Late hydration kinetics: indications from thermodynamic analysis of pore solution data

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1 Abstract

In modern cements, significant amounts of clinker and cementitious materials remain unreacted even after long periods. The origin of the late hydration slowdown is hence of a great importance but not well understood. In this paper, literature data on pore solution concentrations from hours until a year were analyzed by means of thermodynamic modelling. Results revealed that saturation indexes of belite decrease over the hydration time while the ones of calcium aluminosilicate glasses remain constant. Similarly, the C-S-H phase saturation indexes were found to change little over time. Additionally, they are alkali-dependent: two possible explanations for this phenomenon – reduction of capillary tension and changes to the heterogeneous nucleation rate of C-S-H – were proposed. The slowdown of the late hydration could be attributed to the slow transport of elements dissolved from the reactive surfaces to the precipitation/nucleation sites at hydration times greater than one day.

12 Keywords

Saturation indexes; dissolution; precipitation

14 1. Introduction

The solution composition is a crucial feature enabling the understanding of reaction mechanisms in water containing systems. Therefore, the link between the solution chemistry and dissolution-precipitation reactions has been in the scope of researchers in geochemistry for many years [1]–[4]. The experience from the geochemistry has also been used to explain the hydration of Portland cements [5]–[10]. The focus of

19 most studies was on understanding the early hydration of cement and of alite (C_3S) phase as the main
20 component of the Portland clinker.

21 Today, most of the cements produced in Europe and in several other regions are composite binders. The
22 binary, ternary and quaternary blends of the Portland cement clinker and supplementary cementitious
23 materials (SCMs) are used. The trend is to increase the use of the composite cements as it allows the
24 reduction of CO_2 emissions associated with the cement production, among several other advantages of these
25 types of binders [11]. However, the quantity of traditional supplementary cementitious materials beside
26 limestone is not enough for long-term use in concrete. The optimization of their use is necessary to use fully
27 their potential in the future applications [11]. Significant amounts of cement Portland clinker and
28 supplementary cementitious materials remain unreacted because of the late hydration slowdown.
29 Understanding of this phenomenon is an important factor to rationalize and effectively use cement and
30 cementitious materials.

31 The hydration of composite cements is a complex process when the individual cement components interact
32 in the complex microstructure being formed [12][13][14]. Generally, the early hydration of cement clinker,
33 particularly of the calcium aluminate (C_3A) and silicate phases (mainly C_3S), is rapid. After about one to three
34 days from mixing with water, the hydration of cement components continues to slow as these most reactive
35 phases become depleted or almost depleted. In particular, phases like belite (C_2S) or amorphous glasses from
36 SCMs react slowly. The phenomenon occurs despite the hydration degree of these phases is low being in the
37 range of 0 to 10 % [12] [15] [16] [17] [18] at one day. Due to this slowdown, neat Portland cements and
38 composite cements rarely reach full hydration even after years. For the neat Portland cements, final
39 hydration degree of 90 % can be reached while it is even lower for composite cement. This phenomenon is
40 observed although the initial water amount is more than sufficient for complete hydration, i.e. at water to
41 binder ratios (w/b) of 0.5 or higher.

42 The phenomena underlying the hydration kinetics of neat Portland cements or alite pastes at the early times
43 [5]–[10] as well the filler effect arising from the physical interactions among the cement clinker and SCMs

44 have been intensively studied [8][12][19]. Contrary to that, little is known about mechanisms controlling the
45 hydration kinetics beyond one day; i.e. at the time when belite, ferrite, slag and fly ash react [12]. Two views
46 on the origins of this slowdown have been so far discussed. The first theory based its explanation on
47 observations of the porosity refinement until a critical pore size from which no further refinement was
48 observed. The lack of space for hydrates to grow then explained the slowdown [12] [20]. This view has been
49 challenged by Nicoleau and Nonat [5] who suggested that alite hydration is limited by its dissolution kinetics
50 during the so-called deaccelerating phase at later hydration times. No further explanation of the origin of
51 this slowdown of late kinetics has been reported in the available literature. Additionally, the microstructure
52 aspect is missing.

53 In this work, pore solution data available in literature and extracted from cement pastes samples over
54 hydration time from few hours up to several months are analyzed to further improve understanding of the
55 late hydration kinetics. The evolution of the pore solution concentrations in neat and composite Portland
56 cements has been reviewed recently [21] and is not further discussed here, with the exception of the
57 evolution of alkali concentration. Here, the pore solution concentrations are used to calculate saturation
58 indexes which are in turn related to the microstructural features and state of the pore solution in the
59 hydrated cement paste. In this work the data for C_2S , glasses from slag and fly ashes as well as C-S-H phase
60 and portlandite are analyzed. These phases are important for the later hydration times. The data for C_3S have
61 been analyzed elsewhere [5].

62 **2. Pore solution and cement hydration**

63 **2.1. Saturation indexes**

64 Cement hydration is a dissolution-precipitation process [19] and hence the pore solution acts as a reaction
65 vessel. The anhydrous material dissolves in the solution and the hydrates precipitate from the solution.
66 Moreover, the water, being the main component of the pore solution, is also a reactant such that the activity
67 of water in the solution is a decisive parameter as well [22].

68 The hydration reaction proceeds only when the system is out of equilibrium, particularly the following
69 conditions need to be fulfilled [23]:

- 70 • The anhydrous phases need to be undersaturated. For cement, these are calcium (ferrite) aluminates,
71 calcium silicates from the clinker and amorphous component from the supplementary cementitious
72 materials such as fly ash and slag.
- 73 • The respective hydrates need to be supersaturated, i.e. the C-S-H phase, portlandite, AFt and AFm
74 phases. However, note that portlandite and AFt can also be undersaturated depending on the system
75 investigated and time of interest.

76 The saturation index is a useful quantity to determine whether the pore solution is saturated,
77 undersaturated, or supersaturated with respect to the given phase. In this work, the saturation index, SI , is
78 defined as [19]:

$$79 \quad SI = \ln \left(\frac{IAP}{K_{sp}} \right) \quad \text{Equation 1}$$

80 Where IAP is the ion activity product calculated from the measured concentration and K_{sp} is the
81 (theoretical) solubility of a given phase. When:

- 82 • $SI = 0$; $IAP = K_{sp}$, the solution is saturated with respect to given phase, i.e. it is in equilibrium
- 83 • $SI < 0$; $IAP < K_{sp}$, the solution is undersaturated and the solid phase may dissolve
- 84 • $SI > 0$; $IAP > K_{sp}$, the solution is supersaturated and the respective hydrate may precipitate

85 Hence, the analysis of the pore solution composition allows for predicting the phase that may precipitate
86 from the solution or get dissolved by the solution. It is important to notice that the SI not only indicates
87 whether a phase dissolves, is at equilibrium or precipitates, but also can indicate at which rate these
88 processes may occur [5]. This is because the pore solution concentrations mirror the balance between the
89 dissolving and precipitating material. Generally, the rate of a reaction increases when departing further from
90 an equilibrium [1], [2]. There were several attempts to relate the Gibbs free energy (ΔG) of a reaction with
91 its kinetics. Lasaga et al. [2] noted that the reaction mechanism of aluminosilicate minerals leads to a very

strong nonlinear dependence of the dissolution rates on concentrations or saturation levels. Still, there is a general relationship, than can be expressed by the equation 2 [5]:

$$\dot{\alpha} = k \cdot A_{surf} \cdot f(\Delta G) \cdot g(a_i) \quad \text{Equation 2}$$

Where $\dot{\alpha}$ is the rate of the reaction, k is the rate constant, A_{surf} is the reactive surface area and $g(a_i)$ is a function highlighting the catalyzing or inhibiting effect of different ionic species. The ΔG is linked to the saturation index as follows:

$$\Delta G = R \cdot T \cdot \ln\left(\frac{IAP}{K_{sp}}\right) = R \cdot T \cdot SI \quad \text{Equation 3}$$

Where R is the gas constant, T is the absolute temperature

In idealized conditions, the anhydrous phase will dissolve more rapidly, if the solution is more undersaturated with respect to this phase [1], [2] and the hydrates will precipitate more rapidly when the solution is more supersaturated. The hydration of cement is a dynamic process [5]. The continuous dissolution of anhydrous phases increases supersaturation with respect to hydrates. The precipitation of hydrates increase the undersaturation with respect to anhydrous phases.

Hence, slower dissolution of anhydrous phases than the precipitation of hydrates results in a decrease of the supersaturation with respect to the hydrate phases. Similarly, a slow precipitation of hydrates decreases the undersaturation with respect to the anhydrous phases. Both phenomena can result in a hydration slowdown. Nevertheless, the pore solution concentrations remains always between the solubility of anhydrous and hydrated phases [5].

2.2. Effect of pore size and pressure

Already after first hours of hydration, the dissolution-precipitation reactions occur in a confined space [20], [24], [25], i.e. the precipitating hydrates can grow until a certain maximal size to fit into the space available. Additionally, the hydration is influenced by the increasing hydrostatic pressure because of the self-desiccation of cement paste [22], [26]. Overall, the ongoing hydration results in the formation of a fine microstructure that is partially filled with solution which is under the capillary tension. Both parameters, i.e.

116 crystal size and hydrostatic pressure, have impact on the thermodynamic properties of the anhydrous phase
 117 and hydrates and consequently on the properties of the pore solution.
 118 In order to illustrate the impact of the size and hydrostatic pressure on saturation indexes, a simplified system
 119 as shown in Figure 1 was analyzed. This includes a homogenous isotropic crystal (hydrate) in a (pore) solution.
 120 The crystal is assumed to have a spherical shape with a finite size (radius r_c) characterized by the surface
 121 energy crystal – solution (γ_{CL}) and the solubility K_c and does not interact with the wall or the disjoining
 122 pressure is neglected / not existing [27]. The solution is characterized by the *IAP* with respect to the crystal
 123 and is in equilibrium with the air characterized by the RH lower than 100 %, i.e. it is under the capillary
 124 pressure (hydrostatic tension, P_s).

**Figure 1 Illustration of a model system used to analyze
the correlation between the thermodynamic
properties of the crystal, pore solution and the size and
pressure effect.**

125 At equilibrium conditions, the internal pressure in the crystal is given by [27]:

126
$$p_c = p_e + \gamma_{LV} \cdot \kappa_{LV} + \gamma_{CL} \cdot \kappa_{CL} \quad \text{Equation 4}$$

127 where γ_{LV} is liquid-vapour interface energy and κ_{VL} is the curvature of the liquid – vapour interface, κ_{CL} is
 128 the curvature of the liquid – crystal interface and p_e the ambient pressure. The curvature of the liquid-vapour
 129 interface is related to the relative humidity according to the equation [28]:

130
$$\gamma_{LV} \cdot \kappa_{LV} = \frac{R \cdot T}{V_L} \cdot \ln \left(\frac{RH}{100} \right) \quad \text{Equation 5}$$

131 where V_L is the molar volume of the solution. If the solution is supersaturated, then the pressure in the
 132 crystal than can be sustained at this supersaturation is given be the equation [29]:

133
$$p_c = p_e + \frac{R \cdot T}{V_c} \cdot \ln \left(\frac{IAP}{K_c} \right) \quad \text{Equation 6}$$

134 where the p_e is the equilibrium pressure at with the solubility product K_c is measured and V_c is the molar
 135 volume of the crystal. Substituting Equations 1, 3 and 4 into Equation 2 and taking into account that for the
 136 spherical crystal $\kappa_{LV} = \frac{2}{r_c}$, it is possible to provide the relationship between the saturation index, pore size
 137 and capillary pressure, resp. the RH:

$$138 \quad \frac{R \cdot T}{V_c} \cdot \ln \left(\frac{IAP}{K_c} \right) = \gamma_{CL} \cdot \kappa_{CL} + \frac{R \cdot T}{V_L} \cdot \ln \left(\frac{RH}{100} \right) \quad \text{Equation 7}$$

139 And after transforming:

$$140 \quad SI(r_c, RH) = 2 \frac{V_c \gamma_{CL}}{r_c \cdot R \cdot T} + \frac{V_c}{V_L} \cdot \ln \left(\frac{RH}{100} \right) \quad \text{Equation 8}$$

141 Equation 8 enables calculation of the required supersaturation to stabilize a spherical crystal of the given size
 142 at a given capillary pressure resp. RH. This equation indicates that the supersaturation needs to increase in
 143 order to stabilize the decreasing size of the crystal. Additionally, this equation indicates that for RH lower
 144 than 100 % when the solution is under tension, the saturation needed to stabilize a crystal of the given size
 145 is lower [27]. These relationships are further illustrated in Figure 2, which give the saturation index necessary
 146 to stabilize a spherical nano-crystal in the interfacial energy range between 0 and 150 mJ/m² calculated
 147 according to Equation 8 for C-S-H phase and portlandite.

148 At RH = 100 %, relatively low supersaturation levels are needed to sustain a crystal of the size lower than 10
 149 nm and an interfacial energy lower than 50 mJ/m², a needed SI is < 1.0. The value γ_{CL} for the portlandite and
 150 C-S-H phase can be found in the literature. This is about 65 mJ/m² for portlandite [30] [31]. In the case of the
 151 C-S-H phase, the values between 12 and 55 mJ/m² are reported [32] [33] respectively.

Figure 2 Relationship between the crystal size, interfacial energy and saturation index need to sustain the crystal at equilibrium at RH 100 % (left) and 90 % (right). The value γ_{CL} for the portlandite (CH) and C-S-H phase are marked on the graph. The numbers in the white squares are saturation indexes of the isolines.

3. Evolution of saturation indexes based on literature

3.1. Literature data

Pore solution data available in literature were collected and analyzed. The data are summarized in Table 1 including the cement type, its composition (if available), water to binder ratio (w/b), method used to gain

156 the solution (after the setting time) and the curing temperature. The cement compositions were normalized
 157 to 100 % mass excluding the calcium sulfate added as setting time regulator.

Table 1 Details regarding the pore solution data. C –Portland clinker, L – limestone, FA – fly ash, S – slag, w/b water to binder ratio, Lit. – Literature.

Name	Cement type	Cement composition (%)				w/b	Comment	Lit.
		C	L	FA	S			
Neat Portland cements								
1	Neat Portland	+	-	-	-	0.35	Press out, 22 °C	[34]
2	White Portland	+	-	-	-	0.5	Press out, 22 °C	[34]
3	Neat Portland	+	-	-	-	0.4	Press out, 20 °C	[35]
4	White Portland	+	-	-	-	0.5	Press out, 20 °C	[35]
5	Sulphate resistant neat	96	4	-	-	0.4	Press out, 20 °C	[36]
6	Sulphate resistant neat	+	-	-	-	0.5	Press out, 20 °C	[37]
7	Neat Portland	100	-	-	-	0.4	Press out, 20 °C	[38]
8	Neat Portland	96	4	-	-	0.4	Press out, 20 °C	[38]
9	Neat Portland	100	-	-	-	0.5	Press out, 20 °C	[16]
10	Neat Portland	95	5	-	-	0.5	Press out, 20 °C	[16]
Composite cements								
11	Fly ash – Portland	65	-	35	-	0.5	Press out, 20 °C	[16]
12	Fly ash – Portland	65	5	30	-	0.5	Press out, 20 °C	[16]
13	Fly ash – Portland	50	0.2	50	-	0.5	Press out, 23 °C	[39]
14	Slag – Portland	60	-	-	40	0.5	Press out, 20 °C	[18]
15	Composite cement	60	10		30	0.5	Press out, 20 °C	[18]
16	Composite cement	60	20		30	0.5	Press out, 20 °C	[18]

17	Composite cement	50	20	-	30	0.5	Press out, 20 °C	[40]
18	Composite cement	50	15	5	30	0.5	Press out, 20 °C	[40]
19	Composite cement	50	5	15	30	0.5	Press out, 20 °C	[40]
20	Composite cement *	50	-	-	30	0.5	Press out, 20 °C	[40]

* Sample contains quartz as inert material

Commonly, the pore solution data after setting are gained by the steel die method using increased pressures – the co-called press out. The use of high pressure can increase slightly (<10 %) the measured concentrations as discussed in Vollpracht et al. [21] . This influence on the solution concentrations was neglected for the purpose of this work as it is within the accuracy of the pore solution analysis of ± 10 % [21]. The data available in the literature covers the hydration times between about 0.1 to 400 days, however varying depending on the source. In general, the samples are cured sealed.

In general, the pore solution concentrations are given for Ca, Al, Si, Ca, K, Na, sulfate and hydroxide or pH. This allows calculating the saturation indexes for the most important phases like anhydrous calcium silicates, C-S-H, portlandite, ettringite, monosulphate. However, the calculation of saturation indexes for other important phases such as for Fe-hydrogarnet, brucite, hemi- and monocarbonate is not possible because of the lack of the measured concentrations of Fe, C and others. This paper focuses on the saturation indexes of belite, synthetic glass, C-S-H phase and portlandite. C-S-H and portlandite are the main hydration products and are together with belite and the unreacted SCMs the main constituents of the hydrated cement paste at later ages.

3.2. Calculations

Thermodynamic modelling was used to calculate the saturation indexes. The calculations were carried out using the geochemical modelling program GEMS version 3.3 [41][42] with thermodynamic data from the PSI-GEMS database [43][44] supplemented by the cement specific data from CEMDATA18 database [45][46] for C-S-H phase, belite and calcium aluminosilicate glasses as compiled in Table 2. One notes that the calculation

of the thermodynamic properties of the glasses in the fly ashes is not possible since these materials are heterogeneous and consequently, the chemical composition is not known [47]. To cover the compositional ranges of common glasses in the SCMs, three glasses were considered: a synthetic slag taken from [48] and two slag-like glasses (glass 1 and glass 2 in Table 2) whose thermodynamic properties were estimated based on their compositions. The chemical composition of the glass 1 was taken from [18] and of glass 2 from [40], respectively (compare with data in Table 1) . For the both slags, the glass content of the slags according to QXRD was more than 95 %. It was hence assumed that their bulk chemical composition is identical to the glass composition. The thermodynamic properties of the glass phase were estimated using thermodynamic data optimized by the Calphad method [49]. It was assumed that the Gibbs energy data of the liquid slag phase extrapolated to room temperature is close to the one of the corresponding amorphous phase with the same chemical composition. The FTOxid database (version 7.3) as included in the Factsage software [50] was used for the estimation. The calculated Gibbs energy and enthalpy are referred to the stable modifications of the simple oxides. To obtain the data referred to the elements, Gibbs energy data for the simple oxides referred to the elements were added using the same database.

Table 2 Standard thermodynamic properties at 25 °C and 1 bar.

log K _{so}	Δ _f G°	Δ _f H°	S°	a ₀	a ₁	a ₂	a ₃	V°	Ref
	[kJ/mol]	[kJ/mol]	[J/K/mol]	[J/K/mol]	[J/mol/K ²]	[J K/mol]	[J/K ^{0.5} /mol]	[cm ³ /mol]	
Belite: Ca ₂ SiO ₄ ^{a, b}									
-17.41 ^{a, b}									[6]
Synthetic glass: Al _{0.178} Ca _{0.406} Mg _{0.147} Si _{0.358} O _{1.536}									
-4.75	-799.9	-843.5	45	45				19	[48]
Glass 1: Al _{0.143} Ca _{0.443} Fe _{0.004} K _{0.007} Mg _{0.09} Na _{0.002} S _{0.024} Si _{0.364} O _{1.558}									
	-794.2	-835.6	54	45				19	text
Glass 2: Al _{0.1} Ca _{0.404} Fe _{0.003} K _{0.008} Mg _{0.126} Na _{0.008} S _{0.014} Si _{0.397} O _{1.529}									
	-773.0	-813.3	54	45				19	text
Portlandite: Ca(OH) ₂									
-5.20	-897.0	-984.7	83	187	-0.022		-1600	33	[43][44]
<i>C-S-H (CSHQ solid solution)</i>									
TobH (CaO) _{0.67} SiO ₂ (H ₂ O) _{1.5}									
	-1668.6	-1841.5	90	142				55	[46] [51]
TobD (CaO) _{0.83} (SiO ₂) _{0.67} (H ₂ O) _{1.83}									
	-1570.9	-1742.4	122	167				48	[46] [51]
JenH (CaO) _{1.33} SiO ₂ (H ₂ O) _{2.17}									
	-2274.0	-2506.3	143	208				76	[46] [51]

JenD (CaO) _{1.5} (SiO ₂) _{0.67} (H ₂ O) _{2.5}								
	-2169.6	-2400.7	173	233			81	[46] [51]

193 ^alogK_{so} refers to the solubility product expressed with respect to Ca²⁺, Si(OH)₄⁰, OH⁻ and H₂O; calculated from Δ_rG°. ^bThe CaSiO(OH)³⁺
194 and CaSiO₂(OH)₂(aq) complexes present in the PSI thermodynamic data base [43] [44] were deactivated for these calculations to
195 correspond to the Phreeqc thermodynamic data base used by [6]. The solubility of belite from Cemdata (17.43) database agrees very
196 closely to the solubility product of -17.41 (at 25°C from -17.37 at 20°C) derived in [6] based on dissolution experiments.
197

198 Based on the measured concentrations in the pore solution, the activity of water, the partial pressure of
199 gaseous H₂O and thus the relative humidity of the gaseous phase (air) was calculated using GEMS.

200 3.3. Saturation indexes of anhydrous phases

201 The evolution of saturation indexes for belite and the synthetic glass are given in Figure 3. The pore solution
202 data indicate that C₂S is undersaturated as well as the glasses representing the slag or fly ash. In the case of
203 the neat Portland cements, belite phase is supersaturated up to about one day of hydration indicating that
204 belite is unlikely to react during that time. After that, its saturation indexes decrease. Similar phenomena are
205 observed in the case of composite cements. However, the saturation indexes of belite for the system
206 containing slag are more negative when compared to the neat Portland cements, i.e. the pore solutions are
207 more undersaturated with respect to belite. The pore solutions in composite cements are also
208 undersaturated with respect to the glasses representing the slags and fly ashes. The saturation indexes of
209 the glasses are not changing over the hydration time.

Figure 3 Evolution of the saturation indexes over the hydration time for A) C₂S in neat Portland cements, B) C₂S in composite cements, C, D, E) glasses in the composite cements. The numbers in the legend corresponds to the samples listed in the Table 1. Estimated accuracy of calculated SI: ± 0.2 and ± 0.1 for glass assuming 10 % measurement error. See the article text for the colour coding.

3.4. Saturation indexes of C-S-H and portlandite

Saturation indexes for the C-S-H phase and for portlandite are given in Figure 4. In the neat Portland cements, the SI of the C-S-H phase is in the range of 0 to 1.0. For the most of the composite cements, the saturation indexes are lower than in the neat Portland cements. The saturation indexes of portlandite are constant over time in the case of the neat Portland cements, within the accuracy of the method applied. In the case of the composite cements containing slag, the saturation indexes decrease after about half a day of hydration and after 1 – 2 days, the portlandite becomes undersaturated. In the case of fly ashes containing cements, this phenomenon occurs later.

Figure 4 Evolution of the saturation indexes over the hydration time for A) C-S-H in the neat Portland cements, B) C-S-H phase in composite cements, C) portlandite in neat cements, D) portlandite in composite cements. The numbers in the legend corresponds to the samples listed in the Table 1. Estimated accuracy of calculated SI: ± 0.1 assuming 10 % measurement error. For the colour coding, see the article text.

218 The cements investigated can be categorized into two groups, depending on the level of supersaturation,
 219 when analyzing the saturation indexes of the C-S-H phase. In the case of the neat Portland cement and
 220 composite cements, there are groups characterized by lower and higher saturation indexes, respectively.
 221 These two groups are highlighted with the corresponding colour coding in Figure 4 (and Figure 3). Analysis of
 222 the pore solution concentrations reveals that these two groups are characterized by different alkali
 223 concentrations as shown in Figure 5. The cements that are characterized by the higher saturation indexes
 224 have high alkali concentration. Additionally, the alkali concentration in the neat cements is significantly
 225 higher than the one in the composite cements. This phenomenon is further illustrated in Figure 10 in
 226 appendix.

Figure 5 Evolution of the alkali concentration in the investigated cements (sum of K and Na concentrations).

227 The difference in alkali concentrations between neat and composite cements results from the fact that the
 228 most of the soluble alkalis originate from the cement clinker. Additionally, it is reported that the C-S-H phase
 229 in the composite cements binds more alkali when compared to the C-S-H phase in the neat Portland cements
 230 [52].

231 4. Discussions

232 4.1. Saturation indexes and reaction mechanisms

233 Measured pore solution concentrations of Ca, Si, Al, S, K, Na and pH show a considerable scatter because of
 234 the differences in the cement composition including the different cement clinkers and SCMs used and the
 235 different water to binder ratio applied for the sample preparation [21]. However, application of the
 236 thermodynamic modelling revealed that the data could be rationalized. In all samples investigated, the
 237 saturation indexes of the anhydrous (C_2S and glass) as well as of hydrates (C-S-H and portlandite phases) are
 238 similar among the different samples of comparable alkali concentrations. For a given phase, they follow one
 239 master line only depending on the alkali concentration in the case of C-S-H phase and the presence of SCMs
 240 in the case of portlandite.

241 The evolution of the saturation indexes corresponds well to the kinetics of hydration of the cements studied.

242 Initially, belite is supersaturated and only after about one day it becomes undersaturated (c.f. Figure 3). This

243 partially explains the difference in belite kinetics as measured by QXRD in the neat and composite Portland

244 cements shown in Figure 6 as an example [53] [16] [54] [18]. Belite starts to react only at the time when it

245 becomes undersaturated, however with some delay in the composite cements. The continuous

246 undersaturation of the glasses from slag and fly ash corresponds well to the steady, but slow reaction of

247 these materials [15], [17], [18]. Note however, that the slag data was used to approximate solubility of the

248 glasses in fly ashes. During the whole hydration period of neat Portland cements, the C-S-H phase and

249 portlandite are supersaturated. In the case of the composite cements, the portlandite is undersaturated after

250 about 1 day of hydration because of the semi-hydraulic or pozzolanic reaction of the slag and fly ash,

251 respectively.

Figure 6 General overview of the hydration kinetics of Portland cement constituents. A) Hydration degree evolution of the main cement clinker phases in the neat Portland cement (solid lines) and composite cements (dotted lines). Data adopted from [17]. B) Hydration degree evolution of the slag and fly ash in the composite cements. Data adopted from [17] and [16], respectively. The w/b used was 0.5. Note that the hydration degree of the phases can vary depending on the composition and intrinsic properties of the active phases and the replacement ratio, though the general trends are kept.

252 The findings above demonstrate that the pore solution properties obey the predictions and the rules of the
253 thermodynamics, and particularly the mechanisms of the reaction described as the dissolution-precipitation
254 process. Namely that irrespective of the differences in starting materials chemical and mineralogical
255 composition, the hydration is governed by the phases in contact with the pore solution, i.e. the anhydrous
256 phases dissolving and the hydrates forming and by their thermodynamic properties, respectively.

257 **4.2. Space limiting growth vs. saturation indexes evolution**

258 Scrivener and co-workers [20], [55] have investigated the hydration of cements at later hydration times. They
259 demonstrated that during the hydration of neat Portland cements and composite cements, the pore space
260 is gradually filled by hydrates leading to porosity reduction and refinement. Muller et al. [24], [25] have
261 shown with H^1 NMR technique that the water filled capillary pores volume rapidly decreases from the first
262 day of hydration. In parallel to that, the volume of gel pores increases. Consequently, the hydrates
263 precipitate in small pores in the range of tens of nanometer in size, particularly at lower water to cement
264 ratios. The hydrates formed need to be of a small size to precipitate or to grow into the small pores that are
265 filled with water. According to mercury intrusion porosimetry, for composite cements containing slag or fly
266 ash hydrated at water to binder (w/b) ratio of approx. 0.4, the porosity is not refined any more after about
267 28 days of hydration as described by the constant critical pore entry radius [20]. For the system containing
268 reactive metakaolin, the critical pore radius of approximately 3 to 5 nm can be reached as early as after 3
269 days [55]. It was suggested that this phenomenon corresponds to the slowdown or even inhibition of
270 hydration.

271 However, at w/b of 0.5 or higher no such stopping of hydration is observed. The hydration is continuing up
272 to at least 360 days (that is the last measurement point in work [17]), as shown in Figure 6. The hydration of
273 alite reaches its maximum between 2 and 7 days of hydration. The reaction of C_2S and the calcium alumina
274 glasses from slag and fly ash continues. In accordance with the ongoing reaction, the refinement of porosity
275 is observed but the critical pore radius is not reached up to 180 days of hydration [56] as illustrated in Figure
276 7.

Figure 7 Evolution of the pore size distribution of the neat Portland cement (A) and composite cement containing slag as the main SCM. The w/b used was 0.5. Data adopted from [56].

277 Since the microstructure is continuously refined during the hydration, the C-S-H precipitates in more and
 278 more confined space. This requires that the supersaturation for the C-S-H phase needs to increase to account
 279 for the decrease of the pore size, as shown in Figure 2, assuming that the hydration is limited by the growth
 280 of hydrates [12], [20]. Moreover, the undersaturation with respect to the C_2S and glasses should decrease.
 281 Generally, the solution concentrations need to be close to the solubility of anhydrous phases and strongly
 282 supersaturated with respect to the hydrates when the kinetics is limited by the precipitation of hydrates [5].
 283 Contrary to that, the saturation indexes of the C-S-H phase and portlandite in neat cements do not show any
 284 tendencies to increase over the hydration time (c.f. Figure 4), neither for the neat Portland cements nor for
 285 the composite cements containing slag and / or fly ash, irrespective of the w/b used. The supersaturation of
 286 the C-S-H phase rather seems to be a function of the alkali concentration in the solution than of the
 287 refinement of the pore space. Additionally, the undersaturation of belite is slightly decreasing while that of
 288 the glasses does not change during the hydration time.

289 For the cement pastes investigated here, the saturation indexes of the C-S-H phase are close to the solubility
 290 product, i.e. to the equilibrium. This is in agreement with the limited impact of crystal size on the
 291 supersaturation needed to stabilize small crystals as shown in Figure 2 (Section 2.2). The relatively low values
 292 of γ_{CL} , in particular for the C-S-H phase, indicate that the C-S-H particles can precipitate in form of small

crystals of nanometer size. Moreover, the saturation indexes of the C-S-H phase are independent of the initial w/b ratio, in the here investigated range.

The limited changes to the saturation indexes of the C-S-H phase between about 0.5 and 360 days of hydration suggest that the mechanism of the C-S-H phase growth does not change in this period, even if the available space for the growth decreases and refines considerably (Figure 7). The same applies for the portlandite in the neat Portland cements. Since at the early times of hydration, i.e. at the times 0.1 to 0.5 days, it is little probable that the space limits the hydration and the saturation indexes do not change, it is reasonable to state that the space available does not limit the hydration at later times.

This conclusion corresponds to the neat Portland cements hydrated at water to binder ratio of 0.35 to 0.5 and the composite cements at water to binder ratio of 0.5 to 0.6. These water to binder ratios are higher than those used by Scrivener and co-workers [20], [55] to study the hydration of the composite cements, which was mostly 0.4 or lower. It is possible that the evolution of the pore solution concentration is different at such low w/b, although we have not seen any clear trends with changing w/b in the data analyzed. Verification of the effect of w/b is very challenging since it is difficult to obtain the required amount of pore solution at such low w/b. Additionally, at these conditions very high pressures are needed to press out the solution which in turn results in a distortion of the data [21]. Furthermore, we must note that the analyzed systems are homogenized experimentally by the way the pore solution is gained, as well as numerically in the thermodynamic calculations that assume a homogeneous system. In systems such as composite cements with highly reactive calcined clays, thermodynamically incompatible phases – portlandite and strätlingite – coexist [57] [58]. This implies that there must be differences in the local pore solution compositions. These differences are smeared by the current available pore solution sampling methods including the one used. This renders the overall approach used in this paper challenging for such dense systems. Indeed, further advancement in characterization techniques as well as modelling tools is need to further advance the understanding of such heterogeneous cement pastes.

4.3. Effect of pH on the pore solution concentrations and saturation indexes

318 The concentration of alkalis has an important impact on the saturation indexes of the C-S-H phase. It is
319 believed that the high alkali concentration accelerates the cement hydration [59], particularly at early times.
320 However, at later hydration times, this relationship is not necessarily kept. In general, higher alkali
321 concentration in the pore solution results in a reduction of the late compressive strength [59] [60] [61] and
322 the late hydration degree is not increased in the presence of alkalis [53] [60] [61]. The experience of the
323 authors of this contribution **shows** that the higher alkali concentration neither accelerates the reaction of
324 belite nor of slag glass in the neat and composite Portland cements, respectively. In the case of glasses in fly
325 ash, higher alkali accelerate the hydration of these materials. Still, this phenomenon is in general related to
326 the accelerated dissolution of the fly ash glass in these conditions [62] and not to modifications of the
327 precipitation phenomena.

328 The concentration of alkalis in the pore solution has an impact on the tension in the pore solution and has
329 impact on the growth of the C-S-H phase. These two phenomena may explain the higher saturation indexes
330 for the C-S-H phase although similar hydration kinetics was observed.

331 **4.3.1. Tension in the pore solution**

332 During the hydration of sealed samples (these are generally used for the hydration studies) or in concrete
333 cores, the relative humidity rapidly decreases [26]. Hu et al. [26] have shown that RH decreases to 95 % at
334 $w/c = 0.46$ after about 7 days of hydration. For cement samples at low of $w/b = 0.3$, it even drops to values
335 as low as 80 % after the same time of hydration. Similar results are reported for the composite cements
336 containing metakaolin [63]. In the porous body of the cement paste, at RH lower than 100 %, the water starts
337 to evaporate and menisci develop in the pore space [28]. This results in the formation of the capillary
338 pressure resulting from the interaction between the solution and walls of the pores and emptying of the
339 bigger pores.

340 The relative humidity decrease has two causes. It is related to (1) the self-desiccation of the cement paste
341 and to (2) the decrease of the water activity in the pore solution. The second phenomenon is mainly related
342 to the increasing alkali concentration in the pore solution (Figure 5), which lowers the water activity and thus

343 the RH. It is important to notice that only the first contribution results in the increase of the tension [64] of
 344 the pore solution and modifies the pressure in the crystal as explained in section 2.2. Based on the measured
 345 concentrations in the pore solution, the activity of water was calculated when applying the GEMS model. The
 346 results are shown as relative humidity in Figure 8.

Figure 8 Relative humidity calculated based on the activity of water

347 Figure 8 shows the RH at equilibrium with the bulk pore solution, i.e. without considering the formation of
 348 capillary menisci. For the here investigated low alkali systems, the alkalis have only a limited impact on the
 349 water activity and so on the relative humidity that is in the range of 99 %. However for the high alkali systems,
 350 the RH is in the range of 98 - 97 % already after 7 day of hydration. As mentioned, the calculated water
 351 activity reflects neither the self-desiccation nor the presence of capillary menisci and hence cannot explain
 352 the lower RH measured in real systems alone.

353 The measured RH is in the range of 95 % at w/b around to 0.5 after 7 to 28 days of reaction [26]; this includes
 354 the contribution of the self- desiccation as well as the effect of water activity. This shows that the high alkali
 355 concentration considerably reduces the tension in the pore solution when compared to the low alkali
 356 cements. Consequently, the alkalis reduce the positive impact of tension on the oversaturation of the C-S-H
 357 phase and portlandite. This may result in higher saturation indexes for a similar hydration kinetics and explain
 358 the calculation results.

4.3.2. Growth of the C-S-H phase

Labbez et al. [65] [66] postulated that the macroscopic formation (precipitation) of C-S-H phase occurs due to the aggregation of nanoparticles. This is because in the case of the highly charged C-S-H particles, the growth rate is significantly slower than the heterogeneous nucleation rate. This phenomenon is observed even at low supersaturation levels. It means that for a C-S-H particle nucleating on a C_2S surface, the nucleation is faster than its growth at SI equal or higher than 0.04 and on calcite at $SI \geq 0.25$. When the C-S-H particle is nucleating on C_3S , this crossover appears at SI much lower than 0.04 [65]. Knowing that the C-S-H phase has surface properties very close to C_3S , i.e. the hydroxylated calcium silicate surface [67], one can thus argue that secondary nucleation of C-S-H (that is nucleation of new C-S-H particles close to an existing C-S-H particle) is dominating for SI lower than 0.04 [68]. Consequently, in the here investigated range of supersaturations (Figure 4), the conditions in the pore solution favours the heterogeneous nucleation of new C-S-H particles over the growth of already existing C-S-H particles. Nonat and co-workers [52][67] reported that more alkalis are taken up by C-S-H in the presence of a higher alkali concentrations and lower calcium concentration. At these conditions, the alkalis partially replace calcium at the surface of the C-S-H phase [67]. This impacts the interaction free energy at contact between C-S-H particles [67] and hence the heterogeneous nucleation rate of the C-S-H [33]. As the result, higher supersaturations are needed at higher alkali concentration for the same rate of the C-S-H precipitation, respectively its secondary nucleation.

4.4. Effect of Al concentration

The belite reaction is retarded in composite cements when compared to the neat Portland cements [53] [16] [54] [18] (Figure 6), even if the undersaturation which respect to belite is higher (Figure 3). This phenomenon may be explained by the specific interaction of belite hydroxylated surface and anions from the pore solution (Equation 2). Also it was proposed that the aluminate ions bind to surface of calcium silicate phases and inhibit the dissolution [9] [69]. It is noticeable that the alumina concentration in the composite cement is higher than in the neat Portland cements [21] [18] and may delay the belite reaction. This is further supported

383 by the fact that this interaction is particularly strong in mild alkaline conditions [21] that are characteristic
384 for the composite cements.

385 In some cases, belite reacts strongly at later hydration times, i.e. after 28 – 90 days (Figure 6 A), when the
386 alumina concentration is still high [21]. This is associated with the continuously decreasing undersaturation
387 (Figure 3) and the fact that upon progress of hydration and at higher pH values, the binding strength of
388 aluminates to the calcium silicate surfaces decreases so that its passivating effect and retardation are
389 reduced [69]. One notes that during the composite cements' hydration, despite of the fact that the alkali
390 concentration does not significantly change (Figure 5), the pH steadily increases [21]. Hence, the interaction
391 of alumina with hydroxylated belite surface may be responsible for the delay of belite reaction in the
392 composite cements when compare to neat Portland cement.

393 **4.5. Impact of heterogeneous hydration process**

394 The overall rate of hydration reaction is controlled by the slowest of three coupled processes, either the
395 dissolution or the precipitation or the transport of species from the dissolution surface to the precipitation
396 surface [4]. As discussed above, the precipitation of the hydrates (the C-S-H and portlandite phase) is not
397 decisive for the slow hydration at later ages. In the discussion until now, the effect of the transport was
398 neglected. It is discussed in this section.

399 During the calcium silicates hydration, a shell of the hydration products is formed around the anhydrous
400 grains. Consequently, the elements need to dissolve and diffuse across the hydration products (the so-called
401 inner product [70]) to the space initially occupied by water where the hydrates precipitate (the so-called
402 outer product [70]). Additionally, during the hydration, the formation of the Hadley grains is observed [71];
403 i.e. there is a gap between the dissolving surface of the anhydrous material and the layer of the precipitating
404 hydrates.

405 Note, that the state of the solution in the pore space initially occupied by the water, and the space close to
406 the dissolving cement grains can be significantly different. The collected and measured pore solution data
407 correspond to the solution composition in the space initially occupied by water rather than close to the

408 surface of the dissolving anhydrous material. This is because of the press out methodology used to gain the
409 solution gives only about 5 to 10 % of the total solution in the sample according to authors' experience. With
410 this approach, only the easiest available solution is gained, which is the solution in the space between the
411 cement particles and hydrates formed.

412 If the transport of the ions were slow compared to the dissolution and precipitation processes, the
413 concentrations in the space close to the dissolving anhydrous particles would be higher than at the vicinity
414 of the outer product as shown in Figure 9. This means higher supersaturation against the hydrates (C-S-H)
415 and lower undersaturation against the anhydrous phases. The existence of the higher supersaturation in the
416 space close to the anhydrous material is supported by the fact that the inner C-S-H phase has a finer
417 microstructure, i.e. it is characterized by the small crystal size, compared to the outer product [72] [73]. The
418 effect of the slow diffusion on the evolution of the microstructure can be illustrated when analysing
419 metakaolin-containing cements [57], [58], [74]. In these systems, thermodynamically incompatible phases,
420 namely portlandite and strätlingite, co-exist [57], [58] or the reaction of dolomite is limited even in the
421 presence of portlandite [74]. These phenomena are explained by formation of the dense C-S-H matrix
422 resulting in the heterogeneous system in which local equilibria govern the precipitation of the hydrates. The
423 very dense microstructure that is characterized by high tortuosity and is only partially filled with water limits
424 the exchange of ions between the reacting phases. Note that in these works [57], [58], the w/b used was as
425 high as 0.55.

Figure 9 Schematic representation of the of the differences in the pore solution properties close to the outer and inner product (left) and TEM micrograph showing Ip and Op C-S-H present in a hardened C3S paste with $w/c=0.4$ hydrated at 20°C for 8 years. White arrows indicate the Ip–Op boundary [73] (right). Permission of the publisher for the picture is required.

426 Literature data show that total porosity steadily decreases even for samples with fine microstructure [20]
 427 [57] [58], i.e. when the pore threshold diameter does not further decrease or when incompatible phase
 428 assemblage is present. This further supports that the hydration reaction is still ongoing, but its rate is limited
 429 by the transport phenomena.

430 At the relative humidities concerned, pores down to few tens of nanometres are empty. The water layer
 431 thickness is then comparable to the size of individual microstructural features of hydrates (c.f. Figure 9). As
 432 individual surfaces of a crystal might have different energies [75] and hence thermodynamic properties , the
 433 equilibrium pore solution concentrations could be different in the vicinity of the different microstructural
 434 features of a single phase. The presence of the zones with different pore solution concentrations would
 435 effectively hinder the diffusive transport across these regions. Furthermore, the simplified model for
 436 assessing the effect of size and pressure used here is only a rough approximation of the complex interaction
 437 within the geometry shown in Figure 9. It cannot account for the real crystals and interactions of these
 438 crystals with the pore walls. Precipitating C-S-H phases as well as the other hydrates interact with the solid
 439 matrix, which is under compression in the scenario considered in the paper. This interaction can change the

thermodynamic properties of such crystals to a variable extent depending on the local arrangement and the stress history. Understating this phenomenon would allow for a better modelling, explaining the kinetics of the cement hydration and microstructure development.

5. Conclusions

In this paper, pore solution data from literature were analysed by thermodynamic modelling to enhance the ongoing discussions about the limitations of late hydration. The data analysed comprise neat Portland cements as well as composite cements containing slags, fly ashes and limestone additions. They span from half day up to one year and cover water to cement ratios from 0.35 and 0.5 for neat Portland cements and at 0.5 for composite cements respectively.

Despite the large scatter in concentrations of individual elements and differences in cement compositions, the development of saturation indexes follows a master line for a given phase dependent on alkali concentrations. This shows that the methodologies applied, both experimental and modelling, are robust and consistent. It further confirms that the pore solution composition is determined by the phases dissolving in the solution and precipitating from the solution.

In the case of the analysed samples, the development of saturation indexes of anhydrous phases does not support the hypothesis of space-limited growth at later ages as the indexes do not increase in time. The development of saturation indexes of the investigated hydrates (C-S-H and CH) together with their low interfacial energy make the space-limited growth alone improbable explanation. However, in dense systems with spatially heterogeneous pore solution, the local conditions might lead to situations preventing precipitation or growth of certain hydrates other than C-S-H and CH and thus further refinement. In such systems (e.g. composite cements), the total volume of porosity has been reported to decrease without a further decrease of the pore threshold diameter. The pore solution from these dense systems are largely missing since it is too difficult to access. The analysis presented here coupled with the decrease of the pore size show that the overall slowdown of the late hydration can be potentially attributed to the transport of dissolved elements from the dissolution sites to the precipitation sites over a layer of hydrates and thorough

465 partially empty pores. The data suggest that transport starts to play a role at the times as early as one day of
 466 hydration. Though, no direct experimental proof is available and further research is needed.

467 The saturation indexes of the C-S-H phase were found to be alkali-dependent, where higher alkali
 468 concentrations resulted in higher supersaturation. Two possible causes for this dependency were identified:

- 469 • Changes of the water activity and the related reduction of the capillary tension leading to higher
 470 supersaturation needed to stabilize particles of a given small size.
- 471 • Higher supersaturation is required to offset the impact of alkali absorbed on the C-S-H on the
 472 heterogeneous nucleation rate of the C-S-H believed to be the main precipitation mechanism of this
 473 phase.

474 6. Acknowledgement

475 The discussion with Christophe Labbez on the mechanisms of C-S-H growth is greatly appreciated. The
 476 authors would like to thank and acknowledge Alexander Pisch for the calculation of the thermodynamic
 477 properties of the slags.

478 7. Appendix

Figure 10 Dependence of the alkali concentration in the pore solution and saturation indexes of the C-S-H phase. The boxes highlight the ranges of the two groups (low and high alkali systems) of the investigated samples. The colour coding is explained in the text.

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