ZEOLITES

Among the minerals involved in the cement/clay interaction context, zeolites are a group of important phases, which group most of the transition phases between cement and the clayey barrier. Indeed, zeolites are the first products of weathering of clays in a hyperalcaline environment. Gaucher and Blanc (2006) have reviewed the alkaline alteration experiments for clay minerals. Some zeolite phases appear more or less systematically among the reaction products like: phillipsite, chabazite, analcime, in addition to C-S-H phases. The actual nature of zeolite and C-S-H were shown to depend especially on kinetic factors (time, temperature) and on the nature of the alkaline solution. At the cement/clay interface, zeolites can play a major role in the porosity clogging because of the high molar volume of those hydrated phases. In addition, Savage et al; (2007) indicate that cement alteration produces, within the context of deep disposal, zeolites, with a ratio Al/Si that decreases as the alteration proceeds and the pH decreases. However, the hierarchy of secondary minerals of zeolitic nature is extremely difficult to observe and is very sensitive to the chemical and physical factors of primary minerals and the fluids accompanying them. The selection of thermodynamic properties can take advantage of an extensive set of calorimetric measurements carried on natural zeolites in years 1990-2000. The present document represents an effort in selecting the thermodynamic properties of the zeolites of interest within the framework of deep disposal.

1.   Global overview on zeolite stability

Zeolites form an extensive family of minerals. The selection in this document is limited to the phases likely to play a role during the cement/clay interaction in a deep storage, i.e. for temperatures below 150 ° C.

1.1   Brief structural description

Zeolites are part of the largest family of tectosilicates, i.e. that they display a three-dimensional network of silica tetrahedra SiO_4^{-4}. These tetrahedra are partially substituted by aluminum and the charge is compensated by hydrated alkali-alkaline earth cations, located within "cages" formed by the network of tetrahedrons. It is important to note that a zeolite has a variable Si/Al ratio. Moreover, the nature of the compensation cation depends on the composition of the aqueous solution. Finally, the hydration state depends not only the Si/Al ratio but also on the nature of the compensation cation, the relative humidity, pressure and temperature conditions. The hydrated cations are connected to the aqueous solutions and zeolites do exhibit an important exchange capacity about two to three times that of smectites.

1.2   Zeolites phase relations with respect to temperature

The studies from Giret et al. (1992) and Fridriksson et al. (2001) help in selecting the phases of interest:

- T <50 ° C: Phillipsite - Chabazite-Thomsonite (+ formules structurales)

- T <70 ° C: Analcime

- T <90 ° C: Scolecite - Mesolite; Epistilbite

- T <110 ° C: Stilbite, Heulandite, Mordenite

- T <150 ° C: Laumontite.

We have discarded epistilbite and thomsonite from this selection, lacking of measured thermodynamic constants. According to Coombs et al. (1959), the natrolite, together with phases from the serie phillipsite - chabazite, could occur during the low temperature degradation of Roman masonry and clinoptilolite is often associated with analcime in hydrothermally altered volcanic rocks. Gaucher and Blanc (2006) confirm the preceding list of zeolites in the cement/clay interaction context.

In addition, Gaucher and Blanc (2006) have reviewed a set of clay alteration experiments under alkaline conditions. The zeolites which appear almost systematically among final reaction products are: analcime, phillipsite and chabazite. This confirms the importance of the low temperature zeolites in the processes we are interested in.

A last point has to be underlined. Few experimental or field studies can be used for verification purposes. The problem is that thermodynamic properties do apply only to phases of determined compositions. Plain XRD determinations only give the nature of the phase. Punctual analyses are required in order to determine the chemical composition (Fridriksson et al., 2001) and are often not performed, including the amount of bounded water.

1.3   Solubility models

To date, few works have tried to bring some consistency between phase relations within the zeolite family of minerals. Most of the papers published about zeolite stability deal with a single phase, rarely more than three, i.e.:

- Bowers and Burns (1990), for clinoptilolite, wairakite, laumontite, chabazite, phillipsite, mordenite, scolecite, epistilbite, heulandite, stilbite, mesolite, natrolite

- La Iglesia et al. (1991), for chabazite, phillipsite and analcime

- Chipera and Apps (2001) for wairakite, laumontite, heulandite, leonhardite.

The first two groups of authors rely only on estimation methods, phase relations being thereafter verified against field data. Only Chipera and Apps (2001) rely on measured thermodynamic properties and experimental reaction data. However, they propose 5 to 6 sets of thermodynamic properties for each mineral. To date, no solubility model completely meet the needs of ANDRA.

1.4   SELECTION PROCEDURE

The selection of thermodynamic properties is focused on the collection of direct and traceable measurements. Internal calculations are performed by using the properties already selected within the framework of the Thermochimie project. Additionally, the selection is proceeded according to the following guidelines:

- when possible, we avoid fitting LogK(T) functions, as well as averaging equilibrium constants. The aim is to avoid producing new and perhaps confusing data

- when possible, LogK(T) function are calculated by using calorimetric data (and/or estimates) and compared to the results of solution equilibria in order to perform a verification involving different experimental technics

- solution equilibria results are selected according to the electroneutrality condition, the duration of the experiment, the analysis of final solid products and the experimental protocol

- equilibrium constants extracted from solution equilibria are recalculated by using the Thermochimie database

- the selection is finally verified by drawing activity diagrams involving the minerals of interest in the chemical sub systems of concern.

1.5   Predictive models for the properties of formation.

In most of cases the selection for zeolites is based on direct measurements. This situation is completely different than the clay mineral cases where no direct measurement is available for the phases of interest (illite, smectite, vermiculite, …) apart from the measurement performed within the framework of the Thermochimie project. In addition, it is necessary, for clay minerals, to provided the thermodynamic properties of theoretical end members because a mineral like smectite can not display a single, fixed composition. For zeolites, compositions are variable but they are more accurately addressed knowing the nature of the phase because composition domains are less wide. Models can be used for providing data when no other source is available.

In the present case, predictive models are also of use for verification purposes. Since the constraints for verification are lacking, to compare the data from the selection with estimates is a way to discuss the reliability of our choices.

1.6 Main gaps to be filled

Except for phillipsite and gismondine, some calorimetric measurements are available for the phases of interest. But they may not apply to the same compositions (in terms of chemical elements or/and hydration water amounts). Only 5 phases among the 48 natural zeolites have a consistent set of thermodynamic properties, thanks in particular to the work of Johnson and co-workers (1982 to 1992). This applies of course only to a given composition for phases that exhibit extensive composition ranges.

In the present work, either by gathering information from different literature sources or by using estimates, we are trying to complete the thermodynamic data set in a consistent way. The main gap to be filled would rather be the lack of verification cases. We choose to overcome this issue by:

- Investigating zeolite phase relations with respect to literature observations by drawing phase diagrams

- Comparing the selected dataset with respect to estimates.

This cannot replace actual analyses from a well defined verification study but it may at least allow us to discard the main errors from the proposed selection.

2. Data collection and acquisition

Instead of providing an extensive discussion for each of the zeolites, there follows a full discussion concerning analcime, as an example, showing the way we have proceeded. Thereafter, the properties gathered for the other phases will be reported into a single table (Table 1), with specific comments when required.

2.1 Analcime

Analcime $NaAlSi_2O_6:H_2O$ is a particularly widespread mineral at surface's earth and the most common zeolite. A part from the other zeolites, its composition field is rather limited: according to Neuhoff et al. (2004), the number of Si ranges from 1.8 to 2.3 for 6 oxygens. In addition, this phase is sodic only.

2.1.1 Analcime: Available thermodynamic data

A considerable amount of work has been devoted to analcime thermodynamic properties. Johnson et al. (1982) have provided the first complete thermodynamic dataset for hydrated and anhydrous analcime. Those values have then been corrected by Johnson et al. (1992) for the formation enthalpy.

2.1.1.1 Formation enthalpy

It had been directly measured by dissolution calorimetry by several authors:

- using HF dissolution calorimetry, Johnson et al. (1982), then corrected by Johnson et al. (1992) obtained –3305.8 kJ/mol for the composition $(NaAl)_{0.96}Si_{2.04}O_6:1.02H_2O$ and -2979.10 kJ/mol for the anhydrous phase,

- using high temperature drop calorimetry into lead borate, Ogorodova et al. (1995) found -3294.1 kJ/mol for the composition $(NaAl)_{0.95}Si_{2.05}O_6:1.03H_2O$

- finally, using the same technique than Johnson et al. (1982), Neuhoff et al. (2004) acquired five values between -3319.5 and –3298.7 kJ/mol for five composition ranging from 1.98 to 2.05 Si per 6 oxygens.

Neuhoff et al. (2004) were able to explain those differences by considering variations in compositions and in Si,Al state order, meaning that experimental uncertainties are of minor importance there.

2.1.1.2 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 phase, respectively. This is extended to different Si/Al ratio by Neuhoff et al. (2004) thanks to a solid solution model. They also provide configurational entropies for various compositions.

2.1.1.3 Heat capacity

For hydrated and dehydrated analcime, the $Cp°(T)$ function had been directly measured by both Johnson et al. (1982) and Wang (2006), for the respective compositions $(NaAl)_{0.96}Si_{2.04}O_6 : 1.02H_2O$ et $(NaAl)_{0.97}Si_{2.03}O_6 \cdot : 1.02H_2O$. For the anhydrous phase, the functions overlap. This is partly the case for the hydrated phases, except that the functions split as temperature increases. The heat capacity measured by Wang (2006) then increases exponentially. This odd behavior leads us to rather select the functions acquired by Johnson et al. (1982).

2.1.1.4 Equilibrium constants

This is a rare fact for zeolite minerals, two series of experiments have been performed at room temperature by Murphy et al. (1996) and with variable temperature by Wilkins et Barnes (1998), for the respective compositions $Na_{1.02}Al_{1.02}Si_{1.98}O_6 : 0.99H_2O$ and $Na_{0.99}Al_{0.99}Si_{2.01}O_6 : H_2O$. In addition, Murphy et al. (1996) solutions are equilibrated from both under and super saturation.

2.1.2 Synthesis from Neuhoff et al. (2004)

The analcime case is especially favorable for data selection since a full review had already been done concerning its thermodynamic properties by Neuhoff et al. (2004). In addition, the authors have developed a solid solution model and semi empirical relation that allow to predict the thermodynamic parameter values as a function of composition.

Finally the analcime case presents the difficulties that come along with the thermodynamic data selection for zeolites. The only consistent set for a single composition is measured by Johnson et al. (1982, 1922). But more recent works have also been performed to date. In addition, how to compare values acquired for different compositions and how to assess the selected values? The work of Neuhoff et al. (2004) provides extensive answers for analcime but the question has to be answered for each zeolite phase of interest.

2.1.3 Selection and verification

Taking advantage of Wilkin and Barnes (1999) and Murphy et al. (1996) experiments, we choose to verify the selection against their solubility results. This implies to select thermodynamic constants consistent with the analcime composition used by those authors. This can be achieved by using the models and semi empirical relation provided by Neuhoff et al. (2004). Those relations take into account all the previous measurement, including Johnson et al. (1982, 1992) studies. LogK (T) functions are calculated, based on Neuhoff et al. (2004) work, for the composition used in the solubility experiments. The $Cp°(T)$ function used in all case is that measured by Johnson et al. (1982). LogK(T) are reported in Figure 1, together with experimental equilibrium constants. A good agreement is found with experimental data, which confirms our selection. We also retain the composition used by Wilkin and Barnes (1998) because this extends the verification from 25 to 300°C.

Figure 1 also allows realizing the consequences of composition variations in terms of LogK: a variation of 0.06Na modifies by 4 magnitude orders the equilibrium constant at room temperature.
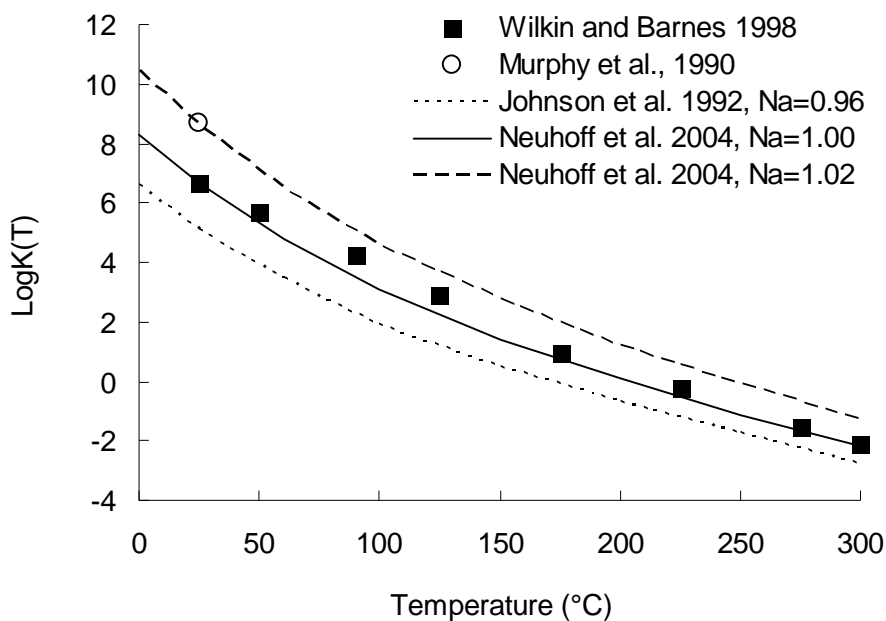
Figure 1   *Analcime LogK(T) function*

2.2   Other zeolites

The thermodynamic constants selected for the other zeolite phases are reported in Table 1, together with the values calculated by prediction models. For each phase, the whole selection process is described in Blanc (2009) and is not fully described into the present document. When necessary, specific comments are given as follows:

Phillipsite

Log K298 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)

Stilbite and stellerite

Thermodynamic function reviewed by Fridriksson et al. (2001)

Mordenite

A complete thermodynamic dataset is given by Johnson et al. (1992). However the LogK(T) function calculated from these data is not compatible with Benning et al. (2000) and Wilkin and Barnes (1998) solution experiments. Constants extracted from Benning et al. (2000) are finally selected.

Clinoptilolite

A full set of thermodynamic parameters is given by Howell et al. (1991). 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, LogK 298 is inferred from phase relation in cementitious systems

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 Drebushchak et al. (2000) and Kiseleva et al. (2001). For pure end members, exchange properties are extracted from the work of Fridriksson et al. (2004).

Gismondine

The selection is rather uncertain for this phase. LogK298 is calculated using a calculation process close to those developed by Hess (1966).

Chabazite

The thermodynamic functions are directly measured by Shim et al. (1999) and Belitsky et al. (2001) on a mineral displaying the same composition in both studies.

Additional details for selection are given in Blanc (2009). As can be seen on Table 1, most of the Cp298 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 LogK(T) function with respect to experimental results from Liou et al. (1971), Zeng and Liou (1982) and Cho et al. (1987).

2.3 A specific issue: the Jonhson et al. (1992) corrections

As previously recalled, only 5 phases among the 48 natural zeolites have a consistent set of thermodynamic properties, thanks in particular to the work of Johnson and co-workers (1982 to 1992). In a last paper in 1992, Johnson and co-workers have proposed to correct all their previous enthalpy measurements by –3.51 kJ/mol(Si). If we integrate this modification:

- the analcime stability field disappear from Figure 4

- scolecite stability field is overlapping those of chabazite and zeolite-CaP in Figure 3

- For mordenite (Johnson et al., 1992), we have calculated the LogK = f(1/T) function with and without this correction. In the latter case, we have obtained a slope close to that of Benning et al. (2000) for the same mineral whereas it differs strongly in the first.

Finally and following Neuhoff et al. (2004), we choose not to take the correction into account for the present work.

3. The use of predicting models for zeolites

The majority of the models developed until now make it possible to evaluate the thermodynamic properties of zeolites, while being based on the polyhedral approach for the enthalpy and the Gibbs free energy (Chermak and Rimstidt, 1989); for the entropy (Holland, 1989; Robinson and Haas, 1983) and for the heat capacity (Berman and Brown, 1985). Estimation methods are specifically devoted to zeolites have also been published. A general evaluation and update of these methods have recently been proposed by Vieillard and Mathieu (2009), Mathieu and Vieillard (2010) and Vieillard (2010) in a consistent set of papers.

A specific care is given to the estimates for entropy and heat capacity since those properties are, in some case, used in the present work in order to complete the set of thermodynamic properties.

3.1 Global overview of Predicting models for zeolites

They have been some few developments of methods devoted especially to zeolites:

- Vieillard (1995) have proposed to estimate the enthalpy of formation with a method based on the electronegativity scale

- La Iglesia and Aznar (1990) have proposed a method for estimating the Gibbs free energy, based on the sum of fictive oxides

- Navrotsky and Tian (2001) developed a model allowing the evaluation of the enthalpy of formation of anhydrous zeolites

- Similarly, Mattigod and McGrail (1999) have updated a fictive oxides and hydroxides summation method (Mattigod and Sposito, 1978), focusing especially on zeolites

- Recently, in a consistent set of articles, Vieillard and Mathieu (2009), Mathieu and Vieillard (2010) and Vieillard (2010) have proposed methods for the prediction of, respectively the enthalpies of hydration, the enthalpies of formation and the entropy and the heat capacity of zeolites, respectively.

These authors have proposed an overview of the existing methods and evaluate their own work by using the most complete set of experimental data. In the selection process for the present work, thermodynamic properties will be completed using their methods. From that point of view, we are restraining the estimates to the entropy and the heat capacity, because their influence on the overall stability is less important, at rather low temperatures, than that of the enthalpy formation.

However, Vieillard and Mathieu (2009) and Mathieu and Vieillard (2010) methods will also be used in the present work, in order to compare their results with the present selection. This is a part of the verification we have performed on the present selection.

3.2   Entropies and heat capacities

Prediction models for the entropy (Holland, 1989, Robinson and Haas, 1983) and for heat capacity (Robinson and Haas, 1983, Berman and Brown, 1985) tested on recent calorimetric data of zeolites (Vieillard, 2010) showed errors up to 5% for the entropy and 10% for the specific heat. Vieillard (2010) have shown that the discrepancies between the measured and estimated values are strongly dependent on the properties of zeolites, in particular concerning the degree of hydration and the structure of the zeolitic framework

In Vieillard (2010) work, many measurements of entropy known as of third law (35 data) and of heat capacity with constant pressure (21 data) were carried on anhydrous and hydrated zeolites. Previous models were primarily based on the polyhedral approach. A improvement can be made by (1) using the thermodynamic properties of silica polymorphs whose the crystal structure are close to those of zeolite, and (2) determining the thermodynamic parameters of the zeolitic water obtained by difference of between zeolites anhydrous and hydrated. Thus Vieillard (2010) has proposed a new set of entropies and Maier-Kelley coefficients a, b and c for the heat capacity function, for the various oxides which compose the 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.

4. Verification

As was already mentioned above, the verification is carried out:

- for individual phase properties when possible,

- by drawing predominance diagrams and investigating phase relations with respect to literature

- by comparing the selection with model predictions.

This exercise is limited by a lack of reliable data (field or experimental), especially within the context of a deep disposal (cement/clay interaction within a confined media). Zeolite composition may vary which has strong consequences on their stability (see the analcime example, Figure 1). Actually, we are lacking for a study including not only fluid compositions and solid material XDR determination but also with a characterization of the mineral chemical compositions.

4.1 Verification using predominance diagrams

4.1.1 CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O system

Predominance diagrams have been built up in order to assess the consistency of our selection. We first investigated the CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O system, as can be seen on Figure 2, gismondine stability field appears rather broad, making chabazite and straetlingite domains almost disappear.

Many authors including Atkins et al. (1994), have reported the precipitation of zeolites in low pH cement. They have also reported the presence of a Ca-P zeolite, which structure would be close to that of gismondine. By using predominance diagrams, we have tried to investigate the solubility of this phase. Considering that the straetlingite is a stable phase at least at 25°C according to Atkins et al. (1994), it should be equilibrated with a low C/S C-S-H and Si substituted katoite. We were able to calculate, based on the diagram shown in Figure 3, this condition gives LogK = 43.3 for the lower limit of the equilibrium constant. Similarly, as C/S is considered by Atkins et al. (1994) as higher than 1, this set up the upper limit to LogK = 47.0. Finally, we have selected an intermediate value, LogK = 45.15, for the Ca-P zeolite equilibrium constant at 25°C. Results are displayed on Figure 3.
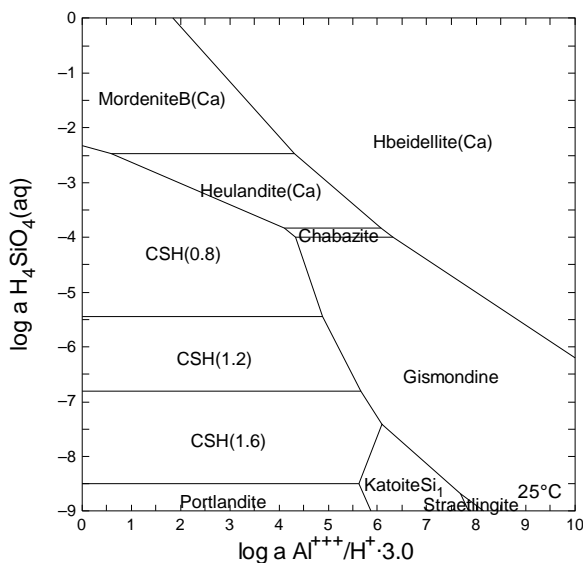
Figure 2   CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O stability diagram at 25°C, Ca^{2+} = 10^{-2}M (without scolecite)
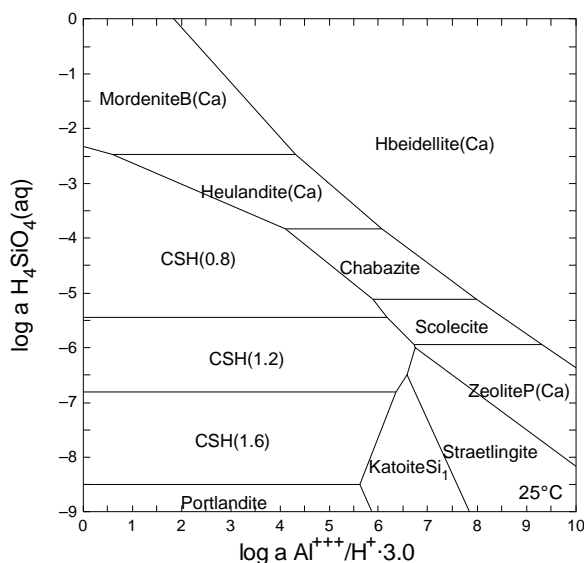
Figure 3   CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O stability diagram at 25°C, Ca^{2+} = 10^{-2}M (without gismondine)

We can observe that the diagrams displayed in Figure 2 and Figure 3 are compatible with previous calculations performed by Damidot and Glasser (1995) and with the Savage et al. (2007) review of the cement/clay interactions. This point was already discussed in the cement material part. Given all the uncertainties, given the assessed values and the lack of data for the verification, it is difficult to claim for the accuracy of the displayed phase relations. But our selection is consistent with previously published works related to cement degradation in the CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O system.

4.2 Na$_2$O-SiO$_2$-Al$_2$O$_3$-H$_2$O system

On Figure 4 is displayed the activity diagram resulting from phases relation calculations in the Na$_2$O-SiO$_2$-Al$_2$O$_3$-H$_2$O system. Globally, the zeolite sequence, from low to high silica activities corresponds to the decrease of the Al/Si ratio highlighted by Savage et al. (2007), for cement degradation.
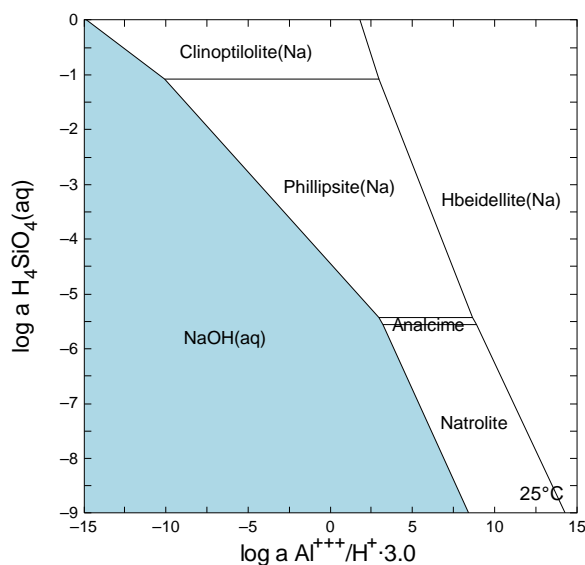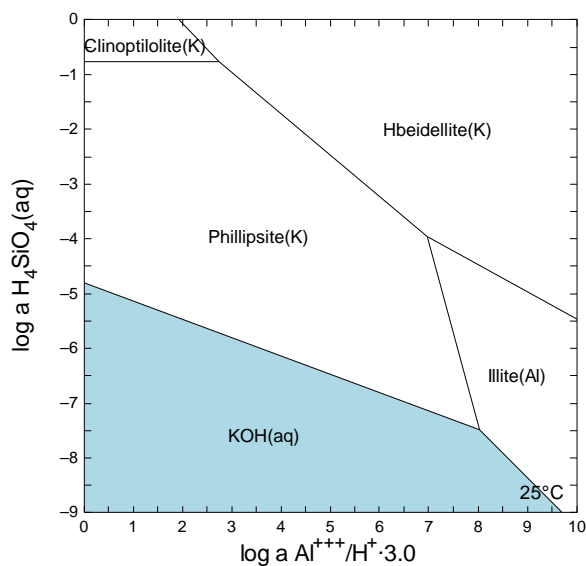

Figure 4   Na$_2$O-SiO$_2$-Al$_2$O$_3$-H$_2$O stability diagram at 25°C, Na$^+$ = 10^{2}M (without paragonite)

However this diagram is also asking for different questions:

- by analogy with the calcic system, the NaOH(aq) domain should be held by sodium silicates (NSH in cement notation), not included in the database, yet,

- Natrolite and phillipsite(Na) are partially overlapping the analcime stability field. Concerning Phillipsite the present selection undergoes uncertainties and an overestimation of the stability of this phase is possible

- - Stilbite is lacking in this diagram. We have based our selection on the main work on that topic (Fridriksson et al., 2001). Refinement of phase relations would require additional experimental data which are currently lacking.

4.3 K_2O-SiO_2-Al_2O_3-H_2O system

On Figure 5 is displayed the activity diagram resulting from phases relation calculations in the K_2O-SiO_2-Al_2O_3-H_2O system at 25°C. As previously, the zeolite sequence, from low to high silica activities corresponds to the decrease of the Al/Si ratio highlighted by Savage et al. (2007).

Figure 5 K_2O-SiO_2-Al_2O_3-H_2O stability diagram at 25°C, $K^+ = 10^{-2}M$ (without Muscovite and Kalsilite)

	LogK (25℃)·	$\Delta H_f°$ kJ.mol^{-1} (1)	Pred. $\Delta H_f°$ kJ.mol^{-1} (2)	S° J.mol^{-1}.K^{-1} (1)	Pred. S° J.mol^{-1}.K^{-1} (3)	V° cm^3.mol^{-1}	Cp J.mol^{-1}.K^{-1} (1)	Pred. Cp J.mol^{-1}.K$^-$ (3)
Analcime	$Na_{0.99}Al_{0.99}Si_{2.01}O_6:H_2O$	6.64	−3308.00	−3300.11	231.08	220.64	97.22	212.38	210.81
Phillipsite−K	$KAlSi_3O_8:3H_2O$	−0.04	−4842.32	−4859.07	390.57	373.17	148.97	351.41	351.41
Philipsite−Na	$NaAlSi_3O_8:3H_2O$	1.36	−4812.12	−4845.83	382.53	365.79	149.69	330.96	330.96
Philipsite−Ca	$Ca_{0.5}AlSi_3O_8:3H_2O$	2.23	−4824.48	−4887.91	342.38	326.89	150.92	321.86	321.86
Natrolite	$Na_2(Al_2Si_3)O_{10}:2H_2O$	16.83	−5732.70	−5738.33	359.73	374.94	169.37	359.23	364.42
Scolecite	$CaAl_2Si_3O_{10}:3H_2O$	14.15	−6063.10	−6055.17	367.42	366.16	172.34	382.81	412.40
Stilbite	$NaCa_2(Al_5Si_{13})O_{36}:16H_2O$	3.74	−22579.71	−22652,5	1622.56	1688,86	668.23	1697.03	1706,55
Stellerite	$Ca_2Al_4Si_{14}O_{36}:14H_2O$	6.90	−21656.24	−21764.82	1604.73	1571.23	663.65	1573.96	1572.62
Mordenite Ca	$Ca_{0.515}Al_{1.03}Si_{4.97}O_{12}:3.1H_2O$	−2.52	−6655.85	−6673.45	484.01	455.04	208.70	443.11	443.11
Clinoptil. Ca	$Ca_{0.55}(Si_{4.9}Al_{1.1})O_{12}:3.9H_2O$	−2.35	−6923.33	−6944.06	498.99	493.57	209.67	481.02	481.02
Clinoptil. Na	$Na_{1.1}(Si_{4.9}Al_{1.1})O_{12}:3.5H_2O$	−0.09	−6782.36	−6789.24	502.72	511.48	214.79	470.38	470.38
Clinoptilolite K	$K_{1.1}(Si_{4.9}Al_{1.1})O_{12}:2.7H_2O$	−1.23	−6568.41	−6568.81	507.66	478.21	214.79	454.31	454.31

Merlinoite-Na	$Na_{1.04}Al_{1.04}Si_{1.96}O_6:2.27H_2O$	10.54	−3681.43	−3690.58	283.43	285.61	113.16	305.68	273.71
Merlinoite-K	$K_{1.04}Al_{1.04}Si_{1.96}O_6:1.69H_2O$	11.59	−3537.60	−3531.59	270.48	261.76	113.16	249.65	266.37
Zeolite CaP	$Ca_2Al_4Si_4O_{16}:9H_2O$	45.15	−11129.11	−11123.65	975.40	796.07	305.70	918.69	918.69
Wairakite	$CaAl_2Si_4O_{12}:2H_2O$	14.41	−6646.70	−6658.84	400.70	365.66	190.67	401.04	403.21
Laumontite	$CaAl_2Si_4O_{12}:4H_2O$	11.66	−7251.00	−7270.20	483.80	471.45	207.53	503.71	503.71
Heulandite Ca	$Ca_{1.07}Al_{2.14}Si_{6.86}O_{18}:6.17H_2O$	2.46	−10667.20	−10712.12	700.94	731.63	315.65	729.87	729.87
Heulandite Na	$Na_{2.14}Al_{2.14}Si_{6.86}O_{18}:6.17H_2O$	2.80	−10612.85	−10636.24	838.29	813.87	315.65	749.34	749.34
Gismondine	$Ca_2Al_4Si_4O_{16}:9H_2O$	38.96	−11179.80	−11203.74	742.24	742.24	315.07	869.26	869.26
Chabazite-Ca	$CaAl_2Si_4O_{12}:6H_2O$	11.51	−7826.44	−7822.83	614.00	588.97	251.16	642.67	642.67

Table 1   Comparison of selected thermodynamic constants (column 1) with predicted values from Vieillard and Mathieu(2009) and Vieillard 2010.

	Formula	LogK	ΔH_f°	Δ	S°	Δ	V°	Cp (25 ˚C)
		(25 ˚C)	$kJ.mol^{-1}$	$kJ.mol^{-1}$	$J.mol^{-1}.K^{-1}$	$J.mol^{-1}.K^{-1}$	$cm^3.mol^{-1}$	$J.mol^{-1}.K^{-1}$
Analcime	$Na_{0.99}Al_{0.99}Si_{2.01}O_6:H_2O$	6.64	−3308.00[a]	3.3	231.08[a]	0.23	97.09[a]	212.38[b]
Phillipsite–K	$KAlSi_3O_8:3H_2O$	0.04[c]	−4841.86		390.57[d]	1.20	148.97[e]	351.41
Phillipsite–Na	$NaAlSi_3O_8:3H_2O$	1.45[c]	−4811.66		382.53[d]	1.20	149.69[e]	330.96
Phillipsite–Ca	$Ca_{0.5}AlSi_3O_8:3H_2O$	2.32[c]	−4824.02		342.38[d]	1.20	151.15[e]	321.86
Natrolite	$Na_2(Al_2Si_3)O_{10}:2H_2O$	19.31	−5718.60[f]	5.5	359.73[f]	0.72	169.20[g]	359.23[f]
Scolecite	$CaAl_2Si_3O_{10}:3H_2O$	16.63	−6049.00[f]	5.5	367.42[f]	0.73	172.30[g]	382.81[f]
Stilbite	$NaCa_2(Al_5Si_{13})O_{36}:16H_2O$	3.74	−22579.71[h]		1622.56[h]		664.70[h]	1697.03[h]
Stellerite	$Ca_2Al_4Si_{14}O_{36}:14H_2O$	6.90	−21656.24[h]		1604.73[h]		666.50[h]	1573.96[h]
MordeniteCa	$Ca_{0.515}Al_{1.03}Si_{4.97}O_{12}:3.1H_2O$	−2.92[i]	−6662.19		493.57[j]		209.80[j]	443.11[g]
MordeniteJ	$Ca_{0.289}Na_{0.362}Al_{0.94}Si_{5.06}O12:3.468H_2O$	−4.18	−6738.44[k]	4.5	486.54[k]	0.97	212.40[k]	484.45[k]
ClinoptiloliteCa	$Ca_{0.55}(Si_{4.9}Al_{1.1})O_{12}:3.9H_2O$	−2.35[i]	−6923.33		498.99[i]		209.66[e]	481.02[j]
ClinoptiloliteNa	$Na_{1.1}(Si_{4.9}Al_{1.1})O_{12}:3.5H_2O$	−0.09[l]	−6782.36		502.72[l]		214.78[e]	470.38[j]
ClinoptiloliteK	$K_{1.1}(Si_{4.9}Al_{1.1})O_{12}:2.7H_2O$	−1.23[l]	−6568.41		507.66[l]		210.73[e]	454.31[j]
MerlinoiteNa	$Na_{1.04}Al_{1.04}Si_{1.96}O_6:2.27H_2O$	10.54	−3681.43[m]		283.43[m]		114.04[m]	305.68[m]
MerlinoiteK	$K_{1.04}Al_{1.04}Si_{1.96}O_6:1.69H_2O$	11.59	−3537.60[m]		270.48[m]		112.91[m]	249.65[m]

	Formula	LogK (25 °C)	ΔH_f° kJ.mol⁻¹	Δ kJ.mol⁻¹	S° J.mol⁻¹.K⁻¹	Δ J.mol⁻¹.K⁻¹	V° cm³.mol⁻¹	Cp (25 °C) J.mol⁻¹.K⁻¹
ZeoliteCaP	$Ca_2Al_4Si_4O_{16}:9H_2O$	45.15[n]	−11129.11[n]		*975.40*		305.70[e]	872.11[j]
Wairakite	$CaAl_2Si_4O_{12}:2H_2O$	*14.42*	−6646.70[p]	6.3	400.70[p]		193.56[e]	401.04[q]
Laumontite	$CaAl_2Si_4O_{12}:4H_2O$	*11.66*	−7251.00[p]	5.6	483.80[r]	2.10	207.53[e]	542.23[j]
HeulanditeCa	$Ca_{1.07}Al_{2.14}Si_{6.86}O_{18}:6.17H_2O$	2.46[n]	−10667.20[s]	8.6	*700.94*		322.06[e]	719.05[j]
HeulanditeNa	$Na_{2.14}Al_{2.14}Si_{6.86}O_{18}:6.17H_2O$	2.80[n]	−10612.85[s]	8.6	*838.29*		325.00[e]	719.05[j]
Gismondine	$Ca_2Al_4Si_4O_{16}:9H_2O$	*38.96*	−11179.80[o]		742.24[j]		315.07[e]	869.26[j]
Chabazite	$CaAl_2Si_4O_{12}:6H_2O$	*11.51*	−7826.44[t]		614.00[u]		251.16[e]	681.19[j]

Table 2- Thermodynamic constants for the final selection.

In italics: internally recalculated values ; (a) Neuhoff *et al.* (2004), based on experimental measurements ; (b) Johnson *et al.* (1982) ; (c) Calcullated by combining data from Hess (1966) et Shibue *et al.* (1981) ; (d) Extracted from Hemingway et Robie (1984) ; (e) from Coombs *et al.* (1997) density value ; (f) Johnson *et al.* (1983) ; (g) Robie et Hemingway (1995) ; (i) This work, after Benning *et al.* (2001) ; (j) Estimated using Vieillard (2010) method ; (k) Johnson *et al.* (1992) ; (l) This work, after Wilkin et Barnes (1998) ; (m) This work, after Donahoe *et al.* (1990) ; (n) This work ; (o) Estimated using Chermak and Rimstidt (1989) method ; (p) Kiseleva *et al.* (1996) ; (q) Neuhoff and Wang (2007) ; (r) Paukov et Fursenko (2000) ; (s) After Kiseleva *et al.* (2001) ; (t) This work, after Shim *et al.* (1999) ; (u) This work, after Belitsky *et al.* (1982).

4.3.1 Comparison with model predictions

On Table 2 are compared the values selected in this study with model predictions. Concerning the enthalpy, in most cases, there is a reasonable agreement between both data set. Specific problems arise from heulandite and phillipsite. Heulandite-Ca stability at least is ensured thanks to the equilibrium with laumontite. This not the case for phillipsite-Ca, which formation enthalpy is deduced from a calculation rather than from direct measurements. The discrepancy with phillipsite reflects this uncertainty. The prediction of enthalpy of formation of phillipsite-Ca and –Na are not very accurate in reason of absence of data about mechanisms of dehydration versus temperature. The molar volume for these minerals are estimated from molar volume of phillipsite-Ba (Cruciani, 2006) and exhibit a difference of 20% between hydrated and anhydrous zeolites in reason of the collapsed structure before total dehydration. This will not be the case for K- and Na bearing phillipsite (Guliev et al. 1999). No data of molar volume of anhydrous Ca-, K- and Na bearing phillipsite are available.

For entropy, discrepancies arise mostly from zeolite CaP and Wairakite. The same point than for phillipsite may be enhanced, related to the way thermodynamic properties of CaP zeolites have been calculated, that influences the entropy value. In addition, the value proposed for the selected entropy includes the configurational entropy which may be high for CaP zeolite (a disordered form of gismondine) and also for wairakite (Neuhoff et al., 2003).

The prediction model of zeolites (Vieillard, 2010) assumes a constant entropy for water ($S°$=54.36 J K^{-1} mol^{-1}) in the zeolite obtained from difference between anhydrous and hydrated analcime, mordenite and clinoptilolite. These three previous zeolites show a continuously varying H_2O. This type of H_2O can be properly referred to as zeolitic. For Wairakite, leonardite and laumontite, they are similar in nature to that found in hydrates because they reflect the observation that dehydration occurs over narrow temperature intervals. This type can be referred to as hydrate H_2O, and their entropy are much lower that those in the zeolitic case. In order to demonstrate that the H_2O resides in a well-defined site and for a given pressure the site is either completely occupied or completely empty depending on the temperature {Neuhoff & Bird , 2001).

Because most of the selected Cp(T) functions are taken from Vieillard (2010) model, the comparison is not really relevant and do not display much differences.

5.   Conclusion

In this chapter is presented a selection of thermodynamic properties for zeolites. The selection focuses on phases which may potentially play a role during the cement/clay interaction, in the context of a deep disposal. Are also presented models for the prediction of the formation enthalpy, the entropy and the heat capacity function.

The verification is carried out through the drawing of predominance diagrams (including cement and clay minerals) and a comparison with predicted values for each thermodynamic parameter. A global agreement is found except for:

- gismondine which has to be discarded from the selection

- the phillipsite(Na) stability domain is also a matter of discussion in that it 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

Given the state of knowledge and the amount of available data, the present study is providing a consistent selection of thermodynamic parameters for zeolites and some predictive tools. Still, some additional work would be required in order to secure the selection for phillipsite, gismondine and chabazite.

In addition, we claim for verification cases coming either from experiments or from field investigations, that would bring us an assessment, including the dependence of the stability domains with respect to minerals composition.

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