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Early hydration of SCM-blended Portland cements: A pore solution and isothermal calorimetry study

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ABSTRACT

In this study the hydration kinetics and the development of concentrations in the pore solution of cement pastes containing different supplementary cementitious materials (blast-furnace slag, Si-rich fly ash, limestone, quartz) at a cement replacement of 50 wt.% were investigated during the first 6 h of hydration. The results indicate that the degree of undersaturation with respect to alite is the primary factor driving the early hydration kinetics. The accelerating effect of the limestone is related to a higher undersaturation. The data reveal also that high aluminium and sulfate concentrations, which depend on the type and chemical composition of the used mineral addition, retard the reaction. High calcium concentrations had no adverse effect on hydration kinetics. The investigations underpin that the mechanisms controlling the early hydration are a complex combination of the filler effect, the pore solution chemistry as well as intrinsic reactivity of the mineral additions and their surface characteristics.

1. Introduction

Due to the possibility to reduce the carbon footprint of cement by blending it with cement replacing materials, supplementary cementitious materials (SCM) are becoming more and more important as mineral additions, especially in Portland cement-based composite cements [1]. SCM affect the reaction of Portland cement (PC) by acting initially as (quasi-)inert addition and at later stage due to their chemical reaction, which depends on the type, fineness and composition of the SCM. Initially where no or little reaction of the SCM occurs, these materials influence the hydration of the PC mainly by the so-called filler effect [2,3] which actually consists of two different aspects:

(i) The presence of additional and different surface sites on the SCM can accelerate the hydration during the first hours as more surface for nucleation and growth of hydrates is present [4–6]. This effect has been observed to be most distinct for calcite but is also generally observed if PC is blended with quartz or blast-furnace slag. For fly ash both, retardation and acceleration have been reported.
(ii) The water-to-(Portland-)cement ratio (w/c) is increased in such blends due to the presence of SCM that initially show little reaction. This additional water promotes the amount of Portland cement reacted after 1 day and longer as more water [7,8] and more space [9–11] for the growth of hydrates is available.

Recent investigations showed that the number of nuclei on the calcite particles is significantly higher than on quartz and blast-furnace slag [12]. While the underlying processes that cause this effect remain unclear, the effect itself explains the accelerating effect of limestone in blended cement [13]. In the case of fly ash a different behavior can be observed. Blending Portland cement with fly ash can lead to retardation of the hydration, especially if a very fine fly ash is used [14]. It has been argued that this effect is caused by interactions of alumina from the fly ash and calcium from the pore solution or by chemisorption of calcium ions on the surface of the fly ash [15–17].

In contrast to the early promotion of PC reaction in the presence of SCM due to the presence of additional nucleation sites, the use of a higher water-to-cement ratio generally retards the early hydration of alite and of PC [7,8,18,19]. A possible explanation could be the higher calcium concentrations due to lower pH values in a diluted system and the absence of additional nucleation sites. In addition to the effect of calcium concentration, also pH, silicon concentrations and the degree of undersaturation of the pore solution with respect to alite can be expected to play an important role.

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The main contribution to the heat of hydration observed during the early reaction of PC is related to the reaction of alite to C-S-H and portlandite, while the reaction of the other clinker phases contributes relatively little to the heat release observed between 1 and 12 h as discussed in detail by Jansen et al. [20]. Thus the changes in the heat observed by calorimetry during the first hours are strongly influenced by the reaction kinetic of alite which is discussed in more detail in the following. Investigations on laboratory synthesized C_3S and C_2S carried out at high water-to-binder ratios showed that higher CaO-concentrations decrease the dissolution rates of C_3S and C_2S significantly [21,22]. Also higher pH values decrease the alite dissolution at constant calcium concentrations [21,22]. In Portland cement where portlandite is present, the pH values influence the calcium concentrations; higher pH values will lower the calcium concentration [14,23] due to the precipitation of portlandite and the common ion effect. It has been argued [24] that the acceleration of the alite hydration in the presence of alkali hydroxides [24–26] could be related to such a decrease of the calcium concentrations caused by the higher pH values. Based on that line of thought a higher w/c which decreases the pH and increases calcium concentrations [14,23] might be expected to retard the alite reaction.

Alite dissolution is fast at high degrees of undersaturation and slow at near equilibrium conditions [21]. The effect of the degree of undersaturation on dissolution kinetics is particularly distinct if the solutions are moderately undersaturated. At high degree of undersaturation the reaction kinetic is rather limited by the number of reactive surface sites than by changes in the degree of undersaturation as discussed in detail in [21,22,27]. The suppressing effect of high calcium concentrations and high pH values discussed above can be rationalized in terms of undersaturation as shown in Nicoleau et al. [21], as pure water is much more undersaturated with respect to alite (which is thus dissolving faster) than saturated lime solutions. Investigations by Bullard et al. [28] indicate that the interplay of undersaturation with respect to C_3S and oversaturation with respect to C–S–H determines the overall hydration kinetics of alite. The presence of more C-S-H nuclei leads to faster C-S-H growth causing lower oversaturation with respect to C-S-H [28]. Lower calcium and silicon concentrations due to faster C-S-H formation result in higher undersaturation with respect to C_3S and thus in faster alite dissolution. This interplay between precipitation and dissolution reactions is the reason why nucleation processes can play such an important role for the reaction kinetics.

Also the concentration of other ions affects the kinetic alite reaction. Aluminium retards alite reaction [22,29,30], which has been related to a hindered growth of C-S-H due to a poisoning by aluminium [29,31,32] and/or to hindered dissolution of alite due to binding of aluminium on the alite surface sites [22]. The retardation of the alite reaction in blended cements containing fly ash could thus be related to the presence of more aluminium in the pore solution. Similarly also sulfate has been reported to retard alite dissolution [22].

While the accelerating effect of limestone has been studied in binary cement blends at a water-to-solid ratio of 0.4 using calorimetric and microscopic techniques, insights into the effect of aluminium, sulfate and calcium result mainly from investigations of dissolution of laboratory synthesized clinker phases in diluted suspensions. The complexity of the systems increases dramatically from pure phases and laboratory synthesized clinkers towards industrial available “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 the present study the early hydration of binary cement-based systems including mineral additions (blast-furnace slag, Si-rich fly ash, limestone and quartz) is investigated by isothermal calorimetry and the composition of the pore solution chemistry is analyzed. Saturation indices are calculated in order to obtain the oversaturation/undersaturation with respect to C_3S and Ca-rich C-S-H.

Table 1
Chemical composition[a] and physical properties of the used raw materials. Data in [wt.%] unless otherwise stated.

	PC	BFS	FA	LS
SiO_2	19.61	39.26	59.68	2.28
Al_2O_3	4.90	8.40	23.33	0.98
TiO_2	0.26	0.29	1.12	0.05
MnO	0.20	0.59	0.03	0.02
Fe_2O_3	3.32	0.38	6.54	0.27
CaO	62.89	38.55	1.61	52.84
MgO	1.39	8.40	1.01	0.45
K_2O	0.58	0.58	2.01	0.22
Na_2O	0.15	0.41	0.45	0.00
SO_3	2.85	1.85	0.15	0.01
P_2O_5	0.18	0.02	0.22	0.03
L.O.I.[b]	1.69	+0.34[g]	2.25	42.41
Total	98.02	98.73	98.40	99.56
CO_2[c]	0.5	0.1	1.1	42.4
C_{total}[d]	n.d.	n.d.	1.41	n.d.
$K_2O_{\text{water soluble}}$[e]	0.40	0.03	0.03	<0.01
$Na_2O_{\text{water soluble}}$[e]	0.04	0.01	0.03	<0.01
$SO_{4\,\text{water soluble}}$[e]	1.20	0.22	0.63	<0.01
Density [g/cm^3]	3.13	2.90	2.33	2.77
d_{50} [μm]	9	14	12	17
SA [cm^2/g][f]	3700	2700	3400	2600

[a] Determined by XRF analysis (wt.%).
[b] 950 °C (PC, BFS), 1050 °C (FA, LS).
[c] Calculated from TGA.
[d] C content determined by combustion analysis. TOC = 1.27 wt.%.
[e] Readily soluble alkalis and SO_3 calculated from the concentrations of alkalis measured in the solution after 5 min agitation at a w/s of 10.
[f] Surface area calculated from PSD and density.
[g] Gain on ignition due to oxidation of S^{2-}.

2. Experimental

2.1. Materials and mix design

An ordinary Portland cement (PC) CEM I 52.5 R was used in this study. Set regulators were 1 wt.% bassanite and 3.1 wt.% gypsum. Different SCM have been considered: blast-furnace slag (BFS), Si-rich fly ash (type V according to EN 197-1) (FA) and limestone (LS) with a calcite content of >95 wt.%. Inert quartz powder (Qz) was used as reference material. The chemical and mineralogical composition of the used materials is presented in Tables 1 and 2.

Table 2
Mineralogical composition of the used raw materials determined by quantitative XRD. Data given in [wt.%].

	PC		BFS	FA	LS
C_3S	68.2	Calcite	1.7	0.9	95.6
α' C_2S	3.0	Gypsum	0.8		
β C_2S	4.1	Hematite		0.6	
C_3A cubic	2.0	Maghemite		0.8	
C_3A othorh.	3.1	Mayenite	0.2		
C_4AF	11.4	Merwinite	0.7		
Arcanite	0.8	Mullite		11.4	
Bassanite	1.0	Others	2.3		3.5
Calcite	1.3	Quartz	0.2	14.3	0.9
Lime	0.6	Amorphous	94.1	72.0	
Gypsum	3.1				
Periclase	0.6				
Portlandite	0.8				
Total	100		100	100	100

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