Application of thermodynamic modelling to hydrated cements

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Abstract

Thermodynamic modelling is essential to understand the effect of binder composition on hydrate assemblage in modern Portland composite cements and its effect on durability. Binary and ternary plots of the hydrates' volumes can visualize the effect of different SCMs at different hydration times. The pore solution data analysis and the derived saturation indices can be used to gain further insights into the processes governing the dissolution and precipitation of hydrates. The modelling of the hydrated cements exposed to different environments has contributed significantly to the understanding of the determining factors governing sulfate, chloride and carbonate attack.

Thermodynamics models and modelling approaches have achieved a mature level. In the last years, more thermodynamic data have become available making thermodynamic calculations more reliable. The main gaps identified include the refinement of models describing the uptake of ions and water by C-S-H, as well as data for ASR products and zeolites.

1. Introduction

The application of thermodynamic methods to investigate cement hydration has a long tradition. Initial attempts to study cementitious systems back in 1965 concentrated on collecting thermodynamic data [1]. These first attempts initiated the process that led to the development of tools and methods enabling the analysis of the complex water-cement systems [2, 3]. Today, these approaches support the understanding of modern hydraulic binders and enable an efficient development of alternative binders.

Hydraulic binders show great variability and include different composite cements based on Portland cement clinkers as well as alternative binders. The first group includes binary, ternary and quaternary blends of Portland clinker with multiple cementitious materials [4, 5]. The second group includes “traditional” alkali activated systems [6, 7] and calcium sulfoaluminate cements which received lately increasing attention in academic as well as industrial research [8-11]. The development of these binders is related to the effort to lower their environmental impact and to contribute to mitigate the climate change leading to a more sustainable future [12]. Despite significant differences between these systems in the physical-chemical reactions involved and the performance evolution, they all share one common characteristic. The empirical data which allowed defining the prescriptive rules for the application norms and codes for Portland cement do not (yet) include these new binders [13, 14]. To address this challenge, the prescriptive building design needs to be replaced by a performance-based design and the long-term experience by predictive modelling of material performance. At the current state of development and maturity, thermodynamic modelling contributes and will continue to significantly contribute to the understanding of the involved reactions and performance evolution.

The composition of hydrating cementitious systems is complex since even common hydrated Portland cement contains at least seven different hydrates, most of them being a solid solution with a variable composition. In multi-component binders, the complexity further increases. Thermodynamic modelling of such multicomponent-multiphase systems together with dedicated experiments promotes the

understanding of the reaction mechanisms and the impact of different factors such as composition, time or temperature. In addition, adequate thermodynamic models allow easy and fast parameter variations enabling predicting the composition of hydrate assemblages under different conditions and to extrapolate it to longer time scales accelerating the experimentation.

Numerous studies have shown that thermodynamic modelling, coupled with accurate and complete thermodynamic databases, can reliably predict hydrated cement phase assemblages and chemical compositions. Thermodynamic calculations and experiments support each other: on the one hand, calculations enable more complete interpretations of limited experimental datasets and help to identify key experiments to be performed. On the other hand, experiments provide the data that are needed to validate calculation results as well as provide model input parameters. Thermodynamics is also an invaluable tool assessing the durability of a cement paste in a given environment. When augmented with transport models, it becomes possible to predict the degradation rate of a cement paste and the evolution of its mineralogy in degraded zones [15-17]. For very long time scales, modelling becomes the only possible mean of estimating the durability of cementitious materials in some very critical applications such as stabilisation and solidification of radioactive wastes.

The purpose of the present paper is to demonstrate how thermodynamic modelling can help achieving a better understanding of hydrating cements both for academic as well as industrial researchers and to point out its limitations. As already mentioned, in recent years thermodynamic modelling has also been successfully used for calcium sulfoaluminate cements [11, 18] and alkali activated systems [6, 19]. However, these applications are not further discussed here, as it is detailed in the papers of Ben Haha et al. [20] and Provis and Shi [21] in this issue. The present paper focusses on how thermodynamic modelling can be applied to understand better the hydration of the modern Portland composite cements concentrating on the most important areas of progress since the last review presented at ICCI in 2011 [3]. The fundamental laws and assumptions are shortly summarised in section 2, while section 3

highlights the application of thermodynamic modelling to Portland and Portland composite cements and to the processes governing the durability of cementitious materials.

2. Basics of thermodynamic modelling in cementitious systems

The simplest way to calculate the composition of a hydrated cement are mass balance calculations based on the chemical composition of the unhydrated cement based on knowledge of the relative stability of the hydrate phases. Alternatively, one might use ternary diagrams as developed by Herfort and co-workers [22, 23] and available online (www.empa.ch/cemdata), where with the help of two ternary diagrams, $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{C}_3\text{A-CaSO}_4\text{-CaCO}_3$, the phase assemblages of hydrated Portland cement, Portland cement containing pozzolans and limestone can easily be obtained. The method is consistent with thermodynamic modelling and provides an effective means of representing the results of thermodynamic modelling graphically. Such calculations have the advantage that they can be carried out in a simple way, but also show several disadvantages. The mass balance calculations do not provide information about the pore solution associated with the given phase assemblage and do not allow for accurate accounting for solid solutions or variations due to temperature or humidity changes. The possible stable phase assemblage has to be known *a priori*. Consequently, the simple mass balance calculations may not be applied for the new type of compositions and binders and/or at high or low temperatures, where the profound knowledge on the relative stability of phases is not yet well established.

The advantage of a thermodynamic calculation is that the phase assemblage does not need to be known *a priori*, but is predicted based on the composition of the starting material or the hydration time. Thermodynamic equilibrium calculations predict, based on thermodynamic databases which are valid for any geochemical system, which solids and solutions are stable under the specific conditions of the experiment. All chemical interactions among solids, solid solutions, gaseous phase and aqueous

electrolytes are considered simultaneously. Thermodynamic modelling is thus based on the knowledge of the thermodynamic data (e.g. solubility or complex formation) of all the solids, aqueous and gaseous species that can form in the system. Geochemical modelling codes (e.g. PHREEQC [24], EQ3/6[25], CHES [26], or GEMS [27, 28]) compute the equilibrium phase assemblage and speciation in a complex system from its total bulk elemental composition and its state, i.e. pressure and temperature. The use of different modelling software leads to very minor differences in the results [29, 30], provided that the same database is used. Even though the approach of thermodynamic modelling has not changed fundamentally, significant progress has been achieved in the last years due to the development of more sophisticated geochemical software [24-28], which enables reliable and very fast calculations, as needed e.g. for transport modelling, or the consideration of solid solution models for various phases.

2.1. Thermodynamic equilibrium calculations

Thermodynamic equilibrium calculations predict the composition in a system composed of aqueous, solid and gaseous phases at the temperature and pressure of interest. Two basic approaches to solve the geochemical equilibrium problem are used in geochemical modelling codes:

- solving the law of mass action (LMA) equations,
- minimizing the Gibbs free energy of the system.

The first approach is common and available in many speciation codes such as PHREEQC [24], EQ3/6[25], or CHES [26] and extensively described in textbooks [31, 32]. It requires $\log K$ values for the aqueous complexes, solids or gases at the temperature and pressure of interest, where K is an equilibrium constant and K_{so} designates the solubility product. To calculate the composition of a system, mass and charge balances equations are solved iteratively using Newton-Raphson iterations.

The Gibbs free energy minimisation approach is represented e.g. by GEMS [27, 28]. Thermodynamic equilibrium in a system is obtained when there is no spontaneous tendency for change anymore, i.e. at

equilibrium the Gibbs free energy of the system is at a minimum. The GEMS approach is based also on a mass and charge balance of the whole system and the equilibrium composition is found from all the stoichiometrically possible phases' combinations.

It is important to realise that the two approaches rely on the same fundamentals properties; the Gibbs free energy of reaction, $\Delta_r G^\circ$, and the mass action constant K are directly related according to:

$$\Delta_r G^\circ = \sum_i \nu_i \Delta_f G^\circ = -RT \ln K$$

where ν_i are the stoichiometric coefficients of the reaction, $\Delta_f G^\circ$ the Gibbs free energy of formation of the individual compound, $R = 8.31451 \text{ J/mol/K}$ is the universal gas constant and T the temperature in Kelvin. For more detailed reading on thermodynamics and thermodynamic modelling of aqueous systems see geochemical textbooks e.g. [31-33].

Both approaches, the LMA approach and the Gibbs free energy minimization approach, give comparable results [29, 30]. While in many cases the LMA might be slightly faster with regard to calculation times, the Gibbs free energy minimization approach has the advantage that no a priori assumptions have to be made about the phases present, the compositions of solid solutions, pH, redox potential and the fugacity of gases but that these parameters are obtained as output parameters.

2.2. Activity corrections for aqueous species

Pore solution of hydrated cements have a high ionic strength, which is especially pronounced for modern cement characterized by the high alkali and sulphur content in the clinker coming from the alternative raw materials and fuels. Solubility products or complex formation constants used in thermodynamic modelling refer to activity of specific species, e.g. to the activity of Ca^{2+} $\{\text{Ca}^{2+}\}$. The activity of $\{\text{Ca}^{2+}\}$ is calculated from the concentration $[\text{Ca}^{2+}]$ by using an activity coefficient, $\gamma_{\text{Ca}^{2+}}$: $\{\text{Ca}^{2+}\} = \gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}]$. The

activity coefficients of ions or complexes account for the electrostatic shielding that occurs in the presence of a charged electrolyte and influences the reactivity of the ions. A number of different equations can be used to account for this effect.

The most common equations used for thermodynamic modelling in cementitious systems are the Davies equation, which is considered to be valid for a ionic strength between 0.1-0.5 molal, and the expanded extended Debye-Hückel equation (WATEQ equation) which is thought to be applicable up to 1 molal ionic strength [34]:

$$\log \gamma_i = \frac{-A_\gamma z_i^2 \sqrt{I}}{1 + \sqrt{I}} - 0.3I \quad (\text{Davies equation})$$

$$\log \gamma_i = \frac{-A_\gamma z_i^2 \sqrt{I}}{1 + B_\gamma a_i \sqrt{I}} + b_\gamma I \quad (\text{expanded extended Debye Hückel equation})$$

where z_i denotes the charge of species i , I the effective molal ionic strength, a_i the ion-size parameter, b_γ is a semi-empirical parameter (0.123 for KOH and 0.098 for NaOH electrolyte at 25°C [35]), and A_γ and B_γ are P,T-dependent coefficients. For uncharged species the expanded extended Debye-Hückel equation corresponds to $\log \gamma_i = b_\gamma I$.

At very high ionic strength, the Pitzer theory might be used, which provides a good fit to experimental data up to 6 molal ionic strength [36]. The Pitzer model uses ion-specific parameters, which describe binary and ternary ion interactions to provide activity coefficients at high ionic strength, as opposed to the non-specific values used in the Debye-Hückel or Davies equations. Using the Pitzer model to determine activity coefficients in alkali activated systems, where in particular at early times high silica and alkali concentration are measured [37], or in salt solutions [38] could improve the accuracy of simulated aqueous compositions. The applicability in cementitious systems is however limited by the current lack of Pitzer parameters describing the specific ion interactions of Al-Si, Ca-Si and Al-K as discussed in more detail in [39].

163 Alternatively, at high ionic strength (up to 3 molal) the specific ion interaction theory (SIT) can be used:

$$164 \quad \log \gamma_i = \frac{-A_\gamma z_i^2 \sqrt{I}}{1+B_\gamma a_i \sqrt{I}} + \sum_k \varepsilon(i, k) m_k \quad (\text{SIT})$$

165 where $\varepsilon(i,k)$ denotes an interaction coefficient which describes the short-range interaction between the
 166 species i and k and m_k denotes the molalities of species k in solution. The SIT model is inherently less
 167 precise than the Pitzer model as it contains fewer parameters, but is in good agreement with Pitzer in
 168 the range $I = 0.1\text{--}3 \text{ M}$ [36, 40]. The deviations observed at the highest ionic strength values can be
 169 attributed to missing interactions of equally charged ions in the SIT theory. The SIT model has been used
 170 e.g. in the NEA thermodynamic database [40] evaluations and in the compilation of the PSI/Nagra 12/07
 171 chemical thermodynamic database [41, 42].

172

173 **2.3. Temperature, pressure and relative humidity**

174 The thermodynamic properties of solids and aqueous species as well as of reactions depend on
 175 temperature and pressure. The dependence of the solubility upon a limited temperature range is often
 176 expressed by the so called 3-term approximation [43]:

$$177 \quad \log K_T = \frac{0.4343}{R} \left[\Delta_r S_{T_0}^\circ - (1 + \ln T_0) \Delta_r C_{p,T_0}^\circ - \frac{\Delta_r H_{T_0}^\circ - T_0 \Delta_r C_{p,T_0}^\circ}{T} + \ln T_0 \Delta_r C_{p,T_0}^\circ \right]$$

178 if the heat capacity of the reaction, $\Delta_r C_{p,T_0}^\circ$, is known at standard temperature and assumed to be
 179 constant in the considered temperature range. The 3-term approximation can be used for temperature
 180 extrapolation for up to $\sim 150^\circ \text{C}$ (Figure 1A). In a more narrow temperature range, also the so called Van't
 181 Hoff equation

$$182 \quad \log K_T = \frac{0.4343}{R} \left(\Delta_r S_{T_0}^\circ - \frac{\Delta_r H_{T_0}^\circ}{T} \right)$$

can be used. The Van't Hoff equation assumes that heat capacity of the reaction, $\Delta_r C_{p,T_0}$, equals to 0 and shows within a narrow temperature interval (± 20 °C), a good agreement with the 3-term extrapolation (Figure 1A); at higher temperature intervals rather the 3-term approximation is recommended. The effect of moderate pressure is less important than the temperature effect [44]. More detailed discussions on temperature and pressure corrections are available in geochemical text books [32, 33, 43] and in earlier review papers [3, 45, 46].

Figure 1: A) Effect of temperature on the solubility products of ettringite (adapted from [3]). B) effect of temperature and relative humidity on the solubility products of monosulfate. The lines indicate the calculated solubility products (as obtained from [29, 47]), while symbols indicate measured data.

Generally, tabulated thermodynamic data refer to the reference temperature of 298.15 K (25°C) and atmospheric pressure. As most cement performance testing (e.g. according to the standard EN-196) and hydration studies are performed at 20 °C, temperature corrections should be applied, in particular for Aft phases as their stability is very sensitive to temperature, even over short ranges of temperatures (Figure 1A, [45, 48]).

199

200 Not only the temperature but also the relative humidity can influence the kind of solids present as
201 recently demonstrated by Baquerizo et al. [47, 49] for AFm and Aft phases. Figure 1B) shows the
202 solubility of monosulfate, a common AFm phase in cements without limestone, as a function of
203 temperature. Monosulfate can contain different amount of water in its interlayer; at high relative
204 humidity (>97%) C_4AsH_{12} , C_4AsH_{14} , or C_4AsH_{16} might be observed, depending on temperature and
205 whether the solid was dried before analysis. Recent investigations [47] indicated that at 25°C and above
206 and 100% relative humidity C_4AsH_{14} is present in solution as shown in Figure 1B). In experimental studies
207 on hydrating cement, however, generally C_4AsH_{12} is reported (e.g. [50]) as the specimens are dried
208 before XRD analysis. The more hydrated C_4AsH_{16} exists below 20°C but has been reported to be unstable
209 at 25 °C and above [47]. The derivation of thermodynamic data [47, 49] for each of the hydration state of
210 monosulfate (and other AFm phases and ettringite) allow now to predict which hydrate is stable at
211 different relative humidity and temperatures as illustrated in Figure 1B).

212

213 **2.4. Kinetics and equilibrium assumptions**

214 By applying thermodynamic modelling to cementitious systems, one implicitly assumes that a
215 constrained thermodynamic equilibrium is present, i.e. that the liquid (pore solution) and the solid phase
216 (hydrates) are in equilibrium. Often also unreacted clinker is still present at the time of interest; in such
217 cases the equilibration of the unreacted clinker with the pore solution is often suppressed in the
218 thermodynamic calculation to mirror the experimentally observed degree of reaction [51]. Even though
219 pore solution is generally somewhat oversaturated with respect to the hydrates forming, particularly at
220 early days of hydration, cementitious systems tend to move close to the thermodynamic equilibrium or
221 at least to a metastable equilibrium so that the assumption of equilibrium conditions is generally spoken

a valid approach. This is confirmed by the several calculation results for traditional Portland cement presented in the literature [51-53].

However, there are several exceptions to this general statement exemplified in the literature where thermodynamically stable phases may not form spontaneously or only very slowly. In Portland based systems, C-S-H is metastable with respect to crystalline calcium silicate hydrate phases; the formation of crystalline C-S-H phases is generally suppressed in thermodynamic calculations to conform to the observations. In calcium aluminate and calcium sulfoaluminate cements the precipitation of amorphous alumina hydroxide is observed instead of the thermodynamically more stable gibbsite, which has significant impact on the resulting phase assemblage. The solubility of precipitated $\text{Al}(\text{OH})_3$ depends on the reaction time. Initially poorly ordered $\text{Al}(\text{OH})_3$ precipitates with a relatively high solubility; with time the degree of ordering increases (microcrystalline $\text{Al}(\text{OH})_3$ is formed), while its solubility decreases [29, 54]. The solubility of gibbsite would be even lower but gibbsite formation is not expected within the timeframe of months to years generally considered for hydrating cements. The high solubility of poorly ordered $\text{Al}(\text{OH})_3$ is responsible for the initial formation of CAH_{10} in calcium aluminate [54] and in calcium sulfoaluminate cements [55], while the formation of less soluble microcrystalline $\text{Al}(\text{OH})_3$ stabilizes C_3AH_6 in the case of CAC and monosulfate in the case of CSA cements [56]. Which $\text{Al}(\text{OH})_3$ modification should be taken into account during modelling depends thus on the timeframe and the temperature considered and can have significant impact on the modelling result [55]. Gibbsite may be allowed to form at temperatures above 60°C but should be suppressed for calculations at ambient temperatures, where microcrystalline $\text{Al}(\text{OH})_3$ will form instead. Within very short timeframes (minutes to hour), possibly only amorphous $\text{Al}(\text{OH})_3$ should be considered in modelling. Similarly, also the formation of some other stable phases such as quartz (SiO_2), goethite (FeOOH) and hematite (Fe_2O_3) might be suppressed in calculations of hydrated cements in favor of their more soluble counterparts: amorphous SiO_2 , microcrystalline FeOOH or microcrystalline or amorphous $\text{Fe}(\text{OH})_3$, depending on the timeframe considered. The

formation of katoite (C_3AH_6) had been often suppressed in thermodynamic calculations, as katoite formation was observed only after a few days at ambient temperature. As discussed above, this apparent kinetic hindrance of katoite formation is related to the stability of $Al(OH)_3$ and the possible formation of katoite should be allowed in thermodynamic calculations. Similarly the formation of mixed Al-Fe-siliceous hydrogarnet ($C_3(A,F)S_{0.84}H_{4.32}$) should be considered, as experimental studies have shown that mixed Al-Fe-siliceous hydrogarnet is the main Fe-containing hydrate after 1 day [57-59], although its presence is difficult to observe by XRD studies due to its poor crystallinity.

The suppression of certain phases (e.g. quartz, dolomite or goethite) and other constraints to be defined by the user of thermodynamic models, introduces an element of expert knowledge or empirics into the otherwise generic approach of thermodynamic modelling, which could lead to biased results. This shows the need to compare the modelling data with the experimental data to validate the calculations as well as the underlying assumptions.

2.5. Thermodynamic databases for cements

The quality of thermodynamic modelling results directly depends on the accuracy and completeness of the thermodynamic database used. Relevant thermodynamic data for solid cementitious substances, such as the solubility products of monosulfate or C-S-H phases, have been compiled in several specific “cement databases” such as in the thermoddem database [60-62] or the cemdata database [29, 45, 46, 51]. In the last decade the thermodynamic databases used became significantly more adequate as the solubility products of more and more minerals present in cementitious systems have been experimentally determined (e.g. [46, 54]) leading to more complete databases and thus to more reliable thermodynamic calculations. Commonly used databases for cementitious systems are

(1) the Cemdata database (<http://www.empa.ch/cemdata>) [29, 45, 46, 51], which is available for GEMS [27, 28] and PHREEQC [24] and includes a comprehensive selection of cement hydrates commonly encountered in Portland cement, calcium aluminate, calcium sulfoaluminate and alkali activated cements in the temperature range of 0 to 100°C and includes data for calcium silicate hydrate (C-S-H), magnesium silicate hydrate (M-S-H), hydrogarnet, hydrotalcite-like phases, some zeolites, AFm and AFt phases. Solid solutions are used to describe the effect of minor elements on the solubility of these phases and data to describe the effect of relative humidity [29, 49] are included. The first version, Cemdata07, was published in 2006 to 2008 [45, 46, 51, 63] and has been updated several times when additional experimental data became available. A major update occurred in 2013/2014 as Cemdata14 [54, 64-67] and in 2018/2019 as Cemdata18 [29]. For alkali activated binders, the calcium (alkali) aluminosilicate hydrate (C-(N-)A-S-H) gel model [68], with lower calcium but higher aluminum and alkali content than in the C-S-H type phase which exists in hydrated PC, and a Mg-Al layered double hydroxide with variable Mg/Al ratio [6], are available.

(2) the Thermoddem (<http://thermoddem.brgm.fr/>) database is available for the Geochemists Workbench® [69] (<https://www.gwb.com/>) and PHREEQC [24] and includes also data for cement minerals as well as crystalline C-S-H phases. Single phase solubilities rather than solid solution are defined. The thermodynamic data for cements have been published in 2010 [61, 62] and in the last years completed with data for zeolites, clay minerals [60] and M-S-H and C-A-S-H phases [70].

Data for cement minerals in two databases are generally comparable, although some differences exist, as discussed in more detail in Damidot et al. [3]. At present, an OECD Nuclear Energy Agency (NEA) database project [71, 72] aims to establish a consistent common thermodynamic database for cement hydrates, which also intends to unify the thermodynamic cement data in Thermoddem and Cemdata databases. Our experience, mainly based on applying Cemdata in thermodynamic modelling

applications, underlines the importance of a careful data selection and evaluation process, and of including sensitivity analyses into the analysis and discussion of results.

The description of C-S-H, hydrotalcite and M-S-H phases by thermodynamic modelling is particularly challenging as their composition varies depending on the availability of Ca, Mg, and Si and the concentrations of other elements such as aluminum or alkali, which can be taken up by the solids [73-78]. This changing solid phase composition can either be taken into account by using a series of different solid compositions and solubility values as e.g. done for C-S-H by [61, 79], by solid solution models [67, 80] or by surface complexation models as e.g. developed by Nonat and co-workers [73]. Several detailed discussions of the different modelling approaches and comparative calculations comparison of the different C-S-H models with and without aluminum have been published in recent years [29, 74, 80]. Many of the C-S-H models available in literature are able to describe the entire range of Ca/Si ratios encountered, but there are only a few C-S-H models which have the ability to predict aluminum and alkali uptake [68, 73, 81], which is of particular importance for blended cements and alkali activated cements with low Ca/Si C-S-H.

3. Application of thermodynamic modelling to cements

This section focusses on how thermodynamic modelling can be used to better understand the hydration of the modern Portland and blended cements. The first part of this section discusses the effect of SCMs on the composition of hydrated cements, while the following parts discuss the changes during hydration in the solid phases and in the pore solution, information which can be obtained from the analysis of pore solution and the use of ternary plots to optimize blended cements. The last section focused on durability.

3.1. Hydrate assemblage

The most common application of the thermodynamic modelling is to calculate the thermodynamically stable phases after a long hydration time, i.e. assuming complete or close to complete hydration. In this case, the results are determined by the initial chemical composition of the investigated samples, the availability of water, pressure and temperature. Consequently, this approach enables an efficient investigation of the effect of the overall chemical composition or temperature on the type and amount of hydrates and the composition of the pore solution.

Perhaps the most successful example of the application of thermodynamic calculations was to understand that calcite is a reactive phase and not only an inert filler. The stable phase assemblage is modified in the presence of calcite, the main mineral component of limestone, when compared to calcium carbonate free cements. It was shown that in the presence of calcite, monocarbonate is stabilized instead of the monosulfate which in turn stabilizes ettringite and prevents its decomposition to monosulfate during ongoing hydration [52, 82, 83]. Overall, these modifications increase the total volume of hydrates, reduce porosity and may increase compressive strength of Portland cement [3, 84]. After these pioneering works, the calculation of stable hydrate assemblage was applied in a number of studies of composite cements containing limestone [85-88].

A typical modeling result of the effect of limestone is also shown in Figure 2 for the limestone - fly ash – Portland cement composite cement from [89]. As in PC, in the absence of any calcite the formation of C-S(A)-H, portlandite, hydrotalcite, monosulfate and katoite is predicted (left hand side of Figure 2). In the presence of 1 to 2 % of limestone the formation of hemiacarbonate and of monocarbonate in the presence of 3% of limestone or more is predicted, which results in the formation of more ettringite and thus more volume. At even higher additions of limestone, less clinker is present leading to a reduction of volume. The calculated volume trends agree well with measured strength data [89].

Figure 2: Thermodynamic modelling of the effect of the limestone content on the Portland cement – fly ash composite cements. Modelled data from [89], Cemdata07 had been used in the modelling.

In blends of limestone with the Portland cement clinker, only a relatively small quantity of calcite reacts to form monocarbonate [52, 90]. The potential of the calcium carbonate reactivity can be more fully used in the systems characterized by the high amount of reactive alumina such as in composite cements containing fly ash [3, 5, 87, 89] and in particular metakaolin [3, 88, 91, 92]. In the case of the slag (GGBFS) - limestone ternary systems, this synergetic effect is limited as the slag contains less aluminum but more magnesium than fly ash or metakaolin. In these systems a significant part of the alumina is bound in hydrotalcite and C-S-H phase [91, 93, 94] limiting the amount of AFm phases and thus the interaction of limestone with slag. However, for slags characterized by high alumina content a similar synergetic effect [93] is observed as in the case of fly ash or metakaolin. The influence of limestone is not only amplified by high reactive Al_2O_3 contents, but also the amount of SO_3 , defined in terms of the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio, plays

an important role. A high $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio results in relatively more ettringite and less monosulphate, so the influence of limestone is less pronounced [3, 90, 95, 96]. A number of studies focused on the effect of dolomite [92, 97, 98] on the hydration and performance of Portland based cements and demonstrated that the main reaction product of dolomite is calcite and hydrotalcite, while some portlandite is consumed. The calcium carbonate from the dolomite reacts with monosulphate to form monocarbonate resulting in the stabilization of ettringite; this effect is identical to the effect of limestone and has the same implications for the cement performance as also confirmed experimentally [97, 99].

Blending of Portland cement with SCMs lowers not only the CO_2 emission per ton of cement but can have also a positive effect on durability (particularly with respect to sulfate resistance and chloride ingress) and can help to prevent alkali silica reaction. The effect of blending of Portland cement with fly ash, silica and slag on the hydrated phase assemblage has been modelled and their effect on C-S-H composition, portlandite content and AFm and AFt phases has been discussed in an earlier review paper [4]. The use of Al_2O_3 and SiO_2 rich supplementary cementitious materials influences not only the amount and kind of hydrates formed but modifies also the composition of the hydrates. Particularly, the Ca/Si ratio in the C-S-H is lower in the composite cements, while Al_2O_3 -rich SCMs increase the Al-uptake in C-S-H. The changes in the phase assemblages observed experimentally are generally well captured by thermodynamic modelling, with the notable exception of aluminium [75] or the sulfate [100] uptake in C-S-H. Thermodynamic calculations are also used to investigate the effect of new type of materials as e.g. effect of municipal solid wastes incineration fly ash [101] on the phase assemblage, the effect of cements composition on the immobilization of waste [102] or binding of hazardous elements in cements [103].

Thermodynamic modelling is also well suited to calculate the effect of temperature on the long-term phase assemblage [45, 48]. Thermodynamic modelling indicates that the temperature has its main impact on the composition of the hydrates containing alumina, while the composition and content of

portlandite and C-S-H phase (if the amount of gel water associated with C-S-H is not considered) do not change in the temperature range 5 – 60 °C (Figure 3) [45, 97, 99, 104]. The main effect of the temperature is that the combination of ettringite plus monocarbonate is destabilized at temperatures higher than about 45 °C in fully hydrated Portland and blended cements, while monosulphate plus calcite is stabilized. Note however, that the amount of gel water in C-S-H decreases strongly at higher temperature [105, 106], which is not captured by the thermodynamic models available at present account neither for the effect of temperature on gel water content of C-S-H [105, 106] or the sulfate adsorption in C-S-H [100] because of the present limitations of available data.

Figure 3: Calculated volume of solids in a hydrated cement paste as a function of temperature. Data from [97]; Cemdata07 had been used in the modelling; the uptake of CO₃ in ettringite has been neglected as well as the uptake of SO₃ in the C-S-H phase.

3.2. Changes in solid phases during hydration

Thermodynamic modelling had been used to quantitatively predict the amount of hydrates formed during the hydration of pure and composite Portland cements. The first attempts were done for the pure Portland and limestone containing composite cements [51-53]. The further development of experimental techniques to investigate the reaction kinetics of poorly crystalline phases such as fly ash, slags and calcined clays [107-113] allowed thermodynamic calculations to also model the changes during hydration for composite cements containing fly ash [50, 87, 114, 115], slag [94, 114, 116-118] or calcined clay [92, 119].

Hydration process calculations are generally done by combining two different models. An empirical model which describes the dissolution of the anhydrous cement components as a function of time is combined with a thermodynamic model which predicts the kind and quantity of hydrates formed assuming equilibrium between the solution and the hydrates [51-53, 120, 121]. These calculations can be conducted at different temperatures, different water to binder ratios and different pressures. This type of calculations enables computation of the time evolution of:

- type and quantities of the hydrate phase and resulting total pore volume and chemical shrinkage
- quantity of the pore solution and concentrations of elements in the solution, including their speciation

Calculation of the changes during hydration requires detailed knowledge of the reaction kinetic of clinker phases and of SCMs. The reaction of the anhydrous clinker phases proceeds at various rates depending on the w/c and the presence of SCMs [122-124]. The blending of SCMs with Portland cement clinker leads to a more complicated system where the hydration of the Portland cement and the reaction of the SCMs occurs simultaneously and influence the reactivity of each other [122, 124-126]. The reaction of most SCMs is slower than the reaction of the Portland clinker [107, 110] with the exception of metakaolin [88, 92, 111, 119, 127], and is influenced strongly by the cement clinker and the presence of

other SCMs [128]. The use of Al_2O_3 and SiO_2 rich supplementary cementitious materials influences not only the amount and kind of hydrates formed but modifies also the composition of the hydrates. Particularly, the Ca/Si ratio in the C-S-H is lower in the composite cements, while Al_2O_3 -rich SCMs increase the Al-uptake in C-S-H [92, 104]. Although the changes in the phase assemblages observed experimentally are generally well captured by thermodynamic modelling, the alkali, aluminum and sulfate uptake in C-S-H is not well captured with the currently available thermodynamic models, such that the C-S-H composition is often corrected manually for the actual aluminum and sulfate uptake determined experimentally. However, in the last years different models to describe aluminum and alkali uptake in C-S-H [6, 73, 74, 81] have become available and further models are in preparation [129].

The calculated composition of the pore solution during hydration can be used to analyze the impact of the specific ions on the microstructure [130] or on the hydration kinetics of the anhydrous phases [128, 131, 132]. As mentioned above it is often assumed that the concentrations in the pore solution are at thermodynamic equilibrium, i.e. they are dominated by the solubility of the hydrates. The good agreement between the calculated pore solution composition and the measured total concentrations confirms the correctness of the assumption of equilibrium [45, 51-53, 133]. However, in systems with very high silica contents predictions are still difficult due to limitations of thermodynamic models for alkali and aluminum uptake in C-S-H [94, 127, 133, 134].

The modeling of the phase assemblage evolution offers multiple possibilities including comparison with experimental results, the investigation of the kind and amount of amorphous phases and volume or mass balance calculations. The comparison of the calculated phase assemblage development during the hydration of four different types of composite cements is shown in Figure 4. The reaction of the anhydrous phases has been measured at different hydration times by XRD-Rietveld (PONKCS) calculations, SEM-BSE/IE or NMR techniques and a kinetic model was fitted to the measured data [87,

117, 119]. In addition, the composition of the C-S-H phase was corrected for the uptake of alumina according the measured Al/Si values.

Figure 4: Thermodynamic modelling of the hydration process of A) a Portland cement (unreacted clinker labelled clinker, data from [117]), composite cements containing B) composite cements containing Portland clinker, slag and limestone (data from [117]), C) Portland clinker, fly ash and limestone (data from [87]), and D) Portland clinker, metakaolin and limestone (data from [119]). C.S.: chemical shrinkage.

During early hydration times where the hydration is dominated by the dissolution of C_3S and C_3A in the presence of calcium sulfate, the model predicts the formation of portlandite, C-S-H and ettringite in all the investigated systems. In the case of PC, at around 1 day, the formation of AFm phases is predicted as shown in Figure 4A; after the first week little changes are predicted in the case of PC. As the content of calcite is relatively small, in addition to hemiacarbonate the formation of some monosulfate is predicted due to the ongoing reaction of aluminate. The total volume of solution is calculated to decrease due to the binding of water in the hydrates formed; also the formation of empty porosity (chemical shrinkage) is calculated as water bound in hydrates has a higher density than free water. This binding of water in the solid hydrates decreases the total pore volume (= empty + water filled porosity) over the hydration time.

For the cements with SCMs the calculations predict significant differences among the cements after longer hydration times i.e. after a few days from mixing with water, when the supplementary cementitious materials contribute significantly to the reaction:

- The reaction of slag results in the formation of more C-S-H phase and hydrotalcite while only little portlandite is consumed. In addition, the content of AFm phases, i.e. monocarbonate in the presence of calcite, is increasing slowly (Figure 4B).
- The reaction of fly ash results in the formation of more C-S-H and monocarbonate in the presence of calcite. This is associated with the consumption of portlandite (Figure 4C).
- In the case of composite cements containing metakaolin, again the formation of more C-S-H phase and monocarbonate is calculated, while portlandite is consumed as in the case of fly ash (Figure 4D). However, the reaction of metakaolin occurs significantly faster than the reaction of the fly ash.

For the composite cements the calculated amount of ettringite remains constant after the first day since its amount is limited by the availability of sulfate and since the presence of calcite prevents the formation

of monosulfate. While little unreacted clinker remains after 1 month and longer in the case of PC, the quantity of unreacted material is more important for the composite cements as shown Figure 4.

The modeled changes of the composition of the solids and liquid phases, of the porosity and the amount of pore solution during hydration have been found to agree well with the experimental data [50-53, 87, 90, 94, 96, 117, 119]. In the presence of metakaolin resulting in very dense systems characterized by low calcium content it was found that not all hydrates were in thermodynamic equilibrium [127]. The very dense microstructure seems to limit the exchange of ions resulting in local heterogeneities such that in the bulk analysis indicates the presence of both strätlingite and portlandite, although the two phases are thermodynamically incompatible in the presence of C-S-H. When modelling such systems additional constraints need to be introduced. Nevertheless, the generally good agreement between experimental and modeled results indicates that the quasi equilibrium approach used in thermodynamic equilibrium calculations is valid for most cement based systems.

The modelled data may also be used for the prediction of compressive strength and elastic properties, i.e. young modulus in hydrated cements, if the calculated volume changes are combined with empirical models relating the pore volume or gel space ratio with strength [45, 87, 114, 115, 117] or with micromechanical models [117, 127, 135]. Figure 5 shows the close relation between both gel space ratio and pore volume with measured compressive strength.

Figure 5: Comparison between the measured compressive strength and calculated a) gel space ratio and b) porosity from the thermodynamic modelling. Data adopted from [114, 117]. The data shown include Portland cements as well as composite cements containing limestone, slag and/or fly ash.

The modelling of the hydration process as a function of time can be used to indirectly assess the hydration of amorphous materials such as fly ash [112, 136], synthetic glasses [93, 137] and metakaolin [138] in cementitious matrixes, by calculating the consumption of portlandite due to their reaction and compare it to the measured portlandite contents. The reaction of SCMs can also be assessed indirectly by comparing the measured increase of the bound water content or chemical shrinkage [112, 136] with thermodynamic modelling or mass balance calculations. Although these modelling or mass balance approaches generally work well, the composition of C-S-H can vary even in the presence of portlandite [139], which has to be taken into account as detailed e.g. in [112, 136, 138]. The kinetics calculated from thermodynamic modeling show good agreement with other methods like Rietveld-PONKCS calculations or NMR [137, 138].

Thermodynamic modelling may also be used to calculate the heat generated due to the dissolution of the cement and the precipitation of hydrates based on measurements of the reaction degree of the cement and using enthalpy values tabulated in thermodynamic databases (e.g. [29, 45, 46]) for all solid and aqueous species. The calculated enthalpy values agree well with total heat measurements after long hydration times [140]. Coupling this approach with quantitative XRD data allows to calculate not only the evolution of the heat flow but also to clearly distinguish the contribution of the different reactions to the total heat flow measured at early hydration times [141-143] as illustrated in Figure 6.

Figure 6: Measured and calculated heat flow curves for hydrating PC (23°C, w/c = 0.5) based on quantitative XRD and enthalpy data; adapted from [141].

3.3. Pore solution

During the hydration the solid hydrates are formed in contact with the surrounding pore solution, thus the pore solution composition mirrors the evolution of the solid phases. Significant changes in the composition of the pore solution can be observed during hydration as exemplified in Figure 7A) for a PC blended with a high volume of a silica fume. The sulfate depletion after a few hours of hydration is well visible by the distinct decrease of the sulfate concentrations. The reaction of the silica fume, which proceeds somewhat slower than the reaction of the PC clinkers, leads to a slow decrease of Ca, K and Na concentrations, while Si and Al concentrations remain relatively low (< 1 mM). The composition of the pore solution can be used to obtain information about whether certain hydration products can form or will be dissolved by comparing the ion activity product (IAP) of a solid with its equilibrium solubility product (K_{so}). The saturation index with respect to a solid can be expressed as $\log(IAP/K_{so})$, e.g. for portlandite:

$$SI_{(portlandite)} = \log\left(\frac{IAP_{(portlandite)}}{K_{so(portlandite)}}\right) = \log\frac{\{Ca^{2+}\}\{OH^{-}\}^2}{K_{so(portlandite)}}$$

Figure 7: A) Measured total concentrations and B) calculated saturation indices as a function of hydration time for a PC blended with a high volume of silica fume; data from [134]. A saturation index of 0 indicates equilibrium, a positive value oversaturation and a negative undersaturation.

The ion activity product IAP is based on the activities of the ions calculated from the measured total concentrations, usually by using thermodynamic modelling (the calculation of activity from concentration is discussed in chapter 2.2). A positive saturation index implies oversaturation and thus the possibility that this phase can precipitate. A negative value means undersaturation with regard to the respective solid indicating that this solid is not stable in equilibrium with such a solution. The data are thus complementary to the mineralogical determination of the solids formed during the course of hydration as illustrated in Figure 7B) by the changes in portlandite saturation for PC blended with a high volume of silica fume [134]. Portlandite was observed during the first days of hydration, where the solution was slightly oversaturated with respect to portlandite ($SI > 0$), but was absent after 28 days and longer [134]. At 7 and 14 days, where the solutions were already undersaturated with respect to portlandite, some portlandite was still observed, but its quantity decreased indicating the slow dissolution of portlandite during this period of time. Also, the change from high Ca/Si C-S-H formed initially in the presence of portlandite to the low Ca/Si C-S-H upon the reaction of SiO_2 can be followed by the SI plotted in Figure 7B). More detailed discussions on how to gain and measure pore solutions, on the calculation of (effective) saturation indices and the changes in the pore solution during the hydration of Portland cement and blended cements are available in literature, e.g. [2, 133, 144].

The kinetics of dissolution and precipitation reactions during cement hydration depends to a large extent on the degree of over- or undersaturation of the respective solids, although it is also influenced by the presence of other ions. Alite dissolution is fast at high degrees of undersaturation and slow at near equilibrium conditions [145-148]; the interplay of undersaturation with respect to C_3S and oversaturation with respect to C-S-H is a major factor determining hydration kinetics of alite [124, 149-

152]. Nucleation processes play an important role for the reaction kinetics; any factor, such as e.g. the presence of limestone, which eases the formation of nuclei [125, 153], leads to faster C-S-H growth and a higher undersaturation with respect to C_3S resulting in its faster dissolution. Also the concentration of other ions such as aluminum and sulfate, which may be bound to the surface, can influence dissolution kinetics of alite [131, 145] and possible also slow down the kinetics of C-S-H formation [154] although the exact mechanisms remain a topic of discussion [155]. This knowledge on the influence of different ions and of under- and oversaturation results mainly from investigations of dissolution of laboratory synthesized clinker phases in diluted suspensions and has been successfully applied to predict the hydration kinetics of alite [149].

The complexity of the systems increases dramatically from pure phases and lab clinkers towards industrially produced “real” materials and blends thereof at realistic water-to-binder ratios where the combination of both dissolution and precipitation reaction determines the observed hydration kinetics. In addition to the calculation of saturation indices discussed above (Figure 7B), the measured concentration data can also be plotted in binary or ternary plots, together with the calculated solubility curves and solubility surfaces of the different solids. Such binary and ternary plots allow to directly visualize how the under- and oversaturation changes during hydration. As an example we reproduce some results of a study investigating the early hydration of PC containing quartz, limestone and fly ash [124]. Plotting the measured calcium and silicon concentrations together with the theoretical solubility curves of C-S-H, portlandite and of C_3S allow to directly visualize the path followed during early hydration as shown in Figure 8. Solid lines show the solubility curves in the absence of alkalis and sulfate, while the dashed/dotted lines show the effect of increased pH as in a cement pore solution (mimicked by 60 mM KOH and 20 mM K_2SO_4 [124]) on the calcium and silicon concentrations. The solutions were in all cases oversaturated with respect to portlandite; which is often observed during the early hydration of PC, as also shown by the saturation indices plotted in Figure 7B). At very early reaction times (5 minutes;

indicated by the lightly colored symbols), the measured calcium and silicon concentrations are near the C_3S surface curve, but with time they move further away from the C_3S curve towards the C-S-H curve, which they follow in direction of the portlandite saturation.

Calorimetric measurements indicated that the early hydration progresses faster in the presence of limestone than in the presence of quartz [124]. The same difference is also visible in the plots of the reaction paths in Figure 8. The squares representing the pore solution measured for PC hydrating in the presence of quartz remain from 5 minutes (light colored square) until 6 hour (black square) in between the C_3S and C-S-H line indicating that the hydration kinetic is determined both by the dissolution of alite and the precipitation of C-S-H. In contrast, the diamonds representing PC in the presence of limestone are after 2 hours and longer near to the solubility line of C-S-H, indicating that the solutions are near equilibrium with C-S-H as limestone offers a very good nucleation surface for C-S-H [125, 153]. This near equilibrium with C-S-H results in a larger distance from the C_3S surface solubility line, thus in a higher undersaturation with respect to alite resulting in faster alite dissolution.

Figure 8: Measured calcium and silicon concentrations in the pore solution during early hydration (light colored symbols correspond to 5 and 30 minutes, dark symbols to 1, 2, 4 and 6 hours) of a

Portland cement blended with 50 wt.% of quartz or limestone compared to the theoretical solubility of portlandite, C-S-H and C_3S . Experimental data and thermodynamic modelling from [124]. Solid lines correspond to the calculated solubility of C-S-H (using the CSHT model [67]), portlandite and C_3S (using the experimental solubility product of the protonated surface as derived in [146]). Dashed/dotted lines show the effect of increased pH in a cement pore solution (mimicked by 60 mM KOH and 20 mM K_2SO_4 [124]) on the calcium and silicon concentrations.

Figure 8 illustrates also the effect of alkalis and sulfate on the solubility lines of portlandite, C-S-H and alite. The presence of 60 mM KOH and 20 mM K_2SO_4 (to mimic the measured concentrations in [124]) leads to an increase in pH and moves the portlandite solubility line towards lower calcium concentrations (indicated by the dotted line). Similar shifts are also observed for the C-S-H and alite curves (dashed lines) illustrating that not only calcium and silicon concentrations are important, but other ions, in particular the pH values, which are strongly influenced by the relative concentrations of sulfate and alkali ions in the solution.

Such binary graphs could also be used for the examination of the effect of other ions such as aluminium in blended PC. Three dimensional graphs representing the solubility surfaces of portlandite, C-S-H or strätlingite can combine more information in one representation and are thus more convenient to visualise simultaneously the effect of varying aluminium and alkalis concentrations. Such three-dimensional solubility surfaces obtained by thermodynamic modelling have been recently developed to better understand the effect of calcium aluminates on the hydration of ye'elimite containing cements [156]. They are plotted here to demonstrate the effect of different alkali concentrations on the solubility surfaces of portlandite, C-S-H and strätlingite. Figure 9A) illustrates the calcium concentrations in equilibrium with portlandite in the presence of 50 to 600 mM KOH and compares it again with the measured calcium, aluminum and silicon concentrations in the pore solution during early hydration (5 minutes to 6 hours) of a Portland cement blended with 50 wt.% of quartz or limestone [124]. Inspection

of the portlandite solubility surface in Figure 9A) shows that increasing KOH concentrations lower the calcium concentrations in equilibrium with portlandite from around 20 mM Ca in the absence of any KOH to below 0.1 mM in the presence of ≥ 400 mM KOH. Comparison with measured data from [124] shows again an oversaturation with respect to portlandite in the presence of 50 mM KOH. The solubility surfaces show also that high concentrations of silicon and aluminium lead to a moderate increase of the total calcium concentrations due the formation of dissolved Ca-silicate complexes and due to lower hydroxide concentrations in the presence of high concentrations of negatively charged Al(OH)_4^- and $\text{SiO}_2(\text{OH})_2^{2-}$ species.

An increase of KOH concentrations and thus of pH has also a strong effect on the solubility surface of C-S-H as shown in Figure 9B). At high Ca/Si ratio the calcium concentrations increase while silicon concentrations decrease, in agreement with the experimental observations reported in [157] for C-S-H. In the presence of low Ca/Si C-S-H, i.e. at low Ca and high Si concentrations, a crossover of the concentrations is calculated, a decrease of calcium and increase of silicon concentrations with increasing pH, again in agreement with the experimental observations reported in [157] for C-S-H. Comparison with measured pore solution data from [124] shows saturation with respect to the C-S-H surface at around 50 mM KOH. As the C-S-H model used does not account for the presence of aluminium in the solid phase, aluminium has only a minor effect on the calculated C-S-H solubility surface plot except at very high aluminium concentrations and low KOH concentrations where high concentrations of negatively charged Al(OH)_4^- lower pH and thus increase calcium and lower silicon concentrations. Figure 9C) shows that strätlingite is expected to be formed at relative high aluminium and silicon concentrations. The strätlingite surfaces Figure 9C) are less affected by pH than those of CH and C-S-H. For strätlingite the measured data from [124] indicate a clear undersaturation, consistent with absence of strätlingite in hydrated Portland cements.

A) CH

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B) C-S-H

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C) Strätlingite

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Figure 9: Effect of KOH, CaO, Al₂O₃ and SiO₂ on the solubility surface of A) portlandite, B) C-S-H (using the CSHQ model [67]) and C) strätlingite; the formation of other solids is suppressed. Measured total calcium, aluminum and silicon concentrations (circle and triangles) in the pore solution during the early hydration of PC blended with quartz or limestone [124].

A combination of the different surfaces allows comparing the pore solution of hydrated PC and blended cements. In Figure 10 the solubility surfaces of portlandite, C-S-H and strätlingite at 600 mM KOH representing the pore-solution of alkali rich PC cements and at 200 mM KOH as typical for low alkali and blended cements are plotted. Figure 10A) illustrates the difference in the long-term (90 to 400 days) pore solution composition between alkali-rich Portland cements [52, 87] and blends with fly ash and limestone [87]. The PC pore solution remains saturated with respect to C-S-H and portlandite, while the fly-ash limestone blended cements have lower calcium concentrations and are partially undersaturated with respect to portlandite, consistent with its dissolution after longer reaction time in the presence of fly ash [87]. In Figure 10B) it is visible that the pore solution of a low-alkali PC remains saturated with respect to C-S-H and portlandite, while the pore solution of ternary and quaternary blends containing Portland cement, slag, fly and limestone with their lower calcium concentrations are undersaturated with respect to portlandite. The blends with metakaolin, which shows a higher degree of reaction than fly ash, are oversaturated with respect to strätlingite indicating that strätlingite is expected to form in these systems in the long term even though strätlingite was not yet clearly visible by XRD [158].

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Figure 10: Effect of CaO, Al₂O₃ and SiO₂ on the solubility surfaces of portlandite, C-S-H and strätlingite in the presence of A) 600 mM KOH representing the pore-solution of alkali rich PC cements and B) 200 mM KOH as typical for low alkali and blended cements. For comparison the measured

concentrations in the pore solution of A) a Portland cement (PC) [52, 87] and a PC blended with fly ash and limestone (FA-L) [87] hydrated between 90 and 400 days and B) low alkali Portland cement (PC) [53], ternary blends containing Portland cement, slag and limestone (S-L) [128, 159, 160] and quaternary blends containing Portland cement, slag, fly and limestone (S-FA-L) [160, 161] and PC blended with metakaolin and limestone (MK) [158] hydrated between 28 and 180 days.

3.4. Ternary plots for phase assemblages

To be able to identify optimized cement composition fulfilling a given target, e.g. blends to further reduce the clinker content in the cement, researchers [55, 162] and later the cement producers [163] have started to use a more flexible approach, adding more than one component to the composite cements and varying the type of the supplementary cementitious materials as shown in Figure 11. Such ternary plots allow understanding the relationship between the cement composition and performance in a broad compositional range, e.g. ternary composite cements composed of cement clinker and two supplementary cementitious materials. Alternatively, the quaternary system can be investigated when e.g. the clinker content is kept constant. In many cases it will be more adequate to perform the modelling at the hydration degrees corresponding to the times of interest instead for fully hydrated systems.

The example of such calculation is shown in Figure 11 for two different composite cements (Portland clinker with limestone and either blast furnace slag or metakaolin after 28 days of hydration). The cement characteristics (chemical and phase composition) as well as the hydration degree after 28 days were adopted from [117, 158, 163]. The reaction degree of the clinker and SCMs is variable depending on the composition of the starting cement. In both cases, the hydration degree of the cement clinker was close to 90 % [117, 158, 163]. The degree of the slag reaction varies between 50 and 65 % [163] and of metakaolin between 30 and 85 % [158]; a higher content of the slag or metakaolin in the starting cement

corresponds to a lower degree of hydration at 28 days and later as detailed in [163]. The sulfate content was kept constant at 3.0 %, in both cases and the calculations were performed at a water to cement ratio of 0.5.

Figure 11 shows the content of the main hydrates portlandite, C-S-H, strätlingite, ettringite and monocarbonate and how they vary depending on the initial cement composition. It is noticeable that despite the apparent similarities between the two composite cements containing either metakaolin or slag, the phase assemblage is significantly different at the investigated hydration time.

Figure 11: Effect of the cement composition on the content of main hydrates and porosity at 28 days of hydration for ternary composite cements containing Portland clinker, limestone and slag (left column, composition and kinetic data from [163]) and Portland clinker, limestone and metakaolin (right column, composition and kinetic data from [158]) as predicted by thermodynamic calculations. Please note that the hydration degree of cement phases corresponds to the 28 day of hydration, i.e. it is not complete.

In the slag containing cement, the C-S-H content increases as a function of the clinker and slag content and decreases with increasing limestone content. The clinker reaches hydration degree of 70 – 80 % while the degree of slag reaction is 40 - 50 % at 28 days [117, 128, 163]. The portlandite content depends

mainly on the clinker content as the slag contains both high amounts of silica and calcium oxide (42 wt.% CaO and 35 wt.% SiO₂ [117, 163]), such that portlandite is produced mainly due to the reaction of Portland clinker and is hardly consumed by the slag reaction. Thus thermodynamic modelling does not predict the formation of strätlingite in the Portland clinker - slag - limestone system in agreement with experimental observations [117, 128, 164-166]. Replacing the slag by metakaolin results in significant modifications; the degree of metakaolin reaction varied between 40 to 90% at 28 days [119, 158] depending on its content. There is a maximum content of the C-S-H phase in the systems containing about 15% of metakaolin and 85% of cement clinker as shown in Figure 11. Increasing limestone results in the reduction of the C-S-H phase content. The portlandite content decreases with the metakaolin content and in the presence of more limestone. Portlandite is not predicted for metakaolin contents higher than about 15%; for metakaolin content higher than 20%, strätlingite is calculated to precipitate. These differences between slag and metakaolin arise from the fact that metakaolin reacts rapidly and provides significant quantities of Al₂O₃ and SiO₂ but no CaO, which together significantly modifies the phase assemblage. Portlandite is consumed as a result of the pozzolanic reaction leading to the formation of significantly more C-S-H and AFm phases than in the case of slag composite cements.

Similar differences occur to the AFt and AFm phases. For the Portland clinker-slag-limestone system the typical scenario is observed: limestone results in the formation of monocarbonate and the stabilization of the ettringite content. Any further limestone present not used for the formation of monocarbonate dilutes the clinkers and leads to less other hydrates. In the metakaolin containing system the maximum monocarbonate content is observed in the area with the maximum C-S-H content. In the presence of little metakaolin, there is less aluminium available to form monocarbonate. At higher metakaolin content monocarbonate is destabilised due to the lack of CaO and strätlingite is formed instead, in agreement with experimental observations [119, 158]. In both systems the amount of ettringite is mainly limited by the availability of sulfate.

Also the variations in the calculated pore volume differ significantly between the slag and metakaolin system. In the slag cements, the lowest porosity is calculated for the high clinker containing compositions (it investigated hydration time), while in the metakaolin systems a minimum is calculated to occur at a significant metakaolin content as well as in the presence of higher limestone contents than for the slag systems.

Overall the modelling data agree well with the experimental data published in the literature [5, 85, 86, 88, 91, 93, 116, 158, 167] further supporting the application of the thermodynamic calculations. However, it needs to be noted that for high metakaolin contents and high metakaolin hydration degrees the calculations results reveal the more discrepancies to the measured phase assemblages as discussed above.

3.5. Durability

Thermodynamics is also an invaluable tool for assessing the durability of a cement paste in a given environment. The coupling of thermodynamic modelling with transport codes makes it possible to calculate the degradation of cement in contact with the environment [16, 168-173] and with sodium chloride [174, 175]. Transport modelling becomes the only possible mean of estimating the durability of cementitious materials in very long timeframes in some critical applications such as stabilisation and solidification of radioactive wastes [17, 170, 172].

Thermodynamic modelling approaches have helped to understand the important role of the available CaO on the resistance of cements against carbonation [168, 171-173, 176-179] as illustrated in Figure 12. The CaO present in the hydrates, with exception of the CaO already associated to carbonate or sulfate, is potentially available to bind CO₂, which increases the carbonation resistance of the binder [176, 177,

180]. Thus many blended cements have a lower resistance towards carbonation, which can however, partially be counteracted by their refined pore structure.

Figure 12: Modelled effect A) of the amount of CO₂ on hydrated Portland cement (adapted from [176]) and B) on the amount of portlandite in Portland cement mortar after 40 years (from [178]).

Thermodynamic calculations have been utilized to understand how salts crystallizing could generate stresses in pores of natural stones or concrete [181-183] and to explain that the expansion caused by ettringite formation is related to the crystallisation pressure generated by the formation of solids at high oversaturation within confined pores [184]. Based on pore solution analysis in calcium sulfoaluminate, calcium aluminate and blended cements, the effect of oversaturation and the so generated crystallisation pressure on expansion as well as of the amount of ettringite and pore size could also be confirmed experimentally [56, 185-188]. Coupled thermodynamic and transport modelling underlined the importance of crystallisation pressure, the amount of ettringite formed as well as the microstructure on expansion [189, 190]. For Portland cements and blended cement it could be shown that the maximum degree of oversaturation with respect to ettringite is lowered if little CaO is available [190-

192], which strongly reduces the expansion related to sulfate ingress. In addition, a low availability of CaO limits the amount of secondary ettringite, thaumasite and gypsum which can be formed [191, 193-195], which also increases sulfate resistance. Thus a reduction of the availability of CaO either by blending Portland cement with silica rich SCMs such as fly ash, SiO₂ or metakaolin or by high concentrations of carbonate in groundwater are efficient counter measures to limit damage due to sulfate [190, 191, 193, 194].

Based on the combination of experimental results with thermodynamic modelling it was found that not only the availability of Al₂O₃ but also of CaO are important. A high availability of CaO can increase the amount of Friedel's salt formed [196, 197] and thus the chloride resistance. This is particularly important for metakaolin blended cements. At intermediate metakaolin content, the binding of chloride increases in the presence of metakaolin, but at high (> 30%) metakaolin contents the Friedel's salt formation is limited by the lack of CaO resulting in lower chloride binding [198, 199], indicating an optimum chloride binding at ≤25% metakaolin content.

The recent updates of thermodynamic databases to include data for zeolites [60, 200, 201] and M-S-H [70, 76, 77, 202] make it possible to better model the complex changes in the solid phases at the surface of hydrated cements upon carbonation [172, 203], at the surface of samples in contact to clay rocks [16], exposed to MgSO₄ solutions [193] or to NaCl and seawater [15] as illustrated in Figure 13.

Figure 13: Modelled difference differences between the effect of NaCl solution and seawater on the phases formed at the surface of exposed Portland cements (reproduced from [15]).

3.6. Future challenges

Thermodynamics models and modelling approaches progressed during last years as more thermodynamic data were determined and different ways of applying them were developed. However, many challenges and open questions are still remaining. Major future challenges include i) the completion of the thermodynamic databases, and application of modelling to ii) understand the factors driving durability and possible mitigation strategies, iii) understanding early and late hydration kinetics and iv) to support the efficient development of new binder types.

Despite significant progress in the determination of thermodynamic data during the last years, several important gaps still exist in thermodynamic databases for cements. In particular, reliable thermodynamic data for water, alkali, anion and cation uptake in C-S-H and on M-S-H, data for hydrotalcite-like phases, data for zeolites derived from experimental solubility measurements as well as data for the reaction products of alkali silica reaction are needed. Further advances in the availability of thermodynamic data

in the coming years may contribute to deepen our understanding of the processes governing corrosion and/or alkali silica reaction (ASR). The solubility of ASR products and their behaviour in different media has been little studied. The through-solution mechanism, which determines the formation of ASR products, suggests that solubility studies could be suitable to study phase equilibria in these systems. The use of thermodynamic models would give the possibility to gain a deeper understanding of the observed phases in model systems and to predict which ASR products could potentially form within concrete. First attempts to use thermodynamic modeling to assess the changes due to ASR have been recently made [204-207]. Kim and Olek [204] used estimated solubilities for two hypothetical ASR products: $\text{K}_2\text{Ca}_4\text{Si}_6\text{O}_{17} \cdot 10.5\text{H}_2\text{O}$ and $\text{Na}_2\text{Ca}_4\text{Si}_6\text{O}_{17} \cdot 10.5\text{H}_2\text{O}$ to describe the sequence of ASR in model systems using a kinetic approach, while Guthrie & Carey [207] used thermodynamic data for magadiite $\text{NaSi}_7\text{O}_{14} \cdot 4.5\text{H}_2\text{O}$ as a crystalline surrogate for an alkali-silicate and okenite $\text{CaSi}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ as surrogate for a high calcium-silicate ASR product, as solubility measurements and solubility products for real ASR products are still missing. These calculations show that it is in principle possible to predict the limiting conditions for formation of ASR products and emphasize the need to determine experimentally realistic composition and solubility products for ASR products containing both calcium and alkali. One way to avoid ASR is increasing the aluminum concentration, which slows down the dissolution of aggregates [208]. Increased aluminum contents are also expected to lead to formation of zeolites in the long term as illustrated in Figure 14, which could further counteract ASR formation.

Zeolites and zeolitic precursors are also formed in alkali-activated cements [6], in the interaction zone between cement and clay rocks [169, 172], at the surface of cements exposed to NaCl [15], to carbonation [171, 203], and in Roman cements [209]. However, their stability is poorly known due to their high structural variability in terms of the Al/Si and extra-framework cations [60, 200, 210]. Further experimentally derived thermodynamic data as well as more in depth understanding of the factors determining their formation kinetics will allow predicting more precisely stability domains of zeolites,

ASR product and C-S-H as also illustrated in Figure 14, to better understand the formation conditions and how to efficiently counteract the expansive alkali silica reaction.

Figure 14: The dominance area of Portland cement, blended cements, calcium sulfoaluminat and calcium aluminate cements, zeolites and ASR products plotted on the CaO–Al₂O₃–SiO₂ ternary diagram of cementitious materials from [23].

Another important field where significant progress is expected is in the use of thermodynamic models to calculate and finally to predict the influence of cement composition and pore solution chemistry on the kinetics of cement hydration. The kinetic of precipitation (or dissolution) of a solid depends on the degree of over- (or under-)saturation, the presence of surface defects such as kink, step or pit sites, the

composition of the solution, diffusion phenomena, the presence of other ions which interact with precipitating and dissolving surfaces and hinder or promote the reaction, pH and temperature [31, 33, 211, 212]. For common minerals such as gypsum [213, 214] or calcite [211, 215] many of the parameters influencing the dissolution/precipitation processes have been investigated and kinetic laws have been formulated, although even for those minerals kinetic data for the high pH conditions relevant for cement systems is scarce. Although our knowledge on the factors determining clinker and SCM dissolution or hydrate precipitation is still limited, considerable progress has been made in recent years e.g. [124, 145, 147, 149, 151], as discussed in chapter 3.3. The complexity however increases dramatically from pure phases and lab clinkers towards industrially produced “real” materials and blends such that predictions of reaction kinetics will remain a considerable challenge.

The further development of measurement techniques allowing to follow the changes in the pore solution during cement reaction directly is expected to enable new insights into the process governing hydration. Static NMR techniques have recently been used to directly follow the Al- and Na-concentrations as well as silica coordination in solution during the hydration in alkali activated systems [216, 217]. Ion selective electrodes have been used to study continuously the concentrations changes in hydration cements in diluted systems [218, 219]. Both techniques allow following the evolution of aqueous concentrations directly as a function of time and avoid the possible artefacts due to the pressing out of pore solutions. The combination of such methods with calorimetric data, mechanical measurements and thermodynamic modelling will help to identify and understand the processes during early hydration.

The reaction of clinker and SCMs is strongly slowed down or stops altogether at later hydration times resulting in an incomplete reaction of clinker and SCMs, which has been attributed (i) to a lack of water, (ii) to difficulties to precipitate hydrates in very small pores [126, 158], or (iii) to increased Al concentrations [128]. Thermodynamic modelling coupled with detailed analysis of pore solution

composition at late ages, humidity and pore size measurements might lead to a clearer understanding of these processes contributing to minimizing the use of clinker and cements.

The combination of thermodynamic modelling, up-to-date thermodynamic databases with dedicated experiments will also be a key parameter to develop and assess efficiently new cement types such as e.g. magnesium carbonate cements [220], magnesium silicate [221], magnesium phosphate cements [218, 222] or other inorganic binders with different chemistry.

4. Conclusions and outlook

The advancement in experimental methods, the understanding of factors affecting reaction kinetics and in thermodynamic data has led to significant progress in application of thermodynamic modelling over the last decade:

- Modern hydraulic binders are of varying composition. Portland cement clinkers are increasingly blended with multiple cementitious materials in binary, ternary and quarterly blends resulting in diverse range of reactivities and cementitious compositions. Also alternative binders such alkali activated systems and calcium sulfoaluminate cements increasingly receive attention due to the effort to lower the environmental impact of cementitious materials. The significant differences between these alternative and blended binders in composition and hydrates formed can be better understood if dedicated experiments are combined with thermodynamic modelling. The use of binary and ternary plots of the hydrate volumes allows to efficiently study the effect of different SCMs and their amount on the total volume, porosity or gel space ratio in the hydrated blends.
- Also the changes during the hydration can be modelled. Such kind of modelling, however, still relies in most cases in combining a thermodynamic model which predicts the kind and quantity

of hydrates formed with an empirical model which describes the dissolution of the anhydrous cement components as a function of time. Our knowledge on the complex interactions between pore solution composition, dissolution and precipitation kinetics is still not yet sufficient to predict hydration kinetics of PC and blended systems although first attempts for simplified systems are promising.

- Plotting of pore solution data and the derived saturation indices as function of time or against solubility curves and surfaces can be used to gain further insights in the process governing the dissolution and precipitation of hydrates.
- The modelling of the processes at the surface of cements exposed to different environments has contributed significantly on our understanding of the determining factors such as e.g. i) the importance of crystallization pressure and microstructure for the expansive reaction due to sulfate, ii) how lowering the availability of CaO can reduce damages due to sulfate attack and iii) the importance of CaO for chloride and carbonate binding in hydrated cements
- The quality of thermodynamic modelling results depends directly on the accuracy and completeness of the thermodynamic database used. In the last decade the solubility products and thermodynamic properties of more and more minerals present in cementitious systems have been experimentally determined leading to more complete databases and thus to more reliable thermodynamic calculations. In recent years also some models able to describe aluminum and alkali uptake in C-S-H have been published and the development of further models to describe the uptake of different cations by C-S-H is expected to make significant progress over the next years.
- Further advances in the availability of thermodynamic data in the coming years may contribute in a similar manner to deepen our understanding of the processes governing corrosion and/or alkali silica reaction (ASR). The use of thermodynamic models would give the possibility to gain a deeper understanding of the observed phases in model systems and to predict which ASR

products could potentially form within concrete. There is a need to determine experimentally realistic composition and solubility products for ASR products containing both calcium and alkali.

- At high aluminum concentrations the formation of zeolites can be expected. Zeolites and zeolitic precursors are formed in alkali-activated cements, in the interaction zone between cement and clay rocks, at the surface of cements exposed to NaCl and during carbonation. Zeolite formation could also potentially counteract the expansive alkali silica reaction. However, the stability of many zeolites is poorly known and further experimentally derived thermodynamic data would allow predicting more precisely the relative stability domains of zeolites, ASR product and C-S-H as illustrated in Figure 14.

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