Characterisation of the fresh and hardened properties of mortars produced with thermoactivated cement

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Abstract

Thermoactivated cement (TAC) from waste cement-based materials has been explored as an alternative binder to ordinary Portland cement (OPC); however, production issues, namely high water demand and rapid setting time, have hindered its application in cementitious materials. This paper adds to the existing knowledge by analysing the influence of replacement rate of OPC with TAC (0, 20, 50 and 100%) on the fresh (flowability and density) and hardened properties (compressive and flexural strength) of mortars produced with TAC with similar flowability and fixed w/b. For replacement rates with TAC up to 50 %, water demand and setting time were only little affected. Moreover, these blended binders with CEM I 42.5R can keep the original strength class. Mortars with 100 % TAC can potentially meet a strength class of 32.5 if initial and final setting times are extended. Moreover, for 20% replacement with TAC, the early age compressive strength was higher than that of control mortars. Low w/b mortars were slightly less influenced by TAC incorporation. In sum, this study confirms the suitability of TAC as a supplementary cementitious material that can accommodate high substitution rates of OPC (up to 50 %), without significant impairment of both fresh and mechanical properties.

Keywords: *thermoactivated cement, thermal activation, recycled cement, rehydration.*

1. Introduction

Recycling the cementitious fraction contained in waste concrete materials has emerged as a possible alternative solution to ordinary Portland cement (OPC). A new thermoactivated cement (TAC) is obtained by recovering the hydraulic binding properties of hydrated cement through thermal activation at much lower temperatures than those currently employed by the cement industry (Carriço, Bogas and Guedes 2020). This route not only reduces the consumption of natural resources, but also the greatest share of CO_2 emissions associated with clinker production caused by the decarbonation of limestone in the kiln at temperatures above 700 ºC (Scrivener Jonh and Gartner, 2018).
Recently, many studies have been directed at developing this recycling methodology, but still mostly focused on the study of the dehydration and rehydration phenomena using cement paste as the precursor material. Most common thermal activation temperatures range between 600-700 ºC, which represent the best compromise between sufficient dehydration and the avoidance of the decarbonation stage (Real et al. 2020). Some consensus has been gathered regarding the higher water demand of these binders due to the increased surface area of the dehydrated compounds after thermal activation (Baldusco et al. 2019). For thermal activation temperatures of 700 ºC there is generally a twofold increase in the water demand compared to OPC (Shui et al. 2009). Therefore, these binders require a high water/cement (w/c) ratio to obtain flowable mortars and guarantee proper compaction. Also, a shorter initial setting time has been reported for TAC, being as low as 17 min, which is much lower than those observed for OPC pastes (~120 min) (Zhang et al. 2019). In cement pastes with TAC as partial cement replacement (5-25%), Yu, Shui and Dong (2013) obtained initial setting times between 5 and 70 % lower than OPC control pastes. Regarding the mechanical strength, 28-days compressive strength ranging between 10-

30 MPa have been reported for mortars with 100% TAC (Serpell and Lopez 2015; Zhang et al. 2018). However, despite the recent research efforts, published studies in this domain are still scarce and perfect knowledge is still a way off. Moreover, most studies do not provide a comparable reference with OPC, making it difficult to establish a performance comparison between these binders. Therefore, the present study aimed to fill that gap by characterising the fresh and mechanical properties of mortars with different replacement rates of OPC with TAC (20, 50 and 100%) in mortars of similar flowability (and varying w/b) or similar composition (fixed w/b).

2. Materials and methods

2.1. Thermoactivated cement production

Source cement paste (SP) was produced with CEM I 42.5 R (herein referred to as CEM I) and a water/cement (w/c) ratio of 0.40. The 28-days compressive strength of SP was 45 MPa. SP was kept in a wet chamber with RH over 95 % for 3 months to achieve a well hydrated and mature cement paste. After this curing period, SP was crushed and grinded using a jaw crusher, a roller press and a ball mill. The jaw crushing stage derived SP particles with size bellow 7 cm, which were passed twice through a roller press, reducing their maximum particle size to 2 cm. After these stages, the particles were ground in a horizontal mill with steel balls for 2 hours. In a last stage, SP was sieved to obtain only particles bellow 125 μm. The thermal treatment was performed in a *Barracha – TERMO-CONTROL 3 PR* electric oven, at a heating rate of 20 ºC/min and a treatment temperature of 700 ºC, residing at this temperature for 5 hours. Cooling to room temperature was performed inside the oven. After the thermal treatment, source cement paste became thermoactivated cement paste (TAC) and was stored in sealed containers until mortar production.

2.2. Mortar compositions

Three mortar series (MI, MII, MIII) were developed to determine the influence of different replacement rates of CEM I with TAC (0, 20, 50 and 100%) on their performance. This analysis was carried out for similar flowability conditions (MI), a fixed high mortar water/binder (w/b) ratio of 0.58 (MII) and a low mortar w/b ratio of 0.40 (MIII). The mortar compositions of each series are presented in Table 1. Mortars were produced with one part cement and three parts of natural siliceous sand, by weight. The sand was dried prior mixing to ensure mixing water was controlled. Mortars with 100% TAC from series MII and all mortars in series MIII required the addition of a polycarboxylic superplasticizer (SP) that was added by weight of binder. A multi-speed planetary mortar mixer was used for mortar production, following the EN 1015-2 (1998).

Table 1 – Composition of mortar mixes produced for this study; with similar flowability (MI), with fixed w/b of 0.58 (MII) and with fixed w/b of 0.40 (MIII).

Designation	**TAC**	**w/b**	**SP**	**M_{TAC}**	**$M_{CEM\ I}$**	**M_{water}**
	%		wt%	(kg/m^3)	(kg/m^3)	(kg/m^3)
MI0	0	0.50	-	0	482	241
MI20	20	0.50	-	96	383	240
MI50	50	0.56	-	231	231	258
MI100	100	0.67	-	432	0	290
MII0	0	0.58	-	0	463	269
MII20	20	0.58	-	92	368	267
MII50	50	0.58	-	228	228	265
MII100	100	0.58	1.0	451	0	262
MIII0	0	0.40	0.4	0	507	203
MIII20	20	0.40	1.3	101	404	202
MIII50	50	0.40	2.0	250	200	200

2.3. Test methods

Normal consistency and setting time of TAC were determined according to EN 196-3 (2016). The flow table test, as described in EN 1015-3 (1999), was employed to assess the flowability of fresh mortars. The bulk density in the fresh state was determined according to EN 1015-6 (1998). After production, mortar prisms were cured in a chamber with RH over 95 % until testing. For each age, mechanical strength was assessed in terms of flexural and compressive strength on three 160x40x40 mm^3 prisms, following what is prescribed in EN 1015-11 (1999).

3. Results and discussion

3.1. Characterisation of thermoactivated cement (TAC)

The normal consistency, setting time and expansion of the binders contained in the mortars produced for this study are presented in Table 2 . As expected, the normal consistency increased with TAC content, being over twice that of CEM I, for 100 % TAC. This high water demand has been attributed to high contents of free CaO leftover from the thermal treatment, and to the great surface area and porous nature of TAC particles (Shui et al. 2009, Bogas, Carriço and Tenza-Abril 2020). Nonetheless, for up to 50 % incorporation of TAC, the rate of increase in water demand was not as pronounced. In this case, fine cement particles might have acted as a lubricant between the TAC particles, reducing friction and improving flowability of the mixtures, which in turn resulted in lower amounts of mixing water to achieve the normal consistency.

Table 2 – Normal consistency, setting time and expansion of binders used in this study.

Designation	**TAC**	**Normal consistency**	**Setting time**		**Expansion**
			Initial	Final	
	%	(w/b)	(min)	(min)	(mm)
100 % CEM I	0	0.268	120	200	1.7
20 % TAC + 80 % CEM I	20	0.325	145	210	-
50 % TAC + 50 % CEM I	50	0.375	125	180	-
100 % TAC	100	0.650	15	32	2.8

The setting time of 100 % TAC, both initial and final, were much lower than those of 100 % CEM I. In fact, the initial setting time of TAC failed to meet the minimum requirement of 45 minutes set by EN 197-1 (2011). However, it has been suggested that a false set might occur in these binders (Serpell and Lopez 2015, Bogas, Carriço and Pereira 2019). Indeed, in samples with 100 % TAC, while the surface of the paste exhibited a quick set, the core remained unreacted. For mortars with 20 and 50 % of TAC, the setting time followed an unclear tendency. However, considering the rapid setting time of 100 % TAC, for up to 50 % TAC, the setting time appears to have been mostly controlled by the setting of CEM I.

As expected, the expansion of 100% TAC was higher than that of pastes with only CEM I. In this regard, TAC contained around 15 % of free CaO, which is known to expand when in contact with water to form $Ca(OH)_2$. Nonetheless, expansion was still lower than the 10 mm limit set by EN 197-1 (2011).

3.2. Flowability and bulk density of fresh mortar

The similar flowability target set for series I mortar mixes (MI) led to varying w/b ratios depending on the incorporation rate of TAC (Fig. 1). While MI20 mortars required no change of the w/b in relation to the control mortar (MI0), MI50 and MI100 mortars had to be produced with w/b ratios that were 12 and 34 % higher than that of MI0, respectively. The high water demand of TAC has been reported in literature (Zhang et al. 2019, Real et al. 2020), being attributed to the extensive surface area and free CaO content in these binders, that results from the thermal treatment.

Figure 2 shows the flow value as a function of the replacement rate with TAC for mortars with fixed w/b (MII and MIII). In mortars with high w/b ratio (MII), for up to 20 % replacement with TAC (MII20), the flowability was not significantly affected. However, MII50 had a flow value 14% lower than control mortars (MII0), and MII100 mortars required 1 wt% of SP to meet the targeted w/b ratio, obtaining flow values similar to those of MII50. In low w/b ratio mortars (MIII), SP had to be added to all mortar mixtures, regardless of replacement rate, to attain a w/b of 0.40. For this series, it was not possible to obtain flowable mixtures with 100 % TAC, showing that for low w/b conditions TAC was only suitable for partial cement replacement as a supplementary cementitious material. Nonetheless, it was possible to obtain flowable MII mortars with up to 50 % TAC, without requiring the addition of SP (MII50).

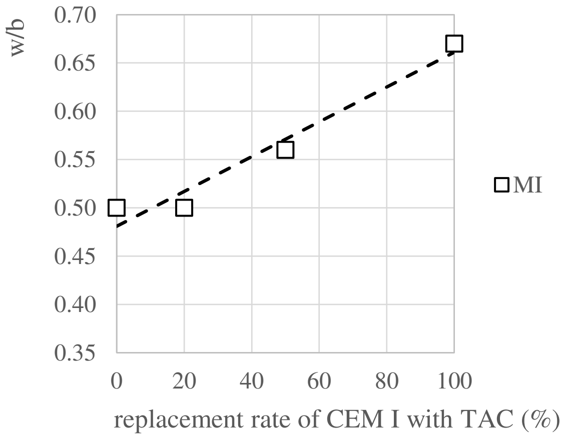

Figure 1. The water to binder ratio of similar flowability mortar series (MI) as a function of the replacement rate of CEM I with TAC.

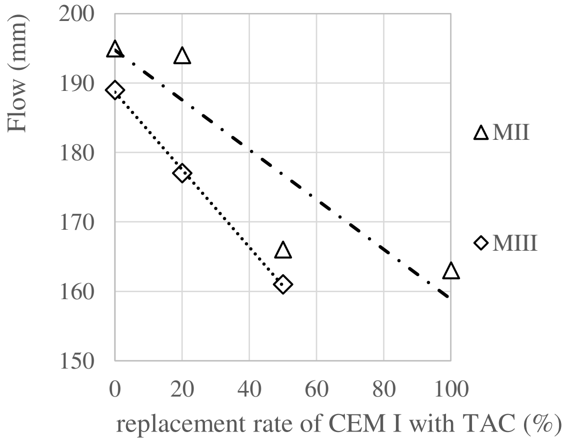

Figure 2. Flow value of fixed w/b mortars series (MII and MII) as a function of replacement rate of CEM I with TAC.

A decrease of the fresh bulk density was consistently observed with increasing the replacement rate of CEM I with TAC for all mortar series (Fig. 2). Besides the higher water demand, the lower particle density of TAC also reduced the paste volume with increasing replacement rate, leading to lower fresh densities than respective control mortars. In MI mortars, fresh density varied linearly with replacement rate with TAC, following the rising w/b necessary to achieve the targeted flow values. In mortars with fixed w/b, for 50% replacement with TAC (MII50 and MIII50), fresh density was 3 and 6 % lower than control mortars, respectively. Despite having a lower w/b, MIII mortars had lower fresh density than MII mortars. In this case, the lower flowability of these mortars reduced the mixture's compactness and increased void content as showed in Figure 4.

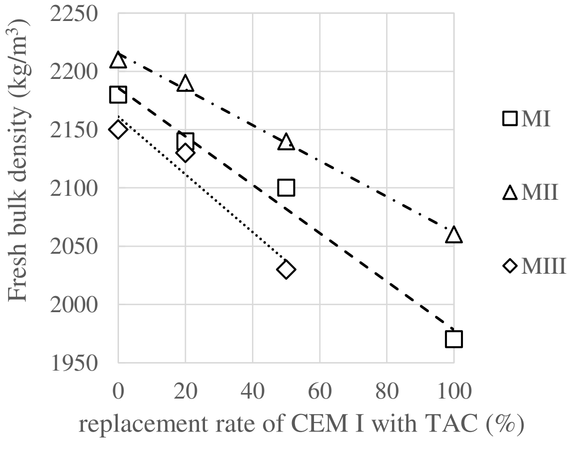

Figure 3. Fresh bulk density of mortars with increasing replacement of CEM I with TAC (0, 20, 50 and 100%) for series I, series II, and series III.

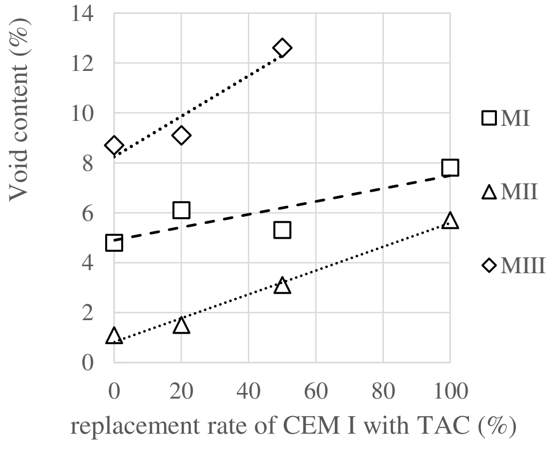

Figure 4. Void content of mortars with increasing replacement of CEM I with TAC (0, 20, 50 and 100%) for series I, series II, and series III.

3.3. Compressive and flexural strength

The compressive and flexural strength of mortars with TAC followed a similar tendency in either mortars with similar flowability (MI) or fixed w/b (MII and MIII). For brevity, only the compressive strength results will be discussed in detail, since the flexural strength results basically follow the same trend. The coefficients of variation of both tests were below 5% for each testing age.

The compressive and flexural strength at 28 days are presented in Figures 5-6, for each mortar series and increasing replacement rates of CEM I with TAC. In general, the 28-day compressive strength decreased with increasing TAC incorporation in all mortar series. As expected, this decrease was more pronounced in mortars with similar flowability (MI) due to the corresponding increase of the w/b with replacement rate. In MI mortars, 28-day compressive strength for 20, 50 and 100 % replacement with TAC was 92, 72 and 35 % that of control samples, respectively. Despite their high w/b (0.67), MI100 mortars with 100% TAC were still able to attain a 28-days compressive strength of as high as 23 MPa.

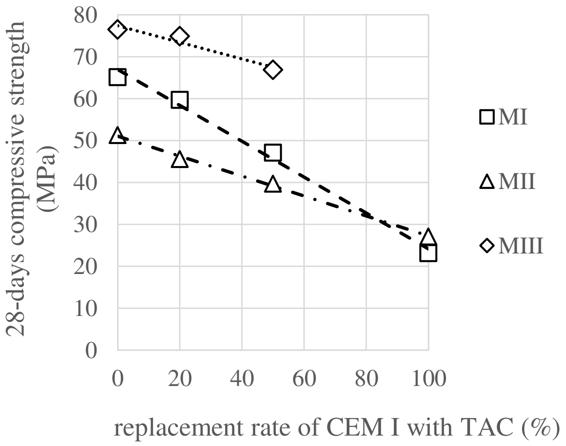

Figure 5. Compressive strength at 28-days for each mortar series as a function of the replacement rate with TAC.

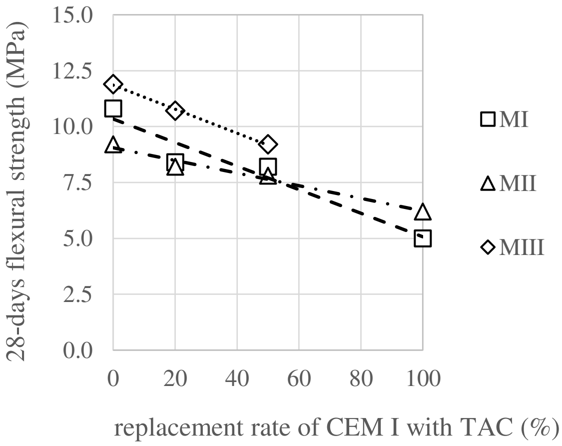

Figure 6. Compressive strength at 28-days for each mortar series as a function of the replacement rate with TAC.

Figures 7-8 show the 7 and 28-days compressive strength of mortars, respectively, for different replacement percentages as a function of the w/b. Overall, there was a reduction of the compressive strength with increasing w/b. The 28-days compressive strength of low w/b mortars (MIII) was slightly less sensitive to TAC replacement than that of high w/b mortars (MII). While the compressive strength of MII20 and MII50 were 11 and 24 % lower than control mortars (MII0), respectively, for MIII20 and MIII50, the compressive strength reduction was only 2 and 12 %, respectively. On the one hand, MIII mortars had varying contents of SP which might have improved the dispersion of TAC and consequently its reactivity. On the other, the smaller particles in TAC might have provided nucleation sites that were more beneficial in denser microstructures.

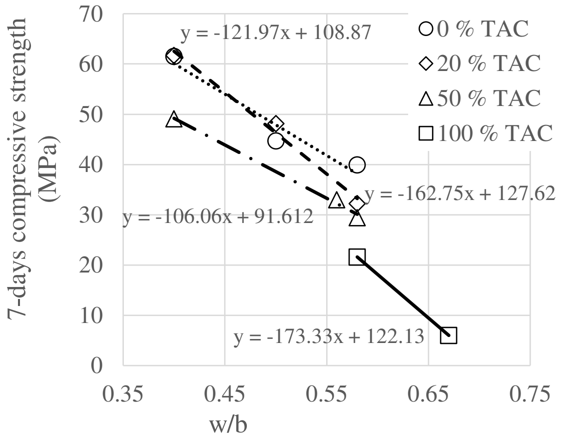

Figure 7. Compressive strength at 7-days for mortars with different replacements of CEM I with TAC as a function of the w/b.

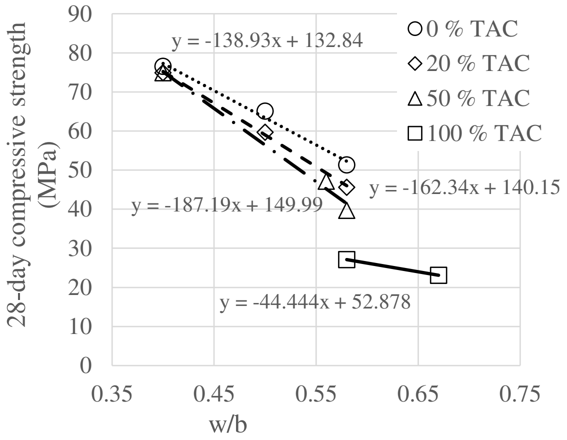

Figure 8. Compressive strength at 28-days for mortars with different replacements of CEM I with TAC as a function of the w/b.

The 28-days compressive strength of mortars with 100 % TAC (MI100 and MII100) was not as significantly affected by the reduction in w/b than remaining mortars, showing a different tendency from mortars with CEM I and lower replacements rates (Figure 8). As reported by Zhang et al. (2018), there might be a threshold strength for these binders due to their low particle hardness, which inevitably stabilizes the compressive strength regardless the w/b ratio. Assuming the compressive strength of mortars with TAC follows the linear regression of Figure 8, the 28-days compressive strength for 20 and 50% TAC incorporation and a w/b ratio of 0.50, would be 59 and 56 MPa, respectively. Therefore, according to EN 197-1 (2011), mortars with 20 and 50 % TAC can potentially meet the mechanical requirements of a 52.5 strength class of blended cements with CEM I 42.5 R. This also attributed to the high strength of the CEM I 42.5 used in this study. Analogously, mortars with 100 % TAC can nearly achieve a standard strength class of 32.5 if the initial setting time is extended.

Figures 9-10 show the compressive strength development of mortars with similar flowability and fixed w/b, respectively. For incorporations of TAC up to 50 %, the strength development was similar to control mortars under both predetermined conditions. Moreover, the compressive strength development of MI20 was quicker than MI0 up to 7 days. These mortars had similar flowability but also the same w/b (0.50), suggesting there might have been other factors that influenced the performance of TAC, such as the w/b and effectiveness of the dispersion.

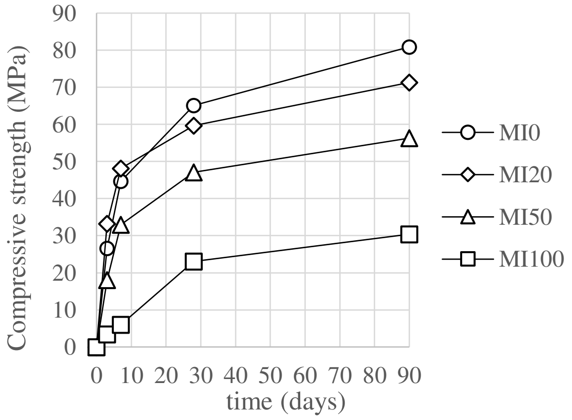

Figure 9. Compressive strength development over time (3, 7, 28 and 90 days) of mortars with similar flowability (MI), for different replacement rates of CEM I with TAC.

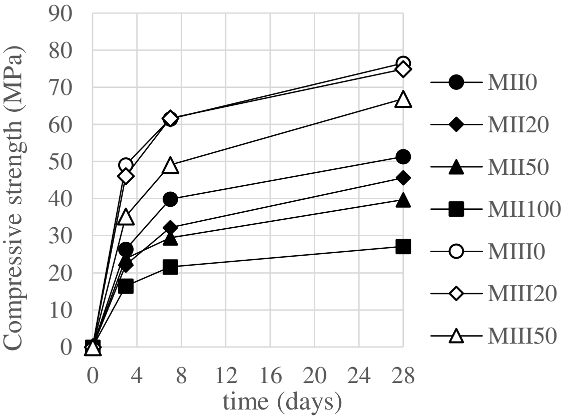

Figure 10. Compressive strength development over time (3, 7 and 28 days) of mortars with w/b of 0.58 (MII) and w/b of 0.40 (MIII) for different replacement rates of CEM I with TAC.

For mortars with 100 % TAC, the strength development was slower than control mortars, especially regarding similar flowability conditions (MI100). In this case, the compressive strengths at 3, 7 and 28 days were 12, 13 and 36 % that of control mortars (MI0). In MII100 mortars (w/b=0.58), at least up to 28-days, the strength development was quicker than in MI100, being 62, 54 and 53 % that of control mortars (MII0). In order to meet the w/b requirement, while maintaining workable mortars, MII100 contained 1 wt% of SP, which might have enhanced the dispersion of TAC particles providing an improved microstructure of these mortars. Nonetheless, the compressive strength development of MI100 after 28-days was not significantly different from that of control mortars with CEM I, and it was similar to that of mortars with up to 50 % TAC (MI20 and MI50) (Fig.9). Therefore, the compressive strength development did not attain a time-dependent threshold value.

4. Conclusions

This paper analysed the influence of different replacement rates of CEM I with TAC in mortars with similar flowability and fixed w/b. The water demand, setting time and soundness of TAC were assessed followed by the characterisation of mortars with 20, 50 and 100 % of this binder in the fresh and hardened state.

The water demand of TAC was higher than CEM I and increased with increasing replacement of TAC. For 100 % TAC, the water demand was more than twice that of CEM I. However, for replacement rates up to 50 %, neither water demand nor setting time were significantly affected by TAC incorporation, showing the potential of these binders as a partial substitute of cement.

The flowability of mortars decreased with increasing incorporation of TAC. For 100 % TAC, mortars required a w/b 34 % higher than control mortars of similar flow. Under fixed w/b conditions, the flowability and fresh density of mortars with 20 % TAC were not significantly affected, and for 50 % incorporation the flowability was only 15% lower than control mortars.

The mechanical strength of mortars with TAC decreased with increasing replacement with TAC. However, for 20% TAC the mechanical strength was very similar to that of control mortars, being even higher than the latter at early ages under similar flowability conditions. Moreover, the compressive strength of mortars with 50% TAC was, on average, 80 % that of control mortars, showing that TAC can be used at high replacement rates of CEM I, without significant impairment of the fresh and mechanical properties.

From this study, it was shown that the cement strength class can be maintained for TAC percentage replacements up to 50%. Moreover, the incorporation of 100 % TAC may be comparable to a low-grade cement with a standard strength class of 32.5.

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