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Activation of LC^3 low-carbon cements by C-S-H seeding

A. Morales-Cantero[1*], A.G. De la Torre[1], A. Cuesta[1], I. Santacruz[1], O. Mazanec[2], A. Dalla-Libera[2], S. Dhers[2], P. Schwesig[2], P. Borralleras[3] and M.A.G. Aranda[1]

[1] *Departamento de Química Inorgánica, Universidad de Málaga, Málaga 29071, Spain*
Email: alejandrom@uma.es, mgd@uma.es, a_cuesta@uma.es, *isantacruz@uma.es, g_aranda@uma.es*

[2] *Master Builders Solutions Deutschland GmbH, Albert-Frank Str, 32, 83308 Trostberg, Germany*
Email: oliver.mazanec@mbcc-group.com, alessandro.dalla-libera@mbcc-group.com, sebastien.dhers@mbcc-group.com, peter.schwesig@mbcc-group.com

[3] *Master Builders Solutions España S.L.U., Carretera de l´Hospitalet, 147-149, Edificio Viena, 1ª planta, 08940*
Cornellà de Llobregat, Spain
Email: pere.borralleras@mbcc-group.com

ABSTRACT

Portland-based Limestone Calcined Clay Cements (LC^3) are attracting a lot of the attention from scholars and field applications due to the reduction in CO_2 emissions. However, their low mechanical strengths at early ages are a key bottleneck for their widespread use. Calcined clays can also lead to a strong reduction of the fluidity in the first hours after mixing, which is an important second drawback. Here, these two issues have been addressed. Three LC^3 binders were prepared based on a PC-52.5R cement and three calcined clays, with variable amounts of kaolinite in the raw materials ranging 29-74 wt%. The particle sizes of the calcined clays were adjusted by milling to $D_{v,50}=13\pm2$ μm. The results show that the loss of fluidity of LC^3 mortars during the first hours can be solved by a recently developed PCE-based superplasticizer, specifically tailored for this application. Moreover, the compressive strengths at 1 day for LC^3 mortars have been boosted by a C-S-H nucleation seeding admixture and the gains are maintained at 28 days. It is noted that the compressive strengths at 1 day and room temperature were increased by 45-100 %, when compared to the corresponding unseeded mortars.

KEYWORDS: *Calcined clay, admixtures, superplasticizer, CO_2 footprint, mechanical strength*

1. Introduction

Calcined clays are a type of widely-available supplementary cementitious material that, combined with Portland cements, are starting to contribute in the reduction of the CO_2 emissions (Juenger et al., 2019). However, the main drawbacks of the resulting LC^3 binders are their poor mechanical strengths at early ages, i.e. 1-2 days (Scrivener et al., 2018), and their severe loss of fluidity during the first hours of hydration (Akhlaghi et al., 2017).

In this work, these two challenges have been addressed with tailored admixtures. On the one hand, and in order to avoid the loss of fluidity during the first hours of hydration, a new commercially available PCE-based superplasticizer, specially designed for this application, was employed. The amounts of this superplasticizer have been optimized for each sample. The performances have been compared to that of a typical PCE. On the other hand, and to improve the mechanical strength at early ages, a commercial accelerator admixture based on C-S-H nucleation seeding has been used (Morales-Cantero et al., 2022a, 2022b).

2. Materials and Methods

2.1 Starting material

A commercial Portland cement, CEM-I 52.5R (PC-Ref) with $D_{v,50}=12(1)$ μm and three raw clays with different kaolinite content, ~74 (CC1), ~49 (CC2) and ~29 (CC3) wt%, have been used to fabricate the LC^3 binders. The clays were calcined at 860 ºC during 4 h, and milled down to $D_{v,50}=13\pm2$ μm. Subsequently, the calcined clays were used to prepare the LC^3-50 binders (52 wt% PC-Ref, 30 wt% calcined clay, 15 wt% limestone and 3 wt% $CaSO_4 \cdot 2H_2O$), (LC^3-CC#). An additional reference sample was prepared by replacing the calcined clay by quartz (inert), with $D_{v,50}$=16(1) μm (PC-Qz).

Three commercially-available admixtures from Master Builders Solutions have been employed in this work, two PCE-based superplasticizers and one C-S-H based strength enhancement agent. SP-1 is a standard one used for years for concrete rheology optimisation. SP-2 is a new superplasticizer specially designed to avoid the loss of fluidity during the first hours of LC^3 hydration. Finally, Master X-Seed 130 (XS130) was used for strength enhancement.

2.2 Analytical techniques

2.2.1 Slump retention

Mortars have been prepared with a water-to-binder mass ratio (w/b) of 0.40 and with a sand-to-binder mass ratio of 1.78, at 20 ºC. For all samples, an optimized amount of SP for an initial constant self-flow, i.e. 200±15 mm, was added. For the samples containing the accelerator, a 2.00 wt% of XS130 by the weight of binder (referred to the commercial suspension) was added. For the mortar preparation, a mortar mixer (Matest, mod. E095) was used according to the following procedure: Step 1: 60 s at 140 rpm (solid, i.e. sand + binder and 80 wt% water); Step 2: 30 s to add the SP and 20 wt% of water for samples without C-S-H seeding or 10 wt% of water for samples with seeding; Step 3: 60 s at 285 rpm; Step 4 (only for samples incorporating C-S-H seeding): 30 s to add the admixture and the 10 wt% of water left; Step 5: 120 s at 285 rpm. After mixing, the mortar was poured in the truncated cone (bottom diameter: 100 mm, top diameter: 70 mm, height: 60 mm) in two steps. The first one, filling up half of the cone and the air bubbles were taken out with a glass rod with 30 vertical punctures. In the second step, the cone was filled up completely and punctured again 30 times. Slump was measured at t_0, 30 and 60 min, at the lab. temperature, 20(2) ºC.

2.2.2 Isothermal calorimetry

An eight channels Thermal Activity Monitor (TAM) instrument with glass ampoules was used. The pastes were prepared with a w/b ratio of 0.35 with the same amount of SP optimized for the mortar slump measurements. Pastes were prepared with a mechanical stirrer (IKA, mod. RW20-D) according to the following procedure: Step 1: 60 s at 800 rpm (binder + 80 wt% water); Step 2: 30 s to add the SP and 20 wt% of water for samples without C-S-H seeding or 10 wt% of water for samples with seeding; Step 3: 60 s at 800 rpm; Step 4 (only for samples with C-S-H seeding): 30 s to add the seeding and the 10 wt% of remain water; Step 5: 60 s at 800 rpm. The heat flow curves were collected up to 7 days at 20 ºC. The first 45 minutes after mixing were not collected to ensure the stabilisation of the equipment.

2.2.3 Compressive strength

Mortars were prepared as described in section 2.2.1. After mixing, the mortars were poured in 4×4×16 cm moulds in two steps, the first, filled up half of the volumes of the moulds. Then, the air bubbles were taken out with a glass rod with 60 vertical punctures. In a second step, the moulds were filled completely and punctured again for 60 times. The moulds were kept in a humidity chamber at 20 ºC and 99 %R.H. during the first 24 h. After that time, they were demoulded and kept underwater up to the selected age. The compressive strength was measured according to EN196-1 in a press (Model Autotest 200/10 W, Ibertest) at a rate of 1.5 $MPa \cdot s^{-1}$. The mortars (three prisms per age) were measured at 1, 7 and 28 days. The reported compressive values are the average of the six specimens, which resulted after flexural tests.

3. Results and discussion

The amounts of SP required for an initial (target) self-flow of 200±20 mm are given Table 1. Moreover, to evaluate the slump retention, the flow values were also measured at 30 and 60 minutes after water mixing. Three main conclusions can be drawn from these data. (1) As previously reported, the fluidity loss for standard PCEs, i.e. SP-1, is extreme for clays containing relatively high amount of kaolinites and/or high BET surfaces. (2) Also as previously published, the amount of required SP is a function of the kaolinite content in the pristine clay which usually correlates with BET surfaces. (3) The novel result here is that SP-2 successfully solved the slump retention problem, see Table 1.

Once the slump retention issue was successfully cleared up, the second drawback was addressed, i.e. the low mechanical strengths at early ages. In order to do so, initially the heat released by the corresponding pastes during the first 7 days were studied. Figure 1 shows the heat flow traces and cumulative heat curves of the pastes without and with C-S-H seeding admixture. Firstly, LC^3 pastes release less heat compared to the PC-Ref, as expected. Secondly, the total heat released by the second reference, PC-Qz, which contains quartz instead of the calcined clay, is lower than that of all LC^3 pastes. After approximately 12 h, the three LC^3 pastes released more heat than PC-Qz which might indicate that the pozzolanic reactions are starting to develop at about 12 hours. Finally, it should be noted that the heat released by PC-Qz is higher than the expected value (i.e. 48% less heat due to dilution), which is very likely due to the filler effect.

Table 1: Optimized amounts of SPs, and slump values, at the given times, for the studied mortars. Values in brackets indicate the standard deviation of the measurements.

Mortars	**SP-1 (wt%)**	**SP-2 (wt%)**	**Slump /mm (at t_0)**	**Slump /mm (at 30min)**	**Slump /mm (at 60min)**
PC-Ref-a	0.34	-	183(1)	156(1)	143(2)
PC-Ref-b	-	1.20	190(1)	264(1)	288(1)
PC-Ref-c	-	0.80	156(1)	203(1)	231(4)
LC^3-CC1	1.00	-	196(2)	106(2)	100(1)
LC^3-CC1	-	1.20	186(3)	210(1)	196(1)
LC^3-CC2	-	1.00	214(2)	271(1)	284(1)
LC^3-CC3	-	0.50	210(1)	267(1)	276(3)
PC-Qz	-	0.40	211(1)	266(1)	283(1)

After C-S-H nucleation seeding with XS130, a clear cement hydration acceleration effect is observed. Firstly, the induction periods are shortened in the seeded pastes as shown by the vertical purple lines (left bottom of Figures 1a and 1c). These times ranged 1.3-2.8 h for the unseeded pastes and 1.0-2.0 h for the seeded ones. Secondly, the seeded samples show higher slopes in the acceleration periods, see oranges lines in Figures 1a and 1c. Thirdly, the C-S-H seeded pastes present larger main peaks at earlier times, see Figures 1a and 1c. This is reflected in larger accumulated heat released at 1 day of hydration, see inset in Figures 1b and 1d. Finally, larger and shaper aluminate-related peaks are observed for the seeded pastes, see Figures 1a and 1c. Because this peak is smaller in PC-Qz, which has the same amount of cement, it is concluded that the C-S-H seeding is also accelerating/enhancing the aluminate dissolution from the calcined clays.

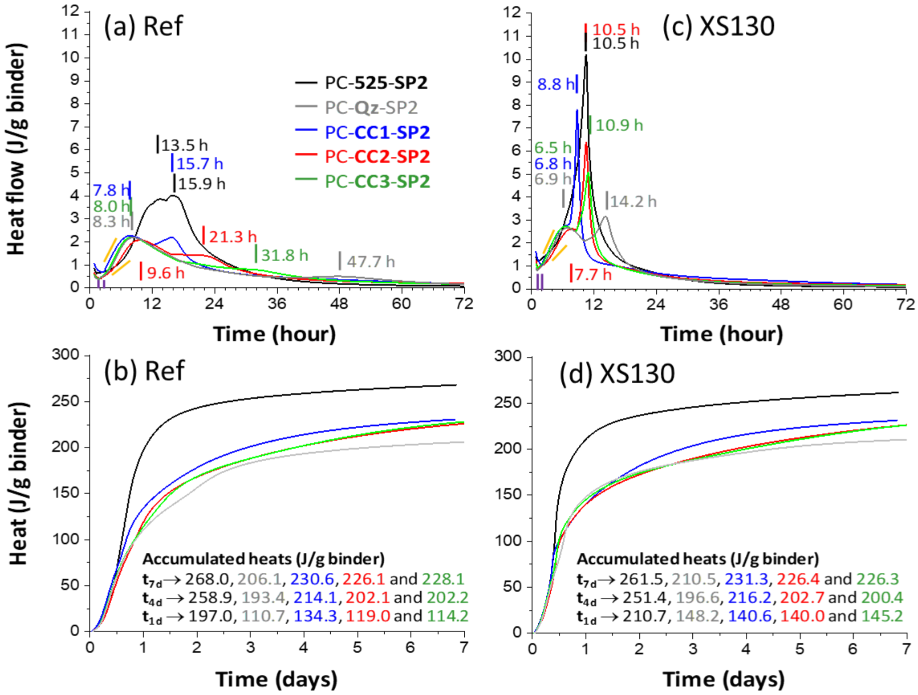

Figure 1: Calorimetric curves for pastes with w/b= 0.35. (a) Heat flow and (b) total heat released for pastes without seeding. (c) Heat flow and (d) total heat released for pastes with seeding.

Finally, the effect of the C-S-H nucleation seeding admixture on the mechanical properties of the mortars was studied. Figure 2a shows the compressive strength values for the studied mortars at 1, 7 and 28 d of hydration. Figure 2b depicts the percentages of compressive strength variation referred to PC-Ref at the same ages. On the one hand, the strengths strongly decrease for the LC^3 binders at 1 day of hydration. The 50% dilution would imply ≈22 MPa at 1 day, but smaller values were measured. Furthermore, clays with lower amounts of kaolinite give lower strengths, as expected. This variation is damped at later ages but invariably LC^3 binders showed lower compressive strengths. On the other hand, the C-S-H seeded mortars showed a very important increase of the compressive strengths, see Figure 2. It is worth noting that the LC^3 binder with high kaolinite content, 74 wt%, surpassed the reference PC at 28 days. It is also remarkable that the LC^3 binder based on a low-content kaolinite clay, 29 wt%, can develop more than 20 MPa at 1 day.

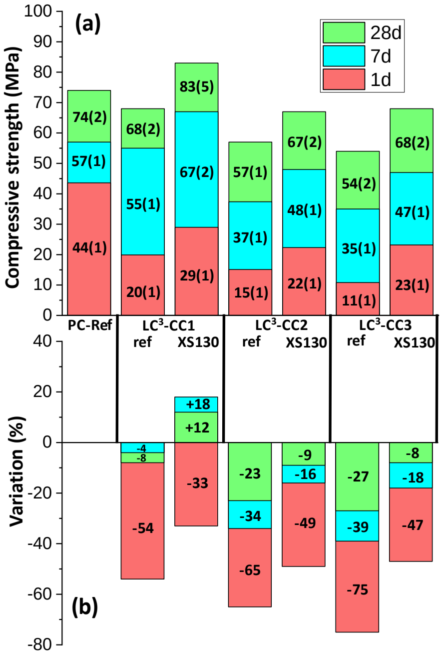

Figure 2: (a) Mortar compressive strengths for LC^3 samples without (ref) and with 2 wt% C-S-H seeding (XS130); (b) Variation of compressive strengths with respect to PC-Ref. Values in the brackets are the standard deviations.

4. Conclusions

Two main conclusions can be drawn from this work.

♦ Firstly, the new PCE-based superplasticizer, specially designed to avoid loss of fluidity during the first hours, successfully solved the slump retention problem of the studied LC^3 binders.

♦ Secondly, C-S-H nucleation seeding boosted the compressive strengths of LC^3 binders at 1 day of hydration by 45-100% respect to the unseeded mortars. The C-S-H seeded LC^3 mortars developed 22-29 MPa at 1 day, which are competitive values for field applications. Moreover, the compressive strength improvements are noticed at all ages. For instance, the relative improvements at 28 days ranged 18-26 %.

Acknowledgements

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References

Akhlaghi, O., Aytas, T., Tatli, B., Sezer, D., Hodaei, A., Favier, A., Scrivener, K.L., Menceloglu, Y.Z., Akbulut, O. (2017) "Modified poly(carboxylate ether)-based superplasticizer for enhanced flowability of calcined clay-limestone-gypsum blended Portland cement", *Cem. Concr. Res.* 101: 114–122.

Juenger, M.C.G., Snellings, R., Bernal, S.A. (2019) "Supplementary cementitious materials: New sources, characterization, and performance insights", *Cem. Concr. Res.* 122: 257–273.

Morales-Cantero, A., Cuesta, A., De la Torre, A.G., Santacruz, I., Mazanec, O., Borralleras, P., Weldert, K.S., Gastaldi, D., Canonico, F., Aranda, M.A.G. (2022a) "C-S-H seeding activation of Portland and Belite Cements: an enlightening in situ synchrotron powder diffraction study", *Cem. Concr. Res.* 161: 106946.

Morales-Cantero, A., Cuesta, A., Torre, A.G.D. la, Mazanec, O., Borralleras, P., Weldert, K.S., Gastaldi, D., Canonico, F., Aranda, M.A.G. (2022b) "Portland and Belite Cement Hydration Acceleration by C-S-H Seeds with Variable w/c Ratios", *Materials* 15: 3553.

Scrivener, K.L., Martirena, F., Bishnoi, S., Maity, S. (2018) "Calcined clay limestone cements (LC3)", *Cem. Concr. Res.* 114: 49-56.