



Portland metakaolin cement containing dolomite or limestone – Similarities and differences in phase assemblage and compressive strength

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HIGHLIGHTS

- Dolomite can replace up to 10% of cement without impairing strength at 20 °C or 38 °C.
- Carbonates delivered by either dolomite or limestone additions stabilize ettringite.
- The reactivity of dolomite can be increased by elevating the curing temperature.
- Limestone and dolomite additions yield similar compressive strength at 20 °C or 38 °C.

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ABSTRACT

The scarceness of high-quality limestone obliges the cement industry to consider alternative supplementary cementitious materials (SCMs) for the production of blended cements. This study investigated the potential usage of dolomite instead of limestone as an addition to Portland metakaolin cement by measuring the development of the compressive strength and phase assemblages at 5 °C, 20 °C or 38 °C. Laboratory grade materials were used to identify potential differences in the impact of the carbonate on the phase assemblages. As with limestone, a strength increase was observed when dolomite is added at temperatures >5 °C due to the formation of additional carbonate AFm phases and the stabilization of ettringite. Differences were observed in the amount and type of the carbonate AFm and AFt phases formed. Thermodynamic modelling in combination with the experimental results indicate that the dolomite and limestone affect Portland metakaolin cement in a similar way, with the reactivity being the major difference between the two carbonate sources. This indicates that with regard to the strength development up to 90 days dolomite can be used instead of limestone to replace parts of a Portland metakaolin cement.

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1. Introduction

There are several ways to minimize the effect of cement production on our climate, one of which is to use supplementary cementitious materials (SCMs) [1]. Limestone is widely used as an SCM. According to the European standard EN197-1, it can replace up to 5%wt clinker in CEM I Portland cements and up to 35%wt in CEM II Portland-limestone cements [2].

The addition of finely ground limestone to Portland cement affects the hydration in two ways. First, there is the physical effect of finely ground limestone, which is also often called the filler effect. The addition of fine materials to Portland cement provides additional nucleation sites, which facilitate the formation of hydrates during the hydration of the cement. Moreover, in systems where parts of the cement are replaced by another material, the water-to-cement ratio increases when the water-to-solid ratio is kept constant. This increases the reaction degree of the cement. The addition of finely-ground limestone is known to enhance the reaction of alite and therefore of Portland cement [3,4], and can also shorten the time necessary to nucleate the first C-S-H phase

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[5], which accelerates the hydration of the cement. However, the filler effect is also always connected with a dilution effect, because the most reactive part of the system is replaced with a less-reactive material.

Second, and contrary to earlier understanding that limestone is an inert material, several authors have reported a reaction of limestone when added to Portland cement [6,7]. Carbonate AFm phases, such as hemiacarbonate and monocarbonate, are formed during the reaction of limestone with pure C_3A or C_3A in Portland cement [8–12]. In the presence of carbonates, these AFm phases are more stable than monosulphate [13]. Consequently, the ettringite does not transform to monosulphate after the sulphate source, e.g. gypsum, is depleted. This chemical effect is called ettringite stabilization and results in a relative increase in the volume of hydrates and leads to an increase in compressive strength at low replacement levels [6,7]. A comprehensive overview of the effect of limestone addition to Portland cement on compressive strength and phase assemblage can be found in [14].

The high-grade limestone required by EN197-1 [2] is not sufficiently available in all parts of the world, so various other carbonate sources are in the focus of ongoing research, with dolomite rock being one promising alternative. Schöne et al. [15] observed similar compressive strength results from cements where 23%wt was replaced with either limestone or dolomite. Moreover, Zajac et al. were able to demonstrate that the effect of ettringite stabilization upon carbonate addition, which has been known for cements containing limestone, is also valid for cements containing ground dolomite rock [16].

The mineral dolomite, which is petrogenetic for dolomite rock, is not stable in the high-alkaline environment of a cement and has been reported to undergo what is known as the dedolomitization reaction [17,18]. In this reaction, dolomite reacts with calcium hydroxide (portlandite) to form calcium carbonate (calcite) and magnesium hydroxide (brucite). However, it has been shown that, in cementitious systems where other ions (Al, Si) are present, the reaction of dolomite produces products similar to those of hydrating Portland limestone cement and hydrotalcite [16,19].

The dissolution of dolomite and calcite in various conditions has been studied before [20]. Pokrovsky et al. were able to show that the dissolution rate of dolomite is significantly smaller than that of limestone at both 25 °C and 60 °C [21]. Moreover, the dissolution rates of both decrease with increasing pH [22] and increase with increasing temperatures from 25 °C to 60 °C [21]. This accords with other authors, who have reported a higher degree of reaction of dolomite with increasing temperatures [19,23].

The positive effect of adding carbonate to ordinary Portland cements is limited because the amount of alumina available is limited in these cements. However, the effect can be amplified by

increasing the aluminium content of the cement by using various aluminium-containing SCMs. This synergetic effect has previously been demonstrated for samples containing limestone and fly ash [24,25] and for combinations of limestone and metakaolin [26–28].

In the present study, we used a calcined clay-containing Portland composite cement with a cement-to-metakaolin ratio of 6:1 to ensure an aluminium-rich cement, referred to in the following as Portland metakaolin cement (CM). We investigated the phase assemblage development of this Portland metakaolin cement with various levels of carbonate addition, either pure dolomite or limestone, in pastes over hydration periods of up to 90 days. We also measured the compressive strength of mortar samples with the same compositions. To investigate the effect of curing at different temperatures, samples were cured at 5 °C and 38 °C as well as the usual 20 °C.

2. Experimental

2.1. Materials

The materials used for this study were Portland cement clinker (C, from Norcem), and laboratory-grade dolomite (D, Magnesia 4179 from Brenntag), limestone (L, Magnesia 4491 from Brenntag) metakaolin (M, Metastar501 from Imerys) and gypsum (S, $CaSO_4 \cdot 2H_2O$, from Merck). The cement clinker was ground in a laboratory ball mill until a Blaine surface area of approx. 400 m^2/kg was achieved. The other materials were used as received. All materials were characterized by means of XRF (Table 1), QXRD (Tables 2 and 3), Blaine specific surface area (Table 1), and laser diffraction (Fig. 1). Laboratory-grade materials were used to make it possible to investigate the effect of dolomite without calcite impurities. The dolomite used was synthesized by precipitation, which is why it has a much finer particle size distribution than the limestone used.

The experimental matrix is given in Table 4. The reference 100CM represents a model composite cement consisting of Portland cement clinker and metakaolin with the mass ratio of 6:1. Levels of 5, 10 or 20%wt of the composite cement were replaced by either limestone or dolomite. To ensure a sufficient sulphate content in the samples, 2.85%wt of laboratory-grade gypsum was added to all mixes.

The paste samples were prepared in the laboratory at 20 °C by mixing binder and water with a w/b ratio = 0.55 (due to the high fineness of the materials used) in a Braun MR5550CA high shear mixer. The mixing procedure was: mixing for 30 s, resting for 5 min, and mixing again for 60 s. The pastes were then cast in 12 ml plastic tubes (diameter 23 mm), which were sealed and stored at the various temperatures over water for up to 90 days.

The mortar samples were prepared in accordance with EN 196-1 [29], except that the w/b ratio had to be increased to 0.55 due to the high fineness of the materials used. After 1 day in a climate chamber (20 °C, >90% RH) the prisms (40 × 40 × 160 mm) were demoulded and stored in big tanks immersed in lime water together with other samples at 20 °C until measurement. Additional samples for the other temperatures (5 °C and 38 °C) were prepared in a similar way, except that they were not stored in a climate chamber for the first day, but in their moulds in a closed box over water at their respective temperatures. After 1 day, they were demoulded and stored immersed in lime water at their respective curing temperatures. The samples cured at 38 °C were stored in 20-litre plastic boxes filled with lime water and not in the big tanks as the other samples. The mortar and paste samples were investigated after 1, 28 and 90 days of hydration at 20 °C. The samples cured at 5 °C and 38 °C were investigated after 28 and 90 days.

Table 1
XRF results [%wt] and Blaine specific surface area of the clinker, dolomite, limestone, metakaolin and gypsum used.

Oxide	Clinker	Dolomite	Limestone	Metakaolin	Gypsum
SiO ₂	20.6	0.01	0.00	52.18	0.02
Al ₂ O ₃	5.6	0.02	0.00	44.92	0.09
TiO ₂	0.29	0.00	0.00	1.14	0.00
MnO	0.05	0.00	0.00	0.00	0.00
Fe ₂ O ₃	3.12	0.00	0.00	0.62	0.00
CaO	63.26	30.32	55.87	0.12	32.66
MgO	2.66	21.59	0.21	0.04	0.06
K ₂ O	1.23	0.00	0.00	0.18	0.01
Na ₂ O	0.51	0.00	0.00	0.17	0.02
SO ₃	1.37	0.00	0.00	0.14	46.47
P ₂ O ₅	0.09	0.00	0.01	0.07	0.00
LOI	-	47.53	43.73	0.29	20.39
Blaine surface area [m^2/kg]	404	1056	482	897	214
Sum (1050 °C)	98.78	99.52	99.82	99.87	99.72

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