

Influence of calcium and magnesium carbonates on hydration kinetics, hydrate assemblage and microstructural development of metakaolin containing composite cements



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ABSTRACT

The hydration of metakaolin composite cements containing quartz, natural limestone and dolomite rock is studied using a multi-method approach and modelling.

The study demonstrates that the calcite present in limestone and dolomite rock is very reactive. Contrary, dolomite does not dissolve. Additionally to the previously reported stabilization of ettringite, the reaction of calcite introduces several changes to the mechanism of metakaolin pozzolanic reaction. Namely, the silicate and aluminate distribution among the hydrates is different. In carbonate containing samples, experimental results supported by the thermodynamic modelling suggest that the silicate mainly precipitates as low Ca/Si C-S-H and additionally the ettringite content is higher. In the case of quartz analogue, the silicates precipitate as strätlingite and C-S-H of higher Ca/Si. These changes cause lower porosity as observed by SEM-BSE and higher strength. High metakaolin reactivity results in a very dense matrix that in turn enables co-existence of phases that are thermodynamically non-compatible.

1. Introduction

Current cements incorporate significant amounts of supplementary cementitious materials (SCMs) as a lever to reduce the environmental footprint associated with the cement production [1] [2].

Supplementary cementitious materials contribute to the mechanical properties of hardened concrete through their hydraulic or pozzolanic properties. Hydration of the cement clinker and the pozzolanic reaction of the SCMs occur simultaneously and may influence the reactivity of each other [3]. The presence of a pozzolan increases the early reactivity of Portland clinker due to the so-called filler effect [4] [5]. Typical pozzolans react slowly achieving substantial reaction degrees only after several weeks [6]. The exception is metakaolin that shows a rapid reaction [7]. The C-S-H with a reduced Ca/Si and increased Al/Si ratio is formed as a result of the pozzolanic reaction [6]. In parallel, additional AFm phases precipitate when reactive alumina is also provided by the SCMs [6]. The presence of reactive pozzolans may limit the late hydration rate of the Portland clinker, i.e. after 28 days [8]. The phase assemblage and microstructure of composite cements can be further changed by the presence of limestone. In Portland cements, the

limestone addition stabilizes monocarbonate in favor of monosulfate hindering the decomposition of ettringite [9]. This effect is even more pronounced in the case of composite cements containing high alumina pozzolans like fly ash or calcined clay [6] [10] [11].

This study reports on the hydration of composite cements containing metakaolin blended with two carbonate rocks (limestone and dolomite) and an inert quartz powder. Dolomite was used since it is frequently associated with calcite in carbonate rocks [12] and is important for industrial applications. In order to reproduce the real industrial conditions, a natural dolomite rock containing also some calcite was used. Additionally, the dolomite mineral is expected to react slower than limestone [13] [14] [15]. As an additional reference, the plain Portland cement was investigated.

Multi-technique approach was used to characterize the mortars and pastes. Mechanical testing of the compressive strength was done on mortar cubes. The hydration of paste samples was investigated by means of thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) and mercury intrusion porosimetry (MIP). In order to enrich the discussion, thermodynamic modelling was carried out.

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Table 1
Chemical composition of the investigated materials (%wt).

	Clinker	Metakaolin	Limestone	Dolomite	Quartz	Anhydrite
LOI 950 °C	0.16	0.98	42.57	46.73	0.15	3.68
SiO ₂	20.86	51.60	1.747	0.18	99.8	2.04
Al ₂ O ₃	4.88	44.06	0.46	0.07	0.0	0.60
TiO ₂	0.37	0.99	0.02	0.0	0.03	0.03
MnO	0.05	0.00	0.02	0.0	0.0	0.0
Fe ₂ O ₃	3.67	0.60	0.20	0.03	0.02	0.23
CaO	63.52	0.00	53.93	32.71	0.0	38.32
MgO	2.57	0.01	0.55	18.99	0.01	1.45
K ₂ O	1.09	0.24	0.07	0.01	0.02	0.16
Na ₂ O	0.55	0.21	0.0	0.0	0.0	0.0
SO ₃	1.22	0.00	0.03	0.0	0.0	52.24
P ₂ O ₅	0.26	0.07	0.04	0.0	0.0	0.02
Sum	99.34	98.75	99.64	98.74	100.03	98.76

2. Materials

Laboratory made composite cements were prepared from Portland cement clinker, anhydrite, limestone, dolomite and ground quartz. The chemical and mineralogical compositions of the materials are given in [Table 1](#) and [2](#), respectively. Particle size distributions are given in [Fig. 1](#).

Metakaolin and Portland cement clinker are commercial products of industrial origin. Quartz, limestone, dolomite and anhydrite used were of natural origin. No analytical materials were used in this contribution; still, the used materials are characterized by their high purity. The clinker, limestone and dolomite were ground in a laboratory ball mill. Metakaolin, quartz and anhydrite were received already ground as commercial products.

The sample matrix is given in [Table 3](#). The cements were homogenized in the laboratory ball mill during 15 min of grinding in order to assure the proper homogeneity of the samples.

3. Methods

3.1. Experimental techniques

3.1.1. Compressive strength

Mortar cubes (20 × 20 × 20 mm) with cement:sand:water proportions of 1:3:0.55 were prepared. Quartz sand with maximal diameter of 0.4 mm was used. No significant bleeding was observed during the mortar sample preparation. The samples were cured at 20 °C and RH = 95% for the first 24 h. Subsequently, the mortars were stored under water at 20 °C. The storage water/mortar ratio was kept constant for all samples. The compressive strength was determined on 7 mortar cubes for each testing age in a way similar to EN 196-1, but with a loading rate of 0.4 kN/s.

3.1.2. Hydration study

For hydration studies, the cement pastes were prepared at w/

Table 2
Mineralogical composition of the cement clinker (%wt).

Minerals	Clinker	Metakaolin	Limestone	Dolomite	Quartz	Anhydrite
C ₃ S	60.8	0.0	0.0	0.0	0.0	0.0
C ₂ S	16.5	0.0	0.0	0.0	0.0	0.0
C ₃ A	6.5	0.0	0.0	0.0	0.0	0.0
C ₄ AF	11.3	0.0	0.0	0.0	0.0	0.0
Calcite	0.0	0.0	98.6	12.5	0.0	0.0
Dolomite	0.0	0.0	0.6	87.5	0.0	5.0
Amorphous	0.0	95.0	0.0	0.0	0.0	0.0
Quartz	0.0	2.0	0.7	0.0	100.0	2.1
Anhydrite	0.0	0.0	0.0	0.0	0.0	90.7
Others	4.9	3.0	0.0	0.0	0.0	2.2

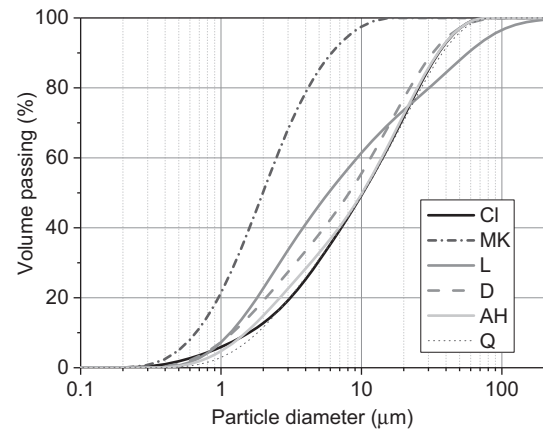


Fig. 1. Particle size distributions of the investigated materials (%wt). CI - Portland clinker, MK - metakaolin, L - limestone, D - dolomite, AH - anhydrite, Q - quartz.

Table 3
Cements composition (%wt).

Samples	Composition (%wt)					
	Clinker	Metakaolin	Limestone	Dolomite	Quartz	Anhydrite
C	95	–	–	–	–	5
C-L-M	56.5	20	20	–	–	3.5
C-D-M	56.5	20	–	20	–	3.5
C-Q-M	56.5	20	–	–	20	3.5
C-40L ^a	56.5	–	40	–	–	3.5

^a Sample used only for compressive strength measurements.

b = 0.55. All pastes were mixed using ULTRA-TURRAX® - IKA mixer to assure homogeneity of the pastes.

For TGA, MIP, XRD and SEM, paste samples were stored sealed at 20 °C in 20 ml plastic vials until testing after 1, 2, 7, 28, 90, 180 and 365 days. At the designated times, discs were cut from the samples and crushed in a mortar. Hydration was stopped by solvent exchange method by keeping crushed samples in isopropanol and flushing them with petroleum ether. TGA was performed on about 30 mg of further ground material at 20 °C/min under a N₂ atmosphere using NETZSCH STA 449F3 device. The amount of calcium hydroxide (CH) and bound water (BW) were calculated from the TG data and expressed as % of the dry sample weight considered as the weight at 550 °C. The crushed and hydration-stopped samples (1 mm to 2 mm) were tested by MIP in Pascal 140/440 Porosimeter from Thermo Scientific up to a maximal pressure of 400 MPa. The pore entry radius was related to the mercury pressure using Washburn equation with surface tension of mercury of 0.485 N/m and contact angle between mercury and cement paste of 141.3°.

XRD was performed on fresh sliced samples and additionally after stopping of the hydration (and intermixing with internal standard). The measurements were conducted using Bruker D8 diffractometer in θ - θ configuration equipped with a CuK α source ($\lambda = 1.54 \text{ \AA}$) and a fixed divergence slit size of 0.5°. Samples were scanned on a rotating stage between 5 and 71° 2 θ using a silicon strip detector with a step size of 0.02° 2 θ and a time per step of 0.4 s.

The quantitative evaluation of the XRD data was performed using Bruker AXS software TOPAS 5 based on the fundamental parameters approach. Rietveld analysis and PONKCS calculations [16] were carried out on in-situ samples (not stopped pastes with a water/binder ratio of 0.55) by using the external standard method [17] already successfully applied to anhydrous ordinary Portland cement clinker [18] and hydrated cementitious materials [18] [19] [20]. For the external standard method, a slice of quartzite rock as secondary standard was used [20], which was calibrated against NIST corundum (SRM 676a). The external

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