Zeolite formation in the presence of cement hydrates and albite

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Abstract

Zeolite formation caused by interactions between cement hydrates and rock forming minerals was investigated by two sets of batch experiments and supported by thermodynamic modelling. The first set of batch experiments investigated the interaction between calcium silicate hydrates (C-S-H) ($\text{Ca}_{0.8}\text{SiO}_{2.8}\cdot 32\text{H}_2\text{O}$) and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}(\text{H}_2\text{O})_{26}$) as cement hydrate minerals and albite ($\text{NaAlSi}_3\text{O}_8$) as a rock forming mineral at 20, 50 and 80°C. The dissolution of C-S-H, ettringite and albite led to relatively high calcium and low silicon and sodium concentrations and to the formation of zeolite P(Ca) ($\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_8\cdot 4.5\text{H}_2\text{O}$) and natrolite ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$).

The second set of experiments used ettringite and silica fume as cement phases and NaAlO_2 to represent a rock forming mineral. High initial sodium, hydroxide and aluminium concentrations were observed leading to the precipitation of zeolite X ($\text{Na}_2\text{Al}_2\text{Si}_{2.5}\text{O}_9\cdot 6.2\text{H}_2\text{O}$) and C-S-H gel at 20 and 50°C where only 40 to 60% of the silica had reacted after 3 years. At 80°C where more silica fume had reacted, the formation of SiO₂-rich zeolite Y ($\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12}\cdot 8\text{H}_2\text{O}$) and chabazite ($\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 6\text{H}_2\text{O}$) was observed.

Solubility products for the zeolite P(Ca), natrolite, chabazite, zeolite X and zeolite Y were obtained from the measured concentrations. Comparison with values published in the literature shows a high

variability due to the flexibility of the Si to Al ratio in zeolite structures and underlines the need for systematic experimental determination of the solubility of different zeolites.

1. Introduction

The interaction of the high pH and alkali content of freshly hydrated Portland cement (PC) porewater with the environment will likely initiate the dissolution of aluminosilicate minerals in the adjacent rock and promote the formation of secondary zeolite minerals (Smellie, 1998). The possible formation of zeolites is of importance in the context of deep underground nuclear waste repositories, where safety has to be evaluated for thousands of years.

In hydrated Portland cements (PC) high alkali concentrations and corresponding high pH values of 13 and above are present (Lothenbach and Winnefeld, 2006; Rothstein et al., 2002). In contact with the environment, the alkalis are leached and the pH is lowered to ≈ 12.5 while portlandite is still present. In a second stage, portlandite is destabilised and in a third stage, decalcification of calcium silicate hydrates (C-S-H) and destabilisation of AFm phases and of ettringite can be expected while the pH drops to 11 or even lower (Berner, 1992; Glasser, 1992; Jacques et al., 2010). Available experimental and modelling studies of the reactions between hyperalkaline leachates from cements and rock forming minerals have focused on either the initial high $\text{pH} > 13$ provided by the dissolution of K and Na components of PC (e.g. Fernández et al., 2010; Rochelle et al., 1998), or on $\text{pH} \approx 12.5$ provided by the dissolution of portlandite ($\text{Ca}(\text{OH})_2$) (e.g. Kaufhold and Dohrmann, 2011; Rochelle et al., 1994). Little focus has up to now been aimed at the less aggressive, alkaline leachate representing degradation of PC in the longer-term or from low-pH cements where a $\text{pH} \approx 11$ is expected to be buffered by the dissolution of C-S-H gel and aluminoferrite minerals such as ettringite (Caudin-Coumes et al., 2006; Lothenbach et al., 2012a; Lothenbach et al., 2014). In the current study the interactions of a simplified, degraded PC/rock system were investigated experimentally at 20, 50 and 80°C and supported by thermodynamic calculation to better understand secondary mineral formation in the longer-term.

2. Materials and methods

2.1 Materials

Batch experiments were set up using natural albite (nominally $\text{NaAlSi}_3\text{O}_8$ from Navarro River, Mendocino Co, California), synthesized ettringite and C-S-H, silica fume (SiO_2 , Aerosil 200) and NaAlO_2 (anhydrous, technical from Sigma Aldrich) as starting materials (Table 1). The natural albite sample was sorted under the optical microscope to remove the main impurities and ground. Even after removal of the impurities, the albite sample still contained a small amount of calcite (0.8 wt.%) and traces of lawsonite and clinocllore. Dissolution of the albite sample in 0.1 M HCl indicated the replacement of 5 mol% of Na by K in albite: $\text{Na}_{0.95}\text{K}_{0.05}\text{AlSi}_3\text{O}_8$. NaAlO_2 contained 6.9 wt.% of water and had an actual composition corresponding to $\text{Na}_{1.33}\text{AlO}_{2.17} \cdot 0.34\text{H}_2\text{O}$ as obtained from thermogravimetric analysis (TGA) and from dissolution of the NaAlO_2 used in 0.1 M HCl.

Ettringite and C-S-H samples were prepared and filtered in a N_2 -filled glove box to minimize CO_2 contamination. Ettringite was synthesized by adding freshly prepared CaO (from CaCO_3 , Merck, pro analysis burnt at 1000°C during twelve hours) and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (Merck, puriss) to MilliQ water. The mixtures were stored for 4 weeks at 20°C in sealed polyethylene (PE) bottles until the solid and the liquid phases were separated by vacuum filtration through $0.45\ \mu\text{m}$ Nylon filters. The solid precipitates were dried for three weeks in N_2 -filled desiccators over saturated CaCl_2 solutions at a relative humidity of approximately 30%. TGA analysis confirmed the formation of ettringite and of a small quantity $\text{Al}(\text{OH})_3$.

Calcium silicate hydrate was synthesised by mixing appropriate quantities of freshly prepared calcium oxide (CaO) and silica fume (SiO_2) to obtain a Ca/Si molar ratio of 0.8. The samples were prepared in PE containers with a water to solid ratio of 45 equilibrated for 1 month and were then filtered with $0.45\ \mu\text{m}$ Nylon filter as detailed in L'Hôpital et al. (2016). To minimise carbonation the still wet C-S-H samples were used directly after filtration; TGA of the slurry indicated high water content: $\text{C}_{0.8}\text{SH}_{32}$.

Batch experiments were set up in a N₂-filled glove box in 3 replicates. For each experiment at 20 and 50°C approximately 3 g of solid were weighed in 100 mL PE vessels as detailed in Table 2 and 90 mL of MilliQ water added. For the samples at 80°C, 30 g of water was added to 1 g of solid in Teflon vessels. Total concentrations present in the batch experiments are summarised in Table 3.

The batches were analysed after 1, 2 and 3 years. The solid and liquid phase were separated by vacuum filtration through 0.45 µm Nylon filters. The solid precipitates were dried for three weeks in N₂-filled desiccators over saturated CaCl₂ solution at a relative humidity of approximately 30%.

Table 1: Summary of solids used

Name	chemical composition	water content [wt.%]	weight [g/mol]	BET surface area [m ² /g]
Albite	Na _{0.95} K _{0.05} AlSi ₃ O ₈	-	262	0.56
Ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O	41.2	1147	5.9
C-S-H	Ca _{0.8} SiO _{2.8} ·32H ₂ O*	84.7	680	273
Silica fume	SiO ₂	-	60	200
NaAlO ₂	Na _{1.33} AlO _{2.17} ·0.34H ₂ O	6.9	88	n.a.

*Water content of C-S-H in the slurry used

Table 2: Set up of batch experiments

Sample name	solid	20°C [g in 90 mL]	50°C [g in 90 mL]	80°C [g in 30 mL]
Alb-ett-CSH	C-S-H	0.180	0.180	0.060
	Albite	2.382	2.382	0.794
	Ettringite	0.573	0.573	0.191
Alb-ett	Albite	2.382	2.382	0.794
	Ettringite	0.573	0.573	0.191
NaAlSi-ett	NaAlO ₂	0.745	0.745	0.248
	Ettringite	0.573	0.573	0.191
	SiO ₂	1.636	1.636	0.545

Table 3: Total element concentrations in the batch experiments based on the mass of starting materials shown in Table 2

Name	Al	Ca	Na	K	Si	SO ₄
		[mmol/l]				
Alb-ett-CSH	112	36	96	5	306	17
Alb-ett	112	33	96	5	303	17
NaAlSi-ett	92	33	107	-	303	17

2.2 Methods

Thermogravimetric analysis was done with a Mettler Toledo TGA/SDTA 851e on 30 to 40 mg of sample using a heating rate of 20°C/min from 30 to 980 °C and N₂ as protective gas. X-ray diffraction (XRD) data were collected with a PANalytical X'Pert Pro diffractometer in a θ –2 θ configuration using CoK α radiation. Infrared (IR) spectra were recorded in the mid-region on a Bruker Tensor 27 FT-IR spectrometer using the ATR technique (attenuated total reflection) on bulk material, and the data are quoted in wavenumbers (cm⁻¹).

Scanning electron microscopy (SEM) analyses were carried out with a Philips ESEM FEG XL 30. A beam voltage of 15 keV was chosen for back scattered electron images (BSE) and element mapping by energy dispersive X-ray spectroscopy (EDS). Analyses were done on powder samples placed on a carbon disc and carbon coated.

Solid state nuclear magnetic resonance measurements using magic-angle spinning (²⁹Si MAS NMR) were performed on a few selected samples. The ²⁹Si MAS NMR experiments were recorded on a Bruker Avance III NMR spectrometer using a 7 mm CP/MAS probe at 79.5 MHz at 4500 Hz sample rotation rate, 20 s relaxation delays and RF field strength of 33.3 kHz during SPINAL64 proton decoupling. The ²⁹Si chemical shifts NMR spectra were referenced to the Aldrich external sample of tetramethylsilane (TMS) with ²⁹Si a chemical shift at -2.3 ppm. The quantification of the ²⁹Si resonances was performed by non-linear least-square fits using the software “DMFIT” developed by Massiot et al. (2002). The amount of unreacted albite was quantified based on the intensity of the resonances at -80.3, -82.0 (small broad signal only), -92.6, -96.9 and -104.6 ppm. Unreacted silica fume was quantified taking into account the shift at -100.9 ppm ((SiO)₃Si-OH from the surface of the amorphous silica (d'Espinose de Lacaillerie et al., 1995; Nied et al., 2016) and the Q⁴ shift at -110 ppm. The relaxation time T₁ of silica fume can be very long and it could be that the amount of silica fume is underestimated.

The pH measurements were carried out immediately after filtration on small aliquots of the pore solution at $23 \pm 1^\circ\text{C}$ using a Knick pH meter (pH-Meter 766) and a Knick SE100 electrode. The pH electrode was calibrated with buffer solutions. A second part of the solution was diluted 1:10, 1:100 and 1:1000 with MilliQ H_2O and used for analysis with ion chromatography (IC). The dissolved concentrations of aluminium, calcium, silicon, sodium and sulfate were quantified using a Dionex DP series ICS-3000 ion chromatograph. Standards from 0.1 to 50 mg/L were used. The measurements are associated with a measurement error of 5-10%.

2.3 Thermodynamic modelling

Thermodynamic modelling was carried out using the Gibbs free energy minimization program GEMS v3.3 (Kulik et al., 2013). GEMS is a broad-purpose geochemical modelling code which computes equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. The thermodynamic data for aqueous species, complexes and solids were taken from the PSI-GEMS thermodynamic database (Thoenen et al., 2014). For cement minerals, the cement database Cemdata07 (Lothenbach et al., 2008) was used and completed with the C-N-A-S-H model from (Myers et al., 2014). Data for albite were taken from the SUPCRT database (Helgeson et al., 1978).

The measured concentrations in the solution were used to calculate saturation indices with respect to amorphous silica (SiO_2), gibbsite ($\text{Al}(\text{OH})_3$), ettringite, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrite (CaSO_4), strätlingite ($\text{Ca}_2\text{Al}_2\text{SiO}_2(\text{OH})_{10} \cdot 3\text{H}_2\text{O}$), albite, low Ca C-S-H ($\text{Ca}_{0.83}\text{SiO}_{2.83} \cdot 1.33\text{H}_2\text{O}$), zeolite P(Ca) ($\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4.5\text{H}_2\text{O}$), and natrolite ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) at 20, 50 and 80°C to assess which solid phases could be stable.

Table 4: Standard thermodynamic properties at 25°C .

Name	composition	$\log K_{\text{S}0}^{\text{a}}$	$\Delta_{\text{f}}G^\circ$ [kJ/mol]	$\Delta_{\text{f}}H^\circ$ [kJ/mol]	S° [J/mol/K]	C_{p}° [J/mol/K]	Ref
Anhydrite	CaSO_4	-4.357	-1322.1	-1435	107	100	PSI ^b
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-4.581	-1797.8	-2023	194	186	PSI ^b

Gibbsite	$\text{Al}(\text{OH})_3$	-1.12	-1151.0	-1289	70	93	PSI ^b
Microcrystalline	$\text{Al}(\text{OH})_3$	-0.67	-1148.4	-1265	140	93	cem ^c
SiO _{2,am}	SiO_2	-2.714	-848.9	-903	41	44	PSI ^b
Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$	-44.9	-15205.9	-17535	1900	2174	cem ^c
C-S-H	$\text{Ca}_{0.83}\text{SiO}_{2.83}\cdot 1.33\text{H}_2\text{O}$	-12.19 ^d	-1744.4	-1916	80	132	cem ^c
Strätlingite	$\text{Ca}_2\text{Al}_2\text{SiO}_2(\text{OH})_{10}\cdot 3\text{H}_2\text{O}$	-23.89 ^d	-5705.1	-6360	546	603	cem ^c
Albite, high	$\text{NaAlSi}_3\text{O}_8$	-20.80 ^d	-3700.8	-3921	219	205	SUP ^e
Zeolite P(Ca)	$\text{CaAl}_2\text{Si}_2\text{O}_8\cdot 4.5\text{H}_2\text{O}$	-20.3±2	-5057.8±11	-5424±16	779±40 ^f	753±40 ^f	g
Chabazite	$\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 6\text{H}_2\text{O}$	-25.8±2	-7111.8±11	-7774±12	581±10 ^h	617±10 ^h	g
Zeolite X	$\text{Na}_2\text{Al}_2\text{Si}_{2.5}\text{O}_9\cdot 6.2\text{H}_2\text{O}$	-20.1±1	-5847.5±6	-6447±8	566±20 ⁱ	586±20 ⁱ	g
Natrolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$	-30.2±1	-5325.7±6	-5728±10	360±10 ^j	359±10 ^j	g
Zeolite Y	$\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12}\cdot 8\text{H}_2\text{O}$	-25.0±2	-7552.5±11	-8327±31	734±100 ⁱ	739±100 ⁱ	g

Data used to calculate C_p° and S° of zeolite P(Ca), chabazite, zeolite X and zeolite Y

Al_2O_3	51.0	79.1	SUP ^e
CaO	39.7	42.8	SUP ^e
K_2O	94.1	84.1	SUP ^e
Na_2O	75.0	68.9	SUP ^e
SiO_2	41.3	44.5	SUP ^e
Zeolitic water H_2O	59.0	47.7	SUP ^e

^a All solubility products refer to the solubility with respect to the species $\text{Al}(\text{OH})_4^-$, Ca^{2+} , Na^+ , $\text{SiO}(\text{OH})_3^-$, SO_4^{2-} , OH^- , or H_2O . ^b GEMS PSI-TDB (Thoenen et al., 2014; Thoenen and Kulik, 2003); ^c Cemdata07 (Lothenbach et al., 2008) + cemdata2014 (Lothenbach et al., 2012b). ^d recalculated in the paper from $\Delta_f G^\circ$. ^e SUPCRT (Helgeson et al., 1978). ^f this study; ^g S° calculated from solubility products at 20, 50 and 80°C; C_p° calculated from Ca-phillipsite, quartz and zeolitic water using the data from (Helgeson et al., 1978). ^h in this study from solubility data. ⁱ recalculated for $\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 6\text{H}_2\text{O}$ from the S° and C_p° measured by Belitsky et al. (1982) for natural chabazite. ^j S° and C_p° calculated from chabazite, Na_2O , CaO , SiO_2 and zeolitic H_2O . ^k S° and C_p° measured by Johnson et al. (1983).

For comparison thermodynamic data for zeolite P(Ca), gismondine ($\text{CaAl}_2\text{Si}_2\text{O}_8\cdot 4.5\text{H}_2\text{O}$), scolecite ($\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$), chabazite ($\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 6\text{H}_2\text{O}$), natrolite, phillipsite ($\text{CaAl}_2\text{Si}_5\text{O}_{14}\cdot 5\text{H}_2\text{O}$) and of analcime ($\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12}\cdot 2\text{H}_2\text{O}$) from Arthur et al. (2011), Blanc et al. (2015), Helgeson et al. (1978) and Neuhoﬀ et al. (2004) are summarised in Table 5. The data for zeolites were mainly derived from phase relations and calorimetric methods and internally consistent.

Table 5: Standard thermodynamic properties at 25 °C for selected zeolites collected from literature

Name	composition	$\log K_{S0}^a$	$\Delta_f G^\circ$ [kJ/mol]	$\Delta_f H^\circ$ [kJ/mol]	S° [J/mol/K]	C_p° [J/mol/K]	Ref
Zeolite P(Ca)	$\text{CaAl}_2\text{Si}_2\text{O}_8\cdot 4.5\text{H}_2\text{O}$	-23.16	-5084.8	-5564.6	397	459	Ther ^b
Gismondine	$\text{CaAl}_2\text{Si}_2\text{O}_8\cdot 4.5\text{H}_2\text{O}$	-26.25	-5102.4	-5589.9	371	435	Ther ^b
Scolecite	$\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$	-29.11	-5598.0	-6049.0	367	383	Ther ^b
Chabazite	$\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 6\text{H}_2\text{O}$	-34.22	-7173.6	-7824.4	614	643	Ther ^b
Chabazite	$\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 6\text{H}_2\text{O}$				640	589	SUP ^c
Ca-phillipsite	$\text{CaAl}_2\text{Si}_5\text{O}_{14}\cdot 5\text{H}_2\text{O}$	-41.10	-8882.4	-9648.0	684	666	Ther ^b

Ca-phillipsite	$\text{CaAl}_2\text{Si}_5\text{O}_{14} \cdot 5\text{H}_2\text{O}$				697	586	SUP ^c
Natrolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$	-26.43	-5316.7	-5718.6	360	359	Ther ^b
Natrolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot \text{H}_2\text{O}$				425	380	SUP ^c
Analcime	$\text{Na}_{1.98}\text{Al}_{1.98}\text{Si}_{4.02}\text{O}_{12} \cdot 2\text{H}_2\text{O}$	-32.46	-6198.2	-6616.0	462	425	Ther ^b
Analcime	$\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$	-33.23	-6176.4	-6613.4	469	424	SUP ^c
Analcime	$\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$	-33.47	-6177.8	-6616.9	459	425	Neu ^d
Analcime	$\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$	-34.74	-6192.6	-6624.0			Art ^e

^a All solubility products refer to the solubility with respect to the species AlO_2^- , Ca^{2+} , Na^+ , SiO_2 , SO_4^{2-} , OH^- , or H_2O ; following the SUPCRT formalism (Helgeson et al., 1978) the notations AlO_2^- (instead of $\text{Al}(\text{OH})_4^-$) and SiO_2 (instead of $\text{Si}(\text{OH})_4^0$) are used. ^b Thermoddem database (Blanc et al., 2015); data for synthetic zeolite P(Ca) and for gismondine (natural mineral) with the same composition are reported. The S° and C_p° values of zeolite P(Ca) and chabazite in Blanc et al. (2015) are misprinted, the correct values are taken from the thermoddem homepage (<http://thermoddem.brgm.fr/>), as well as the solubility products at different temperatures. Note $\Delta_f G^\circ$ of the reference Al^{3+} in the GEMS PSI (Thoenen et al., 2014; Thoenen and Kulik, 2003) and SUPCRT (Helgeson et al., 1978; Shock et al., 1997) thermodynamic database is with -483.7 kJ/mol roughly 4 kJ/mol higher than the -487.6 used in the thermoddem database, and thus rather the log K values should be compared than $\Delta_f G^\circ$ values. ^c SUPCRT (Helgeson et al., 1978). ^d Derived from Neuhoﬀ et al. (2004); ^e Arthur et al. (2011).

The measured compositions of the solution were also used to calculate solubility products for zeolite

The activity of a species i , $\{i\}$, was calculated with GEMS from the measured concentrations considering the formation of aqueous complexes. $\{i\} = \gamma_i \cdot m_i$, γ_i is the activity coefficient and m_i the concentration in mol/kg H_2O . The activity coefficients of the aqueous species γ_i were computed with the built-in extended Debye-Hückel equation with common ion-size parameter a_i of 3.31 Å for NaOH solutions and common third parameter b_y according to equation (1):

$$\log \gamma_i = \frac{-A_y z_i^2 \sqrt{I}}{1 + B_y a_i \sqrt{I}} + b_y I \quad (1)$$

where z_i denotes the charge of species i , I the effective molal ionic strength, b_y is a semi-empirical parameter (~ 0.098 for NaOH electrolyte at 25°C), and A_y and B_y are P,T-dependent coefficient. For uncharged species equation (1) corresponds to $\log \gamma_i = b_y I$. This activity correction is applicable up to approx. 1 M ionic strength (Merkel and Planer-Friederich, 2008).

From the solubility products calculated at different temperatures, the Gibbs free energy of reaction, $\Delta_r G^\circ$, the Gibbs free energy of formation, $\Delta_f G^\circ$, and the entropy, S° , at 25 °C can be obtained according to equations (2) and (3):

$$\Delta_r G^\circ = \sum_i \nu_i \Delta_f G^\circ = -RT \ln K \quad (2)$$

$$\Delta_a G_T^\circ = \Delta_f G_{T_0}^\circ - S_{T_0}^\circ (T - T_0) + \int_{T_0}^T C_p^0 dT - \int_{T_0}^T \frac{C_p^0}{T} dT \quad (3)$$

Using $C_p^\circ = a_0 + a_1 T + a_2 T^2 + a_3 T^{0.5}$ (Berman, 1988), where a_{0-3} are empirical parameters defined for each mineral, then the two integral terms of equation (3) can be solved to give equation (4):

$$\Delta_a G_T^\circ = \Delta_f G_{T_0}^\circ - S_{T_0}^\circ (T - T_0) - a_0 \left(T \ln \frac{T}{T_0} - T + T_0 \right) - 0.5 a_1 (T - T_0)^2 - a_2 \frac{(T - T_0)^2}{2T \cdot T_0^2} - a_3 \frac{2(\sqrt{T} - \sqrt{T_0})^2}{\sqrt{T_0}} \quad (4)$$

where ν_i are the stoichiometric reaction coefficients, $R = 8.31451$ J/mol/K, T the temperature in K and C_p° the heat capacity. A constant $C_p^\circ (=a_0)$ and $a_1=a_2=a_3 = 0$ was assumed for the newly derived data for zeolite as only a narrow temperature range had been studied. The apparent Gibbs free energy of formation, $\Delta_a G_T^\circ$, refers to the free energies of the elements at 298 K. A more detailed description of the derivation of the dependence of the Gibbs free energy on temperature is given in Anderson and Crerar (1993) and Kulik (2002).

3. Zeolites formed in samples containing albite and ettringite

3.1 Analysis of solid phases

In a first series of experiments, the formation of zeolites in the presence of albite, ettringite and in presence or absence of C-S-H (see Table 2) was investigated. In general similar reaction products were observed at all temperatures, independently of whether C-S-H was originally present (samples Alb-ett-CSH) or absent (samples Alb-ett). In both cases, ettringite and a small quantity of $Al(OH)_3$ were still present at 20 °C after 3 years and only a slight decrease of their amount was observed during this time as shown by TGA in Figure 1. At 50°C, the amount of ettringite decreased significantly with time such that only little ettringite remained after 3 years, while the formation of new phases

was observed. At 80 °C ettringite was destabilized within a year (Figure 1). The faster destabilization of ettringite at higher temperature is related to the strong increase of the ettringite solubility with temperature (Lothenbach et al., 2008; Perkins and Palmer, 1999) as well as to the faster reaction kinetics at higher temperature. Higher temperature also accelerated the formation of zeolites such as zeolite P(Ca) which consumed calcium and aluminium from ettringite and $\text{Al}(\text{OH})_3$. Whether C-S-H was also present or not could not be unambiguously determined by TGA as C-S-H shows only a moderate weight loss in the region 50 – 300°C (L'Hôpital et al., 2016), which is overlaid by the ettringite signal.

Figure 1: Effect of time (1, 2 or 3 years) and temperature (20, 50 and 80°C) on the solids observed by thermogravimetric analyses (TGA) of samples containing initially albite and ettringite.

In all cases unreacted albite was present up to 3 years as observed by XRD (Figure 2), by ^{29}Si MAS NMR data (Figure 3) and by FTIR. Deconvolution of the ^{29}Si MAS NMR data indicates that approximately 5% of the albite initially present had reacted at 20°C and 20% at 50 and 80 °C after 3 years (Figure 3). The XRD data confirm that a major fraction of ettringite was still present after 3 years at 20 °C, little ettringite was left at 50°C and none at 80°C. Due to the ettringite dissolution, also the presence of small quantity of gypsum was observed at 50°C and of anhydrite (CaSO_4) at 50 and 80°C as visible by the increase of the peak at 29.6 2theta CoK_α in the XRD patterns (Figure 2) compared to the 20°C samples. In addition, the formation of some calcite was observed at 80°C, less at 50 and 20°C.

The availability of calcium and aluminium from the destabilization of ettringite and of sodium, aluminium and silicon from the dissolution of albite enabled the formation zeolites at 50°C and 80°C in-

dependent of whether some C-S-H was initially present or not. At 50°C, mainly the formation of zeolite P(Ca) was observed by XRD (Figure 2), ^{29}Si MAS NMR (Figure 3), and TGA (Figure 4) although minor quantities of natrolite were also present. The term zeolite P(Ca) is used to designate synthetic gismondine.

The water loss observed at around 320°C in the TGA data is assigned to natrolite (Charistos et al., 1997; Neuhoﬀ and Wang, 2007; Van Reeuwijk, 1972) and those at 110°C and 250°C to zeolite P(Ca), based on the observations of Huo et al. (2013), Nery et al. (2003) and Pal et al. (2013) on substituted zeolite P. The shift at -90 ppm observed by ^{29}Si MAS NMR confirms the formation zeolite P(Ca) as the presence of Na in the pseudo-cage of the gismondine structure would lower the shift to -86.6 ppm (Nery et al., 2003). For natrolite the presence of a weak band at -84.4 ppm (in addition to the main bands at -90 and -95 ppm, Figure 3) indicates a disordering in the Al-Si framework in the natrolite structure as discussed in Neuhoﬀ et al. (2002).

At 80°C in the presence of C-S-H, mainly the formation of natrolite was observed and only little zeolite P(Ca) (Figure 2 - Figure 4), while in the absence of C-S-H mainly zeolite P(Ca) was formed (Figure 1). Whether zeolites had also formed at 20°C is difficult to assess. XRD, TGA and ^{29}Si MAS NMR data indicate that a small quantity of zeolite P and natrolite could have formed at 20°C. Scolecite or faujasite and chabazite (which were present in the samples where NaAlO_2 and SiO_2 have been used as starting materials instead of albite, as discussed below in section 4) were not observed. ^{29}Si MAS NMR data could point towards the presence of some C-S-H in the samples, although an unambiguous assignment is difficult.

Figure 2: XRD patterns of the samples containing initially albite, ettringite and C-S-H equilibrated for 3 years at 20, 50 and 80°C. *: albite, An: anhydrite, Cal: calcite, E: ettringite, Gy: gypsum, N: natrolite (pdf 045-1413), P: zeolite P(Ca)/gismondine (pdf 039-1373)

Figure 3: ^{29}Si MAS NMR spectra of the samples containing initially albite, ettringite and C-S-H equilibrated for 3 years at 20, 50 and 80°C. *: albite; C-S-H: calcium silicate hydrate: -83 and -86 ppm (L'Hôpital et al., 2016); N: natrolite (main signals at -84.4 and -90 ppm in agreement with the chemical shifts reported by Neuhoﬀ et al. (2002), a further less intense signal at -95 is overlaid by albite); P: zeolite P(Ca)/gismondine (main signal at -89.9 ppm comparable to chemical shifts reported by Nery et al., 2003). Silica attributed to unreacted albite equals to 94±2% at 20°C, 78±5% at 50°C and 80±5% at 80°C, indicating a reaction degree of albite of 5, 21 and 19% (±5%) at 20, 50 and 80°C, respectively, taking into account the presence of 1% silicon from C-S-H.

Figure 4: Thermogravimetric analyses of the samples containing initially albite, ettringite and C-S-H equilibrated for 3 years at 20, 50 and 80°C.

The FTIR spectra (data not shown) confirmed the presence of unreacted albite in all samples. For the samples equilibrated at 50 and 80°C, a broadening of the main band at $\approx 955 \text{ cm}^{-1}$ was observed, consistent with the presence of zeolite P(Ca) (Chukanov, 2013). The main bands of natrolite are located at higher wavenumber, $970\text{-}1200 \text{ cm}^{-1}$ (Chukanov, 2013; Huo et al., 2013), and thus cannot be differentiated clearly from the albite signal. In addition, small bands at 875 cm^{-1} and from 1420 to 1530 cm^{-1} characteristic for carbonates (Yu et al., 1999) were observed. SEM/EDS analyses confirmed the previous observations. Mainly albite was present and zeolite P(Ca) and natrolite were observed to grow on its surface (Figure 5). The EDS analyses indicate that the hydrates were richer in sodium (natrolite) or in calcium (zeolite P(Ca)) than alite.

Figure 5: SEM/BSE pictures of natrolite growing on the surface of albite in the presence of ettringite and C-S-H; equilibrated for 2 years at 80°C.

3.2 Solution composition

Figure 6 shows that the composition of the solutions was dominated by sodium from the dissolution of albite and by calcium and sulfate from ettringite dissolution. At 80°C the sulfate concentrations after 1 year were already near to the total amount of sulfate present in the experiments (see Figure 6), consistent with the observed complete destabilization of ettringite at this temperature. After 2 and 3 years somewhat less sulfate was observed in the samples as anhydrite was formed. At 20 and 50°C calcium and sulfate concentrations increased with time (Table 6) consistent with the observed dissolution of ettringite.

Ettringite was the main source of calcium in the experiments. From its dissolution a molar calcium to sulfate ratio of 2 is expected as shown in equation (5) and Table 3. The calcium to sulfate ratio in solution should be even higher in cases where anhydrite precipitated. The presence of less calcium than

sulfate in the solution is a clear indication of the formation of calcium containing phases such as C-S-H or zeolite P(Ca) at all temperatures.

The measured sodium concentrations increased slightly between 1 and 3 years confirming the dissolution of albite ($\text{NaAlSi}_3\text{O}_8$), see equation (6) and Table 3. Based on the sodium concentrations, at least 8% of the albite had reacted at 80°C after 1 year and longer; a higher albite reaction degree can be expected as some of the sodium released is bound in natrolite. In fact, ^{29}Si MAS NMR data (Figure 3) indicates that roughly 20% of the albite had reacted. The concentration of sodium was slightly lower in the sample with C-S-H (Table 6), which agrees with the observed formation of more natrolite in the sample with C-S-H at 80°C as discussed above and shown in Figure 1 and Figure 4. At all temperatures, significantly less sodium was measured after 3 years in the solutions (i.e. 1, 7 and 8 mM Na, respectively, corresponding to at least 1, 7 and 8% albite reaction at 20°C, 50°C, and 80°C) than what could be expected from the dissolution of albite observed by ^{29}Si MAS NMR. This uptake of sodium in the hydrates tentatively indicates the formation of natrolite at all temperatures even at 20°C, e.g. according to equation (7).

Equation (7) indicates that simultaneously to natrolite also zeolite P(Ca) and low Ca/Si C-S-H are expected to form. In fact, the measured silicon and aluminium concentrations are low (Table 6) consistent with the formation of natrolite and zeolite P(Ca). The aluminium concentrations decreased at 50 and 80°C slightly with time, while silicon concentrations increased.

Figure 6: Measured concentrations in the samples containing albite, ettringite and C-S-H equilibrated at 20, 50 or 80°C for 1, 2 and 3 years. The lines indicate the total amount of sodium, calcium, sulfate and aluminium present in the experiments as summarized in Table 3. The total amount of silicon is with approx. 300 mM above the scale shown.

Table 6: Concentrations measured in the batch experiments after different equilibration times. Measurement error $\pm 10\%$.

Time [days]	Na	K	Ca ---- mM ---	Si	SO ₄	Al	OH ^{***} -	pH*
Albite containing samples								
20 °C								
<i>Albite-ettringite-C-S-H</i>								
382	1.52	0.032	3.05	0.105	3.14	0.054	0.093	10.0
781	1.57	0.050	3.89	0.027	3.54	0.228	0.022	9.4
1147	1.69	0.031	4.25	0.010	4.14	0.206	0.039	9.7
<i>Albite-ettringite</i>								
215	1.03	n.a.	4.74	0.006	2.50	1.18	0.010	9.1
382	1.06	<0.001	3.44	0.003	3.22	0.172	0.009	9.0
781	1.08	0.021	4.46	0.002	3.52	1.04	0.025	9.5
1147	1.18	0.027	4.67	0.005	4.97	0.81	0.054	9.8
50 °C								
<i>Albite-ettringite-C-S-H</i>								
382	2.25	0.055	5.24	0.079	6.15	0.210	0.26	10.5
781	4.73	0.090	10.25	0.299	5.40	0.029	0.74	10.9

1147	6.80	0.069	12.48	0.255	13.81	0.029	0.66	10.9
<i>Albite-ettringite</i>								
382	1.64	0.038	5.89	0.015	6.06	1.36	0.11	10.1
781	3.45	0.072	9.09	0.139	4.73	0.084	0.60	10.9
1147	6.36	0.069	12.06	0.235	12.64	0.038	0.85	11.0

80 °C

Albite-ettringite-C-S-H

382	6.35	0.142	10.99	0.484	15.28	0.0085	0.071	9.9
781	7.03	0.193	11.95	1.676	12.03	0.0018	0.007	8.9
1147	7.94	0.091	11.27	2.49	14.11	≤0.0002	0.003	8.6

Albite-ettringite

382	8.30	0.176	11.29	0.72	16.04	0.0014	0.021	9.4
781	8.68	0.138	11.82	1.76	19.79	≤0.0002	0.003	8.6
1147	9.64	0.100	10.37	1.98	14.50	0.0004	0.002	8.4

NaAlO₂ – SiO₂-ettringite

20 °C

382	69.8	<0.001	0.096	0.596	4.77	21.14	9.1	12.0
781	69.1	<0.001	0.046	0.448	7.02	36.26	8.3	12.0
1147	66.4	<0.001	0.008	0.538	5.89	29.40	7.8	12.0

50 °C

382	51.1	<0.001	0.021	1.39	10.64	7.27	8.7	12.0
781	50.2	<0.001	0.106	7.21	14.02	0.239	2.5	11.5
1147	56.7	<0.001	0.216	4.86	13.05	0.841	1.6	11.3

80 °C

382	52.3	<0.001	0.189	18.67	14.33	0.504	0.65	10.9
781	73.9	<0.001	0.417	15.07	20.69	0.170	0.48	10.8
1147	53.9	<0.001	0.485	9.26	15.79	0.723	0.22	10.4

* pH values measured at 23-24°C; ±0.1. ** Hydroxide (OH⁻) concentrations calculated from the measured pH values.

Saturation indices (SI) were calculated from the measured concentrations and pH values in the pore solution considering the presence of carbonates. The SI as compiled in Table 7 confirm the findings from the solid phase analysis. Both solutions, albite-ettringite-CSH and albite-ettringite, were undersaturated with respect to ettringite, consistent with the dissolution observed. At 80°C, where ettringite was absent, a strong undersaturation was observed, while the solutions were saturated with respect to anhydrite. At 20 and 50°C where ettringite continued to dissolve over the 3 years, the solutions were only moderately undersaturated. Saturation with respect to gypsum/anhydrite was only reached at 50°C after 3 years and at 20°C not within the period investigated (Table 7).

The solutions were moderately undersaturated with respect to albite at 20 and 50°C, while at 80°C saturation had been reached, which indicates no or little further albite dissolution is expected at 80°C. The solutions were saturated with respect to C-S-H at 50°C, which made its presence probable in agreement with the ^{29}Si MAS NMR data (Figure 3). At 20 and 80°C, the solutions were moderately undersaturated, although ^{29}Si MAS NMR data tentatively indicate its presence also at 20 and 80°C; this moderate apparent undersaturation could be related to the formation of calcium carbonate. The solutions at 20°C were somewhat oversaturated with respect to gibbsite but near saturation with respect to microcrystalline aluminium hydroxide and at 50°C near saturation with respect to gibbsite (Table 7). Generally at ambient temperatures the formation of microcrystalline aluminium hydroxide was observed due to kinetic reasons, although microcrystalline aluminium hydroxide is thermodynamically slightly less stable than gibbsite as discussed in detail in Lothenbach et al. (2012b).

Table 7: Calculated saturation indices calculated from the measured concentrations (Table 6) and the thermodynamic data given in Table 4. Solid phases observed experimentally are marked as bold

Time days	Albite $\text{N}_{0.5}\text{A}_{0.5}\text{S}_3$	Ettringite $\text{C}_6\text{A}_3\text{S}_3\text{H}_{32}$	Gypsum CsH_2	Anhydrite Cs	C-S-H $\text{C}_{0.83}\text{SH}_{1.3}$	Gibbsite $\frac{1}{2}\text{AH}_3$	Strätl. C_2ASH_8	SiO_2, am S	Zeolite P $\text{CAS}_2\text{H}_{4.5}$	Natrolite NAS_3H_2
Albite containing samples										
20 °C										
<i>Albite-ettringite-C-S-H</i>										
382	-1.0	-4.5	-1.0	-1.3	-1.2	0.4	-2.8	-1.7	-0.3	2.7
781	-1.7	-5.1	-0.9	-1.2	-2.6	1.1	-3.0	-2.2	0.1	2.6
1147	-3.2	-3.8	-0.8	-1.1	-2.7	0.9	-3.0	-2.7	-0.9	1.2
<i>Albite-ettringite</i>										
215	-3.4	-4.9	-1.0	-1.3	-4.2	1.6	-3.0	-3.3	-0.4	2.5
382	-4.4	-7.3	-0.9	-1.2	-4.2	1.2	-5.0	-3.1	-1.8	-0.3
781	-5.8	-3.2	-0.8	-1.1	-4.0	1.4	-3.0	-3.7	-1.5	-0.9
1147	-4.6	-1.9	-0.8	-1.1	-3.0	1.2	-2.1	-3.3	-0.9	0.2
50 °C										
<i>Albite-ettringite-C-S-H</i>										
382	-2.2	-3.2	-0.6	-0.6	-1.3	0.3	-1.7	-2.2	1.3	1.1
781	-2.2	-2.1	-0.5	-0.5	-0.1	-0.4	-1.8	-2.0	0.2	0.6
1147	-2.4	-0.7	-0.2	-0.2	-0.2	-0.3	-2.0	-2.1	0.1	0.5
<i>Albite-ettringite</i>										
382	-4.6	-2.9	-0.6	-0.5	-2.7	0.9	-1.6	-3.0	1.4	0.0
781	-2.6	-1.8	-0.6	-0.6	-0.5	-0.1	-1.4	-2.2	0.6	0.5
1147	-2.4	-0.7	-0.2	-0.2	-0.2	-0.3	-1.7	-2.1	0.1	0.5

<i>80 °C</i>										
<i>Albite-ettringite-C-S-H</i>										
382	-0.9	-7.9	-0.1	0.2	-1.0	-0.5	-4.7	-1.2	1.4	0.5
781	0.3	-11.8	-0.1	0.2	-1.3	-0.5	-6.6	-0.5	1.4	0.9
1147	0.0	-14.9	-0.1	0.2	-1.7	-0.9	-8.9	-0.3	-0.1	-0.3
<i>Albite-ettringite</i>										
382	-1.0	-10.8	-0.1	0.2	-1.3	-0.8	-6.8	-1.0	0.2	-0.4
781	0.2	-13.9	0.0	0.3	-1.9	-0.5	-8.2	-0.5	0.7	0.5
1147	-0.1	-15.7	-0.1	0.2	-2.2	-0.7	-9.4	-0.4	-0.1	-0.2
NaAlO₂ – SiO₂-ettringite										
<i>20 °C</i>										
382	-0.6	-2.3	-2.8	-3.1	-0.7	0.7	1.5	-3.0	0.5	7.3
781	-0.9	-3.5	-3.0	-3.3	-1.2	0.9	1.0	-3.2	0.3	7.3
1147	-0.6	-9.1	-3.9	-4.2	-1.8	0.8	-0.8	-3.0	-0.4	7.4
<i>50 °C</i>										
382	0.1	-11.0	-3.4	-3.3	-1.1	0.3	-1.6	-2.3	1.1	6.2
781	2.3	-11.0	-2.4	-2.4	-0.1	-0.3	-3.0	-1.0	1.2	6.8
1147	2.9	-8.3	-2.0	-2.0	-0.2	0.1	-1.5	-1.0	2.7	7.9
<i>80 °C</i>										
382	3.9	-12.8	-2.0	-1.7	-0.1	-0.4	-3.0	-0.3	3.9	7.3
781	3.5	-11.9	-1.6	-1.3	0.2	-0.6	-3.5	-0.3	3.2	6.6
1147	3.9	-11.4	-1.6	-1.3	-0.2	-0.1	-2.5	-0.3	4.5	7.6

* cement shorthand notation is used: A: Al₂O₃; C: CaO; H: H₂O; N: Na₂O; s: SO₃; S: SiO₂.

3.3 Solubility of natrolite and zeolite P(Ca)

The comparison of the measured concentrations as given in Table 6 with thermodynamic data for zeolites from the literature (Table 5) indicates that the solutions seem to be oversaturated with respect to zeolite P(Ca) at 20 and 50°C, and undersaturated at 80°C (Figure 7). The solutions were also oversaturated with respect to scolecite, but clearly undersaturated with respect to chabazite, zeolite Y, zeolite X and analcime. With respect to natrolite the solutions were calculated to be significantly undersaturated at all temperatures compared to solubility data from literature as visible in Figure 7. This apparent contradiction is related to the high error of the solubility products available in literature for zeolite P(Ca) and natrolite. The solubility products for natrolite have been calculated from measured enthalpy and heat capacity data (Johnson et al., 1983), but not from actual solubility measurements which can, due to the uncertainty associated with the measurements of enthalpy data, lead to significant errors (several log units) on the solubility product as shown e.g. in Lothenbach et al. (2012b).

The only available thermodynamic data for zeolite P(Ca) ($\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4.5\text{H}_2\text{O}$) are based on two single solubility measurements of calcium exchanged sodium-zeolite P with the nominal formula $\text{Ca}_{0.9}(\text{Na}_2)_{0.1}\text{O Al}_2\text{O}_3 (\text{SiO}_2)_{2.66} \cdot 4\text{H}_2\text{O}$ at 25 and 85°C after 1 month equilibration time (Atkins et al., 1993). The thermodynamic data for gismondine or zeolite P(Ca) have been estimated based on the stability of other zeolites as detailed in Blanc et al. (2015). Thus, the measurements of the solution composition reported in Table 6 were used to obtain solubility products of natrolite and zeolite P(Ca) as shown in Figure 7 and Table 8. It should be noted that the calculated solubility products for zeolite P(Ca) could be influenced by the possible uptake of sodium in zeolites P(Ca), as ion exchange is common for zeolite P (Atkins et al., 1993; Nery et al., 2003). For zeolite P(Na) ($\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$) precipitated from oversaturation a much higher solubility (-16.2 at 25°C and -14.5 at 80°C) could be derived based on measurements of Katović et al. (1989) confirming its low stability which makes the formation of zeolite P(Na) less probable in our experiments where higher calcium than sodium concentrations were present (Table 6).

For natrolite, ion exchange with monovalent ions such as K or Cs has been observed, while natrolite does not accommodate any significant amount of bivalent ions such as Ca^{2+} in its structure (Lee et al., 2010; Neuhoﬀ et al., 2002).

Table 8: Solubility products for zeolite P(Ca), natrolite, chabazite, zeolite Y and zeolite X calculated from the measured concentrations (Table 6) at 20, 50 and 80 °C. Solid phases observed experimentally are marked as bold; solid phases absent are printed in italic

Time [days]	Zeolite P(Ca)	Natrolite	Chabazite	Zeolite Y	Zeolite X
Albite containing samples					
<i>20 °C</i>					
<i>Albite-ettringite-C-S-H</i>					
382	-20.5	-28.0	-29.5	-32.5	-25.7
781	-20.1	-28.0	-30.0	-33.0	-25.6
1147	-21.1	-29.5	-32.0	-34.9	-26.8
<i>Albite-ettringite</i>					
215	-20.6	-28.2	-32.7	-34.3	-25.2
382	-22.0	-31.0	-33.6	-36.8	-28.0
781	-21.7	-31.6	-34.7	-38.1	-28.4

1147	-21.1	-30.5	-33.2	-36.6	-27.5
50 °C					
<i>Albite-ettringite-C-S-H</i>					
382	-19.5	-26.9	-28.8	-31.6	-24.6
781	-20.6	-27.5	-29.5	-31.9	-25.3
1147	-20.7	-27.3	-29.7	-31.8	-25.1
<i>Albite-ettringite</i>					
382	-19.5	-28.1	-30.5	-33.6	-25.3
781	-20.2	-27.5	-29.6	-32.2	-25.2
1147	-20.7	-27.5	-30.0	-32.1	-25.2
80 °C					
<i>Albite-ettringite-C-S-H</i>					
382	-20.1	-25.4	-27.2	-28.9	-23.6
781	-20.1	-25.0	-25.8	-27.8	-23.6
1147	-21.6	-26.2	-26.9	-28.8	-24.8
<i>Albite-ettringite</i>					
382	-21.3	-26.3	-27.8	-29.5	-24.7
781	-20.9	-25.4	-26.4	-28.2	-24.0
1147	-21.7	-26.1	-27.1	-28.8	-24.7
NaAlO₂ – SiO₂-ettringite					
20 °C					
382	-19.7	-23.4	-31.2	-29.1	-20.5
781	-19.9	-23.4	-31.8	-29.4	-20.5
1147	-20.7	-23.2	-32.2	-29.0	-20.4
50 °C					
382	-19.7	-21.8	-29.4	-26.7	-19.4
781	-19.6	-21.3	-26.7	-24.8	-19.5
1147	-18.2	-20.1	-25.3	-23.7	-18.3
80 °C					
382	-17.6	-18.5	-22.8	-21.1	-17.3
781	-18.3	-19.3	-23.5	-21.9	-18.0
1147	-17.0	-18.3	-22.3	-20.9	-17.0

The calculated solubility products for zeolite P(Ca) slightly decrease with time at 50 and 80°C while no clear trend can be observed at 20°C as shown in Figure 7A. Although the formation of zeolite P(Ca) at 20°C was not clearly visible in the analysis of the solid phase, the lowering of Ca, Al and Si concentrations in the solution relative to sulfate and sodium as well as the good agreement of the calculated ion activity products with the trends of the solubility products obtained at 50°C and 80°C, make its presence probable. The solubility products calculated from the experiments in the present paper are similar at 80, 50 or 20°C, respectively, and comparable to the value at 85°C derived from

the concentrations measured by Atkins et al. (1993). The value calculated from the concentration measured at 25°C in Atkins et al. (1993) is 3 log units lower than the values determined in this study, which could indicate that in the undersaturation experiments of Atkins et al. (1993) equilibrium was not reached after 1 month at 25°C or it could be related to differences in crystallinity and composition between the pre-synthesized product ($\text{Ca}_{0.9}(\text{Na}_2)_{0.1}\text{O Al}_2\text{O}_3 (\text{SiO}_2)_{2.66} 4\text{H}_2\text{O}$) used by Atkins et al. (1993) and the zeolite P formed from oversaturation during our experiments. Small variation in the silica to aluminium ratio as well as the counter cation can have a large effect (several log units) on the solubility as shown in Blanc et al. (2015) and Neuhoﬀ et al. (2004).

As no measurements of the entropy and heat capacity are available, $S = 779 \text{ J/mol/K}$ and $C_p^\circ = 753 \text{ J/mol/K}$ were estimated from the data of Ca-phillipsite (a doubly connected 4-ring zeolite as zeolite P(Ca), using the data from Blanc et al. (2015) as given in Table 5), quartz and zeolitic water (Helgeson et al., 1978, Table 4), assuming $\Delta_r S^\circ = \Delta_r C_p^\circ = 0$ (Anderson and Crerar, 1993) for the reaction $\text{zeolite P(Ca)} + 3 \text{ quartz} + 0.5 \text{ zeolitic H}_2\text{O} \rightleftharpoons \text{Ca-phillipsite}$. The values obtained are summarized in Table 4. S° and C_p° are higher than the values, $S^\circ = 397$, $C_p^\circ = 459 \text{ J/mol/K}$, estimated by Blanc et al. (2015). As discussed above, the solubility and thus $\Delta_f G^0$ at 25°C are higher than the values estimated based on the single measurement of Atkins et al. (1993). The calculated $\Delta_f H^\circ -5424 \pm 16 \text{ kJ/mol}$ is significantly higher than the $-5614 \pm 38 \text{ kJ/mol}$ obtained from the data reported in Ogordova et al. (2003) from high temperature calorimetry.

The solubility of natrolite increases with temperature (Figure 7B) and the values are roughly 4 log units lower than the one derived in Blanc et al. (2015). Using the $C_p^\circ = 359.2 \pm 0.7 \text{ J/mol/K}$ and $S^\circ = 359.7 \pm 1 \text{ J/mol/K}$ of Johnson et al. (1983), the measured increase of natrolite solubility as a function of temperature is described well. The $\Delta_f H^\circ$ calculated from $\Delta_f G^\circ$ and S° (Table 4) is with $-5728 \pm 10 \text{ kJ/mol}$ in good agreement with the $\Delta_f H^\circ = -5719 \pm 5 \text{ kJ/mol}$ measured by Johnson et al. (1983) and the $-5724 \pm 6 \text{ kJ/mol}$ measured by Wu et al. (2013).

Figure 7: Solubility products for A) zeolite P(Ca): $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4.5\text{H}_2\text{O} \rightleftharpoons \{\text{Ca}^{2+}\} \cdot \{\text{AlO}_2^-\}^2 \cdot \{\text{SiO}_2^0\}^2 \cdot \{\text{H}_2\text{O}^0\}^{4.5}$ and B) natrolite: $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O} \rightleftharpoons \{\text{Na}^+\}^2 \cdot \{\text{AlO}_2^-\}^2 \cdot \{\text{SiO}_2^0\}^3 \cdot \{\text{H}_2\text{O}^0\}^2$ calculated from the measured concentrations from the experiments containing albite as given in Table 6. For comparison, the solubility product calculated from concentrations measured after 1 month from undersaturation (Atkins et al., 1993: triangles) for zeolite P(Ca), the corresponding solubility products from the thermoddb database (Blanc et al., 2015: dashed lines, data in Table 5) and from the data derived in this paper (solid lines) using the data given in Table 4 are shown.

3.4 Thermodynamic modelling of albite reaction

In summary, it was found experimentally that roughly $6\pm 2\%$ of the albite had reacted within 3 years at room temperature and $20\pm 5\%$ at 50 and 80°C. Ettringite had completely reacted at 80°C, mostly at 50°C and only to a small extent at 20°C. This led to the formation of natrolite, zeolite P(Ca), anhydrite and possibly some C-S-H.

The expected changes due to the reaction of albite have been modelled using the derived data for zeolites in Table 4. At all temperature the reaction of albite was calculated to lead to the destabilisation of ettringite as exemplified for 50°C in Figure 8A, while natrolite, zeolite P and C-S-H are precipitating following the general reaction outlined in equation (7). It was calculated that at 20°C, 15% of albite would need to react to destabilise ettringite, 12% at 50°C and 8% at 80°C, as ettringite is more soluble at higher temperature (Lothenbach et al., 2008; Perkins and Palmer, 1999).

Temperature exerts some control over the amount of solids expected. At 20°C, somewhat more C-(N-A)-S-H and natrolite is expected. Above 70°C, higher quantities of zeolite P(Ca) were calculated to form (Figure 8C) and less natrolite, as natrolite is less stable at higher temperatures (Figure 7). Natrolite was calculated to be absent above 85°C. The maximum amount of albite which could react was calculated to be 18, 17 and 14% at 20, 50 and 80°C, respectively. The comparison with the reaction degree obtained by ^{29}Si MAS NMR (Figure 3) data indicates that the reaction degrees at 50 and 80°C ($20\pm 5\%$) were near the maximum reaction degree of albite, while at 20°C (observed reaction $6\pm 2\%$) equilibrium had not yet been reached within 3 years. At 50°C, however, the presence of a small amount of ettringite after 3 years and the formation of mainly zeolite P(Ca) but little natrolite indicated rather an albite reaction of only $\sim 10\%$ (Figure 8) than of $20\pm 5\%$ as observed by ^{29}Si MAS NMR. This could be either related to the error associated with the quantification of ^{29}Si MAS NMR data, to errors in the thermodynamic data or due to a slow dissolution and precipitation kinetic. Sensitivity analysis of the thermodynamic data showed that the solubility product of natrolite (-30.2 ± 1) derived in this study is limited by the stability of albite. An increase of the natrolite solubility by 1 log unit would suppress natrolite formation at 80°C, whereas a decrease by 1 log unit would enable the reac-

tion of all albite at 50 and 80°C. Based on the calculations, more natrolite could be expected to form with time both at 20°C and 50°C as the reaction of albite would proceed.

Figure 8B shows the effect of the reaction of albite on the concentrations. The reaction of albite from 0 to 10% was calculated to increase Na, Ca, Si and sulfate concentrations and to decrease the Al concentrations. A comparison with the changes observed as a function of time at 50°C (Table 6, Figure 6) shows in fact an increase of Na, Ca, Si and sulfate concentrations with time, while the Al concentrations decrease. The measured concentrations after 3 years would be consistent with a silica reaction of approximately 10%.

Figure 8: Composition of A) solid and B) liquid phase as a function of the reaction degree of albite at 50°C and C) effect of temperature on solid phases. Initially 2.4 g of albite, 0.2 g of C-S-H and 0.6 g of ettringite are present in 90 mL of solution as detailed in Table 2. Calculated using the thermodynamic data compiled in Table 4.

4. Zeolites formed from NaAlO_2 , SiO_2 and ettringite

4.1 Analysis of solid phases

In the 2nd series of experiment using starting materials of NaAlO_2 , silica fume and ettringite, only a fraction of the ettringite had reacted after 3 years at 20°C, most had reacted at 50°C and all at 80°C as visible in the TGA (Figure 9) and XRD (Figure 10) data. At 20°C and also at 50°C unreacted silica was observed by XRD with a characteristic broad hump at 20-30 2theta in the XRD pattern. The intensity of the XRD hump related to unreacted silica decreased with time. Deconvolution of the ^{29}Si MAS NMR data indicate that after 3 years 43% (± 8), 66% (± 10) and 83% (± 12) of the silica fume initially present had reacted at 20, 50 and 80°C, respectively (Figure 11). The actual reaction degree could be also somewhat lower as the long relaxation time of silica fume in the ^{29}Si MAS NMR can lead to an underestimation of unreacted SiO_2 . The NaAlO_2 initially present had reacted completely at

all three temperatures while minor amounts of $\text{Al}(\text{OH})_3$ seems to have formed at 20 and 50°C as indicated by the TGA (Figure 9) and XRD (Figure 10) data.

The zeolites formed are clearly different in this second set of experiments. After 3 years at 20 and 50°C, the formation of zeolite X ($\text{Na}_2\text{Al}_2\text{Si}_{2.5}\text{O}_9 \cdot 6.2\text{H}_2\text{O}$) was observed by XRD (Figure 10) and ^{29}Si MAS NMR (Figure 11). After 1 and 2 years at 80°C, chabazite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$) was detected and possibly poorly crystalline zeolite X. After 3 years at 80°C, however, zeolite Y ($\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 8\text{H}_2\text{O}$) and chabazite were present. The fraction of chabazite at 80°C increased with time (Figure 9A). The FTIR spectra (data not shown) tentatively indicated the formation of zeolites as a shift of the band at 1090 cm^{-1} related to amorphous SiO_2 to lower wavenumbers was observed consistent with the presence of faujasite (characteristic band at 1020 cm^{-1} ; Chukanov, 2013; Hincapie et al., 2005) and chabazite (main band at 1035 cm^{-1} ; Chukanov, 2013). The structure of chabazite is based on 6-membered rings. Zeolite X ($\text{Na}_2\text{Al}_2\text{Si}_{2.5}\text{O}_9 \cdot 6.2\text{H}_2\text{O}$) and zeolite Y ($\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 8\text{H}_2\text{O}$) are members of the faujasite group of zeolites, which are also composed of 6-membered rings and exhibit the most open framework of all natural zeolites. The chemistry of faujasite is rather variable, a water loss at 200°C is assigned to the water loss in the supercages, a second minor water loss at around 300°C has been related to more tightly bound water in the sodalite cage (Gottardi and Galli, 1985). These two water loss regions could be identified in the TGA data of the 20 and 50°C samples and in the 80°C sample after 1 year (Figure 9A, B). After 2 and 3 years, the faujasite signal was overlaid by the broad water loss signal of chabazite between 100 and 300°C (Gottardi and Galli, 1985; Neuhoﬀ and Wang, 2007). In addition, the ^{29}Si MAS NMR data in Figure 11 indicate tentatively the formation of C-S-H.

The high initial sodium and aluminium concentrations and the low initial availability of silica seems to have favoured initially the formation of zeolite X ($\text{Na}_2\text{Al}_2\text{Si}_{2.5}\text{O}_9 \cdot 6.2\text{H}_2\text{O}$) and as more silica reacted of zeolite Y ($\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 8\text{H}_2\text{O}$) over natrolite ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$), analcime ($\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$) or phillipsite ($\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16} \cdot 6\text{H}_2\text{O}$). The preferential formation of zeolite Y in-

stead of analcime, which has the same chemical composition but lower water content, was expected (Maldonado et al., 2013). Several authors have reported the formation of zeolite Y at lower temperature (Barth-Wirching and Holler, 1989; Gottardi and Galli, 1985; Wang et al., 2016). Only at temperatures $\geq 100^{\circ}\text{C}$, zeolite Y readily transforms into analcime (Li et al., 2013; Maldonado et al., 2013; Wang et al., 2010).

Figure 9: Thermogravimetric analyses of the samples containing initially NaAlO₂, SiO₂ and ettringite
 A) equilibrated for 1, 2, and 3 years at 80°C and B) equilibrated for 3 years at 20, 50 and 80°C.

Figure 10: XRD patterns of the samples containing initially NaAlO_2 , SiO_2 and ettringite equilibrated for 3 years at 20, 50 and 80°C. C: chabazite (pdf 034-0137), Cal: calcite, E: ettringite, Gib: gibbsite, X: zeolite X/faujasite (pdf 038-0237), Y: zeolite Y/faujasite (pdf 039-1380)

Figure 11: ^{29}Si MAS NMR spectra of the samples containing initially NaAlO_2 , SiO_2 and ettringite equilibrated for 3 years at 20, 50 and 80°C. C: chabazite (main signals -98 and -104 ppm: Lippmaa et al., 1981), C-S-H: calcium silicate hydrate: -83 and -86 ppm (L'Hôpital et al., 2016), X: zeolite X/faujasite (main signal at -84.7 and -89 ppm: Lippmaa et al., 1981; less intense signals at -94, -99 and -103 ppm), Y: zeolite Y/faujasite (main signal at -94.5 ppm, less intense signals at -89, -100 and -105 ppm are overlaid by chabazite: Lippmaa et al., 1981), unreacted SiO_2 at -110(Q^4) and at -100.9 ($\text{Q}^3\text{-OH}$) ppm (d'Espinose de Lacaillerie et al., 1995). Silica attributed to unreacted amorphous silica equals to 57±8% at 20°C, 34±10% at 50°C and 17±12% at 80°C.

4.2 Solution composition

The analysis of the pore solutions (Table 6, Figure 12) showed higher sodium, aluminium and silicon concentrations than in the samples where albite had been present as well as higher pH values. The

composition of the solutions at 20°C was dominated by sodium and aluminium from NaAlO₂ dissolution; calcium concentrations were low with approx. 0.1 mM. The presence of 5 mM sulfate and 0.6 mM Si indicates partial dissolution of ettringite and of the SiO₂ initially present. In fact the solutions were at 20°C undersaturated with respect to ettringite and amorphous SiO₂ (Table 7), consistent with the observed dissolution of these solids. The relatively high undersaturation with respect to silica at 20 and 50°C might be related to the high aluminium concentrations of 1 to 30 mM (Figure 8), as high aluminium concentrations inhibit SiO₂ dissolution (Bickmore et al., 2006). In agreement with the observation of aluminium hydroxide, the solutions were oversaturated with respect to gibbsite, initially also with respect to strätlingite (which was not observed by XRD or TGA) and were near saturation with respect to C-S-H (Table 7). The measured sodium concentrations were with 70 mM clearly lower than the 107 mM Na totally present (Table 3).

At 50 and 80°C higher sulfate concentrations were observed, which increased with time as ettringite dissolved (Figure 9). Lower sodium concentrations than at 20°C were observed, consistent with the presence of a higher quantity of zeolite X and zeolite Y at higher temperature (Figure 11). At 50°C silicon concentrations increased with time, while aluminium concentrations decreased. The solutions were undersaturated with respect to ettringite and silica consistent with the observed dissolution of both solids. At 80°C the solutions were undersaturated with respect to ettringite, strätlingite and gibbsite consistent with the absence of these solids.

The consumption of sodium is consistent with the formation of sodium containing zeolite such as zeolite X (Na₂Al₂Si_{2.5}O₉·6.2H₂O) according to equation (8). At 80°C higher silicon concentrations were observed than at 20 or 50°C as more silica had reacted, which explains the formation of the silica rich zeolite Y (Na₂Al₂Si₄O₉·8H₂O) instead of zeolite X according to equation (9):

Figure 12: Measured concentrations in samples containing initially NaAlO₂, SiO₂ and ettringite equilibrated for 1, 2 and 3 years at 20, 50 or 80°C. The lines indicate the total amount of sodium, calcium, sulfate and aluminium present in the experiments as summarized in Table 3. The total amount of silicon is with approx. 300 mM outside the scale.

Ettringite was the only source of calcium in the experiments and as discussed previously, the lower calcium than sulfate concentrations indicate the formation of calcium containing solids such as C-S-H or chabazite. Ettringite dissolution led in the presence of little SiO₂ to the formation of C-S-H and aluminium hydroxide according to equation (10). In the presence of more silicon, chabazite is expected to form as exemplified in equation (11).

The saturation indices calculated based on the thermodynamic data in Table 4 indicate that the solutions were clearly oversaturated with respect to zeolite P(Ca), scolecite, chabazite, analcime and natrolite at all temperatures. The significant oversaturation with respect to zeolite P(Ca) and natrolite (Table 7) indicates a kinetic hindrance of the formation of zeolite P(Ca) and natrolite under the experimental conditions used. It can be speculated that the low silicon and aluminium concentrations and the presence of albite in the first series of experiments enabled the nucleation of natrolite and zeolite P(Ca) on its surface, while the high pH values, aluminium and silicon concentrations in the experiments starting from NaAlO₂ and SiO₂ favoured the formation of faujasite and chabazite from strongly oversaturated solutions. In fact, Katović et al. (1989) observed a much faster nucleation and growth of zeolite X than of zeolite P. Both faujasite and chabazite remained stable for 3 years in our experiments even though the solutions were clearly oversaturated with respect to natrolite and zeolite P(Ca). Similarly, Barth-Wirsching and Holler (1989) showed that different precursor materials and the resulting different solution compositions affect the kind of zeolites formed. Zeolite formation is found to be dependent on the dominant cation type in solution, Si/Al ratio available in solution, temperature and also on the saturation state with respect to silica (Chipera and Apps, 2001).

4.3 Solubility of chabazite, zeolite Y and zeolite X

The measurements of the solution composition reported in Table 6 were used to calculate solubility products for chabazite, zeolite Y and zeolite X as shown in Figure 13 and in Table 8. The calculated solubility products could be influenced by the possible uptake of calcium in zeolites X and Y, as the exchange of sodium by calcium has been reported for both zeolite X and Y (Barrer et al., 1969; Gottardi and Galli, 1985). In zeolite Y monovalent Na⁺ is preferred over the bivalent Ca²⁺ (Barrer et al., 1968), while zeolite X shows a weak preference for Ca²⁺ over Na⁺ (Barrer et al., 1966). The low Ca/Na ratio of the solution (Ca/Na < 0.01) is expected to lead in all cases to the presence of mainly Na-zeolite X and Y. Also chabazite has been observed to take up other cations (Gottardi and Galli, 1985; Shim et al., 1999; Van Tendeloo et al., 2015). Ca-chabazite, is the most common form observed in nature and $\Delta_f H^\circ$ measurements indicate that Ca-chabazite could be more stable than Na-

exchanged chabazite (Ogordova et al., 2004). To which extent this influences the calculated solubility products, however, remains unclear.

Chabazite was clearly observed only at 80°C, while the ion activity products calculated at 50°C increased with time towards the expected solubility of chabazite as shown in Figure 13A. No other experimental solubility measurements are available in literature to the best of our knowledge. The C_p° and S° had been determined by Belitsky et al. (1982) as $C_p^\circ = 629$ J/mol/K for $\text{Ca}_{0.83}\text{Na}_{0.12}\text{K}_{0.05}\text{Al}_{1.9}\text{Si}_{4.13}\text{O}_{12} \cdot 6.24\text{H}_2\text{O}$ (resulting in 617 J/mol/K for the ideal composition $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$ using the data compiled in Table 4) and as $S^\circ = 597$ J/mol/K (581 J/mol/K for $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$). These values were used to describe the solubility of chabazite as a function of temperature (Figure 13A) resulting in $\Delta_f H^\circ$ of -7774 ± 12 kJ/mol (Table 4). The $\Delta_f H^\circ$ obtained is comparable to the -7790 kJ/mol derived from the measurements in Ogordova et al. (2004), but clearly higher than the value of -7961 kJ/mol derived by Shim et al. (1999) from measurements of dehydrated chabazite or the value of -7826 kJ/mol estimated by Mathieu and Vieillard (2010). The huge variation of reported $\Delta_f H^\circ$ values could be related to the compositional variability of chabazite; Shim et al. (1999) reported a large range of $\Delta_f H^\circ$ values for Ca-chabazite ranging from -7846 to -8582 kJ/mol depending on its aluminium to silica ratio.

Also zeolite Y ($\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 8\text{H}_2\text{O}$) was only observed at 80°C. Its S° and C_p° were calculated based on the data of chabazite, SiO_2 , CaO , Na_2O and zeolitic H_2O as no measured data were available and as both the structures of zeolite Y and zeolite X are based on 6-membered rings similar to the structure of chabazite. The resulting $\Delta_f H^\circ$ of -8327 kJ/mol is lower than the $\Delta_f H^\circ$ of -8160 kJ/mol obtained by Turner et al. (2008) based on high temperature calorimetry or the -8210 kJ/mol derived from the measurements of dehydrated faujasite by Petrovic and Navrotsky (1997).

Zeolite X ($\text{Na}_2\text{Al}_2\text{Si}_{2.5}\text{O}_9 \cdot 6.2\text{H}_2\text{O}$) had formed at 20 and 50°C and possibly at early times also at 80°C. A few solubility data at higher temperature are available in the literature. Šefčík and McCormick (1999) calculated from undersaturation experiments carried out in 2 M NaOH solutions a solubility product of -18.8 ± 0.4 at 80°C after an equilibration time of 3 hours based on the data of

Čizmek et al. (1991), using a different thermodynamic database than in the present work. Using the experimental data given in Čizmek et al. (1991), solubility products from -21.6 to -21.3 in the temperature range 65 to 80°C were obtained in this study (Figure 13C). Katović et al. (1989) observed the precipitation of zeolite X from oversaturation and based on their measurements a solubility product of -19.2 ± 0.4 at 20°C and of -17.3 ± 0.4 at 80°C was calculated, which is comparable to our data. The reason for the observed big difference between undersaturation experiments (Čizmek et al., 1991) and the oversaturation experiments (Katović et al. (1989) and the present work) remains unclear. It could be due to a number of factors including, but not limited to, different crystallinity of the commercial product used in the undersaturation experiments, to slow equilibration or due other factors. In any case, the calculated solubility products for zeolite X increased with temperature; the increase is well described by using the S° and C_p° data obtained from chabazite, CaO, Na₂O and zeolitic H₂O. The calculated $\Delta_f H^\circ$ value of zeolite X (-6447 kJ/mol) is again lower than the $\Delta_f H^\circ$ of -6157 kJ/mol derived from the measurements of dehydrated faujasite by Petrovic and Navrotsky (1997).

Figure 13: Solubility products for A) chabazite: $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O} \rightleftharpoons \{\text{Ca}^{2+}\} \cdot \{\text{AlO}_2^-\}^2 \cdot \{\text{SiO}_2^0\}^4 \cdot \{\text{H}_2\text{O}^0\}^6$, B) zeolite Y(Na): $\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 8\text{H}_2\text{O} \rightleftharpoons \{\text{Na}^+\}^2 \cdot \{\text{AlO}_2^-\}^2 \cdot \{\text{SiO}_2^0\}^4 \cdot \{\text{H}_2\text{O}^0\}^8$; for comparison the solubility of analcime $\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O} \rightleftharpoons \{\text{Na}^+\}^2 \cdot \{\text{AlO}_2^-\}^2 \cdot \{\text{SiO}_2^0\}^4 \cdot \{\text{H}_2\text{O}^0\}^2$, is also plotted using the data from Arthur et al. (2011), Blanc et al. (2015) and Neuhoﬀ et al. (2004) and C) zeolite X(Na): $\text{Na}_2\text{Al}_2\text{Si}_{2.5}\text{O}_9 \cdot 6.2\text{H}_2\text{O} \rightleftharpoons \{\text{Na}^+\}^2 \cdot \{\text{AlO}_2^-\}^2 \cdot \{\text{SiO}_2^0\}^{2.5} \cdot \{\text{H}_2\text{O}^0\}^6$ calculated from the measured concentrations from the experiments containing Na_2AlO_2 and SiO_2 as given in Table 6. For comparison, the solubility product calculated based on concentrations measured from undersaturation (Cizmek et al., 1991: triangles; Sefcik et al., 1999: square) and from oversaturation (Katovic et al., 1989: diamonds) for zeolite X are shown. The solubility products from the data derived in this paper (Table 4) are indicated by the bold lines.

4.4 Thermodynamic modelling of silica fume reaction

The thermodynamic data for zeolites in Table 4 were used to model the expected changes due to the reaction of silica fume as shown in Figure 14A and B for the sample reacted at 50°C; the formation of natrolite and zeolite P(Ca) was suppressed in the calculations. At all temperature the reaction of SiO_2 was calculated to lead to the destabilisation of ettringite (or monosulfate which was stabilised at

50 and 80°C), while initially strätlingite and later C-N-A-S-H gel plus gibbsite precipitated according to equation (10).

The formation of zeolite X was calculated to occur between 20 and 70% of the silica reaction, which agrees with the presence of zeolite X observed at 20°C (43±12% silica reaction, see Figure 11) and 50°C (65±4% silica reaction). At more than 70% silica reaction the formation of chabazite instead of C-N-A-S-H gel and of zeolite Y instead of zeolite X was predicted, in agreement with the observations at 80°C (83±12% silica reaction). At 50°C, the complete reaction of ettringite and the formation of chabazite is expected based on the observed degree of silica reaction (66±10%) but the experimental data show that some ettringite was still present after 3 years and whether any chabazite formed is unclear (Figure 9-Figure 11). These discrepancies might be related to the observed slow dissolution kinetics of ettringite, to the error associated with the quantification of amorphous silica by ²⁹Si MAS NMR data or with the thermodynamic data. The solubility of chabazite is constrained by the solubility of C-S-H gel; a destabilisation of chabazite by 1 log unit would result in the stabilisation of C-S-H instead and in the absence of chabazite at high silica reaction degree. Also the solubility of zeolite Y is closely related to the stability of chabazite and amorphous SiO₂: an increase of the solubility of zeolite Y by 1 log unit would result in the absence of zeolite Y at high silica reaction degree and would limit the maximum silica reaction to 50%.

Figure 14B shows the calculated concentrations at 50°C as a function of the reaction degree of silica. High sodium, sulfate and silicon concentrations were calculated at SiO₂ reaction > 20%. An increase of silicon, sulfate and calcium concentrations is expected as the reaction of silica proceeds, while aluminium and hydroxide are expected to decrease (Figure 14b) which agrees with the changes observed between 1 and 3 years at 50°C (Figure 12). The measured concentrations after 3 years at 50°C (Figure 12) agree relatively well with the concentrations expected at 40% SiO₂ reacted, i.e. before the precipitation of chabazite (Figure 14B).

At maximum reaction of the silica (approx. 70%), somewhat more chabazite and less zeolite Y and C-S-H were predicted (Figure 14C). At all temperatures the formation of zeolite Y instead of zeolite X is expected, although this is associated with some uncertainty as relative small changes in the solu-

bility product would lead to the preference of zeolite X at 20 and 50°C over zeolite Y. This small difference in stability resulting in a small Gibbs free energy gain for the formation of zeolite Y was probably responsible for the slow reaction progress observed at 20 and 50°C, where equilibrium had not yet been reached after 3 years.

Figure 14: Composition of A) solid and B) liquid phase as a function of the reaction degree of silica fume at 50°C and C) effect of temperature on solid phases. Initially 1.6 g of SiO₂, 0.75 g of NaAlO₂ and 0.6 g of ettringite are present in 90 mL of solution as detailed in Table 2. Calculated using the thermodynamic data given in Table 4.

5. Conclusion

The batch experiments showed that zeolitic phases could form in the interaction zones between rock-forming minerals and leached or low-pH cements, respectively, represented by ettringite and C-S-H. The interaction of albite (NaAlSi₃O₈) with ettringite and C-S-H or with ettringite only led to high calcium and low silicon and sodium concentrations in the aqueous solutions and resulted in the formation of a zeolite with a high Ca/Si ratio (zeolite P(Ca): Ca₂Al₂Si₂O₈·4.5H₂O) and low Na/Si ratio (natrolite: Na₂Al₂Si₃O₁₀·2H₂O) at 50 and 80°C, in agreement with the phases predicted by thermodynamic modelling of this system. No clear indication of zeolite formation was observed within 3 years at 20°C, although minor quantities might were present.

Synthesis of zeolites from NaAlO₂, silica fume and ettringite resulted initially in higher sodium and aluminium concentrations while silicon concentrations increased with time and at higher temperature

where more silica fume reaction had occurred. This caused at 20 and 50°C the precipitation of zeolite X ($\text{Na}_2\text{Al}_2\text{Si}_{2.5}\text{O}_9 \cdot 6.2\text{H}_2\text{O}$), C-N-A-S-H gel plus gibbsite. At 80°C, where most of the silica had reacted after 3 years, the formation of more silica rich zeolites, chabazite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$) and zeolite Y ($\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 8\text{H}_2\text{O}$) instead of C-N-A-S-H gel and zeolite X, was observed in agreement with thermodynamic modelling (if the formation of natrolite and zeolite P(Ca) was excluded). Also at 20 and 50°C a similar sequence can be expected with time as the reaction degree of silica increases.

The solutions of a second set of experiments starting from NaAlO_2 and silica fume were even after 3 years significantly oversaturated with respect to zeolite P(Ca) and natrolite although their formation was not observed. The high pH values, aluminium and silicon concentrations in the experiments starting from NaAlO_2 and SiO_2 favoured the formation of chabazite, zeolite X, and zeolite Y, whose nucleation and growth was faster.

Solubility products for the zeolite P(Ca), natrolite, chabazite, zeolite X, and zeolite Y have been calculated from the measured concentrations. The solubility of natrolite, chabazite, zeolite X and zeolite Y increases with temperature, while for zeolite P(Ca) the solubility remains relatively stable. Comparison with the few solubility measurements available in the literature shows a high variability probably related to the structural variability (Si/Al) and the uptake of different cations within the structure of the zeolites. Comparison with thermodynamic data derived from $\Delta_f H^\circ$ and S° data only, shows significant differences in the resulting solubilities and signposts the need for systematic experimental determination of the solubility of the different zeolites. In fact, the derivation of thermodynamic properties for zeolites has been and still is hindered by the variable composition of cations (Ca, Na, K), Al/Si ratios, H_2O contents and structural variability of zeolites. This is further complicated by the commonly encountered slow reaction kinetics, mineral transformations with temperature variation and poorly characterized solids in terms of impurities, order/disorder, crystallite size, and degree of crystallinity.

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