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Ternary cement blends with Fly ash-Calcined clay-OPC: An evaluation on their early age and mechanical properties as binders



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ABSTRACT

The synergetic effect of SCMs, fly ash (F) and calcined clay (C) in ternary mixes at 20% replacement was evaluated. It was found that due to the complementary water demand of F and C, pastes made of ternary blends of FC-OPC showed similar or better rheology than OPC pastes. This was coupled with an increase in heat evolved during early age of hydration and a comparable 28 days compressive strength. The results indicate that ternary mix of FC-OPC can be future green cements, where C can be utilized even in the transition stage with existing SCM, such as F.

Key words: Ternary blended cements, Rheology, Hydration, Compressive strength, Calcined clay, Fly ash, Cement, Supplementary cementing materials, SCM

1. INTRODUCTION

Cement production contributes to ~6% CO₂ emission annually worldwide [1]. To reduce this, greener and more environmentally friendly binders are sought after. Using supplementary cementing materials (SCMs) is one of the main drivers as it results in a direct reduction in CO₂ emission, making them a popular choice in the cement industry for materials development. Calcined clays is one such SCM. It has shown very favourable performance as an SCM to produce favourable or even enhanced mechanical properties and better durability [2,3]. However, implementation of changes requires a transition period, where introduction of new SCMs are most successful when they can be coupled and employed with the existing materials. Additionally, limitations such as decreased workability with calcined clay need to be solved before they can be of significant commercial values. Technically, we have shown that calcined

clay and fly ash possessed contrasting rheological properties when blended as binary cements [4,5]. Additionally, the strength developed for F and C binary cements appeared to be complementary as well.

The purpose of this investigation is thus to highlight the possibility of creating a ternary cement blend based on fly ash (most common commercial SCM) and calcined clay (new promising SCM). The early age rheological behaviours, heat of hydration and 28 days compressive strength will be highlighted in this article.

2. MATERIALS AND EXPERIMENTAL

An OPC and F supplied by Norcem AS (Brevik, Norway), and a smectite rich (~50%) calcined clay (C) from Saint-Gobain Weber (Oslo, Norway) were employed. Detailed chemical compositions of the materials can be found in previous investigations [4]. The specific Blaine surfaces of OPC and F are 382 m²/kg and 357 m²/kg, while that as measured by BET for C is 15.1 m²/g. All materials were utilised as per obtained. Dry powder were manually blended before wetting to produce the binder mixes (Table 1).

Table 1 - Formulation of dry mixes for investigation

Mix [wt.%]	C0F20	C5F15	C10F10	C15F5	C20F0	C100	F100	CF0 (OPC)
C	0	5	10	15	20	100	0	0
F	20	15	10	5	0	0	100	0
OPC	80	80	80	80	80	0	0	100

All cement pastes were prepared at a low w/b of 0.36. Dry powder was added to water and mixed under high shear for 1min, let stand for 5min and a final high shear mixing of 1min to avoid false setting. Rheological measurements were performed with a Physica MCR 300 rheometer (Anton Paar, Graz/Austria) equipped with parallel plate geometry. The Bingham viscosity (μ_2) and dynamic yield point (τ_d) were measured. Calorimetric investigation was conducted using an isothermal TAM Air calorimeter (TA Instrument, New Castle/USA) up to 24h. 28 days compressive strength was measured according to EN197-1. More details on the experimental procedures can be found in previous investigations [4].

3. RESULTS AND DISCUSSION

Workability of pastes: The rheology of reference samples OPC, C and F were first measured. OPC displayed an initial τ_d of 269 Pa and corresponding μ_2 of 0.32 Pa·s. F sample demonstrated an initial τ_d of 26 Pa and corresponding μ_2 of 0.19 Pa·s. The thixotropy of pure C paste was too high for any flow measurements to be registered at the employed w/c of 0.36.

When cement blends containing C-F-OPC with 20% replacement were prepared, the dynamic yield stress of the cement blends varied according to the amount of F and C added. Replacement by 20% F only resulted in a binary paste with $\tau_d = 147$ Pa, which increased linearly ($R^2 = 0.9859$) as C replaces F by weight percentage to a C20F0 paste possessing $\tau_d = 374$ Pa (Fig. 1). This indicated that the impact of C to F ratio on the structural skeleton of the cement matrix is additive, governed by the inherent dynamic yield stress exerted by each individual SCM.

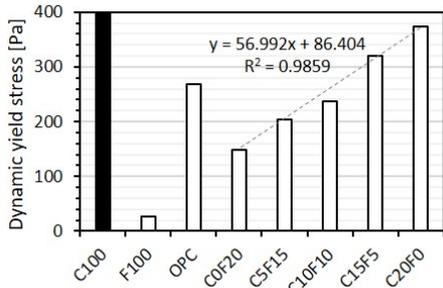


Fig 1 - Dynamic yield stress of cement blends ($w/b = 0.36$)

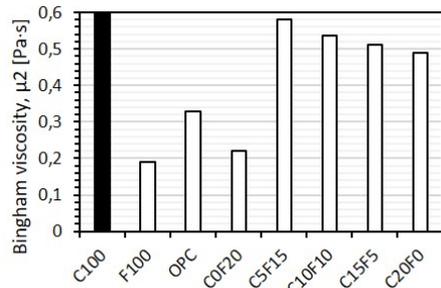


Fig 2 - Bingham viscosity of cement blends ($w/b = 0.36$)

On the other hand, such a trend was absent when Bingham viscosity was measured as shown in Fig 2. COF20 displayed a μ_2 of 0.22 Pa·s, showing high influence of F on the viscosity of the cement blend, possibly a result of the spherical nature of F particles that can 'slip' between particles and decrease the resistance to deformation. Upon replacement with C, a surge in μ_2 was observed to hit a maximum μ_2 of 0.58 Pa·s for C5F15, which decreased to 0.49 Pa·s for C20F0. No explanation is possible at the moment, but it indicated that potential interactions between C and F may be present. Additionally, the results demonstrated that C played a greater role in affecting the viscosity of the ternary blends than F.

Heat of hydration: Both F (3 J/g) and C (6 J/g) showed negligible cumulative amount of heat released by 24h, whereas OPC registered a cumulative heat evolved of 121 J/g as shown in Fig 3. When binary cement blends were measured, the heat evolved was ~15% and 10% lower than that for OPC when F and C were employed respectively, due to a decrease in initial reactivity in the presence of SCM. However, the heat evolved increased when ternary blends were measured, reaching a maximum of 120 J/g for C15F5 (118 J/g for C10F10), comparable to that for OPC. The results confirm that synergetic interaction between C and F occurred, shading light on the variation in Bingham viscosity.

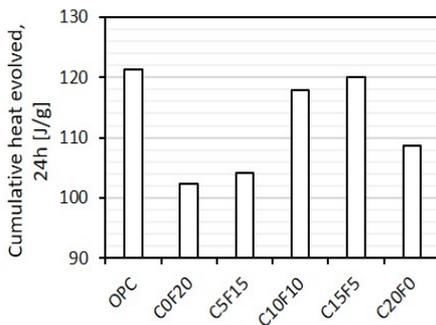


Fig 3 - Cumulative heat evolved at 24h ($w/b = 0.36$)

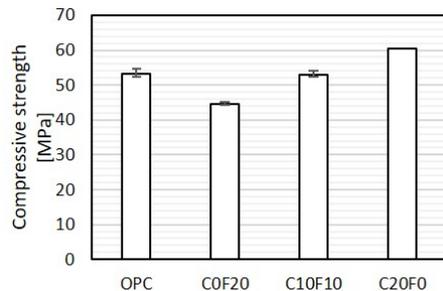


Fig 4 - Compressive strengths at 28 days ($w/b = 0.36$)

Compressive strength analysis: The compressive strengths of OPC, COF20, C20F0 and C10F10 at 28 days were measured (Fig 4). At 28 days, the compressive strength of OPC mortar was 53.2 MPa, whilst that for the binary mixes were 60.4 MPa (C20F0) and 44.7 MPa (COF20)

respectively. The differences in strengths can be attributed to the pozzolanic nature of C, and low reactivity of F. When an equal proportion of F and C (C10F10) were employed to produce the ternary blended cement, the compressive strength was 53.0 MPa, within standard deviation from that for OPC.

4. CONCLUSION

The rheological properties, heat of hydration and 28 days compressive strength of ternary cement blends made from calcined clay, fly ash and ordinary Portland cement were investigated. It has been found that calcined clay-fly ash-OPC ternary blends possess properties, both early age workability and strength comparable to OPC, making them potential candidates as future cements.

This opens up the possibility of a new source of green abundant SCM based on clay that can be employed on a larger scale than current applications, while supporting adaptation of technology when transiting from old to new SCMs.

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