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Influence of limestone and anhydrite on the hydration of Portland cements

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ABSTRACT

The addition of $CaCO_3$ and $CaSO_4$ to Portland cement clinker influences the hydration and the strength development. An increase of the $CaSO_4$ content accelerates alite reaction during the first days and results in the formation of more ettringite, thus in a higher early compressive strength. The late compressive strength is decreased in Portland cements containing higher quantities of $CaSO_4$. The reduced late compressive strength seems to be related to an increase of the S/Si and Ca/Si content in the C–S–H.

The presence of calcite leads to the formation of hemicarbonate and monocarbonate thus indirectly to more ettringite. Only a relatively small quantity of calcite reacts to form monocarbonate or hemicarbonate in Portland cement. Although hemicarbonate is thermodynamically less stable than monocarbonate, hemicarbonate formation is kinetically favored. Monocarbonate is present only after 1 week and longer independent of the quantity of calcite available and the content of sulphate in the cement.

1. Introduction

The addition of $CaCO_3$ and $CaSO_4$ to Portland cement clinker influences the setting behaviour, the progress of hydration and the strength development during hydration. If limestone is added in the small quantities, limestone has a positive impact on the engineering properties of the cement and concretes [1]. The positive impact of limestone on the cement properties was explained as a filler effect [2]. More recent studies showed that calcite is also a reactive cement component [3]. In the presence of limestone, the formation of hemicarbonate ($C_3A{\cdot}0.5CaCO_3{\cdot}12H_2O$) and monocarbonate ($C_3A{\cdot}CaCO_3{\cdot}11H_2O$) is observed instead of monosulphate [4], which prevents the decomposition of ettringite. In contrast, in limestone free cements the further reaction of aluminate phase leads to the destabilization of ettringite and formation of monosulphate, after all gypsum is consumed [5,6]. The stabilisation of the voluminous ettringite instead of monosulphate gives rise to an increase in the total volume of hydration products [5–7] and can thus result in an increase of the compressive strength of mortars [8–11].

Thermodynamic calculations indicate that the main stable phases in hydrated calcite-containing cement are C–S–H, CH, ettringite, monocarboaluminate, and calcite [5,7], while hemicarbonate is calculated to be stable only if no excess calcite is present, i.e. in hydrated Portland cements which contain less than 2–3 wt% of calcite. In experimental studies generally, the formation of hemicarbonate is observed initially [5,6,12,13] in contrast to the thermodynamic calculations. The content of hemicarbonate decreases over the hydration time as monocarbonate is formed instead. The reason for the initial formation of hemicarbonate instead of monocarbonate is unclear. It could be related either to the slow reaction kinetics of limestone at high pH values or to a faster formation kinetic of hemicarbonate when compared to the kinetics of monocarbonate formation.

The amount of calcium sulphate originally added to a Portland cement influences the cement matrix properties. The addition of sulphate regulates not only the setting but also the composition and volume of the hydrate assemblage, the remaining porosity and thus indirectly also compressive strength. In general, more ettringite and an increase of compressive strength are observed in samples containing more SO_3. However, above 3–4 wt% SO_3 content the compressive strength generally decreases [14–18], although the volume of the solid hydrates is expected to increase if more ettringite forms.

In this paper, the hydration of three laboratory limestone cements containing different amounts of $CaSO_4$ as well as industrially produced cements with different quantities of limestone were investigated in order to asses the influence of calcium sulphate and calcium carbonate on hydration and strength development. Thermodynamic modelling has been used to predict the composition

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of the solid phases. Additionally the dissolution of limestone was studied at high pH values.

2. Materials and methods

2.1. Materials

In order to prepare the laboratory cements, Portland cement clinker, natural anhydrite and natural limestone were used. The cement clinker was ground together with the anhydrite in the laboratory ball mill. The cement clinker was homogenized with 15 wt% of ground limestone and different quantities of natural anhydrite (2.5, 3.5 and 4.5 wt%) to give Portland limestone cement. The final sulphate contents of the cements were: 2.1 wt%, 3.0 wt% and 3.8 wt%. The corresponding cements are labelled: L2-15, L3-15 and L4-15, where "L" indicates laboratory cement; the first number corresponds to the approximate content of the sulphate and the second to the content of limestone.

Three commercial cements: CEM I 52.5 R, CEM I 42.5 R and CEM II/A-LL 42.5 R were investigated as well. The cements contain about 3.5 wt% SO_3 and 1, 3 and 9 wt% of limestone, respectively. These cements are labelled: C3.5-1, C3.5-3 and C3.5-9, where again the first number corresponds to the content of the sulphate and the second to the content of the limestone.

The chemical composition determined by XRF and the physical properties of the materials are given in Table 1. The mineralogical composition of cement clinker and commercial cement was obtained from XRD – Rietveld analysis (Table 2). The particle size distributions of laboratory and commercial cements determined by laser granulometry using a Malvern Mastersizer are given in Fig. 1. The $CaCO_3$ content of the natural limestone, determined by XRD – Rietveld analysis, is about 97 wt%. The limestone had a Blaine fineness of 7000 cm^2/g and a d_{50} of 8 μm.

The fineness of the limestone fraction of the commercial cements is not known. As the limestone, sulphate and clinker were co-ground during the production of the cements it is expected that the limestone is very fine as it is easier to grind than the cement clinker phases [19,20].

The distribution of the alkalis between sulphates and oxides in the unhydrated cement was determined based on the measured concentration of the readily soluble alkalis in double distilled water at w/c (water to cement ratio) of 10 after an equilibration time of 5 min.

Table 2
Mineral composition of the cements determined by XRD-Rietveld analysis.

Sample	Phase contents (wt%)							
	C_3S	C_2S	C_3A	C_4AF	Anhydrite	Bassenite	Calcite	Others
L2-15	51.7	17.3	9.8	1.7	2.8	0	15	1.7
L3-15	51.1	17.1	9.7	1.6	4.3	0	15	1.2
L4-15	50.5	16.9	9.6	1.6	5.6	0	15	0.8
C3.5-1	65.5	9.0	8.2	9.3	0.5	3.4	1.1	3.0
C3.5-3	57.6	14.4	8.7	8.8	0.6	3.0	2.8	4.1
C3.5-9	54.2	14.0	8.4	7.8	2.1	1.5	8.7	3.3

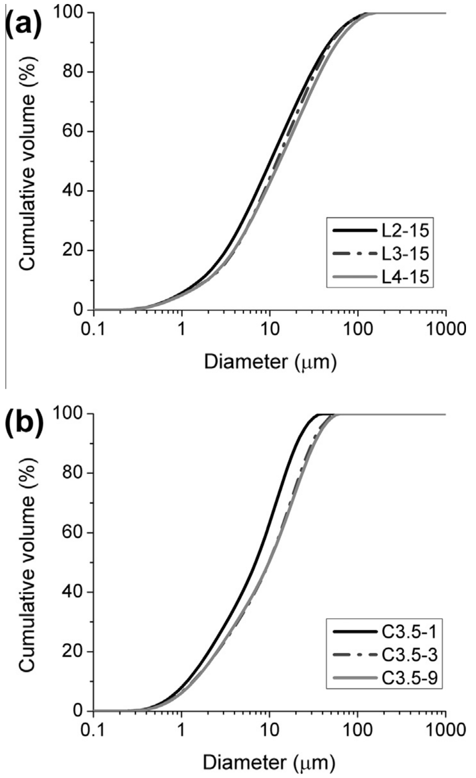

Fig. 1. The particle size distribution of investigated (a) laboratory cements, and (b) commercial cements determined by laser diffractometry.

Table 1
Chemical composition of the used materials.

Parameter	Unit	L2-15	L3-15	L4-15	C3.5-1	C3.5-3	C3.5-9
SiO_2	wt%	18.9	18.5	18.1	19.32	19.35	18.49
Al_2O_3	wt%	4.7	4.5	4.5	5.32	5.47	5.27
TiO_2	wt%	0.2	0.2	0.2	0.26	0.27	0.26
MnO	wt%	0.0	0.0	0.0	0.04	0.04	0.03
Fe_2O_3	wt%	1.6	1.5	1.4	2.88	2.83	2.71
CaO	wt%	63.7	63.2	62.7	63.2	62.0	61.2
MgO	wt%	1.0	0.9	1.0	2.14	2.3	2.12
K_2O	wt%	0.7	0.6	0.6	0.78	0.99	0.99
Na_2O	wt%	0.2	0.2	0.2	0.06	0.06	0.05
SO_3	wt%	2.1	3.0	3.9	3.58	3.5	3.45
P_2O_5	wt%	0.3	0.3	0.3	0.11	0.2	0.22
LOI 950 °C	wt%	6.6	6.7	6.7	2.07	2.59	4.55
Total	wt%	100.0	99.8	99.7	99. 8	99.6	99.4
CO_2(TG)	wt%	6.2	6.3	6.2	0.7	1.8	4.3
Readily soluble alkalis							
Na_2O	wt%	0.07	0.07	0.07	0.05	0.05	0.05
K_2O	wt%	0.5	0.5	0.5	0.5	0.6	0.62
Physical parameters							
Blaine surface area	cm^2/g	4873	4550	4669	6450	4990	5080
Density	g/cm^3	3.00	3.00	3.00	3.12	3.11	3.07
d_{50}	μm	10.1	11.7	12.0	7.0	9.9	9.5