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Limestone reaction in calcium aluminate cement–calcium sulfate systems

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ABSTRACT

This paper reports a study of ternary blends composed of calcium aluminate cement, calcium sulfate hemihydrate and limestone. Compressive strength tests and hydration kinetics were studied as a function of limestone and calcium sulfate content. The phase evolution and the total porosity were followed and compared to thermodynamic simulation to understand the reactions involved and the effect of limestone on these binders. The reaction of limestone leads to the formation of hemicarboaluminate and monocarboaluminate. Increasing the ratio between sulfate and aluminate decreases the extent of limestone reaction.

1. Introduction

Ternary blends composed of calcium aluminate cement (CAC), calcium sulfate (C$[1]) and Portland cement (PC) are widely used in dry mix mortars. These systems have special properties, such as fast setting, rapid strength development and shrinkage compensation that justify their use despite the higher costs with respect to plain PC.

In this study PC is replaced by limestone in ternary blends. Limestone is a low cost and a low environmental impact material. The literature on blends of calcium aluminate cement, calcium sulfate and limestone is scarce, nevertheless there are various studies with calcium sulfoaluminate cement (CSA) blended with calcium sulfate and limestone. Previous studies done by Pelletier-Chaignat et al. [1] on systems with similar chemical compositions containing CSA, gypsum and limestone or quartz filler indicate that limestone gives higher strengths compared to quartz. Hemicarboaluminate and monocarboaluminate are formed and there is less monosulfoaluminate. The impact of calcium sulfate on the limestone reaction was not discussed. Other studies on blends of CSA with calcium carbonate [2,3] and of blends of CAC with calcium sulfate [4] showed that calcium sulfate has a strong impact on the reaction of calcium carbonate; the amount of reacted limestone decreases with the calcium sulfate content.

Limestone addition in cement has been widely studied in PC based systems [5–7]. These studies indicate that:

- The addition of calcite reduces ettringite dissolution when sulfate is depleted. Aluminate reacts with carbonates to form the AFm phases monocarboaluminate and hemicarboaluminate instead of consuming ettringite to form monosulfoaluminate.
- The formation of carboaluminates and increased amount of ettringite increase the volume of hydrates, decrease the porosity and increase the strength at modest levels of addition.
- The amount of calcite which can react is limited by the reactive aluminate and sulfate content in the system. Above a critical sulfate to aluminate ratio, calcite acts as inert filler.

The main difference between PC and CAC-C$ based systems is that the latter clearly contains much higher quantities of aluminate, mainly in the form of monocalcium aluminate, so there is potential for much higher amounts of calcite to react and contribute to strength development.

The hydration of systems composed of CAC and calcium sulfate leads to the formation of ettringite and amorphous aluminium hydroxide as shown in reaction (1):

$$3CA + 3C\$H_x + (38-3x)H \rightarrow C_3A \cdot 3C\$ \cdot H_{32} + 2AH_3 \tag{1}$$

where x = 0 for anhydrite, x = 0.5 for hemihydrate and x = 2 for gypsum.

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[1] Cement notation: C: CaO, A: Al_2O_3, \$: SO_3, S: SiO_2, c: CO_2, F: Fe_3O_4, H: H_2O.

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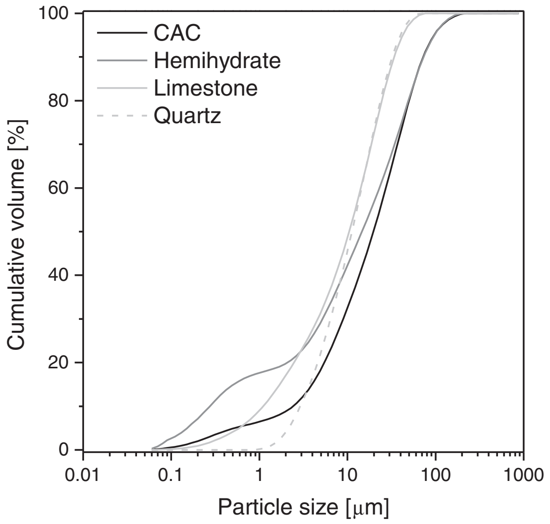

Fig. 1. Particle size distributions.

When calcium sulfate is depleted and there is an excess of monocalcium aluminate, ettringite is consumed and forms monosulfoaluminate and aluminium hydroxide according to reaction (2):

$$C_3A \cdot 3C\$ \cdot H_{32} + 6CA + 16H \rightarrow 3\ C_3A \cdot C\$ \cdot H_{12} + 4AH_3. \qquad (2)$$

When limestone is added to the system, the formation of hemicarboaluminate (reaction (3)) and/or monocarboaluminate (reaction (4)) is thermodynamically more favourable compared to the formation of monosulfoaluminate (reaction (2)), which is not stable anymore.

$$3CA + 0.5Cc + 18H \rightarrow C_3A \cdot Cc_{0.5} \cdot H_{12} + 2AH_3 \qquad (3)$$

$$3CA + Cc + 17H \rightarrow C_3A \cdot Cc \cdot H_{11} + 2AH_3 \qquad (4)$$

The main objective of this study is to investigate the effect of variable calcium sulfate and limestone content on strength development and link this to hydration kinetics, phase formation and the reaction of limestone. Thermodynamic simulation is used to understand the impact of calcium sulfate content on the phase assemblage of these systems and to estimate the maximal amount of reacted limestone.

2. Materials and methods

Calcium aluminate cement (CAC, Ternal RG from Kerneos), was blended with calcium sulfate β-hemihydrate (HH, Prestia Selecta from Lafarge). Six systems with variable calcium sulfate content were studied; three without any substitution and three with 20 wt.% (weight percent) of limestone (Cc, natural crushed calcite, Durcal 15 from Omya). Systems substituted with quartz (Q) instead of limestone were also prepared for compressive strength tests and isothermal calorimetry measurements. This was done to separate the physical and the chemical effects of the substitution. The physical filler effect is the extra space due to dilution and the addition of surfaces for nucleation. The chemical effect is due to the reaction of limestone [8]. To have comparable physical effects it is important to have similar particle size distributions for quartz and limestone as shown in Fig. 1.

The oxide composition of the different materials obtained with X-ray fluorescence (XRF) spectrometry is given in Table 1. The mineralogical compositions of the CAC cement, hemihydrate and limestone were obtained by XRD Rietveld analysis and are presented in Table 2. CAC contains some $C_{12}A_7$ (about 1.4%) and is included in the column “other phases”. Note that hemihydrate contains 3.5 wt.% of calcite. The compositions of the systems studied are listed in Table 3. The sample names are composed of the molar percentage of CA relative to HH and the wt.% of limestone substitution (Cc). Limestone is composed of 99.8% of calcite, therefore the terms limestone and calcite are used without distinction in this paper. Molar amounts of calcium sulfate are used to indicate the relative amount of aluminate and sulfate; the stoichiometry of reaction (1) is 50 mol% aluminate and 50 mol% sulfate. An additional system with 50CA–50HH was tested for compressive strength. Moreover different substitution levels (10, 20 and 40% Cc) were tested in compression at 28 days of hydration.

All experiments were carried out at 20 °C. Paste samples were cast with a water to binder ratio (w/b) of 0.4 and were used for all the experiments except compressive strength tests which were done on mortars. The dry powders were weighted in a recipient of 250 ml and dry mixed for 30 s before mixing all the powders with water for 2 min using a paddle mixer at 1600 rpm.

For the strength measurements, mortars were cast according to European standard EN 196-1 with a water to binder ratio of 0.5 (because of the interfacial transition zone a w/b of 0.5 in mortar is comparable to 0.4 in paste). Three mortar bars of 40 × 40 × 160 mm^3 were cast from a blend of 1350 g of normalized sand with 450 g of binder and 225 g of water. The mixing protocol was: 30 s at low speed to blend the dry powders, water added and mixed for 30 s at low speed, the sand is then added and mixed for 30 s at low speed followed by a break of 15 s and 60 s at high speed. The mixing duration was reduced from that specified in the norm because of the rapid setting of the systems. No setting regulating admixtures were used. After one day the bars were unmoulded and cured in a high humidity environment (96% R.H.). The results at each time are an average of four compression tests.

Hydration kinetics were followed by isothermal calorimetry (TAM Air from TA Instruments). 10 g of cement paste (mixed outside the calorimeter) was introduced in a glass ampoule which was then sealed with a cap and placed in the calorimeter.

For SEM, XRD, TGA and MIP measurements, the samples were cast in polystyrene cylinders (35 mm ⌀ × 50 mm). These cylinders were immediately placed in a water bath at 20 °C to maintain a constant temperature for the first 24 h. Then they were demoulded and placed in cylindrical recipients of 37 mm of diameter containing around 8 g of demineralized water per 95 g of sample mass to ensure a continuous supply of water while minimizing leaching. At each age, three slices of 2–3 mm thickness were cut from the cylinders and then immersed in isopropanol to stop the hydration. After 7 days in the solvent, they were stored in a desiccator under vacuum and over silica gel for 2 days to remove the alcohol, prevent carbonation and remove possible moisture. Stopping the hydration with isopropanol and storing the samples under vacuum have a detrimental effect on the crystallinity and

Table 1
XRF oxide composition (expressed in wt.%) and mass attenuation coefficients referring to CuKα radiation (MAC).

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	TiO_2	P_2O_5	CO_2	MAC
CAC	36.6	4.1	40.3	16.3	0.1	0.0	0.0	0.3	1.8	0.2	–	97.4
HH	38.5	0.9	0.0	0.0	0.2	0.0	0.0	52.8	0.0	0.0	–	73.3
Cc	57.3	0.1	0.1	0.0	0.4	0.1	0.2	0.0	0.0	0.0	40.9	76.1
Q	0.0	97.9	1.0	0.0	–	–	0.8	–	0.0	0.0	–	–
MAC [cm^2/g] [9]	124.0	36.0	31.7	214.9	28.6	25.0	122.3	44.5	124.6	39.7	9.4	–