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Hydration, shrinkage, and durability of ternary binders containing Portland cement, limestone filler and metakaolin

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HIGHLIGHTS

- Designed cement-based materials incorporate metakaolin and limestone up to 45% total proportion.
- The portlandite consumption is higher in ternary binders.
- The actual performances depend on metakaolin chemical and physical properties.
- Metakaolin-based mixtures showed lower ultimate shrinkage.
- Lower water-to-binder ratio improves short-term strength and resistance to carbonation.

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ABSTRACT

A partial replacement of the clinker by latent hydraulic or pozzolanic materials is encouraged due to environmental and specific technical requirements. Such substitution remains limited to a relatively low level (less than 30% by mass of cementitious materials). An experimental research work was carried out on mortars made with binary and ternary binders (Portland cement; metakaolin; limestone filler) to reach 45% total replacement. In order to investigate the activating effect of reduced water-to-cement ratio, two series of mixtures were designed with W/C_0 of 0.42 and 0.5. Their heat of hydration, portlandite content, shrinkage, porosity, and carbonation were monitored. The tests were performed to understand the evolution of their relative strength (activity index) and durability parameters. The strength development of mortars with ternary binders was found to depend on metakaolin properties, including manufacturing process and particle size distribution. Reducing W/C_0 ratio accelerated pozzolanic reaction and allowed improving early-age strength and durability parameters.

1. Introduction

The use of alternative materials as a substitution to clinker is now a major issue to reduce CO_2 emissions from cement production [1–4]. In addition to conventional supplementary cementitious materials (SCMs) such as silica fume, blast furnace slag, fly ash, etc. [5,92], the use of metakaolin (MK) appears today as a promising alternative to produce "eco-materials". Raw material, mainly kaolin-rich soil, is locally abundant, and the manufacturing process based on calcination at less than 1000 °C consists in dehydroxylation without CO_2 emission, thus metakaolin presents a lower carbon footprint than Portland cement [6]. The replacement of MK and LF does not systematically reduce the emission of CO_2 and improve the durability of the related cement-based materials. The production of MK itself leads to lower CO_2 emissions than cement production; one ton of MK represents 175 kg of CO_2 released [7]. It also requires less thermal energy than clinker production. San Nicolas et al. [8] showed that a French installation consumes 2.2 MJ/t of MK, which is 80% less than the energy consumed during cement production. At the level of concrete, the CO_2 emissions and the cost-effectiveness of a ternary system [9] depend on the distance between the production plants. The CO_2 emissions should be compared at equivalent durability, thus it is necessary to assess the actual performances of these cement-based materials.

Most of existing studies agree on the significant pozzolanic reactivity of metakaolin compared to other mineral additions [10,11]. Metakaolin is actually an artificial pozzolan, i.e. it can react with Portlandite (CH) from the cement hydration and form

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additional C-S-H or C-A-S-H [8]. This allows metakaolin to improve greatly the mechanical performance and durability of cementitious materials.

Experimental studies of concrete or mortar incorporating metakaolin show that up to an optimum level of substitution, the compressive strength of these materials increases significantly (even at early age) compared to that of the reference concrete/mortar (without metakaolin) [12–17]. There is no consensus on the value of this optimum rate, probably because of the variability of MK and cement, mixture proportioning of concrete (W/C ratio, cement content, chemical admixtures, etc.). Nevertheless, all the works agree on the fact that this optimum is connected to the microstructure of the material which itself depends on three main factors: the filler effect, the acceleration of cement hydration (at very early age) and the pozzolanic reaction of the metakaolin with CH (significant at long-term) [12,15]. It is generally located between 10 and 20% [14,16]. Below this threshold, the incorporation of the MK has been shown to produce finer pores and a segmentation of the capillary porosity [18,19]. The latter is at the origin of gas permeability and water absorption decrease in the concretes incorporating MK [20]. Therefore, these concretes showed better durability and resistance to aggressive agents [21–25].

The use of high MK content as partial replacement of Portland cement in mortar or concrete can lead to a significant drop in materials performances. One of the reasons is the depletion of portlandite produced by cement hydration. The Portland cement substitution rate ***p*** necessary to consume all the portlandite (CH) produced can be estimated by the following equation [26]:

$$\alpha \times \frac{\beta}{M_{AS_2}} \frac{p}{1-p} = (3-n)(1-p) \times \frac{\%_{C_3S}}{M_{C_3S}} + (2-n)(1-p) \times \frac{\%_{C_2S}}{M_{C_2S}} \tag{1}$$

where $n = C/S$, M is the molar mass (g/mol), β is the amorphous content of MK and α is the ratio between CH produced and AS_2 contained in MK.

Through this equation, a rate of approximately 30% is obtained with n = 1.75, $\beta = 0.55$, $\alpha = 3$, $\%C_3S = 65$ and $\%C_2S = 5.5$. The studies carried out on binary mixtures (PC + MK) show that this value is an upper limit of the MK content that can be added in mortar without lowering its performance. Ambroise et al. [27] and Khatib et al. [28] actually showed that the compressive strength was lower than that of the reference mortar, with more than 30% of Portland cement replacement by MK.

Recent work shows that it is possible to go beyond the 30% substitution of OPC, thus to decrease carbon footprint, by combining metakaolin with a moderate amount of limestone filler [29–31]. For instance, Antoni et al. [29] showed that ternary binders (PC + MK + LF) lead to higher performances than binary binders in terms of heat release and mechanical strength. However, these performances depend both on mix-design parameters (cement content, water-to-binder ratio, etc.) and on the physicochemical properties of the materials.

It is important to note that data on the durability and long-term shrinkage of ternary binders incorporating limestone filler and metakaolin are very scarce in literature. Drying shrinkage remains a major issue for concrete durability. It has been widely investigated for binary binders, whereas only Barluenga et al. [32] and Brook et al. [21] focused on ternary binders (OPC + MK + Filler). Similarly, very few studies have been carried out on porosity [33], permeability [34] and carbonation [33] of these ternary binders. High substitution of Portland cement by mineral additions generally results in relatively low early-age strength, which is of major concern for durability due to hydration-drying coupling. The reduction of water-to-binder ratio allows optimizing the composition of these materials to meet specifications on early-age strength and durability [5,35]. There are a limited number of references on the influence of water-to-binder ratio on performances of metakaolin-based materials [36].

The paper investigates the feasibility of substituting 45% by mass of ordinary Portland cement by mineral additions while keeping or enhancing mechanical performances and durability. Three sets of mineral additions have been studied, namely: metakaolins, limestone fillers, and siliceous fillers. They were characterized by different chemical compositions, particle size distributions and specific surfaces. They were first used separately as a substitution of Portland cement, and siliceous filler and limestone filler were associated to metakaolin in order to understand the synergistic effect of these materials. Then, the influence of the quality of metakaolin (purity of kaolin and manufacturing process) on the relative strength was studied. Finally, the major originality of this work consists of an experimental study of the drying shrinkage, water porosity and carbonation of ternary binders (OPC + MK + Filler) and an investigation on the effect of water-to-binder ratio on these parameters.

2. Experimental program

The chemical compositions of metakaolin and limestone filler make it an interesting combination as a substitute for Portland cement. Their SiO_2 and CaO contents are complementary in order to make an effective mixture thereof as a substitute for the cement. The high crystallized silica content of the Siliceous Filler (SF) makes it valuable as an inert substituent, thus highlighting the possible chemical interaction of limestone filler on Portland cement and Metakaolin.

The different stages of the study presented in this paper are summed up in Fig. 1. Metakaolin (MK), limestone filler (LF and μLF) and siliceous filler (SF1 and SF2) were used as partial replacement of ordinary Portland cement (PC). In the first part, the effects of inert minerals additions and pozzolanic addition (MK) on cement hydration and compressive strength development are quantified by means of isothermal calorimetry, compressive tests and thermogravimetric analyses (TGA). The tests were carried out both on binary and ternary binders' mixtures. The objectives were defined as follows.

- The combination (PC + MK) allows highlighting the effects of MK on cement hydration.
- The comparison between LF and SF in binary mixture allows demonstrating how the limestone fillers are likely to influence cement hydration.
- (PC + MK + LF) and (PC + MK + SF) allow studying the impact of LF on pozzolanic reactions and its interaction with MK.
- The comparison between LF/μLF and SF1/SF2 in binary and ternary mixtures shows the effect of fineness on the properties of the cementitious matrix.

This analysis leads, in the second part, to the choice of the best combination (PC; MK; X = {LF, μLF, SF1, SF2}), which can be used for the study of the influence of metakaolin quality on hydration and compressive strength. Finally, the metakaolin MK3 which exhibited the best mechanical performance was used to highlight the effect of water-to-binder ratio (noted W/C_0) on durability properties of binary and ternary mixtures including MK.

2.1. Materials

The chemical compositions and physical properties of the ordinary Portland cement (PC), metakaolins (MK), limestone fillers (LF) and siliceous fillers (SF) are given in Table 1. Three metakaolins