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Processing and hydration activation of limestone calcined clay belite-rich cements

C. Redondo-Soto[1*], N. Fernández-Pérez[1], A. Cuesta[1], I. Santacruz[1], D. Gastaldi[2], F. Canonico[2], and M.A.G. Aranda[1]

[1] *Departamento de Química Inorgánica, Cristalografía y Mineralogía, Universidad de Málaga, Málaga, Spain*
Email: cinthyars@uma.es, noe.fernandez98@uma.es, a_cuesta@uma.es, isantacruz@uma.es, g_aranda@uma.es
[2] *BUILT – Buzzi Unicem Innovation Lab and Technology, Vercelli, Italy*
Email: dgastaldi@buzziunicem.it, fcanonico@buzziunicem.it

ABSTRACT

Belite-rich limestone calcined clay cements, BR-LC^3, could be an alternative for low carbon binders with potentially very good durability properties, given the high amount of C-S-H gel from the cement hydration with additional C-(A)-S-H from the pozzolanic reaction. Nevertheless, BR-LC^3 phase hydration rates at early ages are slow and they must be enhanced, for instance by using C-S-H nucleation seeding admixtures. In this work, a BR-LC^3 binder was prepared using a clinker-activated Belite-rich cement, BC (58 wt%), kaolinitic calcined clay (26 wt%), limestone (13 wt%) and gypsum (3 wt%). Pastes were prepared with a water-to-binder (w/b) ratio of 0.40 and superplasticizer. Mortars were prepared with the w/b=0.40 and having a target slump self-flow of 210±20 mm. Paste hydration characterization was carried out by thermal analysis, Rietveld quantitative phase analysis and mercury intrusion porosimetry. The compressive strengths of the mortars were also determined. Remarkable compressive strength improvements at 7 and 28 days are shown by using a C-S-H seeding admixture. The improvement of mechanical strengths is not related to belite phase hydration acceleration but mainly to lower porosity.

KEYWORDS: *low-carbon cement, calcined clay, chemical admixture, pozzolanic reaction*

1. Introduction

Clinker replacement by the combination of limestone and kaolinite-containing calcined clays is one of the foremost approaches for minimizing cement CO_2 emissions because of its wide availability and the resulting mechanical strength performances at 3 days or later, Scrivener et al (2019). These materials benefit from the pozzolanic reaction, i.e. the chemical reaction of metakaolin, and related amorphous alumina-silicate(s), with portlandite (CH) to yield calcium silicate aluminate hydrate (C-A-S-H) gel which has very good cementing and pore-refining properties. Moreover, lower limestone demand cements, such as BCs, present advantages for developing low-carbon binders and possibly extending infrastructure service lives, Cuesta et al (2021). However, BCs have slow strength development at early ages that can be enhanced with admixtures.

One possibility, which does not compromise durability performances, is the use of C-S-H nucleation seeding admixtures. These admixtures behave according to two principal mechanisms in cement hydration: i) modifying the pore solution ion contents, and ii) supplying additional nucleation sites. These features lead to an enhancement of the hydration of Belite-rich cements, Morales-Cantero et al (2022a, 2022b). Moreover, two BR-LC^3 binders have been prepared very recently and accelerated with a C-S-H seeding admixture, Redondo-Soto et al (2023). The aim of the present project is to complement that previous work by employing a different admixture, Master X-Seed STE53, which is tailored for strength enhancement of low-carbon cements. BR-LC^3 mortars have been prepared with similar self-flow slump values and hence very similar rheological features.

2. Materials and Methods

2.1 Materials. The employed BC was a CEM I 42.5 N-like, provided by Buzzi Unicem SpA with the following mineralogical composition: 28.4wt% of C_3S, 50.6wt% of β-C_2S, 11.6wt% of C_4AF, 2.3wt% of

C_3A, 2.2wt% of $C_4A_3\underline{S}$, 1.6wt% of MgO, 1.5wt% of $C\underline{C}$ and 1.8wt% of $C\underline{S}$. The key textural features are: $D_{v,50}$=12.8 μm and a Blaine value of 502 m^2/kg. The remaining materials were: i) a 80 wt% kaolinitic clay from Caolines de Vimianzo; ii) an 96 wt% limestone (LS) by Omya; and iii) a 96 wt% gypsum (Gy) by Fábrica de yesos y escayolas La Maruxiña. The raw clay was calcined at 860ºC to yield the calcined clay (CC). Additionally, a polycarboxylate superplasticizer based on poly(ethylene glycol) polyacrylate ether sodium salt (PCE) from Master Builders Solutions was employed to obtain the slump target for mortars. The C-S-H seeding admixture was Master X-Seed STE-53 (STE53) provided by Master Builders Solutions. Further information and characterization of these materials have been previously reported, Redondo-Soto et al (2023) and Morales-Cantero et al (2022b).

2.2 Pastes and mortars preparation. BR-LC^3-42 binder was prepared using 58 wt% of BC, 26 wt% of CC, 13 wt% of LS and 3 wt% of Gy. Mortars were prepared using sand-to-binder (s/b) ratio of 1.78 and w/b ratio of 0.40. The steps were as follows: i) homogenization of the binder with sand, in a plastic bag, and addition of the 80 wt% of the water mixing at 140 rpm for 60 s; ii) addition of the PCE with a syringe and of the residual 20 wt% of the water; and iii) stirring at 285 rpm for 180 s. When using STE53, the water is added in three stages: a) addition of SP and 80 wt% of the water followed by stirring at 140 rpm for 60 s; b) addition of the PCE with a syringe and 10 wt% of the water and then mixing at 285 rpm during 60 s; and finally, c) addition of STE53 with a syringe and 10 wt% of the water, stirring at 285 rpm for 120 s. The amount of PCE for each sample was optimized to yield a free-flow value of 210±20 mm. 2 wt% of STE53 was added, when required. The amounts of both admixtures are referred to the binder amount, correspond to the as-received products, and their water contents were considered for w/b calculations. The same mixing procedure was carried out for the cement pastes.

2.3 Analytical techniques. Hydrated pastes characterization was carried out at 2, 7 and 28 days by thermal analysis (TA) and laboratory X-ray powder diffraction (LXRPD) with Rietveld quantitative phase analysis (RQPA). Moreover, some microstructural features were characterized by mercury intrusion porosimetry (MIP). Resulting mortars properties were studied by compressive strength measurements. More details related to the employed analytical techniques are given in Redondo-Soto et al (2023). Slump free-flow measurements were performed pouring the mortar in the cone, UNE-EN 1015–3 standard, previously moistened, in two steps: i) filling it up to 80 % of its volume and removing the air bubbles with a glass rod: 15 vertical punctures and then, ii) filling the cone completely and making another 15 vertical punctures. Once the cone was leveled using a spatula, it was gently lifted, and the diameter of the mortar after flowing was measured in two perpendicular directions. The free-flow values were obtained for BC-ref, BR-LC^3-42, and BR-LC^3-42-STE53 by adding 0.27, 0.76 and 0.81 wt% of PCE, respectively. The weight percentage of PCE used for each sample will not be detailed next for sake of simplification.

3. Results and discussion

3.1. Calorimetry study of the pastes. The heat development of the pastes is shown in Figure 1. The BC is used as reference, and it develops a cumulative heat of hydration of 208 J/g at 7 d. This value is much smaller than those of typical PC 42.5 at that age, about 300 J/g. The maximum of the heat flow trace for BC, see Fig. 1, is located at ~24 h. As it can be seen, and as expected, BR-LC^3-42 develops less heat, 172 J/g-of-binder at 7 d. This lower heat is undoubtedly due to the dilution of the belite cement by the mixture of limestone and calcined clay. However, it must be noted that the induction period is largely reduced for the BR-LC^3 binder, see Fig. 1. This is likely due to the filler effect because the fine particle sizes of the employed calcined clay and limestone. As the developed heat was low, binder activation was carried out with STE53 as previously reported for neat PC and BC by Morales-Cantero et al (2022b). The heat of hydration for BR-LC^3-42-STE53 was 181 J/g-of-binder at 7 d. The admixture addition moved the maximum of the aluminate peak from 25 to 19 h, it becomes more intense and sharper. The maximum of alite peak, located at ~10 h, was not influenced by the STE53 addition, see Fig. 1. Hence, the acceleration/activation of the hydration of this BR-LC^3 binder is demonstrated and it mainly involved the aluminate-rich phase(s).

3.2. Phase evolution with hydration for the studied pastes. Paste hydration characterization was carried out by RQPA to obtain the degree of hydration (DoH) of the main cement phases. Additionally, TA was performed to follow the pozzolanic reactivity by measuring the portlandite contents. Table 1 shows the most important results from both techniques. From the inspection of Table 1, the following conclusions concerning the DoHs can be drawn. i) Alite hydration rates are very high and similar for the three samples. ii) Belite phase, which was activated at the clinkering stage, reacts faster than in PC but its hydration rate does not increase when STE53 admixture is employed. iii) The DoH of C_4AF is larger and it clearly increases with C-S-H seeding. Focusing on TA result, the Portlandite (CH) content increases with time for BC-ref, but it is very small and it decreases in BR-LC^3-42 seeded and unseeded pastes. These results are a proof of the pozzolanic reaction and they are in full agreement with our previous report for related samples, Redondo-Soto et al (2023).

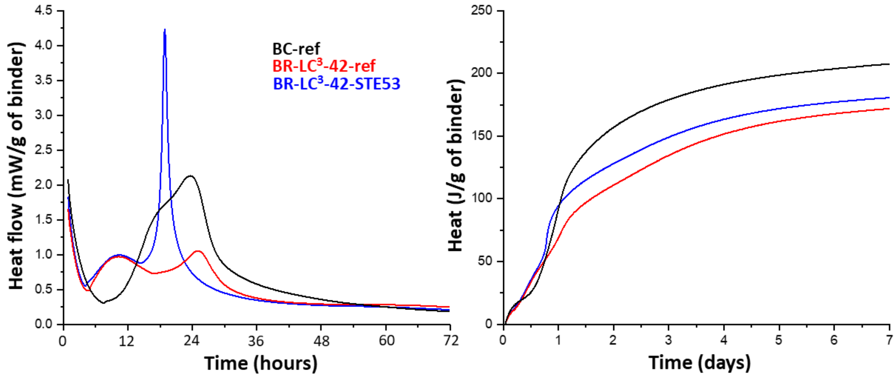

Figure 1. Calorimetric study for BR-LC^3-42 pastes, w/b=0.40. Left: Heat flow curves shown up to 3 days for better visualization. Right: Cumulative heat traces. Both plots contain the data for neat BC as reference.

Table 1. DoH (%) of the most important cement phases as determined by Rietveld quantitative phase analyses. The CH contents (wt% referred to 100 g of paste) determined by TA are also shown.

	Degree of hydration (%) from LXRPD-RQPA			CH (wt%) from TA
	C_3S-M3 2 – 7 – 28 /d	β-C_2S 2 – 7 – 28 /d	C_4AF 2 – 7 – 28 /d	2 – 7 – 28 /d
BC-ref	89 – 94 – 94	3 – 37 – 46	44 – 86 – 86	4.1 – 4.7 – 5.4
BR-LC^3-42-ref	92 – 94 – 95	22 – 37 – 42	76 – 86 – 88	1.0 – 0.8 – 0.0
BR-LC^3-42-STE53	91 – 95 – 96	23 – 27 – 43	96 – 96 – 98	1.3 – 0.8 – 0.0

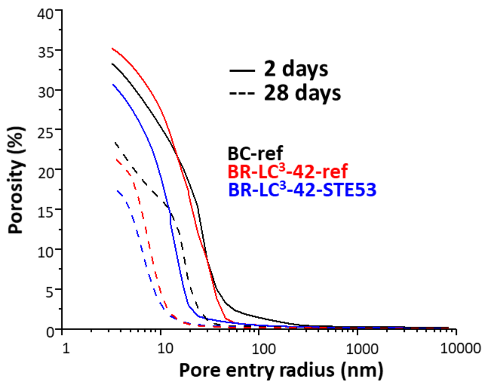

Figure 2. Mercury intrusion porosimetry results for the pastes at 2 and 28 days.

3.3 Microstructural evolution from MIP. MIP traces are given in Figure 2. At early ages, i.e. 2 d, the overall porosity of BR-LC^3-42 is slightly larger than that of BC-ref reflecting the lower amount of cement and the reduced rate of pozzolanic reaction. Interestingly, BR-LC^3-42-STE53 paste at 2 d showed smaller pore entry size threshold value and lower overall porosities. This clearly shows the benefits of C-S-H nucleation seeding by refining the porosities. At later ages, i.e. 28 days, the overall porosities of BC-ref and BR-LC^3-42 are similar but the pore entry threshold value for BR-LC^3-42 is smaller, which is a signature of the pozzolanic reaction. BR-LC^3-42-STE53 showed the lowest overall porosities showing the benefits of C-S-H seeding.

3.4 Mechanical strength investigation for the mortars. To compare the mechanical strength performances, mortars with very similar viscosity have been prepared. The workability is also an important parameter. Therefore, these values were determined here. The free-flow values for BC were 224(3), 169(2) and 164(1) mm at mixing time (t_0), 30 and 60 min, respectively. For BR-LC^3-42, these values were 202(1), 172(1) and 162(1) mm at t_0, 30 and 60 min, respectively. The corresponding results for BR-LC^3-42-STE53 were 210(2), 191(1) and 178(1) mm, respectively. These values reflect a small slump retention loss but much less severe than those observed in Portland-based LC^3 using the same type of PCE. The values in parenthesis are the standard deviation of the slump measurements.

Compressive strength results are shown in Figure 3. For the BR-LC^3-42 binder, the compressive strength at 2 d was low, 14 MPa, reflecting the slow hydration rate of belite and that the contribution of pozzolanic reaction is not important at this age. This is a 46 % decrease respect to BC-ref, a consequence of the 42 wt% cement replacement. At 7 d, the compressive strength was 28 MPa, 26 % lower than the value for BC-ref. At this age, the pozzolanic reaction is contributing. Finally, at 28 d, the corresponding value for BR-LC^3-42 was 53 MPa, just 12 % less than that of BC-ref. Thus, the contribution of the pozzolanic reaction at this age is relatively more important. In any case, the compressive strengths for BR-LC^3-42 were low and therefore, strength enhancement by C-S-H nucleation seeding was attempted as described above. For BR-LC^3-42-STE53, the compressive strength value at 2 d was the same than that of the unseeded LC^3 mortar within the variability of the measurements. Therefore, it is concluded that if a hydration acceleration has taken place, its effect on the mechanical strength is only shown at ages earlier than 2 days.

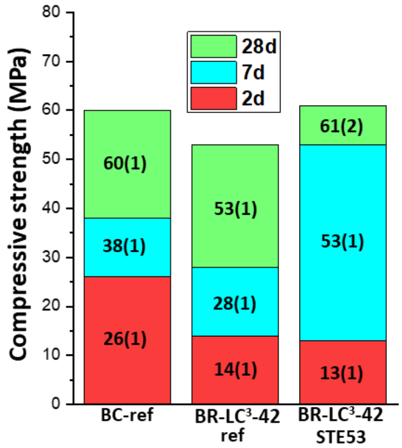

Figure 3. Compressive strength data for the studied mortars at 2, 7 and 28 days.

Conversely, the consequences of C-S-H nucleation seeding is remarkable at 7 d. This C-S-H seeded low-carbon binder develops 53 MPa at 7 d, a 39 % increase over BC-ref despite containing 42 wt% less cement. Moreover, the compressive strength increase compared to the unseeded binder, BR-LC^3-42, was 89 %. Clearly, the pozzolanic reaction is already significantly contributing at this age, and C-S-H seeding is enhancing it, likely through a more homogenous distribution of the hydrates in agreement with MIP results. However, spatially resolved techniques is required to firmly establish this key point. The mechanical strength for BR-LC^3-42-STE53 at 28 d was 61 MPa, presenting the same value as BC-ref, within the variability of the measurements. BR-LC^3-42-STE53 performs better than the unseeded binder by 8 MPa, which indicates the long-term benefits of C-S-H seeding.

3. Conclusions

Belite-rich limestone calcined clay cement binders have been prepared with similar fresh properties. The compressive strengths were measured at 2, 7 and 28 days of hydration. The use of STE53, a C-S-H nucleation seeding admixture, highly improves the compressive strength at 7 days. An 89% enhancement respect to the unseeded binder was measured. An improvement, relatively lower, is also measured at 28 days. Thermal and Rietveld analyses have been employed to determine the degree of reactions. This study indicates that the improvement in the performances, when using STE53, does no relate to belite phase hydration acceleration but partly due to accelerated C_4AF hydration and likely to a more homogenous hydration product arrangement within the matrix. Mercury intrusion porosimetry clearly shows lower porosities for the C-S-H seeded pastes.

Acknowledgements

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