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► **To cite this version:**

Guillermo Puerta-Falla, Magdalena Balonis, Gwenn Le Saout, Narayanan Neithalath, Gaurav Sant. The Influence of Metakaolin on Limestone Reactivity in Cementitious Materials. 1st International Conference on Calcined Clays for Sustainable Concrete, Jun 2015, Zurich, Switzerland. pp.11-19, 10.1007/978-94-017-9939-3_2. hal-02914818

HAL Id: hal-02914818

<https://hal.science/hal-02914818>

Submitted on 10 Nov 2021

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The Influence of Metakaolin on Limestone Reactivity in Cementitious Materials

Guillermo Puerta-Falla, Magdalena Balonis, Gwenn Le Saout,
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Abstract Recent studies have demonstrated that in the presence of limestone (CaCO_3), carbonate-AFm phases (i.e., hemi- and/or mono-carboaluminate) may be stabilized at the expense of sulfate-AFm, which is more commonly found in cement systems. This suggests that enhancing AFm phase formation may be a novel way of incorporating increased quantities of limestone as a reactive component in cement-based systems. Often, in an ordinary portland cement (OPC), the quantity of the AFm hydrates formed is limited by the availability of aluminum. Therefore, as means of enhancing AFm phase formation, this paper evaluates metakaolin addition to determine how it affects limestone reactions and carbonate-AFm formation in the OPC systems. The results of a multi-method study including: X-ray diffraction with Rietveld refinement (QXRD), strength measurements, thermogravimetric analysis, and thermodynamic calculations are used to quantify solid phase constitutions, and the extent of limestone that has been consumed in reaction. Obtained results suggest that pozzolanic reactions which occur when metakaolin is used as an aluminous source are observed to be beneficial in offsetting the dilutive effects of OPC replacement noted in blended cement formulations.

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1 Introduction

CO₂ pressures facing the construction industry are providing an increasing impetus to reduce the use of ordinary portland cement (OPC) as the primary binder phase in concrete [1]. Towards reducing OPC use, emphasis has been placed on replacing OPC with supplementary cementitious materials (SCMs) in the form of: fly ash, blast furnace slags, silica fume, etc. [2, 3]. While capable of providing suitable properties, quantities of common SCMs available to replace OPC, are often, especially at local scales, inadequate to satiate the desired OPC replacement demand [4]. Due to concerns of the limited/localized availability of SCMs, there is interest in using limestone (CaCO₃), an abundant mineral, to reduce the clinker factors of OPC, and thus OPC use in concrete. The replacement of OPC by limestone induces a variety of effects ranging from: (a) dilution and strength reduction [5, 6], to (b) accelerated hydration at early ages that results from the so-called filler effects [7]. Of these effects, dilution, i.e., the reduction in strength that accompanies OPC replacement is a considerable issue, as technologically this is the most significant limitation which has ensured that, in practice, OPC replacement by CaCO₃ remains limited [8]. OPC is comprised of four main phases tricalcium silicate (C₃S), dicalcium silicate (C₂S), tricalcium aluminate (C₃A) and the ferrite (C₄AF) phases, wherein the kinetics of hydration of each phase differs from the others¹ [9]. Hydration of the C₃A in the presence of sulfate ions, provided by gypsum (C \bar{S} H₂), forms ettringite (C₆A \bar{S} ₃H₃₂, AFt) at early ages and the monosulfoaluminate (C₄A \bar{S} H₁₂, SO₄-AFm, Ms), at later ages when gypsum is exhausted. However, in cases where carbonate ions may be present, e.g. as provisioned by the dissolution of limestone, C₃A reacts with such species to form the CO₃-AFm phases instead of SO₄-AFm and ettringite is stabilized to accommodate sulfate ions [10–12]. In general, monocarboaluminate (C₄A \bar{C} H₁₁, Mc) forms when there is an abundance of the (calcium) carbonate source present, and hemicarboaluminate (C₄A \bar{C} _{0.5}H₁₂, Hc) forms in the case of carbonate-deficient conditions [12]. In typical OPCs, the aluminate (mainly C₃A) phase content is regulated by governing standards [10]. This ensures that the extent of CaCO₃ that can react in a typical OPC is quite small and in the range of 2–5 % (by mass) [12]. As such, if it is desirable to increase CaCO₃ reactivity and thus OPC replacement levels, it is necessary to enhance the quantity of aluminous phases that can provide sufficient Al(OH)₄⁻ (aluminate) species, which under conditions of portlandite saturation would react with CaCO₃ to produce the CO₃-AFm phases. In this work metakaolin (MET) is evaluated as aluminous agent which can extend the limestone reactivity in portland cement systems.

¹Standard cement chemistry notation is used: C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, H = H₂O, \bar{S} = SO₃ and \bar{C} = CO₂.

Table 1 The oxide composition of materials utilized in this study as determined by X-ray fluorescence (XRF)

Oxide (%)	Type I/II OPC	MET
SiO ₂	20.54	51.36
Al ₂ O ₃	4.97	47.60
Fe ₂ O ₃	3.10	0.39
CaO	65.75	0.02
MgO	2.43	0.09
SO ₃	2.75	0.08
Na ₂ O	0.18	0.28
K ₂ O	0.29	0.18

2 Materials and Methods

An ASTM C150 compliant Type I/II ordinary portland cement (OPC) and commercially available limestone (nominally pure: >95 % CaCO₃, d₅₀ = 3 μm) were used. The oxide compositions of the OPC and metakaolin (MET) are presented in Table 1. A series of cementitious mixtures were prepared using de-ionized (DI) water at a fixed water-to-solids ratio ($w/s = 0.45$) as described in ASTM C305. The series of mixtures produced comprised of: (a) plain OPC, pastes in which: (b) 30 % of the OPC is replaced by limestone² (c) 5-to-15 % of the OPC is replaced in 5 % increments by MET (d) 5-to-15 % of the OPC is replaced in 5 % increments by MET and an additional 30 % of the OPC is then replaced by limestone.

Compressive strength measurements were carried out at 90 days using cubic specimens (50 mm × 50 mm × 50 mm) cured at 25 ± 1 °C in lime water as described in ASTM C109 [8].

For thermal analysis (TG/DTG) a Perkin Elmer STA 6000 thermal analyzer with a Pyris data acquisition interface was used to determine solid phase quantities in cementitious mixtures.

To arrest hydration, solvent exchange was as described by Zhang and Scherer [13]. Quantitative X-ray diffraction analyses were carried out on powdered cementitious mixtures at desired ages using a Bruker D8 Advance diffractometer using Cu-Kα ($\lambda = 1.54 \text{ \AA}$) radiation. Care was taken to minimize preferred orientation errors by texturing the sample surface, and using a rotating sample stage. X-ray structure information for the relevant anhydrous and hydrated crystalline phases was sourced from standard databases or from the literature [14, 15]. Rietveld analysis was carried out using the X'Pert HighScorePlus© [16].

Thermodynamic calculations were carried out using a geochemical speciation code, GEMS-PSI: version 2.3.1 [17]. Thermodynamic data of solid and aqueous

²All replacements in this study are performed on a mass basis; some pastes were prepared with quartz instead of limestone to enable comparison of compression strength for blends containing reactive component (limestone) versus inert filler (quartz).

species are sourced from the GEMS-PSI database, and amended with additional information relevant to cementitious systems [12]. Calculations were performed under conditions of 1 bar, 25 °C and CO₂-free air.

3 Results and Discussion

As showed on Fig. 1, the replacement of OPC by metakaolin results in improved strength. Such beneficial effects of metakaolin addition, have also been highlighted by Vance et al. [18, 19] and Antoni et al. [20] and attributed to the pozzolanic character of metakaolin, and the formation of the Hc/Mc phases. This is significant in that in spite of very substantial reductions in the cement factor (CF), mechanical properties near equivalent to the pure OPC mixtures can be achieved. Figure 2 shows representative DTG traces at 90 days, and the portlandite content normalized by the cement factor (CF) for metakaolin containing mixtures. It is noted that portlandite contents of a given mixture decrease with increasing OPC replacement by metakaolin, even when dilution is accounted for. This is indeed expected due to the pozzolanic nature of metakaolin, which would consume lime to form a low(er) Ca/Si (and potentially higher Al-substituted) C-S-H phase which ensures that metakaolin containing mixtures show reduced decreases in compressive strength, in spite of the substantial OPC replacement. Figure 3 shows XRD patterns for the metakaolin containing mixtures after 90 days of hydration. It is noted that the portlandite content of a given mixture, in both limestone deficient/excess cases, reduces with increasing metakaolin content. Mc exists as the dominant phase, only when excess limestone is added to the system.

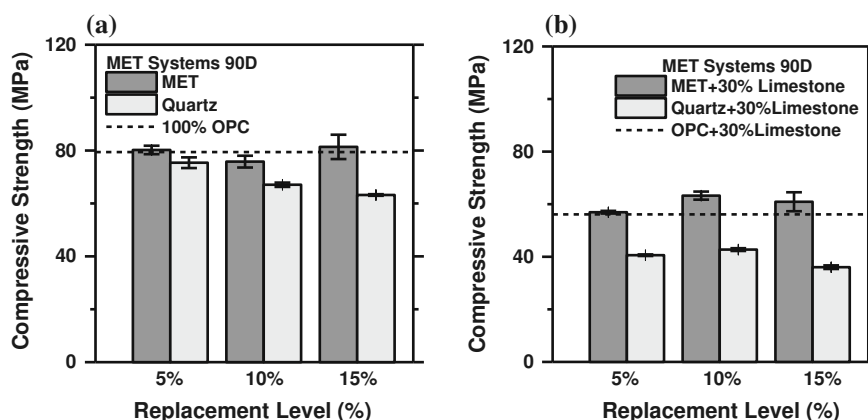


Fig. 1 Compressive strength at 90 Days for: **a** OPC systems **b** OPC + 30 % Limestone systems, at different levels of replacement by metakaolin (*MET*); results compared against quartz which is not reactive and acts as inert filler

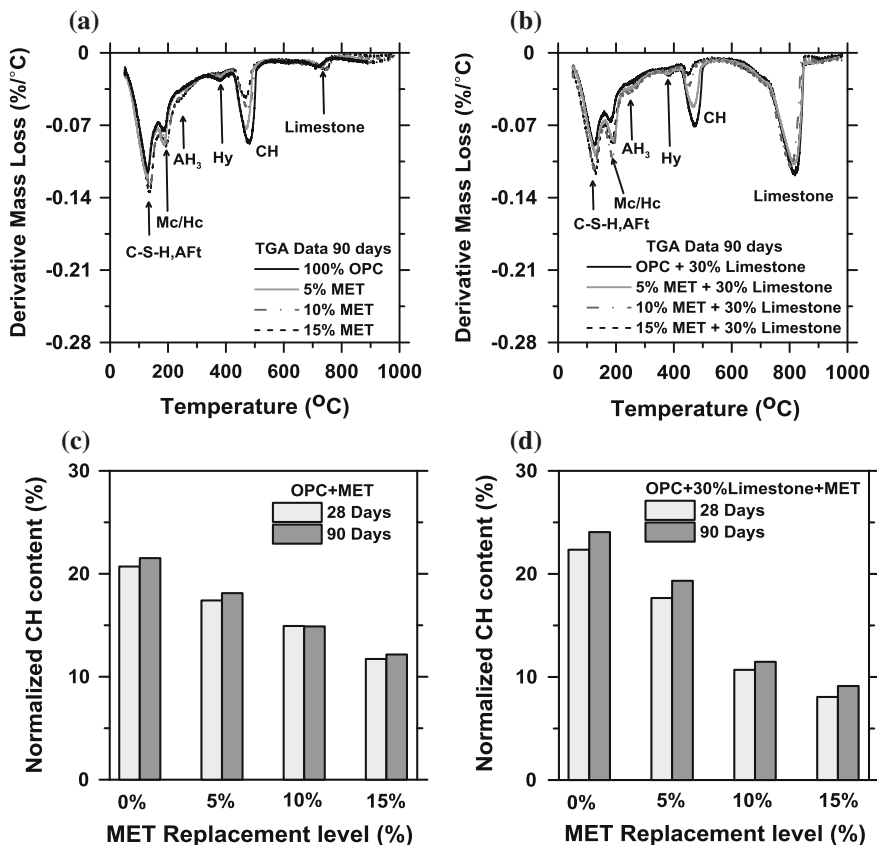
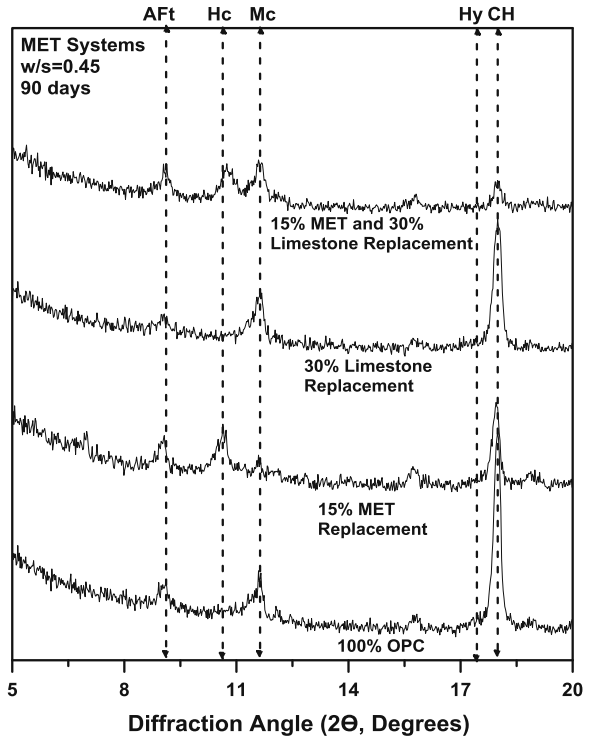


Fig. 2 Representative DTG curves for OPC mixtures for: **a** 0-to-15 % MET replacement, **b** 0-to-15 % MET replacement with additional 30 % of limestone dosed by OPC replacement. The normalized (by CF) portlandite contents for OPC mixtures for: **c** 0-to-15 % MET replacement, **d** 0-to-15 % MET replacement with additional 30 % of limestone dosed by OPC replacement. The portlandite contents were determined by thermal analysis (TGA/DTG)

When only limestone intrinsic to the OPC (limestone deficient system) is present, Mc is stabilized only when no metakaolin is added. However, when OPC is replaced by metakaolin, in increasing proportion, Hc is stabilized as stable and dominant phase. This is in line with the observations made by Antoni et al. [20] and Vance et al. [18, 19]. Contents of the CO₃-AFm (i.e., Hc/Mc) phases, reflect trends in limestone consumption. More CO₃-AFm phases form with increasing metakaolin content, and when excess limestone is present. It should be noted that while these trends follow evolutions in the equivalent CO₂/Al₂O₃ ratio, limestone reaction is limited, likely on account of its low dissolution rate. In spite of the near consumption of portlandite, e.g., in the 15 % metakaolin mixture containing excess limestone, strätlingite is not observed in the XRD patterns. It was noted that

Fig. 3 XRD patterns for the plain (100 % OPC), limestone enriched (30 % OPC replacement by limestone) and MET enriched mixtures composed for limestone deficient and excess conditions. Hemicarboaluminate (*Hc*), monocarboaluminate (*Mc*), portlandite (*CH*), ettringite (*AFt*) and hydrogrossular (*Hy*)



ettringite is present in both the deficient and excess limestone cases, wherein the release of sulfate ions, due to preferred CO_3^{2-} ion uptake into the AFm phase, stabilizes ettringite in these systems. Figure 4 shows volumetric phase assemblages, calculated using GEMS, for 15 % OPC replacement by metakaolin in either limestone deficient or excess conditions. The systems presented show (determined by the portlandite match-point from TGA data) a degree of metakaolin reaction of 37 and 31 %, in limestone deficient and excess scenarios respectively.

Due to pozzolanic reaction, metakaolin ensures consumption of lime and increased formation of C-S-H formed, albeit, of a lower Ca/Si ratio and potentially also higher Al substitution. In agreement with XRD data, both C_2ASH_8 and Hydrogrossular phases are not predicted to form for relevant levels of metakaolin reaction. In contrast to the observations herein, XRD data of Antoni et al. [20] showed the presence of C_2ASH_8 and portlandite in coexistence with each other. While this is in violation of thermodynamic phase relations established by Damidot et al. [21], it may be on account of the somewhat higher metakaolin contents used in their study, or inhomogeneous reaction zones. This discrepancy could however, also be on account of uncertainties in determination of solubility data, small variations in which could alter stability fields dramatically. For example, as noted in the simulations shown herein (Fig. 4), strätlingite is predicted to form only when portlandite is consumed. When only limestone intrinsic to the OPC is present (see

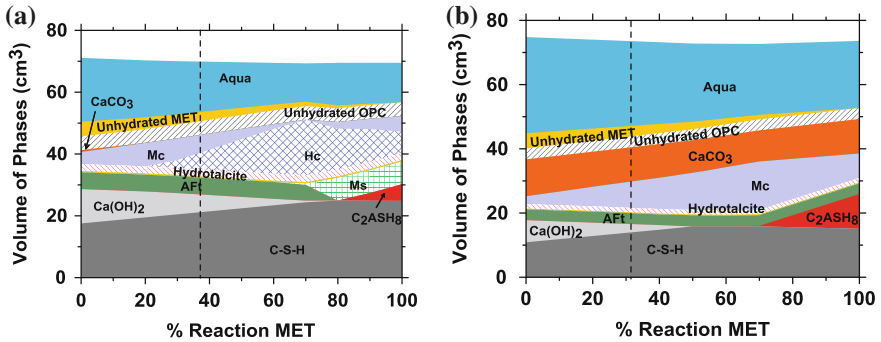


Fig. 4 Phase assemblages calculated using GEMS by incremental reaction of MET for **a** 15 % MET and **b** 15 % MET and additional 30 % limestone replacement of OPC. Monosulfoaluminate (*Ms*), ettringite (*AFt*), monocarboaluminate (*Mc*), hemicarboaluminate (*Hc*), strätlingite (*C₂ASH₈*), and hydrotalcite (*M₄AH₁₀*) are denoted. The *dashed lines* locate the estimated phase assemblage and MET degree of hydration, after 90 days

Fig. 4a), at low levels of metakaolin reaction, *Mc* is stabilized. With the passage of time and increase in metakaolin reaction the phase relation changes and *Hc* becomes dominant with *Mc* existing as the minor $\text{CO}_3\text{-AFm}$ phase. For the degree of metakaolin reaction ascertained herein, *Mc* and *Hc* appear to exist in equivalent volumetric quantities, though on a mass basis this would translate to a larger quantity of *Mc* (the denser $\text{CO}_3\text{-AFm}$ phase), in contrast to the XRD data shown in Fig. 3. While this may indicate that the ascertained degree of metakaolin reaction is lower than reality, it may also suggest kinetic restraint in the formation of *Hc*, from the *Mc*, *Ms* and portlandite (or vice versa depending on the chemical environment).

When excess limestone is present, *Mc* is predicted to be the dominant AFm phase (Fig. 4b). This is once again in contrast to the XRD observations in Fig. 3, where even under limestone excess conditions, when (15 %) metakaolin is present, *Hc* and *Mc* are noted to coexist; the reasoning for which is discussed above. It is seen that, at any degree of metakaolin reaction, a large quantity of limestone remains unreacted, ensuring modest levels of *Hc/Mc* formation. This leads to the idea that the compensation in mechanical properties (see Fig. 1), produced by the combined replacement of OPC, by limestone and metakaolin, is dominantly on account of the pozzolanic nature of metakaolin and less due to the formation of $\text{CO}_3\text{-AFm}$ phases.

4 Conclusions

Metakaolin was evaluated in blended binder formulations in terms of its ability to enhance the reaction of limestone in cementitious systems. Such enhancements in limestone reaction are provoked by systematic manipulation of the binder

chemistry, e.g., in terms of the $\text{SO}_3/\text{Al}_2\text{O}_3$ and $\text{CO}_2/\text{Al}_2\text{O}_3$ ratios of the binder. It is noted that in spite of the provision of sufficient aluminium, calcium and water, the extent of limestone reacted is limited, mostly on account of its low reactivity (i.e., dissolution rate, and solubility). Due to reasonable (reactive) aluminum content metakaolin has shown to increase limestone reactivity and resulting formation of the $\text{CO}_3\text{-AFm}$ (hemi- and/or mono-carboaluminate). On the account of its pozzolanic nature, it is also effective at ensuring strength equivalence, or improvement (in spite of reductions in the OPC content) as compared to the pure OPC formulations.

Acknowledgments Authors acknowledge full financial support provisioned by the NSF (CMMI: 1066583).

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