5 M NaOH/0.5 M KOH	91.6	7.3	0	0	0	0	0	1.1	0

Table S5. Continued.

Synthesis solution	**C-(N,K-)A-S-H (wt.%)**	**CH (wt.%)**	**C_3AH_6 (wt.%)**	**Calcite (wt.%)**	**Aragonite (wt.%)**	**Vaterite (wt.%)**	**Natrite (wt.%)**	**Thermonatrite (wt.%)**	**Trona (wt.%)**
Ca/Si* = 1.6									
Water	*100*	*0*	*0*	*0*	*0*	*0*	*n/a* [a]	*n/a* [a]	*n/a* [a]
0.1 M NaOH	*≥89*	*9*	*0*	*≤ 2* [d]	*≤ 2* [d]	*≤ 2* [d]	*0*	*0*	*0*
0.1 M KOH	*88*	*12*	*0*	*0*	*0*	*0*	*n/a* [a]	*n/a* [a]	*n/a* [a]
0.5 M NaOH/0.5 M KOH	*87*	*13*	*0*	*0*	*0*	*0*	*0*	*0*	*0*

[a] n/a = not applicable; no Na was added during synthesis (<0.6 mM Na is present as an impurity in the 0.1 M KOH synthesis solution).

[b] peaks tentatively assigned to K-natrolite in the diffractogram of this sample were excluded from Rietveld analysis.

[c] peaks tentatively assigned to carbonated calcium hemicarboaluminate in the diffractogram of this sample were excluded from Rietveld analysis.

[d] a small amount of $CaCO_3$ was detected in this sample by TGA (total $CaCO_3$ mass estimated to be ≤ 2 wt.% of the sample).

[e] a small amount of $C_3AH_6/Al(OH)_3$ was detected in this sample by TGA (phase mass estimated to be ≤ 2 wt.% of the sample), which is assigned here to C_3AH_6.

Appendix S4. Thermogravimetric analysis

The results of analysis of the solid samples by TGA (Figures S1-S6) are consistent with the XRD data in Figure 2. C-(N,K-)A-S-H is the dominant solid phase in each sample, as identified by the main mass loss peaks centred between 80°C and 200°C in the DTG traces. Portlandite is identifiable by mass loss peaks at ~450°C; these peaks are generally much larger in the samples synthesised with 0.5 M NaOH/0.5 M KOH. Superficial carbonation products are identified between 600°C and 700°C in some samples but are most prominent at Ca/Si* = 0.6 and 1.2, which is also consistent with the XRD results. The peaks located between 800°C and 900°C are assigned to decomposition of C-(N,K-)A-S-H to wollastonite.[19-21] Additional peaks marked by #, † and ‡, and centred at 150-250°C, ~350°C and ~400°C in some of the differential mass loss traces in Figures S1-S6, are tentatively assigned to thermal decomposition of C-(N,K-)A-S-H.[19]

Katoite is identified in the TGA results for the Al-containing C-(N,K-)A-S-H samples synthesised with Ca/Si* = 0.6, 1 and 1.2, and 0.5 M NaOH/0.5 M KOH (Figures S1-S6). This phase is identified via the mass loss peaks at ~300°C;[12] this assignment does not preclude the additional presence of small amounts of poorly-crystalline $Al(OH)_3$, which has a characteristic mass loss peak at ~275°C.[12]

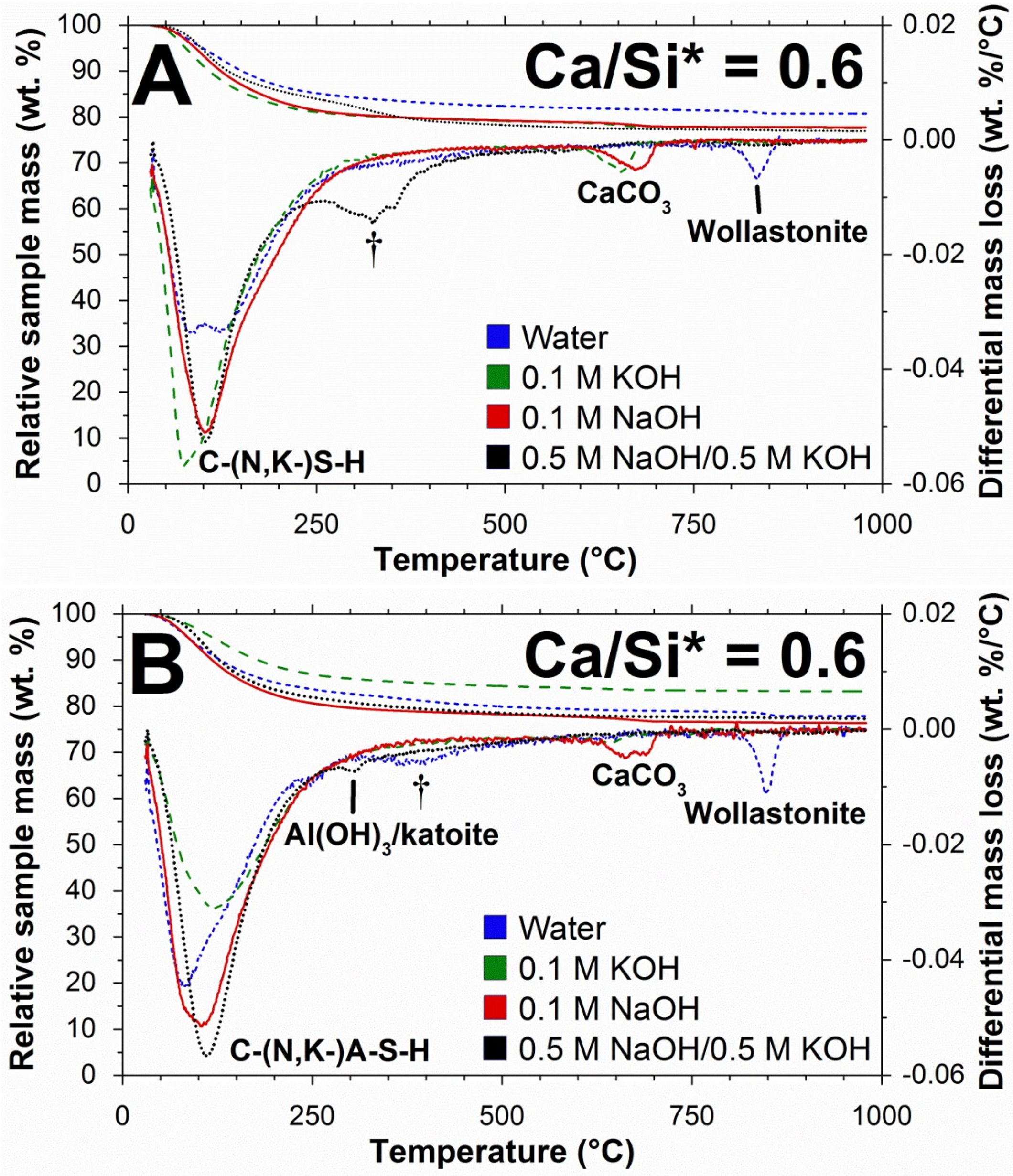


Figure S1. TGA results for C-(N,K-)A-S-H sample synthesised with Ca/Si* = 0.6 and A) Al/Si* = 0 or B) Al/Si* = 0.05. The peaks marked by † are tentatively assigned to dehydration of C-(N,K-)A-S-H. Ca/Si* = bulk Ca/Si. Al/Si* = bulk Al/Si.

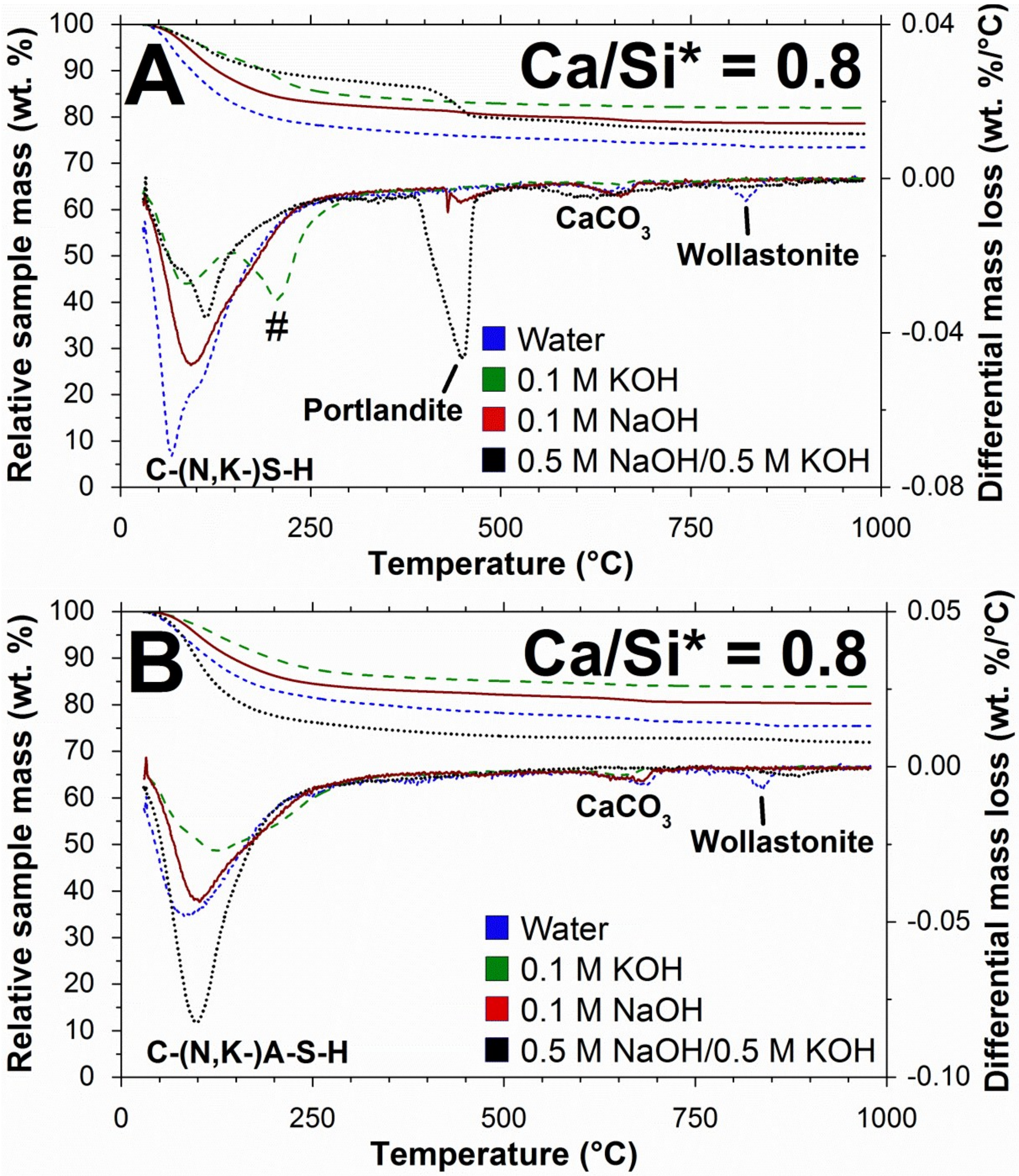


Figure S2. TGA results for C-(N,K-)A-S-H sample synthesised with Ca/Si* = 0.8 and A) Al/Si* = 0 or B) Al/Si* = 0.05. The peak marked by # is tentatively assigned to dehydration of C-(N,K-)A-S-H. Ca/Si* = bulk Ca/Si. Al/Si* = bulk Al/Si. An additional major phase, possibly a zeolite, was formed in addition to C-(N,K-)S-H in the sample synthesised with Al/Si* = 0 and 0.5 M NaOH/0.5 M KOH.

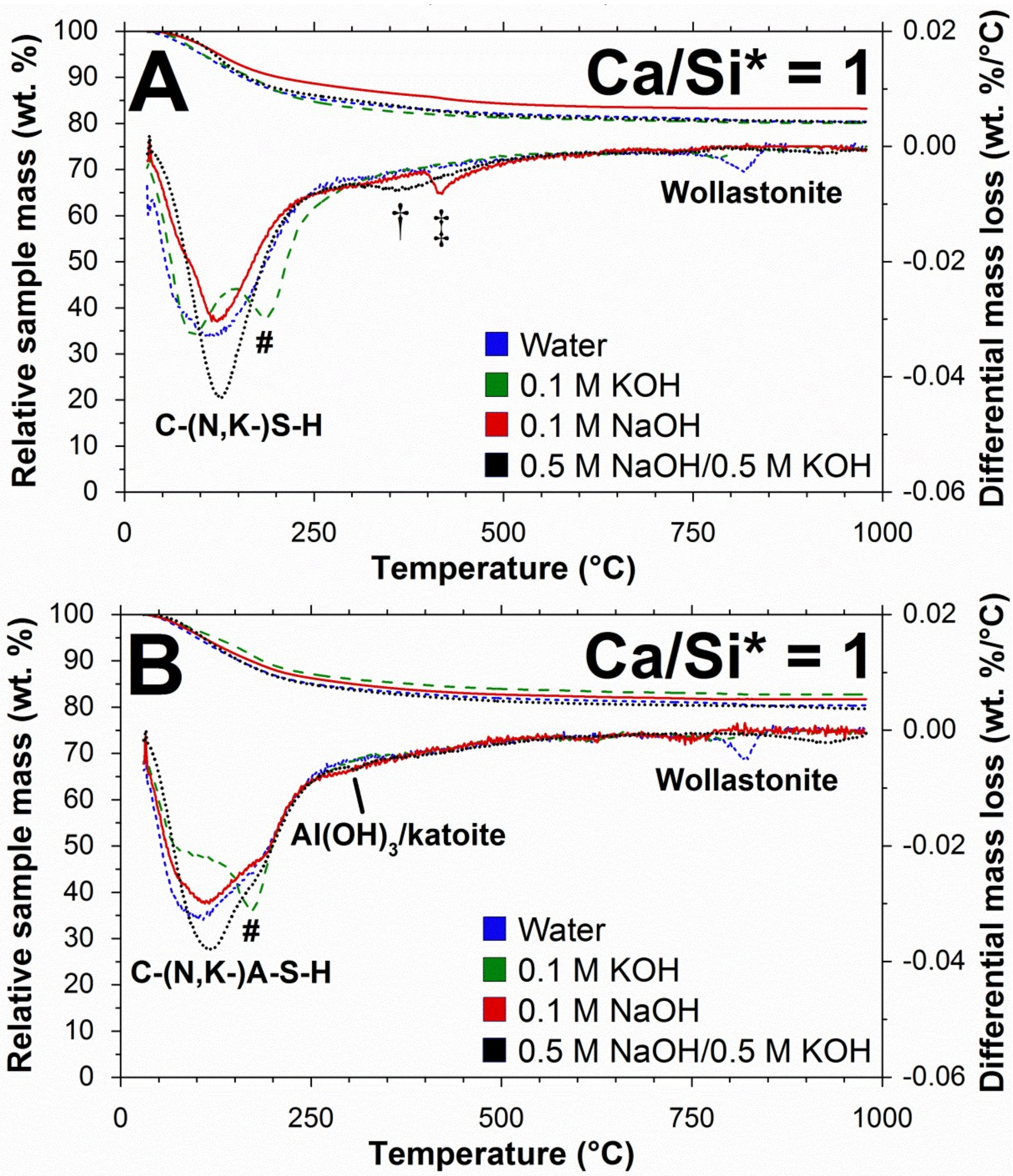


Figure S3. TGA results for C-(N,K-)A-S-H samples synthesised with Ca/Si* = 1 and A) Al/Si* = 0 or B) Al/Si* = 0.05. The peaks marked by #, † and ‡ are tentatively assigned to decomposition of C-(N,K-)A-S-H. Ca/Si* = bulk Ca/Si. Al/Si* = bulk Al/Si.

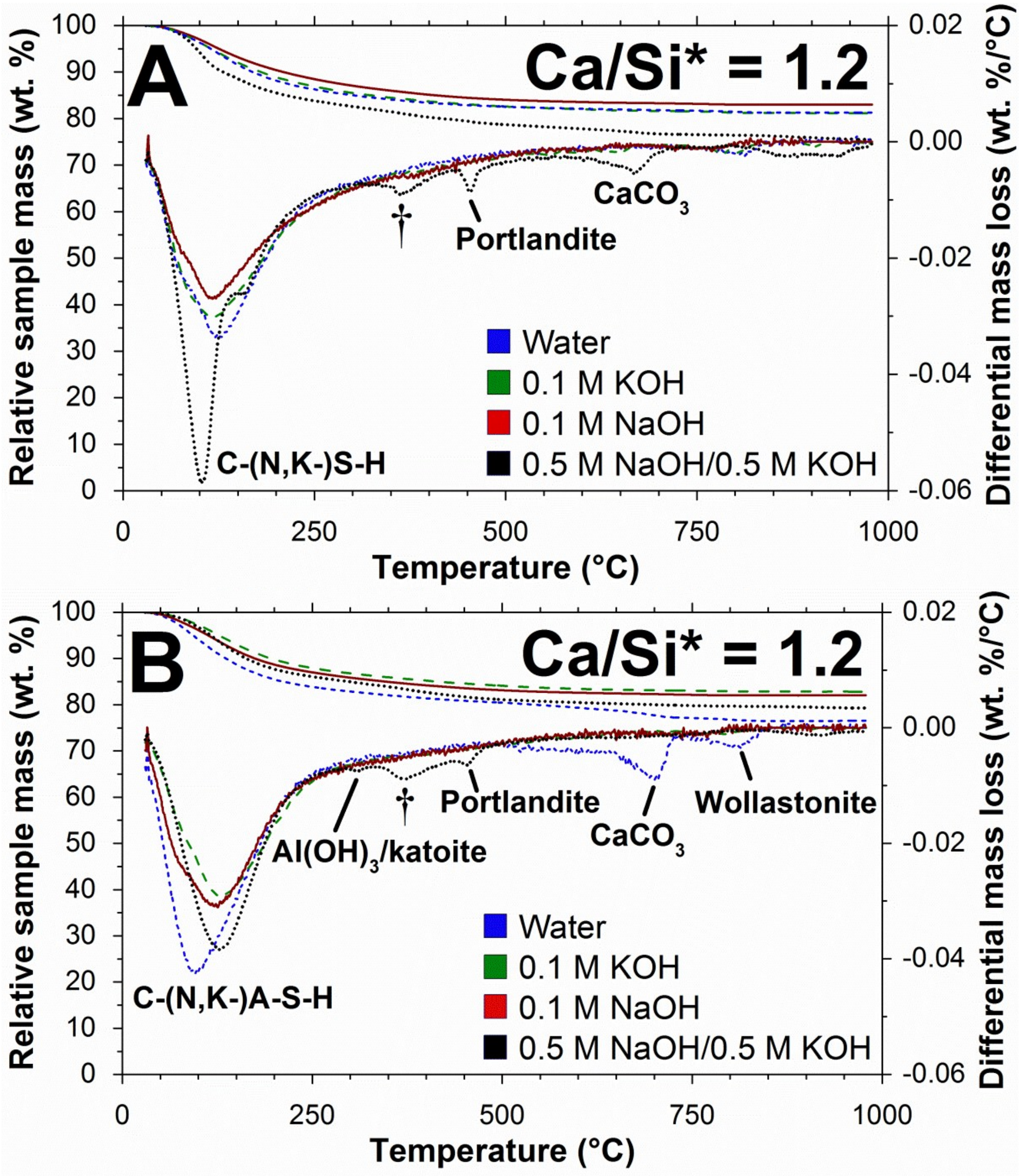


Figure S4. TGA results for C-(N,K-)A-S-H samples synthesised with Ca/Si* = 1.2 and A) Al/Si* = 0 or B) Al/Si* = 0.05. The peaks marked by † are tentatively assigned to decomposition of C-(N,K-)A-S-H. Ca/Si* = bulk Ca/Si. Al/Si* = bulk Al/Si.

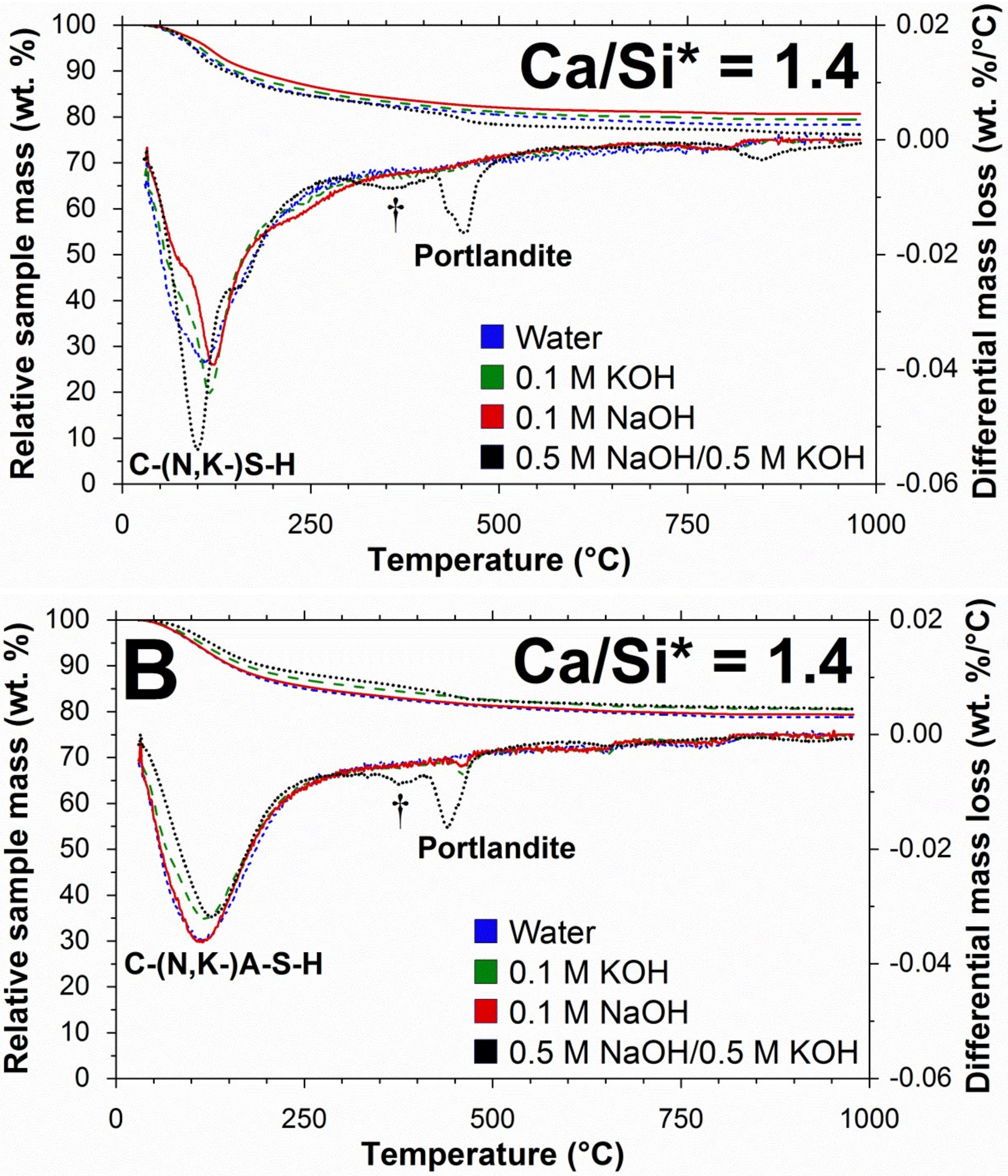


Figure S5. TGA results for the C-(N,K-)A-S-H sample synthesised with Ca/Si* = 1.4 and A) Al/Si* = 0 or B) Al/Si* = 0.05. The peaks marked by † are tentatively assigned to decomposition of C-(N,K-)A-S-H. Ca/Si* = bulk Ca/Si. Al/Si* = bulk Al/Si.

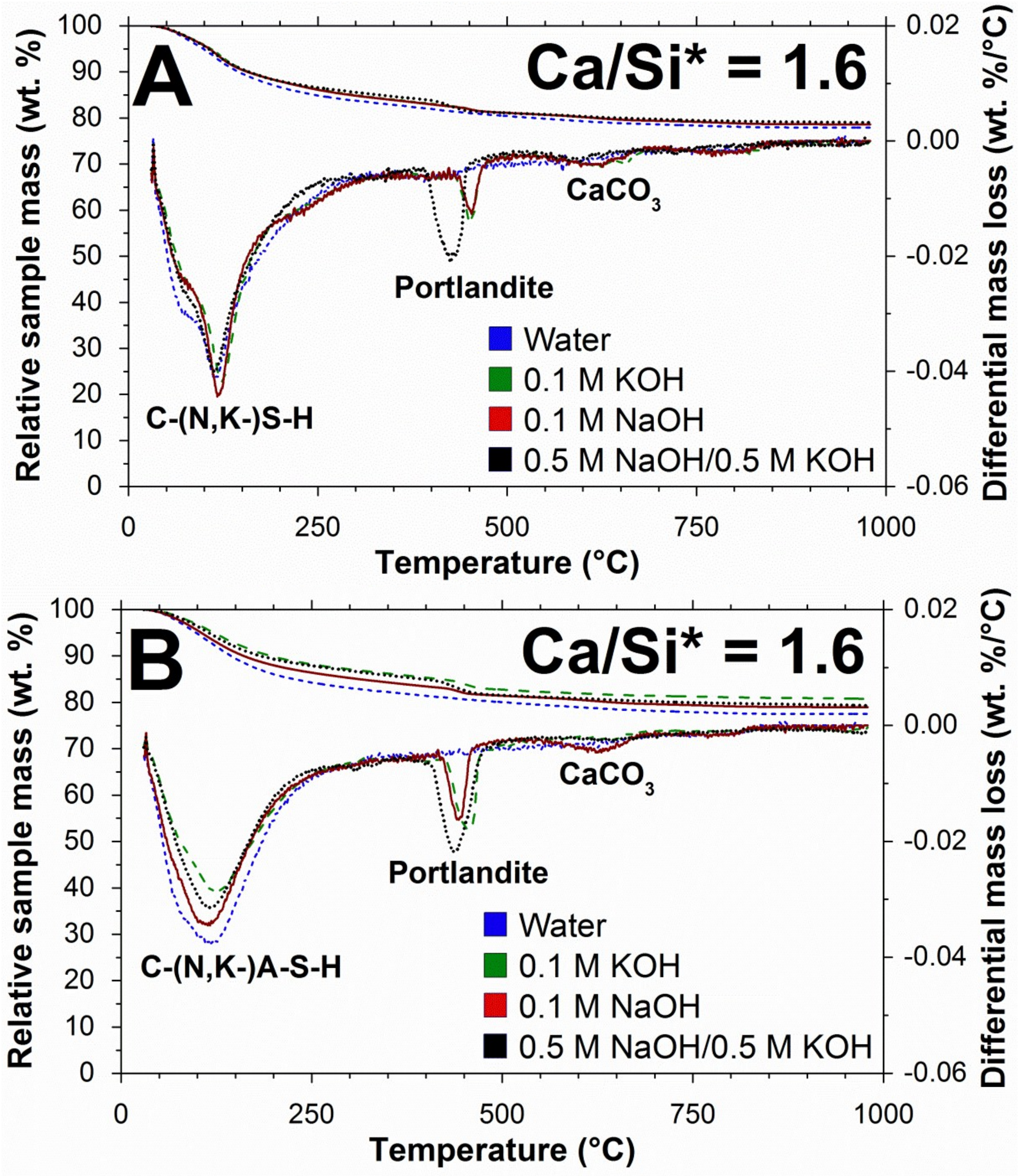


Figure S6. TGA results for the C-(N,K-)A-S-H sample synthesised with Ca/Si* = 1.6 and A) Al/Si* = 0 or B) Al/Si* = 0.05. Ca/Si* = bulk Ca/Si. Al/Si* = bulk Al/Si.

The TGA data show that between 15.1% and 24.7% of the total mass in each sample is lost due to dehydration and dehydroxylation of reaction products. The central positions of the differential mass loss peaks assigned to C-(N,K-)A-S-H, and the total mass lost from room temperature to 980°C, do not vary systematically as a function of the Ca/Si* ratio or alkali concentration, because the water content of the samples are much more strongly influenced by the drying method used. The same observation has been made for C-(N,K-)A-S-H samples prepared at 20°C.[22] Here, the measured mass losses reflect the removal of bulk water (freezedried for 7 days and equilibrated at ~30% RH), partial dehydration of adsorbed water, and little or no removal of structurally-bound water from the C-(N,K-)A-S-H products [19, 23] by the drying protocol used prior to analysis.

Appendix S5. Saturation indices

Effective saturation indices (SI*) were calculated using eq.(S1):

$$SI_i{*} = \frac{1}{n_i}\log_{10}\left(\frac{IAP_i}{K_{s,i}}\right)$$ * MERGEFORMAT (S1)

where IAP_i is the ion activity product of the i^{th} solid phase, $K_{s,i}$ is the solubility product of the i^{th} solid phase, and n_i is the total stoichiometric number of ions in the dissolution reaction defined for the i^{th} solid phase. The dissolution reactions used in calculations here are shown in Table S3 (Appendix S2). Solid phases with positive SI* values can be expected to precipitate from solution (super-saturation), while negative SI* values indicate the likelihood of dissolution (under-saturation). A 'near-saturation' range of $-0.5 \leq SI^* < 0$, where precipitation may potentially take place, is also defined to account for the uncertainty in the modelling calculations and experimental measurements.

Effective saturation indices (SI*) were calculated from the measured dissolved Si, Ca, OH^- and Al concentrations, using eq.(S1), to assess the proximity of the samples to equilibrium (Tables S6-S7).

Table S6. Effective saturation indices (*SI**) for relevant solid phases in the C-(N,K-)S-H samples (Al/Si* = 0), calculated from the filtrate chemical compositions in Figure 3 and Appendix S6 (Electronic Supporting Information). Bold text indicates solid phases that are observed in the TGA and/or XRD results of the respective samples (C-(N-)A-S-H is represented by end-members of the CNASH_ss thermodynamic model [17]). A 'near-saturation' condition of $-0.5 \le SI^* < 0$ is assumed, as discussed in the text.

Synthesis solution	**$CN_{0.3125}S_{1.5}H_{1.1875}$** [a]	**$C_{1.5}SH_{2.5}$** [a]	**$CS_{1.5}H_{2.5}$** [a]	**CH**	**SiO_2** [b]
Ca/Si* = 0.6					
Water	n/a [d]	**-0.7**	**0**	-1.6	-0.1
0.1 M NaOH	**-0.1**	**-0.9**	**-0.4**	-1.6	-0.5
0.1 M KOH	n/a [d]	**-0.9**	**-0.4**	-1.7	-0.5
0.5 M NaOH/0.5 M KOH	**≤-0.1** [c]	**≤-0.6** [c]	**≤-0.8** [c]	≤-0.8 [c]	-1.8
Ca/Si* = 0.8					
Water	n/a [d]	**-0.6**	**-0.1**	-1.5	-0.3
0.1 M NaOH	**-0.3**	**-0.8**	**-0.8**	**-1.2**	-1.4
0.1 M KOH	n/a [d]	**≤-1.0** [c]	**≤-0.9** [c]	≤-1.3 [c]	-1.4
0.5 M NaOH/0.5 M KOH	**-0.1**	**-0.6**	**-0.8**	**-0.8**	-1.8
Ca/Si* = 1					
Water	n/a [d]	**-0.3**	**-0.5**	-0.7	-1.6
0.1 M NaOH	**-0.2**	**-0.3**	**-0.7**	-0.5	-1.9
0.1 M KOH	n/a [d]	**-0.2**	**-0.8**	-0.3	-2.3
0.5 M NaOH/0.5 M KOH	**-0.4**	**-0.5**	**-1.1**	-0.4	-2.6
Ca/Si* = 1.2					
Water	n/a [d]	**-0.2**	**-0.7**	-0.3	-2.1
0.1 M NaOH	**-0.3**	**-0.2**	**-0.7**	-0.3	-2.2
0.1 M KOH	n/a [d]	**-0.2**	**-0.8**	-0.3	-2.3
0.5 M NaOH/0.5 M KOH	**-0.4**	**-0.4**	**-1.1**	**-0.3**	-2.7
Ca/Si* = 1.4					
Water	n/a [d]	**-0.2**	**-0.9**	-0.2	-2.6
0.1 M NaOH	**-0.4**	**-0.2**	**-0.9**	-0.1	-2.6
0.1 M KOH	n/a [d]	**-0.2**	**-0.9**	-0.1	-2.6
0.5 M NaOH/0.5 M KOH	**-0.4**	**-0.3**	**-1.1**	**-0.2**	-2.8
Ca/Si* = 1.6					
Water	n/a [d]	**-0.3**	**-1.1**	-0.1	-2.8
0.1 M NaOH	**-0.5**	**-0.1**	**-0.9**	**0**	-2.8
0.1 M KOH	n/a [d]	**-0.2**	**-1.0**	**0**	-2.8
0.5 M NaOH/0.5 M KOH	**-0.4**	**-0.3**	**-1.2**	**-0.1**	-2.9

[a] $CN_{0.3125}S_{1.5}H_{1.1875}$, $C_{1.5}SH_{2.5}$ and $CS_{1.5}H_{2.5}$ are the INFCN, T2C* and TobH* end-members of the CNASH_ss thermodynamic model,[17] respectively

[b] Amorphous SiO_2

[c] The values shown are calculated at the detection limit for Ca (~0.004 mM) because dissolved Ca concentrations were below the detection limit

[d] n/a = not applicable: no Na was added to the system (<0.6 mM Na is present as an impurity in the 0.1 M KOH synthesis solution)

Table S7. Effective saturation indices (SI^*) for relevant solid phases in the C-(N,K-)A-S-H samples (Al/Si* = 0.05), calculated from the filtrate chemical compositions in Figure 3 and Appendix S6. Bold text indicates solid phases that are observed in the TGA and/or XRD results of the respective samples (C-(N-)A-S-H is represented by end-members of the CNASH_ss thermodynamic model [17]). A 'near-saturation' condition of $-0.5 \le SI^* < 0$ is assumed, as discussed in the text.

Synthesis solution	**$C_{1.25}A_{0.125}SH_{1.625}$ [a]**	**$CA_{0.15625}S_{1.1875}H_{1.65625}$ [a]**	**$CN_{0.3125}S_{1.5}H_{1.1875}$ [a]**	**$C_{1.5}SH_{2.5}$ [a]**	**$CS_{1.5}H_{2.5}$ [a]**	**½AH_3 [b]**	**C_3AH_6**	**CH**	**SiO_2 [c]**
Ca/Si* = 0.6									
Water	**≤-0.5** [e]	**≤-0.1** [e]	n/a [f]	**-0.8**	**-0.1**	≤-0.8 [e]	≤-1.7 [e]	-1.7	-0.1
0.1 M NaOH	**-0.6**	**-0.4**	**-0.1**	**-0.8**	**-0.4**	-0.8	-1.6	-1.5	-0.7
0.1 M KOH	**-0.8**	**-0.5**	n/a [f]	**-0.9**	**-0.5**	-1.1	-1.7	-1.6	-0.8
0.5 M NaOH/0.5 M KOH	**≤-0.6** [d]	**≤-0.7** [d]	**≤-0.1** [d]	**≤-0.6** [d]	**≤-0.8** [d]	**-1.2**	**≤-1.1** [d]	≤-0.9 [d]	-1.8
Ca/Si* = 0.8									
Water	**≤-0.4** [e]	**≤-0.3** [e]	n/a [f]	**-0.5**	**-0.1**	≤-1.7 [e]	≤-1.8 [e]	-1.4	-0.4
0.1 M NaOH	**≤-0.7** [d]	**≤-0.6** [d]	**≤-0.4** [d]	**≤-0.8** [d]	**≤-0.7** [d]	-0.8	≤-1.3 [d]	≤-1.2 [d]	-1.3
0.1 M KOH	**≤-0.8** [d]	**≤-0.7** [d]	n/a [f]	**≤-0.8** [d]	**≤-0.8** [d]	-1.0	≤-1.3 [d]	≤-1.2 [d]	-1.5
0.5 M NaOH/0.5 M KOH	**≤-0.7** [d]	**≤-0.8** [d]	**≤-0.3** [d]	**≤-0.7** [d]	**≤-1.0** [d]	-1.2	≤-0.9 [d]	≤-0.7 [d]	-2.1
Ca/Si* = 1									
Water	**-0.2**	**-0.3**	n/a [f]	**-0.4**	**-0.4**	-1.0	-0.9	-0.8	-1.4
0.1 M NaOH	**-0.4**	**-0.5**	**-0.2**	**-0.4**	**-0.7**	**-1.4**	**-0.9**	-0.6	-1.9
0.1 M KOH	**-0.3**	**-0.6**	n/a [f]	**-0.3**	**-0.7**	-1.4	-0.7	-0.4	-2.1
0.5 M NaOH/0.5 M KOH	**≤-1.0** [d]	**≤-1.1** [d]	**≤-0.5** [d]	**≤-0.8** [d]	**≤-1.3** [d]	**-1.7**	**≤-1.1** [d]	≤-0.7 [d]	-2.5
Ca/Si* = 1.2									
Water	**≤-0.2** [e]	**≤-0.4** [e]	n/a [f]	**-0.2**	**-0.6**	≤-1.4 [e]	≤-0.8 [e]	-0.5	-1.9
0.1 M NaOH	**-0.3**	**-0.5**	**-0.2**	**-0.2**	**-0.7**	-1.7	-0.8	-0.3	-2.2
0.1 M KOH	**-0.3**	**-0.6**	n/a [f]	**-0.2**	**-0.7**	**-1.8**	**-0.8**	**-0.3**	-2.2
0.5 M NaOH/0.5 M KOH	**-0.5**	**-0.8**	**-0.3**	**-0.3**	**-1.0**	-1.7	-0.6	**-0.2**	-2.7

Table S7. Continued.

Ca/Si* = 1.4									
Water	**≤-0.4** [e]	**≤-0.6** [e]	n/a [f]	**-0.4**	**-0.8**	≤-1.4 [e]	≤-0.8 [e]	-0.5	-2.1
0.1 M NaOH	**≤-0.3** [e]	**≤-0.7** [e]	**-0.5**	**-0.1**	**-0.9**	≤-1.9 [e]	≤-0.6 [e]	**-0.1**	-2.7
0.1 M KOH	**≤-0.3** [e]	**≤-0.8** [e]	n/a [f]	**-0.1**	**-0.9**	≤-1.9 [e]	≤-0.6 [e]	**0**	-2.8
0.5 M NaOH/0.5 M KOH	**-0.5**	**-0.8**	**-0.3**	**-0.3**	**-1.0**	-1.7	-0.6	**-0.1**	-2.8
Ca/Si* = 1.6									
Water	**≤-0.5** [e]	**≤-0.8** [e]	n/a [f]	**-0.4**	**-1.1**	≤-1.5 [e]	≤-0.6 [e]	-0.2	-2.7
0.1 M NaOH	**≤-0.4** [e]	**≤-0.8** [e]	**-0.5**	**-0.2**	**-1.0**	≤-1.9 [e]	≤-0.6 [e]	**0**	-2.8
0.1 M KOH	**≤-0.4** [e]	**≤-0.8** [e]	n/a [f]	**-0.2**	**-1.0**	≤-1.9 [e]	≤-0.5 [e]	**0**	-2.8
0.5 M NaOH/0.5 M KOH	**-0.4**	**-0.8**	**-0.3**	**-0.3**	**-1.0**	-1.7	-0.6	**-0.1**	-2.8

[a] $C_{1.25}A_{0.125}SH_{1.625}$, $CA_{0.15625}S_{1.1875}H_{1.65625}$, $CN_{0.3125}S_{1.5}H_{1.1875}$, $C_{1.5}SH_{2.5}$ and $CA_{1.5}H_{2.5}$ are the 5CA, INFCA, INFCN, T2C* and TobH* end-members of the CNASH_ss thermodynamic model,[17] respectively

[b] Microcrystalline $Al(OH)_3$

[c] Amorphous SiO_2

[d] The values shown are calculated at the detection limit for Ca (~0.004 mM) because dissolved Ca concentration was below the detection limit

[e] The values shown are calculated at the detection limit for Al (~0.003 mM) because dissolved Al concentration was below the detection limit

[f] n/a = not applicable: no Na was added to the system (<0.6 mM Na is present as an impurity in the 0.1 M KOH synthesis solution)

The defined near-saturation condition of $-0.5 \leq SI^* < 0$ accounts for the uncertainty in the modelling calculations and experimental measurements, indicating that solid phases with SI^* values within this range can potentially precipitate at equilibrium, even though the calculated saturation index is slightly negative. This interpretation means that C-(N,K-)A-S-H is expected to form in every sample, while portlandite could precipitate in the alkali-containing samples at Ca/Si* = 1 without Al, in the Al-containing sample synthesised with 0.1 M KOH at a Ca/Si* = 1, and in all Ca/Si* ≥ 1.2 samples (Tables 1-2). Portlandite is generally only identified in samples with Ca/Si* ratios ≥ 1 (Figure 2 and Appendices S3-S4), and C-(N,K-)A-S-H is formed in all of the specimens, in good agreement with the expected equilibrium phase assemblages and this interpretation of near-saturated SI^* values. Amorphous SiO_2 is only predicted to be near saturated in the Ca/Si* ≤ 0.8 C-(N,K-)A-S-H samples synthesised with water. A small amount of partially dissolved amorphous SiO_2 has been observed in samples synthesised at 20°C and Ca/Si* = 0.6 using the same protocols that were applied here,[22] which indicates that precipitation of C-(N,K-)A-S-H is strongly preferred at Ca/Si* ≤ 0.8.

Small amounts of katoite (C_3AH_6) are identified in some of the Al-containing samples by XRD and TGA (Figure 2 and Appendices S3-S4), but this phase is predicted to be undersaturated at equilibrium in every sample that this phase was observed (Table S7), which indicates that not all samples have yet reached equilibrium. The calculated SI^* values predict that strätlingite is undersaturated in all samples, in good agreement with the XRD and TGA results, where this phase is not identified. Si-hydrogarnet is predicted to be near-saturated in the Al-containing samples at Ca/Si* ratios ≥ 1 except the sample synthesised with 0.5 M NaOH/0.5 M KOH at Ca/Si* = 1, but this phase is not identified in the XRD or TGA results, which suggests that it is kinetically hindered from forming under the synthesis conditions used here. This result is consistent with the higher temperatures (110°C) needed experimentally to form Si-hydrogarnet in the CaO-Al_2O_3-SiO_2-H_2O system within a laboratory timeframe.[16]

Appendix S6. Tabulated supernatant compositions and solubility products

Aqueous phase compositions and pH results for the C-(N,K-)S-H (Al/Si* = 0) and C-(N,K-)A-S-H (Al/Si* = 0.05) samples are shown in Tables S8 and S9 respectively. Solubility products (K_s) for C-(N,K-)A-S-H, calculated using the chemical compositions determined by mass balance and reported in Tables 1-2, are shown in Table S10.

Table S8. Aqueous phase compositions and pH results for the C-(N,K-)S-H samples (Al/Si* = 0, Ca/Si* = 1) equilibrated at 50°C.

Synthesis solution	**[Si] (mM)**	**[Ca] (mM)**	**[Al] (mM)**	**[K] (mM)**	**[Na] (mM)**	**$[OH^-]$ (mM)**	**pH [a]**
			Ca/Si* = 0.6				
Water	4.72	1.50	0	0	0	0.0471	9.70
0.1 M NaOH	35.3	0.008	0	0	54.8	14.1	12.1
0.1 M KOH	30.8	0.006	0	45.4	0.291 [c]	18.4	12.2
0.5 M NaOH/0.5 M KOH	43.6	b.d.l. [b]	0	462	470	576	13.7
			Ca/Si* = 0.8				
Water	2.75	1.22	0	0	0	0.113	10.1
0.1 M NaOH	2.65	0.004	0	0	61.8	50.3	12.6
0.1 M KOH	2.13	b.d.l. [b]	0	57.0	0.430 [c]	57.0	12.7
0.5 M NaOH/0.5 M KOH	0.386	0.074	0	485	486	639	13.7
			Ca/Si* = 1				
Water	0.091	2.77	0	0	0	5.93	11.7
Water	0.112	2.59	0	0	0	4.55	11.7
0.1 M NaOH	0.336	0.147	0	0	77.2	72.5	12.8
0.1 M KOH	0.079	0.540	0	75.3	0.489 [c]	79.1	12.8
0.5 M NaOH	0.560	0.039	0	0	444	390	13.5
0.5 M KOH	0.288	0.132	0	432	0	431	13.5
0.5 M NaOH/0.5 M KOH	1.31	b.d.l. [b]	0	451	442	645	13.7
0.5 M NaOH/0.5 M KOH	1.23	0.031	0	460	453	639	13.7
			Ca/Si* = 1.2				
Water	0.038	6.29	0	0	0	11.3	12.0
0.1 M NaOH	0.124	0.533	0	0	91.7	87.0	12.9
0.1 M KOH	0.090	0.517	0	90.4	0.493 [c]	97.0	12.9
0.5 M NaOH/0.5 M KOH	0.69	0.058	0	465	460	639	13.7
			Ca/Si* = 1.4				
Water	0.013	9.91	0	0	0	17.5	12.2
0.1 M NaOH	0.040	1.37	0	0	100	99.9	12.9
0.1 M KOH	0.032	1.34	0	95.5	0.515 [c]	105	12.9
0.5 M NaOH/0.5 M KOH	0.491	0.103	0	467	464	639	13.7
			Ca/Si* = 1.6				
Water	0.006	13.1	0	0	0	24.1	12.4
0.1 M NaOH	0.023	2.69	0	0	102	105	12.9
0.1 M KOH	0.016	2.40	0	97.3	0.544 [c]	110	12.9
0.5 M NaOH/0.5 M KOH	0.433	0.125	0	592	577	639	13.7

[a] pH measured at ~24°C

[b] b.d.l. = below detection limit (~0.004 mM for Ca)

[c] A small amount of Na is present as an impurity in the 0.1 M KOH synthesis solution

Table S9. Aqueous phase compositions and pH results for the C-(N,K-)A-S-H samples (Al/Si* = 0.05, Ca/Si* = 1) equilibrated at 50°C.

Synthesis solution	**[Si] (mM)**	**[Ca] (mM)**	**[Al] (mM)**	**[K] (mM)**	**[Na] (mM)**	**$[OH^-]$ (mM)**	**pH [a]**
Ca/Si* = 0.6							
Water	4.25	1.27	b.d.l. [b]	0	0	0.060	9.80
0.1 M NaOH	23.2	0.008	0.086	0	45.8	22.7	12.4
0.1 M KOH	18.6	0.004	0.036	46.0	0.303 [c]	23.4	12.3
0.5 M NaOH/0.5 M KOH	48.9	b.d.l. [b]	1.38	447	447	613	13.7
Ca/Si* = 0.8							
Water	2.13	1.19	b.d.l. [b]	0	0	0.158	10.2
0.1 M NaOH	2.89	b.d.l. [b]	0.235	0	55.0	61.5	12.8
0.1 M KOH	2.04	b.d.l. [b]	0.104	60.2	0.392 [c]	51.9	12.7
0.5 M NaOH/0.5 M KOH	10.0	b.d.l. [b]	0.708	425	422	635	13.7
Ca/Si* = 1							
Water	0.104	2.36	0.003	0	0	5.29	11.6
Water	0.160	1.76	0.008	0	0	2.98	11.5
0.1 M NaOH	0.417	0.092	0.026	0	77.4	88.5	12.9
0.1 M KOH	0.162	0.227	0.031	78.7	0.51 [c]	71.6	12.8
0.5 M NaOH	0.780	0.036	0.194	0	448	408	13.5
0.5 M KOH	0.537	0.074	0.082	441	3.28 [c]	448	13.5
0.5 M NaOH/0.5 M KOH	1.78	b.d.l. [b]	0.057	454	444	658	13.8
0.5 M NaOH/0.5 M KOH	1.48	b.d.l. [b]	0.121	453	446	645	13.7
Ca/Si* = 1.2							
Water	0.057	4.16	b.d.l. [b]	0	0	8.11	11.9
0.1 M NaOH	0.159	0.414	0.008	0	86.9	97.0	12.9
0.1 M KOH	0.125	0.488	0.005	93.7	0.518 [c]	84.1	12.9
0.5 M NaOH/0.5 M KOH	0.744	0.087	0.085	457	445	658	13.8
Ca/Si* = 1.4							
Water	0.016	3.84	b.d.l. [b]	0	0	17.0	12.2
0.1 M NaOH	0.025	2.53	b.d.l. [b]	0	93.0	116	13.0
0.1 M KOH	0.022	2.38	b.d.l. [b]	103	0.558 [c]	94.9	12.9
0.5 M NaOH/0.5 M KOH	0.563	0.128	0.062	461	452	682	13.8
Ca/Si* = 1.6							
Water	0.005	8.89	b.d.l. [b]	0	0	29.5	12.4
0.1 M NaOH	0.018	2.90	b.d.l. [b]	0	95.4	122	13.0
0.1 M KOH	0.018	2.85	b.d.l. [b]	103	0.553 [c]	98.8	12.9
0.5 M NaOH/0.5 M KOH	0.520	0.152	0.059	458	448	682	13.8

[a] pH measured at ~24°C

[b] b.d.l. = below detection limit (~0.004 mM for Ca and ~0.003 mM for Al)

[c] A small amount of Na is present as an impurity in the 0.1 M KOH synthesis solution

Table S10. Solubility products (K_s) for the C-(N,K-)A-S-H products synthesised at 50°C, with chemical compositions (Tables 1-2) determined by TGA, IC and pH measurements (italic font), and TGA, XRD, Rietveld analysis, IC and pH measurements (normal font), which refer to the reaction given by eq.(5) and Ca^{2+}, SiO_3^{2-}, AlO_2^-, Na^+, K^+, OH^- and H_2O.

Synthesis solution	**$\log_{10}(K_s)$**	
	Al/Si* = 0	**Al/Si* = 0.05**
Ca/Si* = 0.6		
Water	-4.6	≤-5.1 [a,b]
0.1 M NaOH	-8.9	-9.7
0.1 M KOH	-9.6	-9.8
0.5 M NaOH/0.5 M KOH	≤-8.3 [a,c]	≤-10.0 [a,c]
Ca/Si* = 0.8		
Water	*-6.7*	*≤-7.5* [a,b]
0.1 M NaOH	*-10.1*	*≤-11.1* [a,c]
0.1 M KOH	*≤-10.8* [a,c]	*≤-10.9* [a,c]
0.5 M NaOH/0.5 M KOH	*-5.9* [d]	*≤-11.8* [a,c]
Ca/Si* = 1		
Water	-8.6	-9.2
0.1 M NaOH	-10.2	-10.8
0.1 M KOH	-10.3	-10.9
0.5 M NaOH/0.5 M KOH	-10.9	≤-12.4 [a,c]
Ca/Si* = 1.2		
Water	*-9.9*	*≤-10.7* [a,b]
0.1 M NaOH	*-10.6*	*-11.7*
0.1 M KOH	*-10.9*	*-11.4*
0.5 M NaOH/0.5 M KOH	*-11.1*	*-12.2*
Ca/Si* = 1.4		
Water	-11.3	≤-12.6 [a,b]
0.1 M NaOH	-11.4	≤-12.6 [a,b]
0.1 M KOH	-11.8	≤-12.0 [a,b]
0.5 M NaOH/0.5 M KOH	-11.0	-13.0
Ca/Si* = 1.6		
Water	*-12.5*	*≤-13.7* [a,b]
0.1 M NaOH	*-11.3*	*≤-12.4* [a,b]
0.1 M KOH	*-11.6*	*≤-11.8* [a,b]
0.5 M NaOH/0.5 M KOH	*-11.5*	*-13.4*

[a] Maximum values. Activities of Ca^{2+}, SiO_3^{2-}, AlO_2^-, Na^+, K^+, OH^- and H_2O were calculated using [b] [Al] = 0.003 mM or [c] [Ca] = 0.004 mM, as the measured concentrations of these elements in the supernatants were below the detection limit.

[d] An additional major phase, possibly a zeolite, was formed in this sample in addition to C-(N,K-)S-H.

Appendix S7. Additional data for the Al/Si* = 0 and 0.1, Ca/Si* = 1 C-(N,K-)A-S-H samples studied by ^{29}Si MAS NMR

The TGA results shown in Figure S7 support the slight discrepancies between the Al/Si ratios determined through the ^{29}Si MAS NMR deconvolution analysis presented in the main body of the paper and the Al/Si* ratios used during synthesis, via the identification of C_3AH_6 and/or $Al(OH)_3$, and C_4AcH_{11} secondary products.

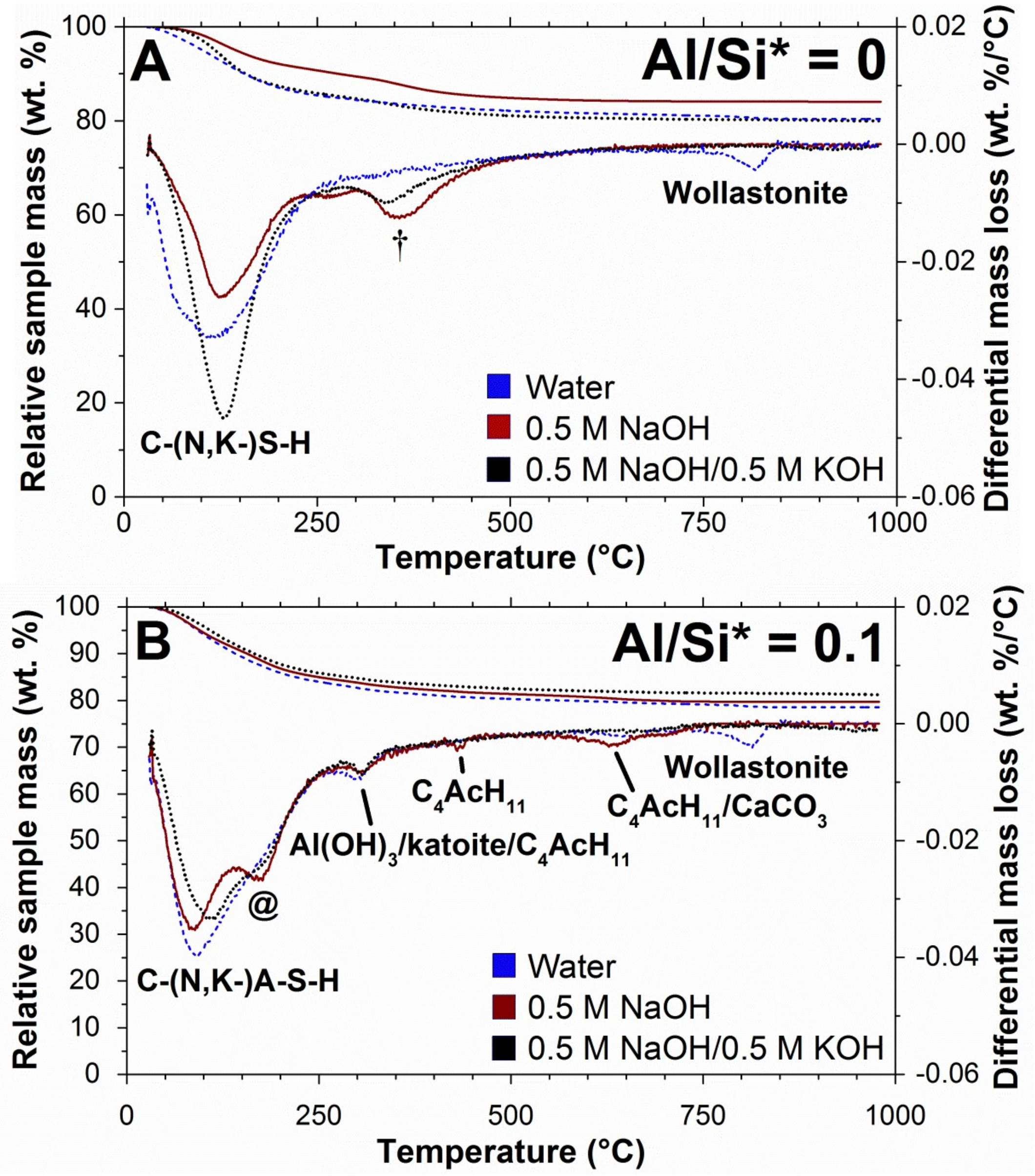


Figure S7. TGA results for C-(N,K-)A-S-H samples equilibrated at 50°C with Ca/Si* = 1, and A) Al/Si* = 0 and B) Al/Si* = 0.1. The peak marked by † is tentatively assigned to thermal decomposition of C-(N,K-)S-H and the peak marked by @ is tentatively assigned to thermal decomposition of C-(N,K-)S-H and C_4AcH_{11}. Ca/Si* = bulk Ca/Si. Al/Si* = bulk Al/Si.

Additional solubility data for the alkali and Al-containing C-(N,K-)A-S-H products studied by ^{29}Si MAS NMR (Figures 8 and 9) are shown in Table S11.

Table S11. Aqueous phase compositions and pH results for C-(N,K-)A-S-H samples (Al/Si* = 0 and 0.1, Ca/Si* = 1) equilibrated at 50°C studied in the ^{29}Si MAS NMR component of this work.

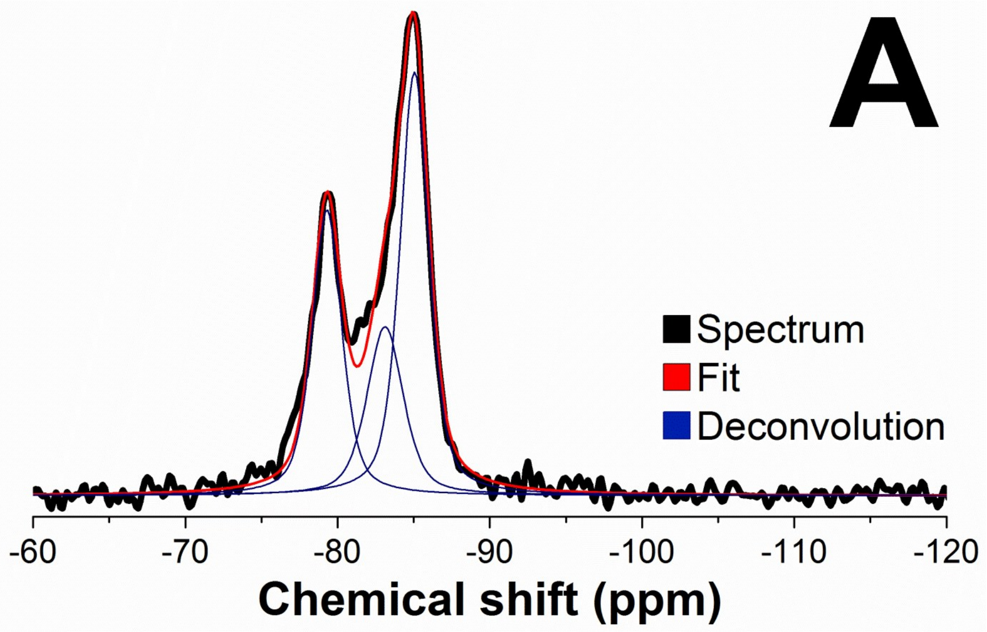
Synthesis solution	**[Si] (mM)**	**[Ca] (mM)**	**[Al] (mM)**	**[K] (mM)**	**[Na] (mM)**	**[OH^-] (mM)**	**pH** [a]
			Al/Si* = 0				
Water	0.112	2.59	0	0	0	4.55	11.7
0.5 M NaOH	0.560	0.039	0	0	444	390	13.5
0.5 M NaOH/0.5 M KOH	1.31	b.d.l. [b]	0	451	442	645	13.7
			Al/Si* = 0.1				
Water	0.175	1.51	0.028	0	0	3.47	11.5
0.5 M NaOH	0.792	0.031	0.122	0	436	408	13.5
0.5 M NaOH/0.5 M KOH	1.38	b.d.l. [b]	0.250	449	445	668	13.7

[a] pH measured at ~24°C

[b] b.d.l. = below detection limit (~0.004 mM for Ca)

Appendix S8. Detailed ^{29}Si MAS NMR spectral deconvolution results

The deconvoluted spectra for the Al-free C-(N,K-)S-H samples and C-(N,K-)A-S-H samples (Al/Si* = 0.1) are shown in Figures S8 and S9 respectively. The spectral deconvolution results are tabulated in Table S12.



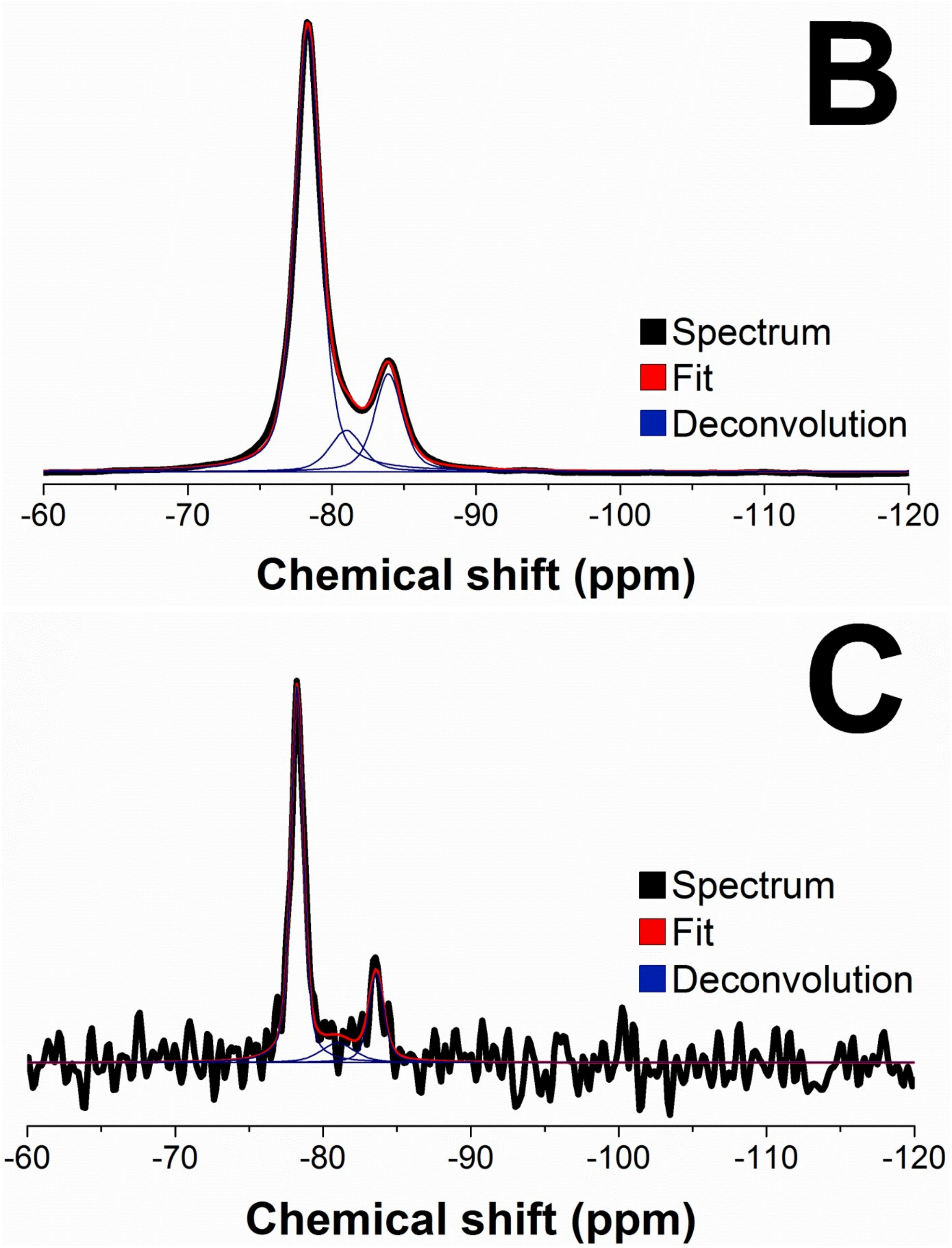
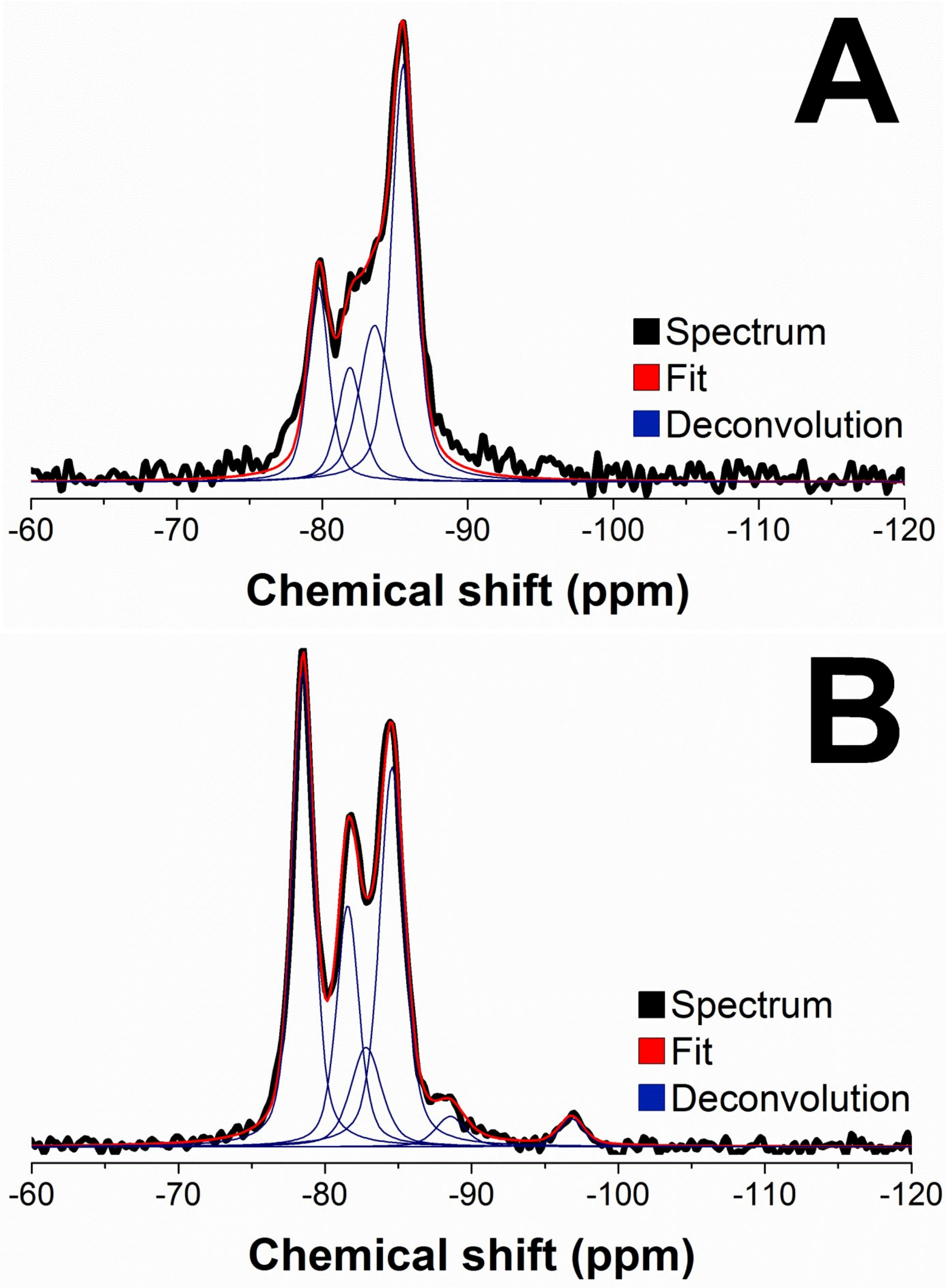


Figure S8: Solid-state ^{29}Si MAS NMR spectra of C-(N,K-)S-H samples synthesised with Al/Si* = 0, Ca/Si* = 1 and A) water, B) 0.5 M NaOH, and C) 0.5 M NaOH/0.5 M KOH, and equilibrated at 50°C.


A
■ Spectrum
■ Fit
■ Deconvolution
-60
-70
-80
-90
-100
-110
-120
Chemical shift (ppm)
B
■ Spectrum
■ Fit
■ Deconvolution
-60
-70
-80
-90
-100
-110
-120
Chemical shift (ppm)

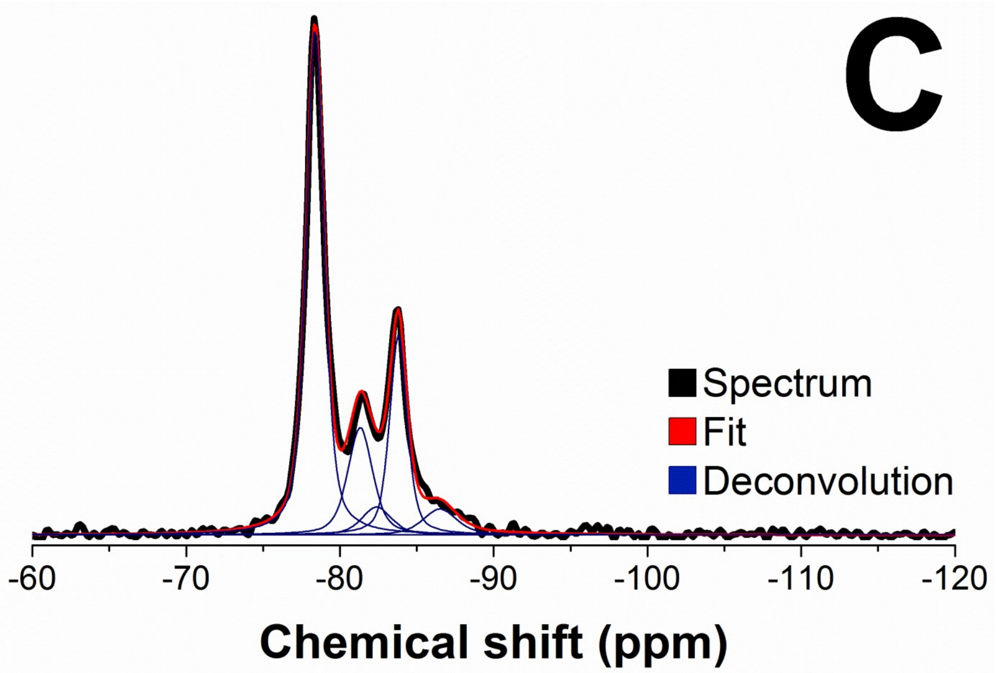


Figure S9. Solid-state ^{29}Si MAS NMR spectra of C-(N,K-)S-H samples synthesised with Al/Si* = 0.1, Ca/Si* = 1 and A) water, B) 0.5 M NaOH, and C) 0.5 M NaOH/0.5 M KOH, and equilibrated at 50°C.

Table S12. Deconvolution results for the ^{29}Si MAS NMR spectra of C-(N,K-)A-S-H samples synthesised with Ca/Si* = 1 and equilibrated at 50°C. The estimated error in absolute site percentages is ±0.02. Al/Si* = bulk Al/Si.

Al/Si*	**Alkali solution type**	**Q^1 -79.0 ±0.7 ppm**	**Q^2(1Al) -81.7 ±0.4 ppm**	**Q^2_b -82.4 ±1.3 ppm**	**Q^2_p -84.4 ±0.8 ppm**	**Q^3(1Al) -87.6 ±1.1 ppm**	**Q^3 -96.8 ppm**
0	Water	0.32	0	0.23	0.46	0	0
0	0.5 M NaOH	0.74	0	0.09	0.18	0	0
0	0.5M NaOH/ 0.5 M KOH	0.70	0	0.10	0.20	0	0
0.1	Water	0.20	0.16	0.21	0.43	0	0
0.1	0.5 M NaOH	0.34	0.18	0.10	0.32	0.031	0.024
0.1	0.5M NaOH/ 0.5 M KOH	0.54	0.16	0.05	0.20	0.052	0

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