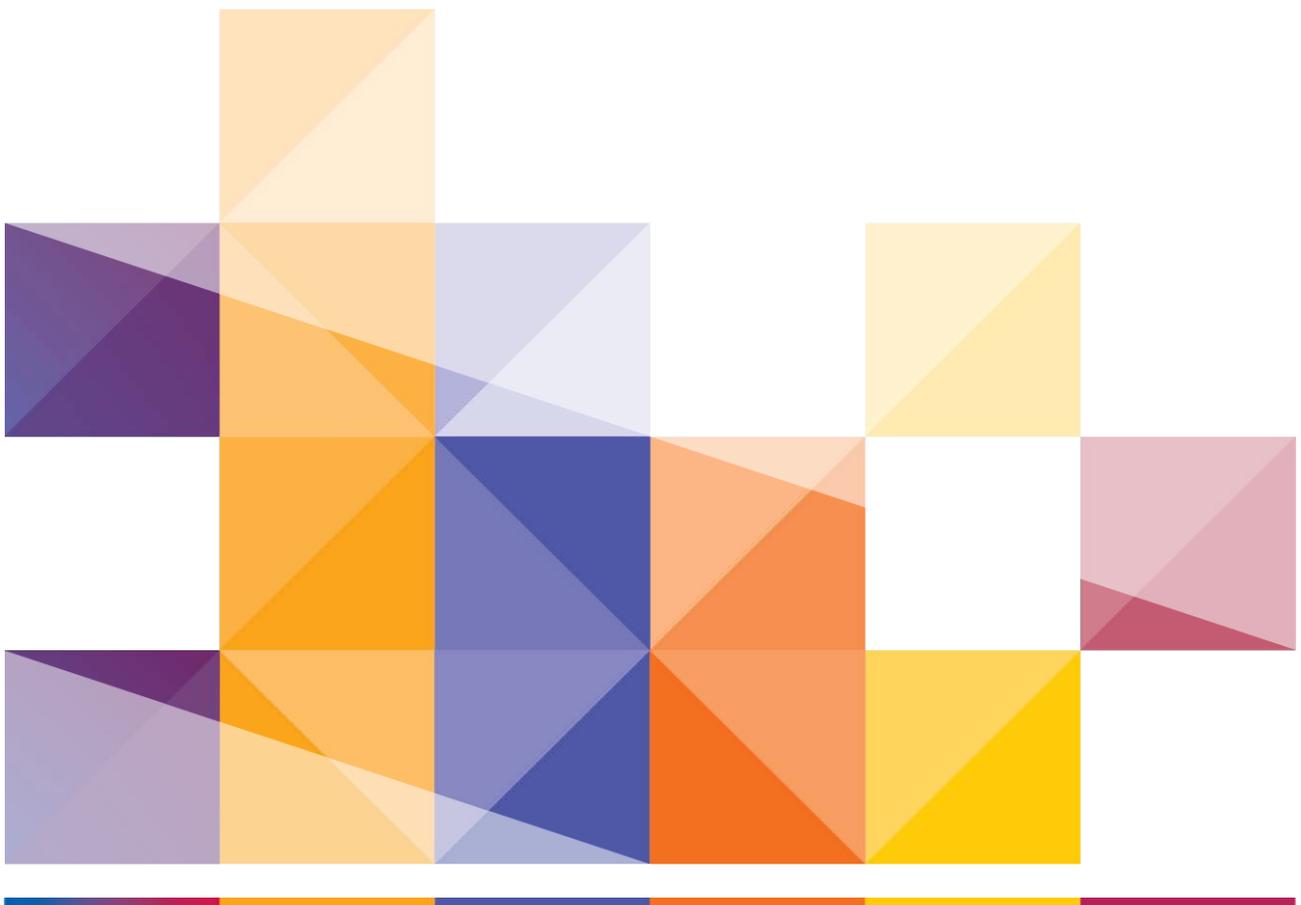


ThermoChimie

Technical report

Zeolite documentation



The ThermoChimie database was first developed in 1995 by Andra, the French national radioactive waste management agency. They have since been joined by Radioactive Waste Management (RWM) from the UK, and ONDRAF/NIRAS from Belgium.

ThermoChimie provides an accurate and consistent set of data specifically chosen for use in modelling the behaviour of radionuclides in waste packages, engineered barriers, and both the near surface and deep geosphere. The database can be used to model the speciation and solubility of a wide range of stable and radioactive elements, organics, and solid phases including cements, clay minerals and degradation products (such as zeolites). The database is suitable for use within the range of conditions expected in both near-surface and geological disposal facilities: pH 6-14, ionic strength up to 5M, Eh within the stability fields of water, and temperatures from 15 to 80°C.

ThermoChimie is intended for use across the radioactive waste management community, to support repository performance assessment, research and development activities and decision making. To maximise their utility the data are therefore provided in formats suitable for use with common geochemical modelling codes. The database can be viewed and downloaded from the project website: <https://www.thermochimie-tdb.com/>, where additional information and supporting documents are also available.

In the context of an underground storage, zeolites are a group of important phases, which includes most of the transition phases between cement and the clayey barrier. Indeed, zeolites are the first alteration products of clays in a hyperalkaline environment. Gaucher et al. (2004) shown that the contact with cement based materials induced transformation in both sides of the cement / clay interface, producing zeolites. Those latter, as 3D framework silicates, are indeed stabilized in alkaline environments and they were found in many experiments where clay minerals were put in contact with alkaline solution (Gaucher and Blanc, 2006). Within the framework of the ThermoChimie project, much efforts has been put to fill up the gaps in thermodynamic databases (TDB) (Blanc et al. 2012; Giffaut et al. 2014), especially for clay minerals, cement minerals and zeolites. The selection of thermodynamic properties for zeolites was achieved in 2008-2009 (Blanc, 2009; Blanc and Vieillard, 2008) and it was published in 2015 (Blanc et al., 2015). The work establishes the consistency within the selections for clay, zeolites and cement phases. Tentative work in that line were recently achieved for the Cemdata18 database (Ma and Lothenbach, 2020a; Ma et al., 2020), which now includes high solubility zeolites and clay phases from ThermoChimie TDB. With respect to recent solubility determinations, the present selection focuses on terminal solubility phases, that is minerals which display the highest stability, consistently with long period of equilibrium time. In addition, this selection is limited to the phases likely to play a role during cement/clay interaction in deep disposal, i.e. for temperatures below 100°C.

Instead of providing an extensive discussion for each of the zeolites, the selection is described in detail for two examples, analcime and mordenite. Thereafter, the properties gathered for the other phases are reported with specific comments and referrals to the documented selection (Blanc, 2009).



1. Zeolites in waste disposal concepts

Zeolites belong to the extensive mineral family of tectosilicates. They display a three-dimensional network of silica tetrahedra SiO_4^{4-} , partially substituted by aluminum with a variable Si/Al ratio. The charge deficit is compensated by hydrated alkali and alkaline earth cations, located within "cages" formed by the network of tetrahedrons. The nature of the hydrated compensation cation depends on the composition of the aqueous solution. Zeolites exhibit an exchange capacity about two times higher than that of smectites (Fridriksson et al., 2004).

From the studies by Giret et al. (1992) and Fridriksson et al. (2001), we can classify the different zeolites according to their formation temperature:

- T <50°C: Phillipsite – Chabazite - Thomsonite
- T <70°C: Analcime
- T <90°C: Scolecite - Mesolite; Epistilbite
- T <110°C: Stilbite, Heulandite, Mordenite
- T <150°C: Laumontite.

All those phases were considered in this selection, apart from epistilbite and thomsonite because of a lack of measured thermodynamic constants in the literature. The review by Gaucher and Blanc (2006) also confirms the presence of analcime, phillipsite and chabazite as products of smectite alteration by alkaline solutions. In addition to the previous minerals, natrolite was observed by Coombs et al. (1959), associated with phases from the phillipsite – chabazite series, in cases of meteoritic low temperature degradation in ancient Roman masonry examples. The same authors also determined the presence of clinoptilolite associated with analcime among the hydrothermal alteration products of a volcanic rock. Natrolite and clinoptilolite were added to the list of the minerals investigated.

A last point has to be underlined. Few experimental or field studies can be used for verification purposes because mineralogical determination often relies on XRD analyses only. This very useful technique brings quite few information concerning the chemical composition of the zeolite, which is a difficulty, given the composition variability of such minerals. This leads to strong uncertainties concerning the thermodynamic properties and prevent direct verification from field determinations.

2. Context of the selection

Zeolite thermodynamic data selection is specifically hindered by the large composition domain for these phases. This concerns the various type of zeolites but, even within a given zeolite group, the composition domain may be wide and strongly impacts the thermodynamic properties and the overall stability of the phase. Blanc et al. (2015) have provided an illustration of this for analcime. The variability in composition strongly limits the comparisons and global assessment of thermodynamic properties. In addition, few experimental or field studies can be used for verification purposes. A typical problem arises when mineralogical determinations are based on XRD alone, as it does not provide precise enough information for chemical composition and degree of hydration.

The thermodynamic properties of zeolites have been the subject of numerous experimental studies either using calorimetry or solution equilibria (Johnson et al. 1982, 1983, 1985, 1991, 1992 ; Belitsky et al. 1982 ; Hemingway and Robie 1984 ; Donahoe et al. 1990 ; Kiseleva et al. 1996, 2001 ; Shim et al. 1999 ; Drebushchak et al. 2000 ; Ogorodova et al. 2003 ; Neuhoff et al. 2004 ; Neuhoff and Wang 2007). However, problems still arise with the completeness of the thermodynamic datasets, especially with properties being measured on minerals displaying slightly different compositions. Only five phases among the 48 natural zeolites have a consistent set of thermodynamic properties, measured by calorimetry on the same sample (Johnson et al. 1982, 1983, 1985, 1991, 1992).

More recent work investigated the solubility of high solubility (synthetic) zeolites, like the experiments performed by Ma and Lothenbach (2020a) and Ma and Lothenbach (2020b)). Indeed, the solubility of those synthetic phases had been the topic for a large suite of publications:

- Lothenbach et al. (2017), Ma and Lothenbach (2020a) and Ma and Lothenbach (2020b): synthesis and solubilities at different temperatures for 22 zeolites, synthetic and natural phases of short period of equilibration times,
- Van Tendeloo (2016), Wey et al. (1980), Petrovic et al. (1993), Qiu et al. (2006), Xiong (2013) and Wu and Navrotsky (2016) : thermodynamic properties for synthetic zeolites Si, A, Y, X, involving calorimetric measurements.

The work listed before are underlying an additional difficulty in selecting thermodynamic data for high solubility phases. On that regards, the work proposed by Dimitrijevic et al. (2006) and Abdullah et al. (2019) clearly indicates that increasing the equilibration time and/or the temperature leads to the appearance of new zeolite types or even to the decomposition of the mineral itself (into kaolinite and quartz for Dimitrijevic et al., 2006). In the present work, the focus was specifically put on the lowest solubility phases and calorimetric measurements, thus avoiding the uncertainty coming from kinetically dependent solubility determinations.

For such low solubility zeolites, few critical selections have been proposed so far for these minerals. The selection by Bowers and Burns (1990) is substantially based on estimates. Savage (1998) proposed a compilation from five different sources, still including a significant proportion of estimated data. Chipera and Aps (2001) have made a selection for calcic zeolites only. As an improvement, the present work proposes a selection of thermodynamic data for 22 zeolites. The selection is performed using direct measurements (calorimetry) and following guidelines described by Giffaut et al. (2014). In order to complete the thermodynamic datasets, when necessary, missing heat capacities were estimated using the model developed by Vieillard (2010).

3. Examples of detailed selection

3.1. ANALCIME

Analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), a sodic zeolite, is among the most common zeolites. Its composition domain is rather narrow: according to Neuhoff et al. (2004), its number of Si atoms ranges from 1.8 to 2.3 for six oxygen atoms. A considerable amount of work has been published concerning the measurement of its thermodynamic properties by calorimetry means. Johnson et al. (1982) provided the first complete thermodynamic dataset for hydrated and anhydrous analcime.

3.1.1. Thermodynamic properties from the literature

The enthalpy of formation was directly measured by dissolution calorimetry by several authors:

- using HF dissolution calorimetry, Johnson et al. (1982) obtained -3305.8 kJ/mol for the composition $(\text{NaAl})_{0.96}\text{Si}_{2.04}\text{O}_6 \cdot 1.02\text{H}_2\text{O}$ and -2979.10 kJ/mol for the anhydrous phase
- using high temperature drop calorimetry into lead borate, Ogorodova et al. (1996) found -3294.1 kJ/mol for the composition $(\text{NaAl})_{0.95}\text{Si}_{2.05}\text{O}_6 \cdot 1.03\text{H}_2\text{O}$

Finally and using the same technique as Johnson et al. (1982), Neuhoff et al. (2004) acquired five values ranging between -3319.5 and -3298.7 kJ/mol for five compositions, from 1.98 to 2.05 Si atoms per six oxygen atoms. Neuhoff et al. (2004) were able to explain these differences by considering the variations in compositions and in the Si/Al ordering state.

For entropy, the only direct measurement of the parameter is given by Johnson et al. (1982): 226.75 and 171.71 J/mol.K for the hydrated and anhydrous phases, respectively. This measurement could be extended to different Si/Al ratios by Neuhoff et al. (2004) by using a solid solution model. They also provide configurational entropies for various compositions. For hydrated and dehydrated analcime, the $C_p(T)$ function was directly measured by both Johnson et al. (1982) and Wang (2006), for the respective compositions $(\text{NaAl})_{0.96}\text{Si}_{2.04}\text{O}_6 \cdot 1.02\text{H}_2\text{O}$ and $(\text{NaAl})_{0.97}\text{Si}_{2.03}\text{O}_6 \cdot 1.02\text{H}_2\text{O}$. For the anhydrous phase, the functions are in close agreement. The heat capacity measured by Wang (2006) for hydrated analcime increases exponentially as temperature increases. This unusual behavior leads us to prefer the function measured by Johnson et al. (1982).

3.1.2. Synthesis from Neuhoff et al. (2004) and verification

Analcime is especially favorable for thermodynamic properties selection since Neuhoff et al. (2004) had already fully reviewed its thermodynamic properties, depending on its composition. In that case, the verification step is limited to verifying the solubility calculated by using the model proposed by Neuhoff et al. (2004). Two series of experiments could be gathered from the literature, at room temperature by Murphy et al. (1996) and from 25 to 300°C by Wilkin and Barnes (1998), for the respective compositions $\text{Na}_{1.02}\text{Al}_{1.02}\text{Si}_{1.98}\text{O}_6 \cdot 0.99\text{H}_2\text{O}$ and $\text{Na}_{0.99}\text{Al}_{0.99}\text{Si}_{2.01}\text{O}_6 \cdot \text{H}_2\text{O}$. In addition, the Murphy et al. (1996) solutions were equilibrated from both under- and supersaturation. The $\text{Log}K(T)$ function was calculated using the Neuhoff et al. (2004) model, according to the composition of the samples retained by Murphy et al. (1996) and Wilkin and Barnes (1998). These are reported in Figure 1 and display good agreement with experimental results. From this figure we can see the consequences of composition variations in terms of $\text{Log}K$: a variation of 0.06Na modifies the equilibrium constant by four orders of magnitude at room temperature.

A recent determination by Ma and Lothenbach (2020a) is to be discussed in this section. The authors have synthesized analcime by hydrothermal treatment of a solution during 24 hours, at 200°C. The resulting solid displays a Si/Al ratio 1.91, which is especially low, compared with the composition gathered by Neuhoff et al. (2004). The duration of the equilibration experiment was 1 month, while it last up to 13 months for Wilkin and Barnes (1998) and 31 months for Murphy et al. (1996) experiments. Finally, the ionic activity product (IAP) was calculated for the idealized Si/Al = 2, even if the actual solid composition corresponded to a lower Si/Al ratio. They calculated an equilibrium constant 5 orders of magnitude higher than the value selected in this selection for Si/Al = 2.01. Such a difference can be explained by the short equilibration time. Their calculated equilibrium constant is also affected by the approximation they rely on: to calculate an IAP based with stoichiometric coefficient from an idealized formula (Si/Al = 2), different from that of the actual mineral (Si/Al = 1.91). Indeed and as reported previously, a modification of this atomic ratio by 0.06 units induces a modification of the equilibrium constant by 4 orders of magnitude (see Figure 1). The conclusion is that the extensive work carried out by Ma and Lothenbach (2020a) is suitable for our purposes. It would be very interesting, though, when considering higher solubility zeolites, of which type can precipitate at rather low temperature (and reaction times), in cementitious environments.

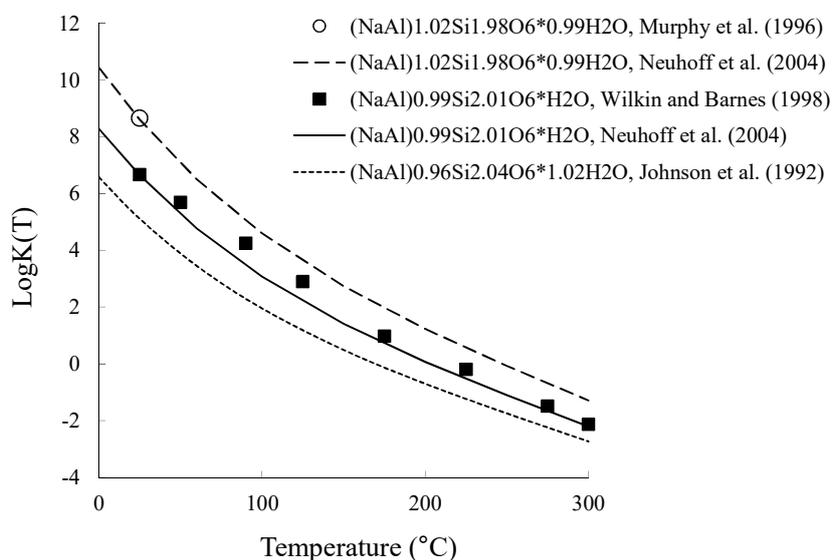


Figure 1 - Equilibrium constant of analcime as a function of temperature

3.2. MORDENITE

Mordenite is a rather common zeolite, which typically forms in a hydrothermal setting (Coombs et al., 1959). Its chemical composition is close to the following ideal formula $(Ca,Na,K)AlSi_5O_{12} \cdot 3.5H_2O$, which indicates a strong variability in the type of charge compensating cation.

The selection for mordenite thermodynamic properties is based on two main works. First, Johnson et al. (1992) obtained, by calorimetry, a full set of thermodynamic parameters for a sample with the composition $Ca_{0.29}Na_{0.31}Al_{0.94}Si_{5.06}O_{12} \cdot 3.47H_2O$, for both hydrated and dehydrated states. In addition, Benning et al. (2000) carried out solution experiments, from 25 to 325°C for a mineral displaying the composition $Ca_{0.52}Al_{1.03}Si_{4.97}O_{12} \cdot 3.1H_2O$. To extract thermodynamic parameters, we applied the following process:

- Cp(T) is estimated using the Vieillard (2010) method and ΔH_f^0 and S^0 are adjusted using solubility data from Benning et al. (2000)

- only experiments at $T > 90^\circ\text{C}$ are considered, lower temperatures being suspected to present deviation from thermodynamic equilibrium given the equilibration period (Blanc, 2009).

The results of the refinement are given in Figure 6 for mordenites. From the Johnson et al. (1992) data, the mordenite LogK(T) function was calculated with and without correcting the ΔH_f^0 by $-3.51 \text{ kJ/mol}(\text{SiO}_2)$, as recommended by the authors. The agreement with mordenite(Ca) is better without considering the correction. Neuhoff et al. (2004) also came to the same conclusion for analcime. This silica correction is not applied in this work. The thermodynamic properties and the calculation process are summarized in Table 1. The thermodynamic constants selected for the other zeolite phases are reported in Table 2 and the references are given, for ΔH_f^0 , S^0 and Cp respectively in Table 3.

Table 1 - Calculation of thermodynamic constants for mordenite

Property	Value
$\text{Ca}_{0.52}\text{Al}_{1.03}\text{Si}_{4.97}\text{O}_{12} \cdot 3.1\text{H}_2\text{O}$	
S° : Estimated from Vieillard (2010)	$S^\circ = 493.57 \text{ J/mol.K}$
$C_p(298.15 \text{ K})$: Estimated from Vieillard (2010)	$C_p(298.15 \text{ K}) = 443.11 \text{ J/mol.K}$
ΔH_f^0 : Adjusted from Benning et al. (2001) experiments	$\Delta H_f^0 = -6651.87 \text{ kJ/mol}$
$\text{Ca}_{0.29}\text{Na}_{0.31}\text{Al}_{0.94}\text{Si}_{5.06}\text{O}_{12} \cdot 3.47\text{H}_2\text{O}$	
S° and $C_p(298.15 \text{ K})$: Measured by Johnson et al. (1992)	$S^\circ = 486.54 \pm 0.97 \text{ J/mol.K}$ $C_p(298.15 \text{ K}) = 484.33 \pm 0.97 \text{ J/mol.K}$
ΔH_f^0 : Measured by Johnson et al. (1992), without considering the silica correction	$\Delta H_f^0 = -6738.4 \pm 4.5 \text{ kJ/mol}$

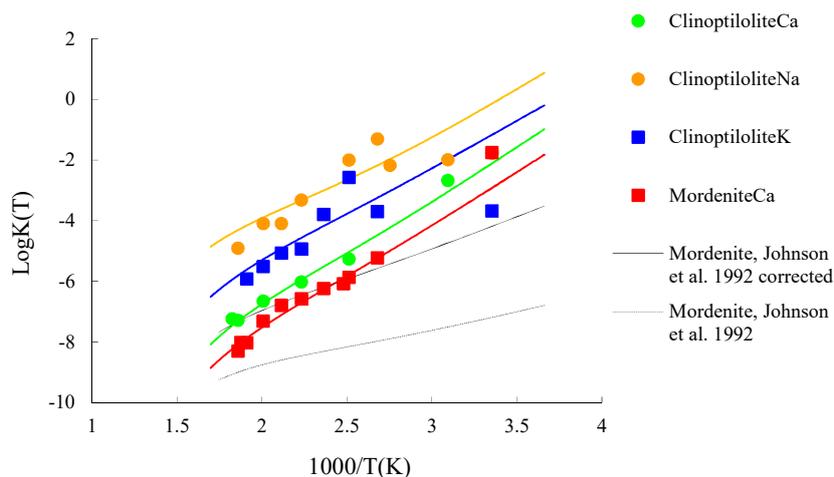


Figure 2 - Refinement of the thermodynamic constants for mordenite and clinoptilolite zeolites, from solution experiments by Wilkin and Barnes (1998) and Benning et al. (2000).

Table 2 - Thermodynamic properties of zeolites (adapted from Blanc et al. (2015)).

Mineral	Formula	LogK	ΔH_f^0	\pm	S^0	\pm	V^0	Cp (298.15 K)
		(298.15 K) ⁽¹⁾	kJ/mol	kJ/mol	J/mol.K	J/mol.K	cm ³ /mol	J/mol.K
Analcime	Na _{0.99} Al _{0.99} Si _{2.01} O ₆ *H ₂ O	6.64	-3308.00	3.3	231.08	0.23	97.09	212.38
Phillipsite(K)	KAISi ₃ O ₈ *3H ₂ O	0.04	-4841.86		390.57	1.20	148.97	351.41
Phillipsite(Na)	NaAISi ₃ O ₈ *3H ₂ O	1.45	-4811.66		382.53	1.20	149.69	330.96
Phillipsite(Ca)	Ca _{0.5} AlSi ₃ O ₈ *3H ₂ O	2.32	-4824.02		342.38	1.20	151.15	321.86
Natrolite	Na ₂ (Al ₂ Si ₃)O ₁₀ *2H ₂ O	19.31	-5718.60	5.5	359.73	0.72	169.20	359.23
Scolecite	CaAl ₂ Si ₃ O ₁₀ *3H ₂ O	16.63	-6049.00	5.5	367.42	0.73	172.30	382.81
Stilbite	NaCa ₂ (Al ₅ Si ₁₃)O ₃₆ *16H ₂ O	3.74	-22579.71		1622.56		664.70	1697.03
Stellerite	Ca ₂ Al ₄ Si ₁₄ O ₃₆ *14H ₂ O	6.90	-21656.24		1604.73		666.50	1573.96
Mordenite(Ca)	Ca _{0.515} Al _{1.03} Si _{4.97} O ₁₂ *3.1H ₂ O	-2.92	-6662.19		493.57		209.80	443.11
Mordenite	Ca _{0.289} Na _{0.362} Al _{0.94} Si _{5.06} O ₁₂ *3.468H ₂ O	-4.18	-6738.44	4.5	486.54	0.97	212.40	484.45
Clinoptilolite(Ca)	Ca _{0.55} (Si _{4.9} Al _{1.1})O ₁₂ *3.9H ₂ O	-2.35	-6923.33		498.99		209.66	481.02
Clinoptilolite(Na)	Na _{1.1} (Si _{4.9} Al _{1.1})O ₁₂ *3.5H ₂ O	-0.09	-6782.36		502.72		214.78	470.38
Clinoptilolite(K)	K _{1.1} (Si _{4.9} Al _{1.1})O ₁₂ *2.7H ₂ O	-1.23	-6568.41		507.66		210.73	454.31
Merlinoite(Na)	Na _{1.04} Al _{1.04} Si _{1.96} O ₆ *2.27H ₂ O	10.54	-3681.43		283.43		114.04	305.68
Merlinoite(K)	K _{1.04} Al _{1.04} Si _{1.96} O ₆ *1.69H ₂ O	11.59	-3537.60		270.48		112.91	249.65
Zeolite P(Ca) ⁽²⁾	Ca ₂ Al ₄ Si ₄ O ₁₆ *9H ₂ O	45.15	-11129.11		975.40		305.70	872.11
Wairakite	CaAl ₂ Si ₄ O ₁₂ *2H ₂ O	14.42	-6646.70	6.3	400.70		193.56	401.04
Laumontite	CaAl ₂ Si ₄ O ₁₂ *4H ₂ O	11.66	-7251.00	5.6	483.80	2.10	207.53	542.23
Heulandite(Ca)	Ca _{1.07} Al _{2.14} Si _{6.86} O ₁₈ *6.17H ₂ O	2.46	-10667.20	8.6	700.94		322.06	719.05
Heulandite(Na)	Na _{2.14} Al _{2.14} Si _{6.86} O ₁₈ *6.17H ₂ O	2.80	-10612.85	8.6	838.29		325.00	719.05
Gismondine	Ca ₂ Al ₄ Si ₄ O ₁₆ *9H ₂ O	38.96	-11179.80		742.24		315.07	869.26
Chabazite	CaAl ₂ Si ₄ O ₁₂ *6H ₂ O	11.51	-7826.44		614.00		251.16	681.19

⁽¹⁾ In the equilibrium reactions, the following primary species are used: K⁺, Na⁺, Ca⁺², H₄SiO₄, Al⁺³, H⁺ and H₂O

⁽²⁾ Tentative values (see text for additional explanations, LogK(298.15 K) uncertainty assessed to ± 2 log units)

Table 3 - References for the selection of the thermodynamic properties of zeolites.

Mineral	LogK (298.15 K)	ΔH_f^0 reference	S^0 reference	Cp (298.15 K) reference	Specific comment
Analcime		Neuhoff et al. (2004)	Neuhoff et al. (2004)	Neuhoff et al. (2004)	
Phillipsite(K/Na/Ca)	Hess (1966)		Hemingway and Robie (1984)	Hemingway and Robie (1984)	Properties extrapolated to Na and Ca pure end-members after Shibue (1981)
Natrolite		Johnson et al. (1983)	Johnson et al. (1983)	Johnson et al. (1983)	
Scolecite		Johnson et al. (1983)	Johnson et al. (1983)	Johnson et al. (1983)	
Stilbite		Fridriksson et al. (2001)	Fridriksson et al. (2001)	Fridriksson et al. (2001)	
Stellerite		Fridriksson et al. (2001)	Fridriksson et al. (2001)	Fridriksson et al. (2001)	
Mordenite(Ca)	Extracted from Benning et al (2000)		Vieillard (2010) estimate	Vieillard (2010) estimate	
Mordenite(J)		Johnson et al. (1992)	Johnson et al. (1992)	Johnson et al. (1992)	Without considering corrections for silica contribution by Johnson et al. (1992)
Clinoptilolite(Ca)	Extracted from Benning et al (2000)		Extracted from Benning et al (2000)	Vieillard (2010) estimate	
Clinoptilolite(Na/K)	Extracted from Wilkin and Barnes (1998)		Extracted from Wilkin and Barnes (1998)	Vieillard (2010) estimate	
Merlinoite(Na/K)		After Donahoe et al. (1990)	After Donahoe et al. (1990)	After Donahoe et al. (1990)	End members properties extracted from linear relations with composition
Zeolite P(Ca)		Tentative values deduced from phase relation considerations (see text)		Vieillard (2010) estimate	Phase introduced as an alternative to gismondine
Wairakite		Kiseleva et al. (1996)	Kiseleva et al. (1996)	Neuhoff and Wang (2007)	(*)
Laumontite		Kiseleva et al. (1996)	Kiseleva et al. (1996)	Kiseleva et al. (1996)	(*)
Heulandite(Ca/Na)		Kiseleva et al. (2001)	Drebushchak et al. (2000)	Drebushchak et al. (2000)	Properties extrapolated to pure end-members after Fridriksson et al. (2004)
Gismondine	Hess (1966)		Vieillard (2010) estimate	Vieillard (2010) estimate	The selection is uncertain (see text)
Chabazite		Shim et al. (1999)	Belitsky et al. (1982)	Belitsky et al. (1982)	(*)

(*) For chabazite, heulandite, laumontite and wairakite, the phase transition temperatures were checked by Blanc (2009) with respect to the experimental results obtained by Liou et al. (1971), Zeng and Liou (1982) and Cho et al. (1987).

4. Other zeolites

The thermodynamic constants selected for the other zeolite phases are reported in Table 2, together with the values calculated by prediction models. For each phase, the whole selection process is described in Blanc (2009). When necessary, specific comments are given as follows:

Phillipsite

LogK₂₉₈ is issued from a calculation process from Hess (1966) that states for equilibrium with microcline in saline lakes.

Scolecite and natrolite

For both phases, a complete set of measurements is provided by Johnson et al. (1983) and corrected by Johnson et al. (1992). This latter correction is not retained in the present selection, as explained earlier.

Stilbite and stellerite

Thermodynamic functions have been measured and reviewed by Fridriksson et al. (2001).

Clinoptilolite

A full set of thermodynamic parameters is given by Howell et al. (. Unfortunately, the natural sample chosen contains Ba and Sr which poses problems for future modeling. Instead, we have extracted thermodynamic functions from Benning et al. (2000) and Wilkin and Barnes (1998) solution experiments.

Merlinoite

For this phase, the selection holds on a single experimental work from Donahoe et al. (1990).

Zeolite CaP

Because of a lack of experimental data, LogK₂₉₈ is inferred from phase relation in cementitious systems (see Blanc 2009 and Blanc et al. (2015)).

Wairakite

The thermodynamic functions are taken from calorimetric measurements by Kiseleva et al. (1996).

Laumontite

The selection is based on the direct measurement performed by Kiseleva et al. (1996) and Paukov and Fursenko (2000).

Heulandite

The selection is based on the experimental work of Drebuschak et al. (2000) and Kiseleva et al. (2001). For Na, K and Ca pure end members, exchange properties are extracted from the work of Fridriksson et al. (2004).

Gismondine

The selection is rather uncertain for this phase. Enthalpy of formation measured by Ogorodova et al. (2003) overestimates the stability of the mineral. Instead, LogK₂₉₈ is calculated using a process similar to the method proposed by Hess (1966). Entropy and heat capacity are calculated using Vieillard (2010) model.

Chabazite

The thermodynamic functions are directly measured by Shim et al. (1999) and Belitsky et al. (1982) on a mineral displaying the same composition in both studies.

As can be seen in Table 2, most of the C_{p298} are estimated with the model developed by Vieillard (2010). Moreover, for chabazite, heulandite, laumontite and wairakite, the phase transition temperature could be checked by calculating their $\text{LogK}(T)$ function with respect to experimental results from Liou (1971), Zeng and Liou (1982) and Cho et al. (1987).

5. Estimating zeolites Entropies and heat capacities

As can be seen from Table 3, thermodynamic datasets have to be completed, in some cases, for entropy and heat capacity. In spite of recent developments concerning estimate models for zeolites (Arthur et al., 2011; Ma et al., 2020; Voskov, 2020), entropy nor heat capacity estimate was the topic of such developments. In that regard, the methods developed consistently by Vieillard and Mathieu (2009), Mathieu and Vieillard (2010) and Vieillard (2010) provide an accurate estimated for these thermodynamic functions.

The S° and $C_p(T)$ estimation model from Vieillard (2010) work uses 35 measured entropy values and 21 data sets for heat capacity, measured at constant pressure. The model is based on the polyhedral approach. An improvement was proposed by (1) using the thermodynamic properties of silica polymorphs with a crystalline structure are close to that of zeolite, and (2) determining the thermodynamic parameters of the zeolitic water obtained by difference between anhydrous and hydrated zeolites. Finally, Vieillard (2010) could propose a new set of entropies and Maier-Kelley coefficients a , b and c for the heat capacity function, for the various oxides which compose zeolites. With the new sets of values, predictions errors decrease to less than 3% and less than 4% for the entropy and the specific heat, respectively. The comparison with other models available for entropy (Holland, 1989; Robinson and Haas, 1983) and for heat capacity (Berman and Brown, 1985; Robinson and Haas, 1983) tested by Vieillard (2010) showed errors reaching 5% for the entropy and 10% for the heat capacity. This is the reason why we selected Vieillard (2010) model over other available works.

6. Verification and consistency with clay and cement minerals

The verification of the selected datasets is carried out by establishing predominance diagrams in chemical sub-systems of interest (K_2O - Na_2O - CaO - SiO_2 - Al_2O_3 - H_2O). Consistency with clay and cement minerals is checked similarly. Especially for clay minerals, the component MgO is added to the verification system.

6.1. VERIFICATION OF THE ZEOLITES THERMODYNAMIC DATASETS

Verification by drawing activity diagrams is performed for chemical systems including the components K_2O , Na_2O and CaO . The corresponding diagrams are calculated at room temperature and they are displayed in Figure 3. Globally, the clay minerals' stability domains are located in low alkaline activity areas consistently. Phillipsite and clinoptilolite appear as the main Na- and K-bearing zeolite phases. This is consistent with Savage et al. (2007) review, who report these phases as usual, especially when volcanic rocks are altered by brines, in salt lakes areas. Natrolite and analcime also appear in equilibrium with solutions at low dissolved silica activities. The size of the stability domain of analcime strongly increases with temperature, reaching $\log(a_{H_4SiO_4}) = -3.5$ at $150^\circ C$, which is consistent with the observations reported for clay mineral alkaline-alteration experiments in the review proposed by Gaucher and Blanc (2006).

6.2. CONSISTENCY WITH CLAY AND CEMENT MINERALS

The stability domains of zeolites allows to check the consistency of phase relations between the clays, zeolites and cement minerals because zeolites are intermediates between clays and cement minerals when considering the alteration of the latter by neutral pH solutions (Savage et al., 2007; Gaucher and Blanc 2006).

The compositions of the main minerals in the chemical system K_2O - Na_2O - CaO - SiO_2 - Al_2O_3 - H_2O are plotted in Figure 4, depending on their respective amount of silica and alkaline/alkaline earth elements. From the review by Savage et al. (2007), it appears that:

- the alkaline compositions are related to minerals that equilibrate with high pH solution, for instance portlandite or C-S-H1.6,
- compositions rich in silica are more likely to equilibrate with basic to neutral pH.

Based on composition only, the minerals in Figure 4 are located along a general trend where their alkalinity decreases as silica increased. This tendency could be associated with the alteration of cementitious materials by lower pH solutions, as can be found in clayey formations (7.0 to 7.5 for the Callovo-Oxfordian formation, see Gaucher et al. (2009)).

To check if this tendency can be reproduced by calculating the stability domains of the main minerals in the CaO - MgO - SiO_2 - Al_2O_3 - H_2O systems, predominance diagrams are calculated using the present selection and they displayed in Figure 5.

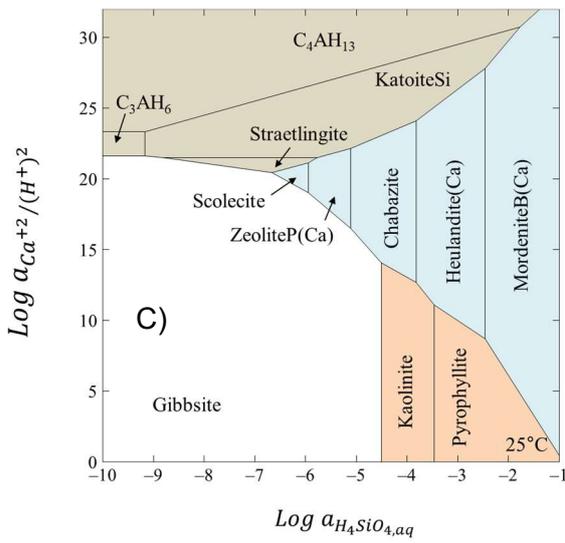
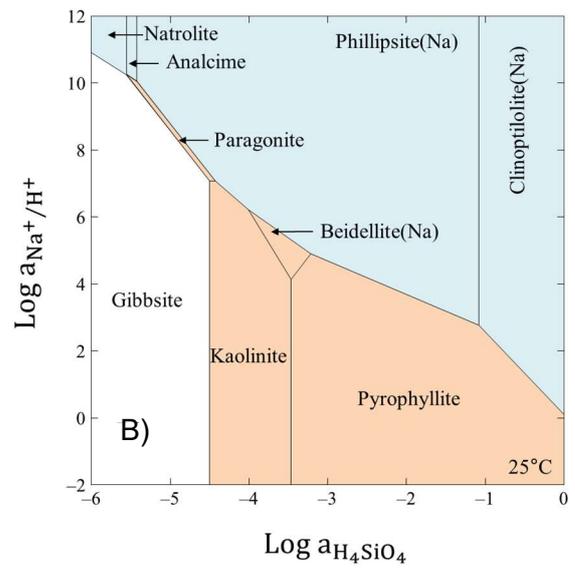
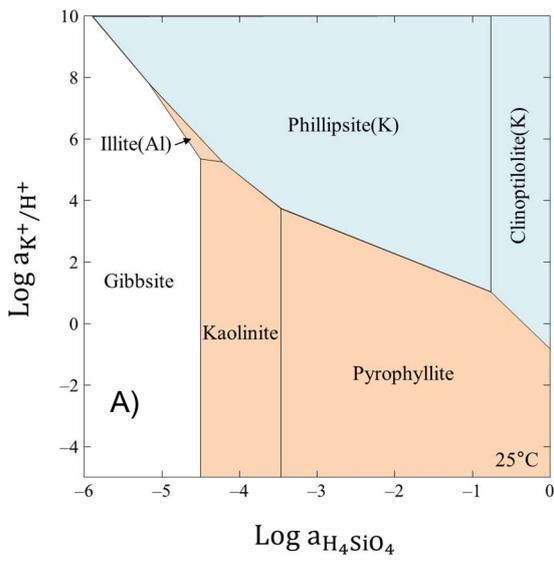
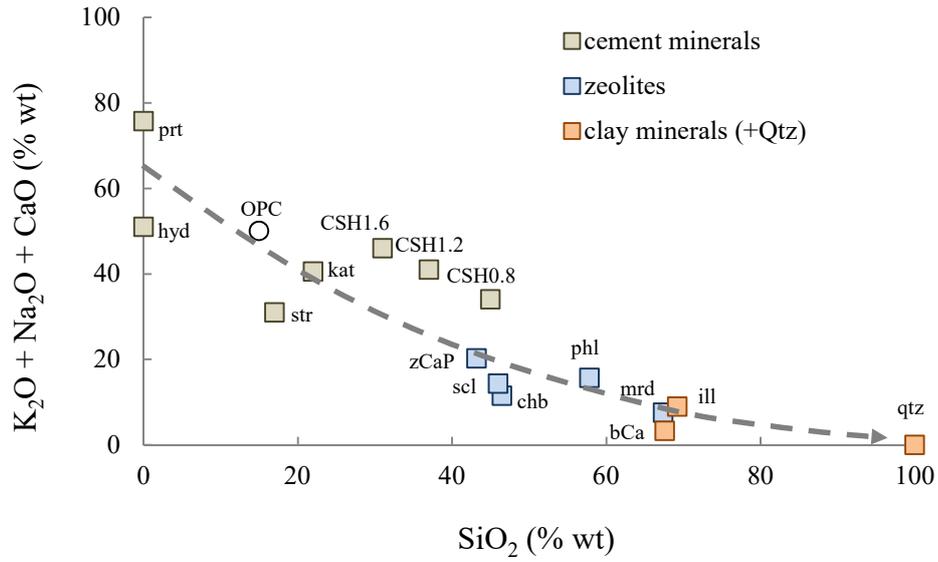


Figure 3 - Predominance diagrams at 25°C: A) the $\text{K}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system; B) the $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system; C) the $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$.



prt: portlandite; hyd: hydrogarnet; OPC: ordinary Portland cement; kat: katoite; str: straetlingite; zCaP: zeolite P(Ca); scl: scolecite; chb: chabazite; phl: phillipsite; mrđ: mordenite; bCa: beidellite(Ca); ill: illite; qtz: quartz.

Figure 4 - Composition of the minerals in the $K_2O-Na_2O-CaO-SiO_2-Al_2O_3-H_2O$ chemical system.

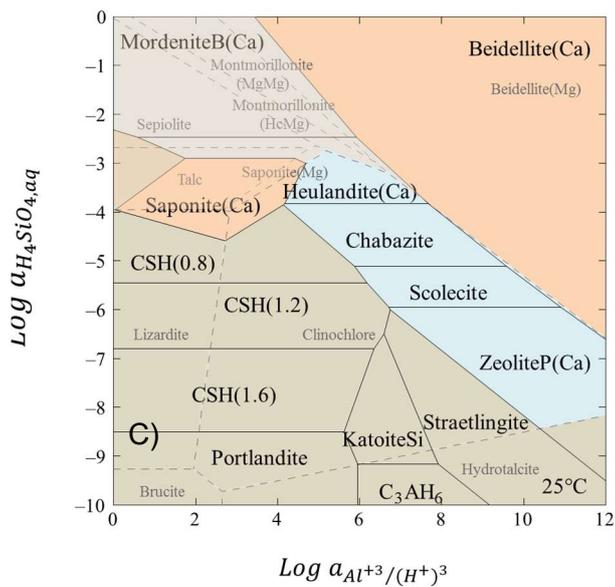
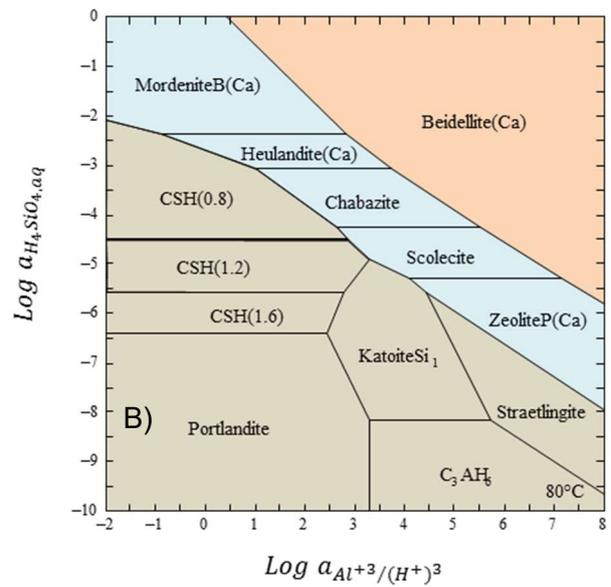
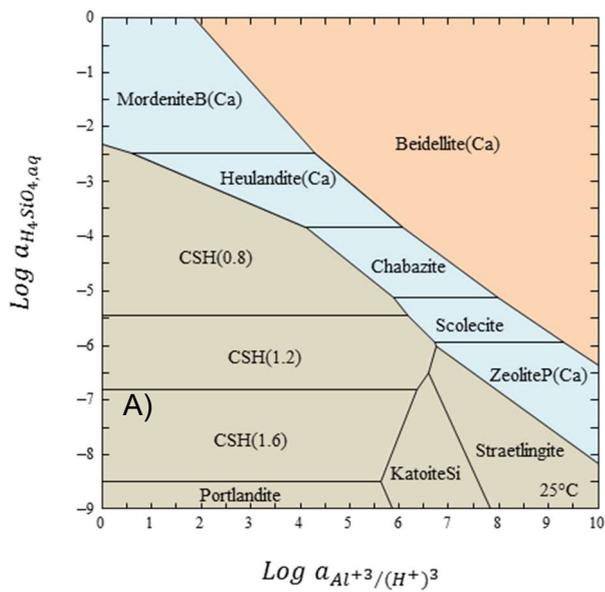


Figure 5 - Predominance diagrams in the CaO-SiO₂-Al₂O₃-H₂O chemical system. A) At 25°C, displaying the erroneous gismondine stability field; B) At 80°C, displaying the zeolite P(Ca) stability field; C) At 25°C, displaying the zeolite P(Ca) stability field; D) At 25°C, with zeolite P(Ca) and saturated with Mg (the stability fields of the Mg-bearing minerals are indicated by dashed lines).

Indeed, phase relations from Figure 5A to C are consistent the mineral sequence displayed in Figure 4:

- The succession from CSH(1.6) to CSH(0.8) in Figure 5A corresponds to increasing silica activity, consistent with the trend displayed in Figure 4;
- The stability domains of the C-S-H phases are limited by zeolites displaying higher Si/Al ratios as the silica activity increases, consistently with Figure 4 and in agreement with the alteration sequences in salt lakes reported by Savage et al. (2007);
- The arrow in Figure 4 ends with clay minerals in the high silica domain. In Figure 5A and B, beidellite(Ca) actually occupies the highest silica activity domain. This is even clearer in Figure 5C where the presence of magnesium allows montmorillonites, saponites and talc to appear. All of these occupy the upper, acidic part of the diagram, consistently with mineral compositions displayed in Figure 4.

6.3. INFLUENCE OF DISSOLUTION AND PRECIPITATION RATES

Globally, Blanc et al. (2015) have shown that natural analcime and clinoptilolite dissolution rate is close to that of smectite. This indicates that, for natural zeolites, the duration of the equilibration experiment should be similar. The order of magnitude for clay minerals at room temperature is at least 1 year for clay minerals (Gaboreau et al., 2020). This also implies that the appearance of zeolites in cementitious materials, from precipitation, is dependent on kinetic factors like time and temperature.

The appearance of zeolites have been a matter of debate in the deep disposal context (Dauzères, 2010; DeWindt et al., 2004; Savage, 2013; Shao et al., 2013). The present selection is clearly adapted to long-term calculations, with duration consistent with zeolite precipitation, even at low temperatures. For example, in the case of Searles Lake (California), the precipitation phillipsite and merlinoite, from the alteration of volcanic ashes, occurs between 10,000 and 100,000 years (Savage et al., 2007).

7. Conclusion

The selection of thermodynamic properties for zeolites focuses on phases which may potentially play a role during the cement/clay interaction, in the context of long-term deep disposal. The verification is carried out using predominance diagrams. The consistency between the three groups of minerals is also checked by drawing similar diagrams. A global agreement is found except for gismondine, which was finally discarded from the selection, and phillipsite(Na) of which stability domain partially overlaps that of analcime.

Experimental data are lacking in order to address more accurately the stability domains of phillipsite, chabazite and gismondine, which are among the phases of interest. The introduction of new datasets, from short duration experiments must be discussed regarding for the influence of kinetics on the equilibrium achievement and regarding the application concerned.

Still, given the state of knowledge and the amount of available data, the present study is providing a consistent selection of thermodynamic parameters for natural zeolites.

8. References

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