Reutilisation of hazardous spent fluorescent lamps glass waste as supplementary cementitious material

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HIGHLIGHTS

- Spent fluorescent lamps glass (SFLG) waste successfully used to replace PC.
- No prior treatment required to reduce the mercury content of SFLG.
- Similar pozzolanic activity observed with manual and mechanically treated SFLG.
- Strength results came close to 100% PC, with up to 35% SFLG after 90 curing days.
- SFLG waste generally prolonged the setting time of the blended pastes.

GRAPHICAL ABSTRACT
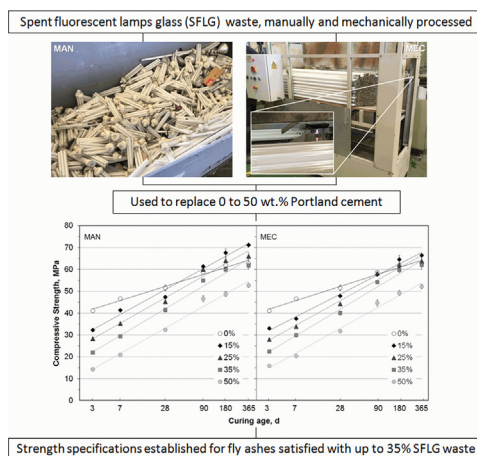
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ABSTRACT

Spent fluorescent lamps glass (SFLG) waste, manually and mechanically processed in a lamps waste treatment plant, was used to partially replace up to 50 wt% Portland cement (PC). Both waste types exhibited similar pozzolanic activity. The mortars containing up to 35 wt% SFLG met the specifications for other pozzolanic materials (e.g. fly ash) and, after 90 curing days, their compressive strength values were similar to or higher than those of the 100% PC sample (58.8 MPa). Our results provide an alternative reutilization process for this hazardous waste to reuse SFLG as-received (no washing to reduce mercury) and contributes to less PC use.

1. Introduction

Discharge and fluorescent lamps contain chemical elements, such as mercury and phosphorous dust, to generate light. Given the high toxicity of mercury, European Directive 2011/65/EU [1], which restricts the use of certain hazardous substances in electrical and electronic equipment (EEE), limits mercury concentrations

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according to the type of lamp and its power. As described by Rey-Raap and Gallardo [2], part of the mercury contained in discharge and fluorescent lamps generates visible light, while another part interacts with glass and phosphor powder. In lamps treatment plants, where glass waste is separated and recovered, the dust inside lamps is collected by blowing in order to reuse mercury in new lamps. Therefore, the glass collected after treating lamps contains both the mercury diffused into glass and that coming from the dust residue that could not be completely removed. According to the data reported by Rey-Raap and Gallardo [3], the mercury concentration in spent fluorescent lamps (SFL) falls within the 2. 37 ± 0.50 mg/g range (average of compact and linear lamps from various manufacturers, places and years). As these authors concluded [2], at the end of lamps' useful life 13.66% of mercury diffused in glass during the working hours, while phosphor powder contains 85.76% of mercury (the remaining 0.58% lies in the vapour phase). Consequently, this glass waste is classified as hazardous, with code *20 01 21 - Fluorescent tubes and other waste containing mercury* according to Spanish order MAM/304/2002 [4]. As reported by Ambilamp (www.ambilamp.es), a non-profit Spanish association composed of more than 400 up-lighting companies, 2,616 tonnes of lamps were separately collected in 2018, of which 152.2 tonnes were light-emitting diode (LED) lamps and the remaining 2,483 tonnes (93.87%) were non-LED lamps (composed of 80.66 wt% of glass) [5]. The data provided by the Integrated Industrial Register [6] showed that 5,475.0 tonnes of lamps (discharge, fluorescent and LED) were placed in the Spanish market in 2019. This implies that approximately 93.87% of them (5,139.38 tonnes) contained mercury and, consequently, 4,145.4 tonnes of glass contaminated by this toxic element (80.66 wt% of the lamps) will be generated at the end of their useful life.

Although glass can generally be recycled several times with no loss of quality, according to Mehta and Ashish [7] the remelting process is very sensitive to any contamination (only 5 g of contaminated glass may influence a tonne of material during manufacturing). Besides, different reviews [8–10] have summarised the different construction applications in which glass has been successfully reused: as recycled aggregate in asphalt mixtures, as fine aggregate in concrete, to produce foam glass and lightweight aggregates, to manufacture clay bricks, as a raw material in ceramic glaze (partially replacing common frits), to synthesise heat storage materials, as a raw material in eco-cement, as recycled aggregates in road bases and subbases [11], as a precursor in geopolymers [12] or to partially replace Portland cement (PC). However, the mercury contained in spent fluorescent lamps glass (SFLG) waste limits its reutilisation possibilities, especially in applications that require high temperatures (i.e. glass or frits) as mercury gases can be released. As reducing mercury content in SFLG waste is expensive and difficult, the reutilisation of this hazardous waste is limited, so it is usually dumped in landfills with hazardous waste. As explained by Rey-Raap and Gallardo [3], although some technologies have attempted to remove or reduce mercury content in SFLG waste, most of them cannot completely eliminate the phosphor powder attached to glass [2]. This makes the possibility of reusing and valorising SFLG waste to partially replace PC particularly interesting, because its reutilisation as a pozzolanic admixture would allow large amounts of a hazardous waste to be reused as-received, without having to wash or apply additional treatments to remove either the phosphorous powder adhered to surfaces or the mercury diffused in glass. There is even the possibility of mercury being encapsulated in the cementitious matrix at the end of the mortar or concrete's useful life, which would convert hazardous waste into inert. However, to avoid overextending this work, mercury leaching in the SFLG/PC binders developed will be presented in another supplementary publication.

Other benefits gained from partially replacing PC with SFLG waste are those that derive from reducing the amount of employed cement. As previously reported, between 560 and 710 kg CO_2 per tonne of produced cement were released to the atmosphere in 2017 (net CO_2 emissions, variation depending on the production region) [13]. According to the European Cement Association based in Brussels [14], almost 4 billion tonnes of cement were produced worldwide in 2018, which implies that approximately 2.3–2.9 billion tonnes of CO_2 were globally released by the cement industry in this period. Therefore, reusing SFLG as a supplementary cementitious material will also contribute to preserve natural resources and to minimise energy and the carbon footprint associated with PC production [2,7–10].

The pozzolanic activity of different glass waste types has been successfully proven in previous research [7–9,15–21]. Several of these studies [10,16,18–20] concluded that the reactivity of glass depends considerably on the curing temperature, chemical composition and particle size of powder. Mohajerani et al. [9], who reviewed using waste glass in construction applications, observed that previous research mainly focused on soda-lime glass, the most frequently used. Hence given the strong influence of glass composition on its pozzolanic behaviour [19,20], together with the nature of the SFLG waste herein used (hazardous), the present study may contribute new significant knowledge to existing research.

As possible drawbacks that may arise when partially replacing PC with SFLG waste, various studies draw our attention to alkali-silica expansive reactions (ASR), which take place between alkalis provided by glass particles (alkali-rich) and silica [7,9,10,15,22–24]. However, all these studies agree that ASR occur mainly when glass is used to replace natural aggregates, and no deleterious expansion by ASR is observed below a certain particle size. Although no consensus has been reached on the recommended maximum size to be employed for avoiding ASR, the most restrictive (minimum) reported particle size is 100 μm [9]. As the SFLG waste particles used in this study were crushed and milled below this limit to promote their reactivity, expansive ASR has not been evaluated.

In short, the present work aims to use SFLG waste to partially replace PC which, apart from reducing the amount of employed PC, would provide a reutilisation alternative for a waste that is generally deposited in hazardous landfills because removing its mercury demands specific and expensive treatment. No previous treatment to minimise the mercury content (diffused in glass, or provided by the attached phosphorus dust) will be applied prior to its use in the PC blended binders. Additionally, if mercury is encapsulated by the binding matrix and the amount of leached mercury is below the limits set out in regulations [25], this hazardous waste could become inert at the end of the cementitious component's useful life. However, these complementary studies will be the target of future work.

2. Experimental

2.1. Experimental flow chart

Fig. 1 summarizes the experimental process followed to conduct the present research. As shown, two different types of SFLG waste, manually and mechanically processed (MAN and MEC, respectively) were used. They were crushed and milled to reduce their particle size and increase their reactivity and, after their characterization, they were used to develop SFLG/PC blended binders (0 to 50 wt% PC replacement). Pastes and mortars were prepared to assess the pozzolanic activity of the MAN and MEC glass waste, by means of microstructural and mechanical characterization tests.
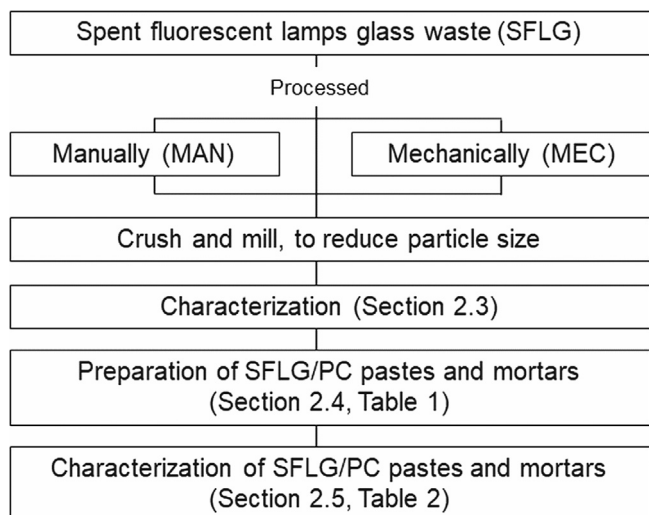
Fig. 1. Experimental process followed to assess the pozzolanic activity of the SFLG waste, manually and mechanically processed.

The different stages of the process are properly described in the following Sections 2.2 to 2.5.

2.2. Materials

In this study, two different hazardous glass waste types were supplied by VAERSA, a company that treats lighting and energy accumulators waste in the Valencian Community (east Spain). Glass waste was recovered from spent fluorescent lamps (SFL), which had reached the end of their useful life, following two different treatments: manual (MAN, Fig. 2a) and mechanical (MEC, Fig. 2b). As explained by Rey-Raap and Gallardo [2,3], during the mechanical process, the ends of the SFL are cut with a flame. Some phosphor powder, which was introduced to provide light during the lamps' useful lives, is blown and recovered with compressed air. Then negative pressure is applied to break tubes. The remaining materials (glass, plastic, metal) are separated by elecromagnetism and density differences. The supplied glass pieces fell within the 2–5 cm range and were used as-received, without washing or applying additional treatments to remove the phosphor powder attached to their surfaces. Samples were prepared with PC type CEM I 42.5R, which complies with UNE EN 197-1:2011 specifications. Siliceous sand with a fineness modulus of 2.74 and particles smaller than 2 mm was used in mortars.

2.3. Spent fluorescent lamps glass waste preparation and characterisation

SFLG was crushed in a BB200 Retsch jaw crusher (Ibertest) and particles were sieved until they were all smaller than 2 mm. These particles were milled for 8 h in an Orto-Alresa ball mill, where 1,110 g of glass waste and 4,860 g of alumina balls (diameters ranging from 15 to 40 mm) were used. The granulometric distribution of the milled glass waste was determined by laser diffraction in a Mastersizer 2000 (Malvern instruments). The chemical composition of both SFLG waste types was evaluated in a Bruker S4 Pionner spectrometer, and their crystalline phases were analysed by X-ray diffraction (XRD) in a Brucker AXS D4 Endeavor powder difractometer with Cu Kα radiation at 20 mA and 40 kV, from 5° to 55° 2 theta degrees. An scanning electron microscope (SEM) JEOL JSM-7001F, electron gun within the 0.1–30 kV range, equipped with an EDX-WDX detector and the INCA 350 software (Oxford), was used to investigate the morphology of the milled MAN and MEC powders. Thermogravimetric analyses (TG) of the glass waste were performed in a TGA/SDTA851e/LF/1600 (Mettler Toledo) using alumina crucibles in an air atmosphere at a heating rate of 20 °C/min, from 35 °C to 1,000 °C.

2.4. Sample preparation

Mortars were prepared following the process established in Standard UNE EN 196–1:2005 using a binder:sand:water ratio of 1:3:0.5 (in weight). The SFLG waste, manually (MAN) and mechanically (MEC) obtained, was used to replace 0 to 50 wt% PC CEM I 42.5R. Pastes and mortars were cured under controlled conditions at 20 °C and 95% relative humidity for 365 days. Table 1 summarises the variables of this study.

2.5. Pastes and mortars characterisation

Table 2 summarises the different tests herein run. The setting time was investigated in pastes following Standard UNE EN 196–3:2005. The amount of water was kept constant (147.5 g) and the initial PC content (500 g) was replaced with the different percentages of SFLG waste (0 to 50 wt%). The equipment and test conditions employed for the SEM and XRD analyses were those previously described in Section 2.3. Although the same equipment was also used for the thermogravimetric tests, the TG tests in pastes were run from 35 to 600 °C in a N$_2$ atmosphere at a heating rate of 10 °C/min in aluminium crucibles (100 µl) with manually perforated lids.

Fig. 2. The original spent fluorescent lamps: a) Manually processed; b) Mechanically processed.

Table 1
Variables of the process used to develop SFLG/PC blended samples.

Glass waste type	Designation	Binder:sand:water ratio	PC Replacement, wt.%	Curing temperature, °C	Curing time, days
–	REF	1:3:0.5	0	20	3, 7, 28, 90, 180 and 365
Manual	MAN15		15		
	MAN25		25		
	MAN35		35		
	MAN50		50		
Mechanical	MEC15		15		
	MEC25		25		
	MEC35		35		
	MEC50		50		

Table 2
Tests performed to characterise the developed SFLG/PC blended samples.

Designation	Pastes				Mortars
	Setting time	TG, Curing age	XRD, Curing age	SEM, Curing age	Compressive Strength, curing age
REF	√	7, 28, 90, 365	7, 28, 90, 365	28	3, 7, 28, 90, 180, 365
MAN15	√	7, 28, 90, 365	7, 28, 90, 365	–	3, 7, 28, 90, 180, 365
MAN25				28	
MAN35				–	
MAN50				28	
MEC15	√	7, 28, 90, 365	7, 28, 90, 365	–	3, 7, 28, 90, 180, 365
MEC25				28	
MEC35				–	
MEC50				28	

The compressive strength of the developed mortars was evaluated from 3 to 365 curing days in a MEH-3000PT/W (Ibertest) following Standard UNE EN 196–1:2005. The Strength Gain attributed to the pozzolanic reaction (SG, calculated according to Eq. (1)) and the Strength Activity Index (SAI, relative strength between the blended SFLG/PC and REF mortars) were determined for each waste type, PC replacement and curing age.

$$SG(\%) = \frac{S_{POZ} - (S_{REF} \cdot PC)}{S_{REF} \cdot PC} \cdot 100 \qquad (1)$$

where:

S_{POZ} = compressive strength of the SFLG/PC blended mortar, MPa
S_{REF} = compressive strength of the reference mortar, MPa
PC = percentage of Portland cement in the SFLG/PC blended mortar, per unit.

3. Results and discussion

3.1. Characteristics of the spent fluorescent lamps glass waste

The MAN and MEC glass waste was milled for 8 h. As reported in Table 3, the milled powders had a mean diameter close to 20 μm, with 10 vol% of particles under 2 μm and 90 wt% vol. below 60 μm.

According to the studies by Jiang [8] or Mirzahosseini and Riding [18], glass particles below 75 μm exhibit pozzolanic reactivity

and inhibit an alkali silica reaction (ASR). Mirzahosseini and Riding [18], who investigated the influence of particle size (63–75 μm, 25–38 μm and 0–25 μm ranges) on the pozzolanic activity of green glass powder, concluded that smaller particle sizes significantly improved pozzolanic reactivity because a bigger surface area of particles facilitates glass dissolution and, consequently, improves the kinetics of the reaction and strength development. Shi et al. [26] investigated the partial replacement of PC with glass waste with the same chemical composition, but four different finenesses. They also observed that replacing PC with ground glass powder reduced ASR-induced expansion. These results were corroborated by the review by Mohajerani et al. [9], in which deleterious ASR were not reported in the literature when using glass powder with a particle size smaller than 100 μm.

Table 4 shows the chemical composition of the two SFLG waste types herein used (MAN and MEC). Both glass types were composed of approximately 75% of SiO_2, and presented relatively high Na_2O contents (7.6% and 12.2% for MAN and MEC, respectively). This chemical composition comes close to that reported by Mohajerani et al. [9] for soda-lime glasses (containers, light bulbs, etc.), whose SiO_2 and Na_2O contents fell within the 66–75% and 12–17% range, respectively. However, the CaO content was lower than that expected for these glass types (5–12%) [7–9]. As highlighted by Mejdi et al. [15], the relatively high SFLG waste alkali content increases the risk of deleterious alkali silica gels forming (N,K-(C)-S-H). However, the scientific community acknowledges that below a given particle size (which oscillates from 0.1 to 1 mm,

Table 3
Granulometric parameters of the MAN and MEC SFLG waste milled for 8 h.

PFLG waste	Mean diameter, μm	d_{10} μm	d_{50} μm	d_{90} μm
MAN	20.30	1.87	10.90	49.10
MEC	22.60	1.85	11.70	59.60

Table 4
Chemical composition of the SFLG waste, MAN and MEC, wt.%

SFLG waste	SiO_2	Na_2O	CaO	Al_2O_3	MgO	K_2O	BaO	ZnO	ZrO_2	PbO	Other	LOI*
MAN	75.7	7.6	2.9	5.2	1.0	2.6	2.4	1.0	0.35	0.32	0.25	0.65
MEC	74.2	12.2	4.4	3.1	1.9	1.8	1.3	0.2	0.05	0.06	0.55	0.36

*Loss on ignition determined at 1,000 °C.

depending on the study performed [9]), the pozzolanic reaction generally occurs faster than ASR, which reduces the expansion risk [7,10,15,16,22–24]. As 90 vol% of the SFLG waste particles used herein were smaller than 60 μm (Table 3), no ASR expansion was expected. Previous studies confirm that using glass waste as a supplementary cementitious material (SCM) even reduces ASR between glass aggregates and the cementitious matrix [9,10,16,22–24].

As Fig. 3 shows, both the MAN and MEC glass waste exhibited a significant deviation from the baseline, differentiated as two bands: from 5 to 15 and from 15 to 40 2θ degrees. As expected from previous studies [7,8,15], this corroborates the essentially amorphous structure of the glass waste. Although minor signals

originated by the diffraction of crystalline vaterite (V, $CaCO_3$, PDF #330268), hydrotalcite (T, $Mg_6Al_2CO_3(OH)_{16}\cdot 4(H_2O)$, PDF #141191) and natron (N, $Na_2CO_3\cdot 10H_2O$, PDF # 15800) were also distinguished, they were attributed to carbonation of the sample during storage and handling. In agreement with Mohammed [27], the fact that the sum of SiO_2 + Al_2O_3 exceeded 70% (80.9% and 77.3% for the MAN and the MEC glass waste, respectively), together with the insignificant amount of crystalline phases in the material, they are good indicators of a possible pozzolanic reactivity.

Fig. 4 shows the micrographs of the milled glass powder. Both waste types MAN and MEC exhibited a similar morphology, with fine irregular particles with sharp edges, as well as flat and smooth surfaces.

3.2. Setting time of the SFLG/PC blended pastes

Fig. 5 shows the variation in the initial and final setting times (IST and FST, respectively) with the different amounts (0 to 50 wt%) and types of SFLG waste (MAN and MEC). All the pastes complied to UNE EN 197–1:2011 specifications as they presented an IST longer than 60 min. The IST of the REF paste (165 min) became slightly shorter with the partial PC substitution with the MAN waste, and progressively prolonged with the mechanically processed glass (MEC, up to 200 min). The FST generally prolonged with the partial PC replacement with both waste types: from the 210 min recorded for the REF paste, up to the maximum 270 min exhibited by paste MEC50. The time under the plastic condition generally prolonged in the SFLG/PC blended pastes. Although it slightly varied when up to 25 wt.%MAN waste was incorporated (up to 55 min vs. the 45 min exhibited by the REF paste), it progressively prolonged with higher MAN glass waste contents (up to 80 min with 50 wt%) or in the samples prepared with mechanical waste (within the 70–75 min range, whatever the MEC glass waste content).

The results obtained with up to 25 wt% MAN waste were similar to those previously reported by Kamali and Ghahremaninezhad [22], who observed no significant variations in the IST and a minor reduction in the FST when replacing up to 20% PC in concrete with
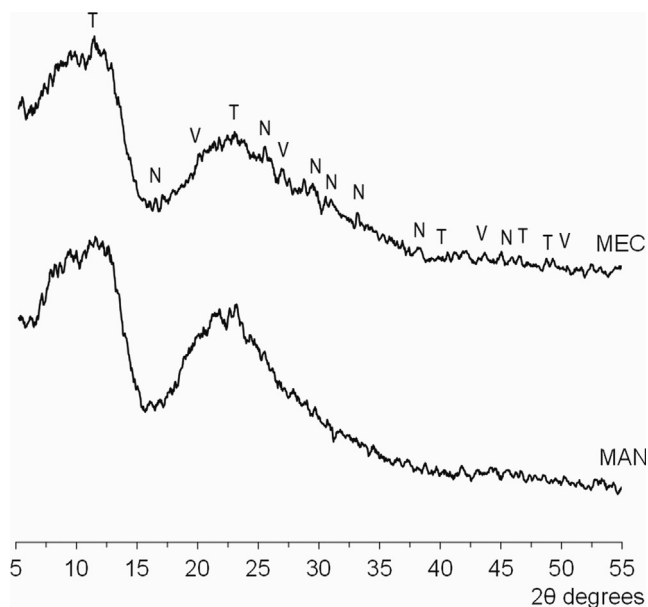

Fig. 3. X-ray diffractogram of the SFLG waste types MAN and MEC. V, vaterite ($CaCO_3$); T, hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}$ $4(H_2O)$); N, natron ($Na_2CO_3\cdot 10H_2O$).
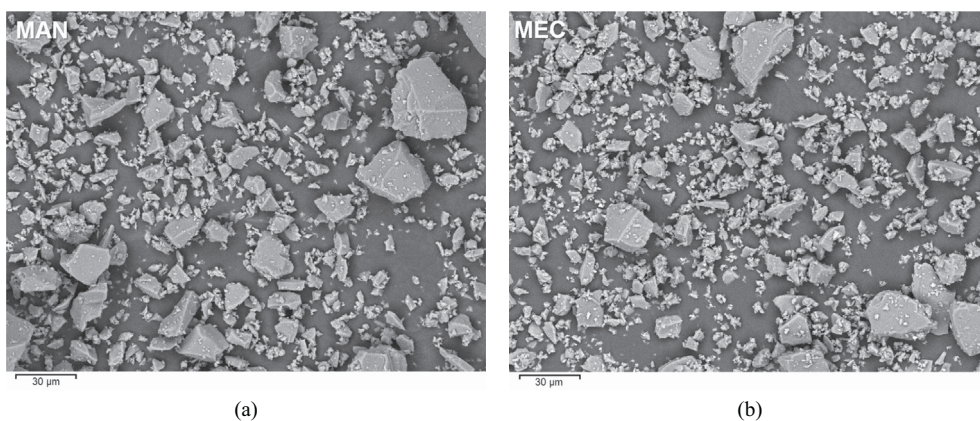

(a)   (b)

Fig. 4. Scanning electron microscope images of the milled SFLG waste: a) MAN; b) MEC.
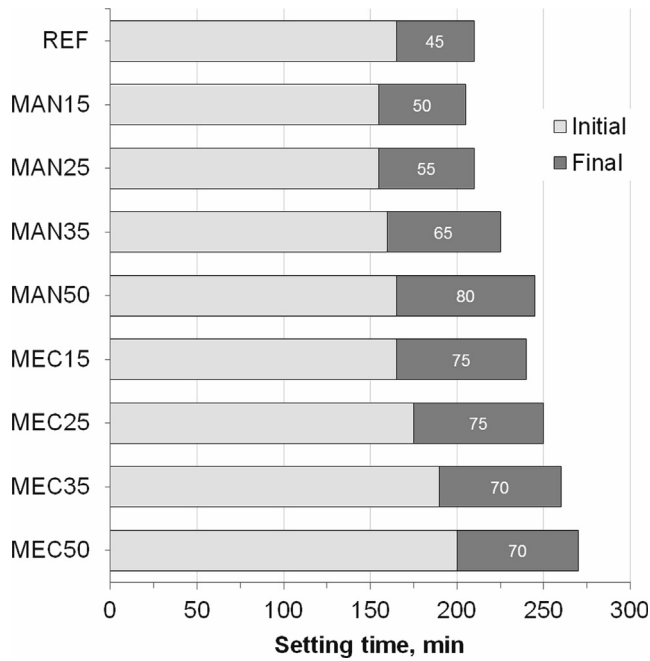
Fig. 5. Setting time of the SFLG/PC blended pastes, made with the MAN and MEC glass waste.

two different glass powder types (derived from glass fibre waste and recycled glass). The setting times recorded with higher MAN contents or with the MEC glass waste came closer to those previously reported by Elaqra et al. [16] or Patel et al. [28], who observed a slight delay in PC hydration when replacing PC with up to 30% and 20% glass powder, respectively. As suggested by Patel et al. [28], this delay could be explained by the dilution effect as pozzolanic reactions do not occur in such short curing times.

3.3. Compressive strength of the SFLG/PC blended mortars

Figs. 6 to 8 summarise the compressive strength (MPa), strength gain (SG, %) and strength activity index (SAI, %) results obtained when replacing 0 to 50 wt% PC with the MAN and MEC glass waste.

As Fig. 6 shows, similar compressive strength results were obtained for a given percentage of PC substitution and curing time, no matter what the employed SFLG waste type. Although the SPLG/PC blended mortars exhibited significantly lower mechanical properties for up to 28 days than those given by the reference sample, after 90 curing days the strength of the mortars containing up to 35 wt% glass waste was similar to or even greater than that presented by the reference sample. The positive results obtained after medium-long curing ages suggest that SFLG waste has a medium reactivity, comparable to that of other widely studied pozzolans, such as fly ash [29].

Both glass waste types MAN and MEC similarly contributed to the strength of the blended mortars (SG, %). Although the results reported in Fig. 7 show negative SG values after 3 and 7 curing days, this trend reversed after approximately 20 days. Consequently, a positive contribution of the MAN and MEC glass waste to compressive strength was observed after 28 curing days, which became more significant after longer curing times or with higher PC replacements.

Fig. 8 shows the SAI values determined for the SFLG/PC blended mortars, prepared with 0 to 50 wt% MAN or MEC glass waste, and cured for up to 365 days. The mortars containing up to 35 wt% glass waste met the specifications established for fly ash (UNE EN 450–1) [29] as their SAI values were higher than 75% and 85% when cured for 28 and 90 days, respectively. These values fell within the 100–110% range in the mortars blended with 25 wt% glass waste cured for 90 days. Although minor improvements were observed with additional curing times (up to 365 days), the obtained results implied that the mortars with 65 wt% PC exhibited a maximum 10% compressive strength reduction after 90 curing days, or 3% after 1 year.

The strength parameters correlated with curing age by means of simple linear equations (2), which were established for both SFLG waste (MAN and MEC) types and for all the PC substitution percentages.

$$S_{PAR} = a \cdot \ln(t) + b \tag{2}$$

where:

S_{PAR} = Strength parameter to be analysed: compressive strength (MPa), SAI (%) or SG (%);
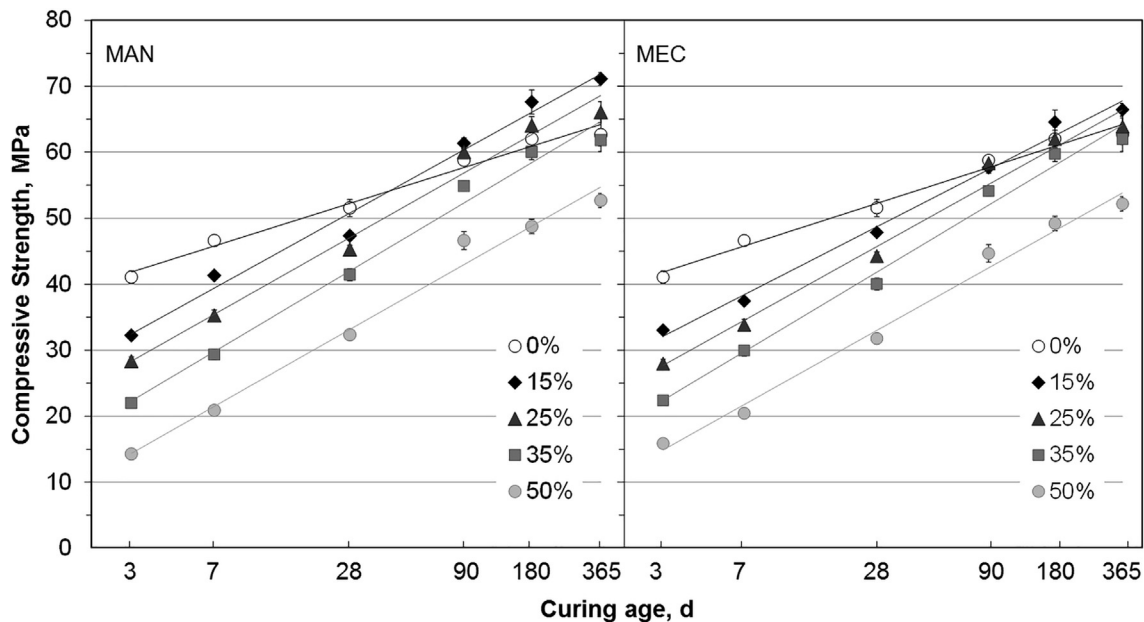

Fig. 6. Compressive strength of the mortars prepared with 0 to 50 wt% SFLG waste, MAN and MEC, cured from 3 to 365 days at 20 °C.
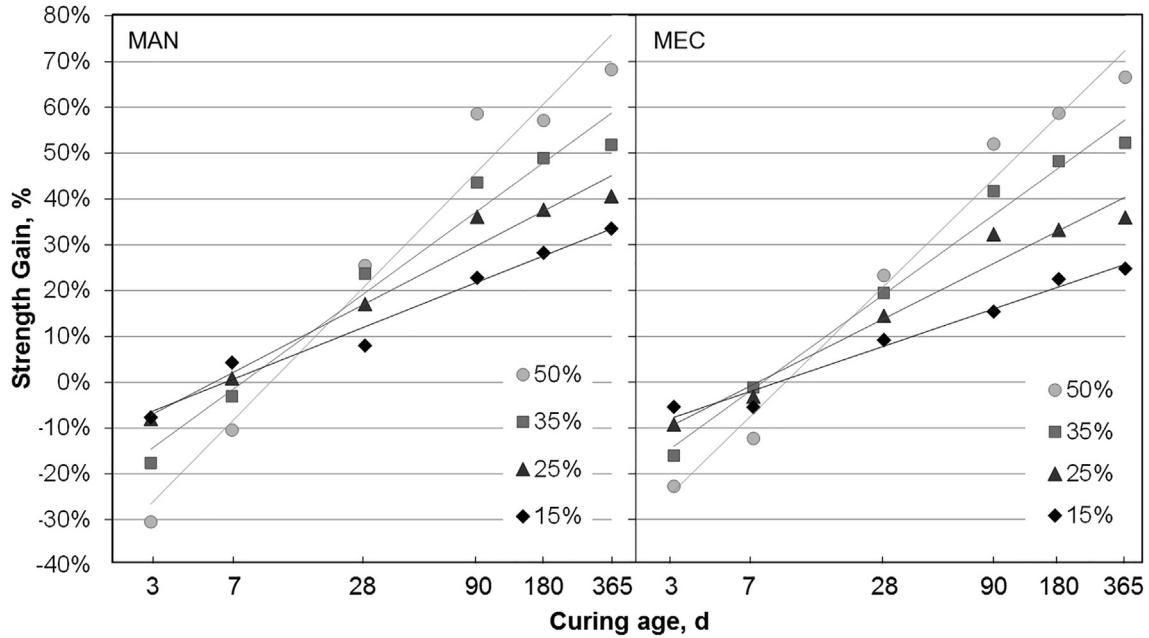
Fig. 7. Strength gain of the mortars prepared with 0 to 50 wt% SFLG waste, MAN and MEC, cured from 3 to 365 days at 20 °C.
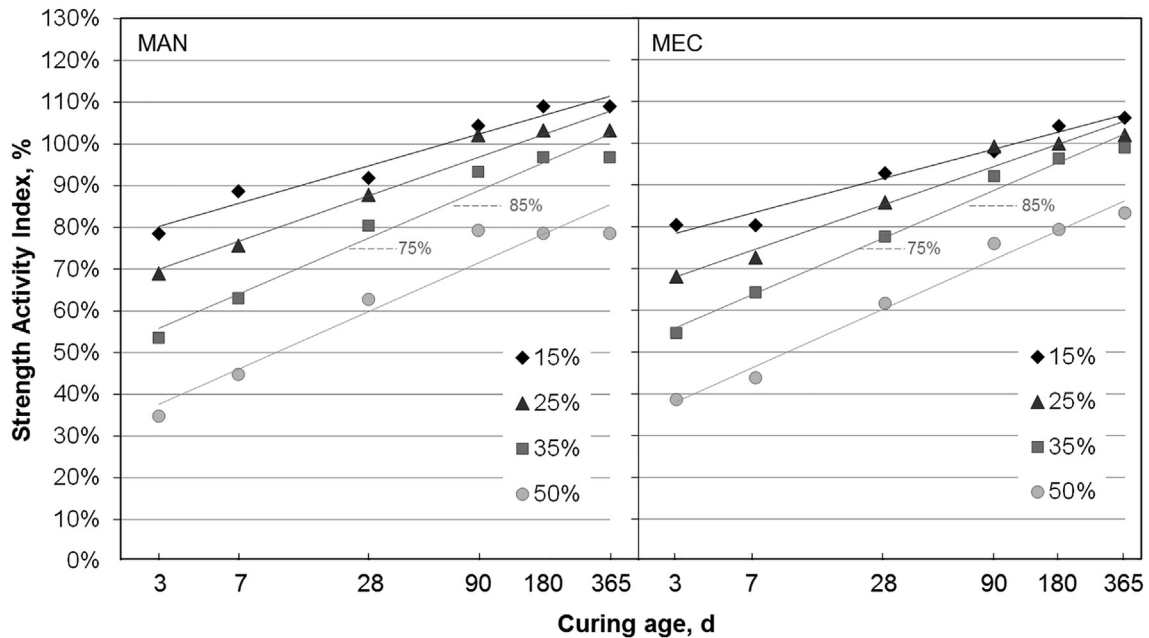

Fig. 8. Strength activity index of the mortars prepared with 0 to 50 wt% SFLG waste, MAN and MEC, cured from 3 to 365 days at 20 °C.

t = curing age, days
ln = natural based-e logarithm
a constant = linear regression slope
b constant = intercept between the strength parameter and the
Y axis

As shown in Table 5, a coefficient of determination R^2 higher than 0.97 was generally obtained, which indicates that the simple linear regression between the based-e logarithm of the curing age and strength parameters (compressive strength, SAI or SG) was good. Similar regression values were obtained regardless of the process followed to obtain the glass waste (MAN or MEC), which confirms that no significant differences were observed between

these SFLG waste types from a strength development point of view. The B-intercept values lowered with increasing glass waste amounts, which denotes reduced pozzolanic activity at short curing ages when the amount of portlandite released by PC hydration and, consequently, available for the pozzolanic reaction, was still small. In other words, the dilution effect prevails over the pozzolanic reaction for early curing ages. Although the slope of the compressive strength linear adjustments (σ_C 'a' constant) hardly varied with glass waste content or type (all the values recorded for the SFLG/PC blended mortars fall within the 7.43–8.82 range), the obtained values were considerably higher than those recorded for the reference sample (4.66), which denotes a greater improvement in strength with curing time in the pozzolanic mortars. Con-

Table 5
Linear regression data for the compressive strength, SG and SAI of the MAN and MEC SFLG/PC blended mortars.

Strength	Regression	MAN					MEC				
		PC substitution, wt.%					PC substitution, wt.%				
		0	15	25	35	50	0	15	25	35	50
σ_C, MPa	a	4.66	8.20	8.39	8.82	8.41	4.66	7.43	8.06	8.69	8.11
	b	36.74	23.45	19.12	12.62	5.14	36.74	23.97	18.87	12.89	5.99
	R^2	0.98	0.98	0.98	0.99	0.99	0.98	0.99	0.98	0.99	0.99
SAI, %	a	–	0.065	0.079	0.097	0.100	–	0.059	0.078	0.097	0.100
	b	–	0.73	0.61	0.45	0.27	–	0.72	0.60	0.45	0.27
	R^2	–	0.96	0.95	0.96	0.93	–	0.97	0.97	0.99	0.98
SG, %	a	–	0.083	0.109	0.153	0.213	–	0.070	0.103	0.148	0.200
	b	–	−0.16	−0.19	−0.31	−0.50	–	−0.15	−0.21	−0.30	−0.46
	R^2	–	0.97	0.97	0.97	0.97	–	0.97	0.97	0.99	0.98

trarily to the compressive strength 'a' values, the slope of the SAI and SG linear adjustments progressively increased with glass waste content. This indicates that the contribution of pozzolan to the system's mechanical properties increases with the amount of glass waste and curing time.

The obtained results agree with the reviews by Chandra et al. [23] and Jiang et al. [8] who concluded that, although increasing glass waste contents generally reduced early age strength, mechanical properties improved with curing age. Kamali and Ghahremaninezhad [22] also observed the strength differences between the blended and reference cements diminish with curing time, so that after 28 curing days mortars containing 20 wt% glass waste showed better compressive strength results than the reference sample. The results obtained herein came close to those obtained by Bignozzi et al. [19] who, after analysing the influence

of replacing 25% PC with four different glass waste types (crystal glass from home items, glass from cathode ray tubes, fluorescent lamps and soda-lime glass) observed that the strength of the blended mortars was generally lower than that of the reference sample for up to 60 curing days at 20 °C. Patel et al. [28] also found that the strength of mortars containing 20% glass powder came close to that presented by the reference mortar after 90 curing days. The SAI values reported in their study [28] fell within the 76–100% range in the samples cured from 7 to 90 days. Similar results have also been reported by Khmiri et al. [30], who evaluated the pozzolanic behaviour of different finenesses glass, and obtained SAI within the 82–102% range in mortars blended with 20% glass powder and cured from 7 to 90 days. In short, as Mohajerani et al. [9] concluded in their review, although strength results strongly depend on the type of glass and powder fineness, the con-
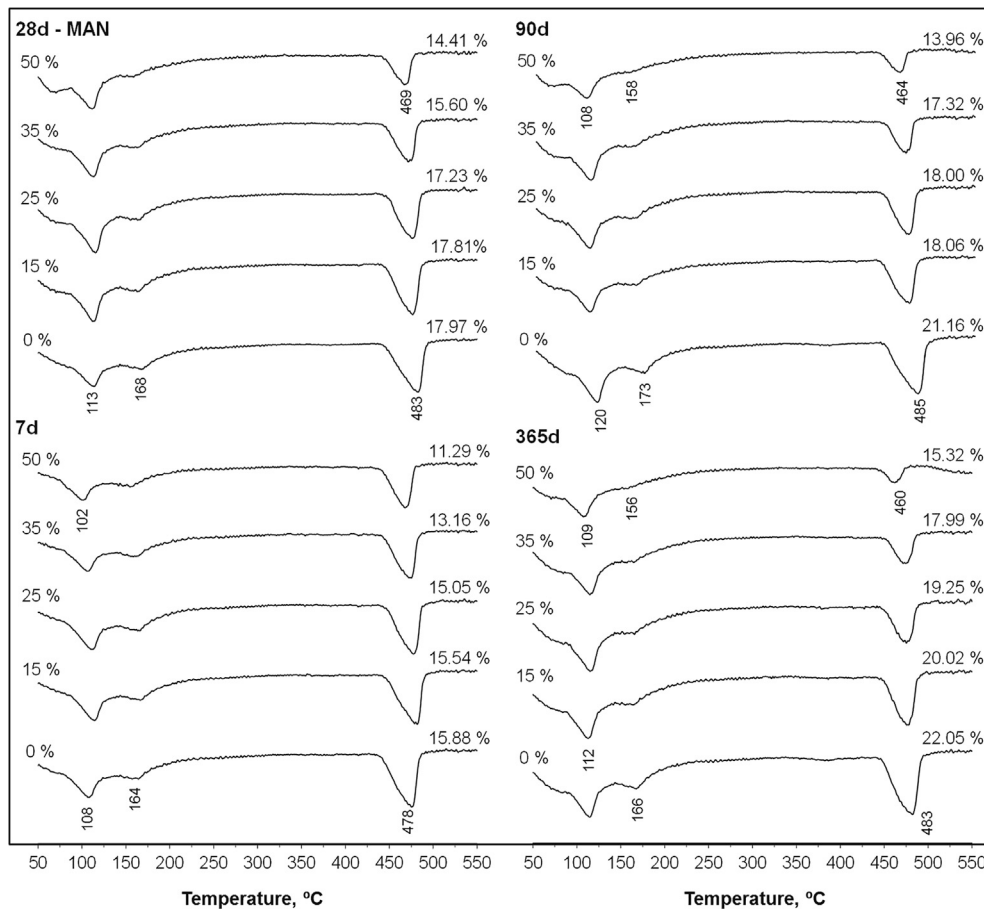

Fig. 9. DTG curves of pastes with 0 to 50 wt% MAN glass waste, cured at 20 °C from 28 to 365 d.

crete or mortar samples containing glass waste as a pozzolanic admixture generally met the requirements for fly ashes (ASTM C618, UNE-EN 450–1, or equivalents), where a minimum SAI value or 75% is required after 28 curing days.

3.4. Thermogravimetric analyses

Figs. 9 and 10 plot the derivative thermogravimetric curves (DTG) for the SFLG/PC blended pastes cured at 20 °C from 28 to 365 days. PC replacement and total weight loss (TWL) are indicated as percentages. In agreement with compressive strength evolution, similar thermogravimetric results were obtained for a given PC substitution and curing age, no matter what the used SFLG waste type was. For a given curing time, TWL diminished with increasing amounts of glass waste, which denoted fewer hydrated phases. Signals arising from 100 to 120 °C are assigned to the dehydration of ettringite and calcium silicate hydrates (CSH), and those originated at ≈170 °C originate from the dehydration of calcium aluminate and calcium aluminosilicate hydrates (CAH and CASH, respectively) [31,32]. The slightly lower temperatures herein obtained compared to those indicated by the authors [31,32] for the corresponding bands are explained by the manual perforation of the lids, which modifies the atmosphere generated inside the capsule and makes the obtained results less accurate. These bands intensified with curing time, which corroborates the formation of hydrates that provide the binder with strength. Signals within the 470–480 °C range are attributed to the dehydroxylation of Ca (OH)$_2$ and, as expected [31,32], their intensity lowered with increasing amounts of SFLG waste. As Chandra et al. [23] explain in their review, at short curing ages the smaller amounts of port-

landite recorded in the blended pastes are explained by the dilution effect of PC, while at later curing ages the lower portlandite content derives from the pozzolanic activity of the SFLG waste, which react with the Ca(OH)$_2$ released during PC hydration to provide new compounds with binding properties.

Fig. 11 summarises the percentage of fixed lime (FL, Ca(OH)$_2$) attributed to pozzolanic reactions in the SFLG/PC blended pastes, cured at 20 °C for up to 365 days. This parameter was determined according to Eq. (3):

$$FL = \frac{CH_C \cdot PC - CH_{POZ}}{CH_C \cdot PC} \cdot 100 \tag{3}$$

where:

CH$_C$ = amount of calcium hydroxide in the reference paste, determined for each curing age
CH$_{POZ}$ = amount of calcium hydroxide in the SFLG/PC blended paste, determined for the same curing age as the reference paste
PC = percentage of PC in the blended paste, per unit

Negative fixed Ca(OH)$_2$ values were generally recorded for the pastes cured up to 28 days, which denotes the presence of larger amounts of lime than those theoretically expected in a sample prepared with the same amount of PC than the blended paste, but with no pozzolanic additions. As previously observed by Cyr et al. [33] and Payá et al. [32], negative FL values are explained by the prevalence of the particle effect over the pozzolanic reaction as SFLG waste particles provide additional nucleation sites that facilitate PC hydration. However, while the 7 days cured pastes
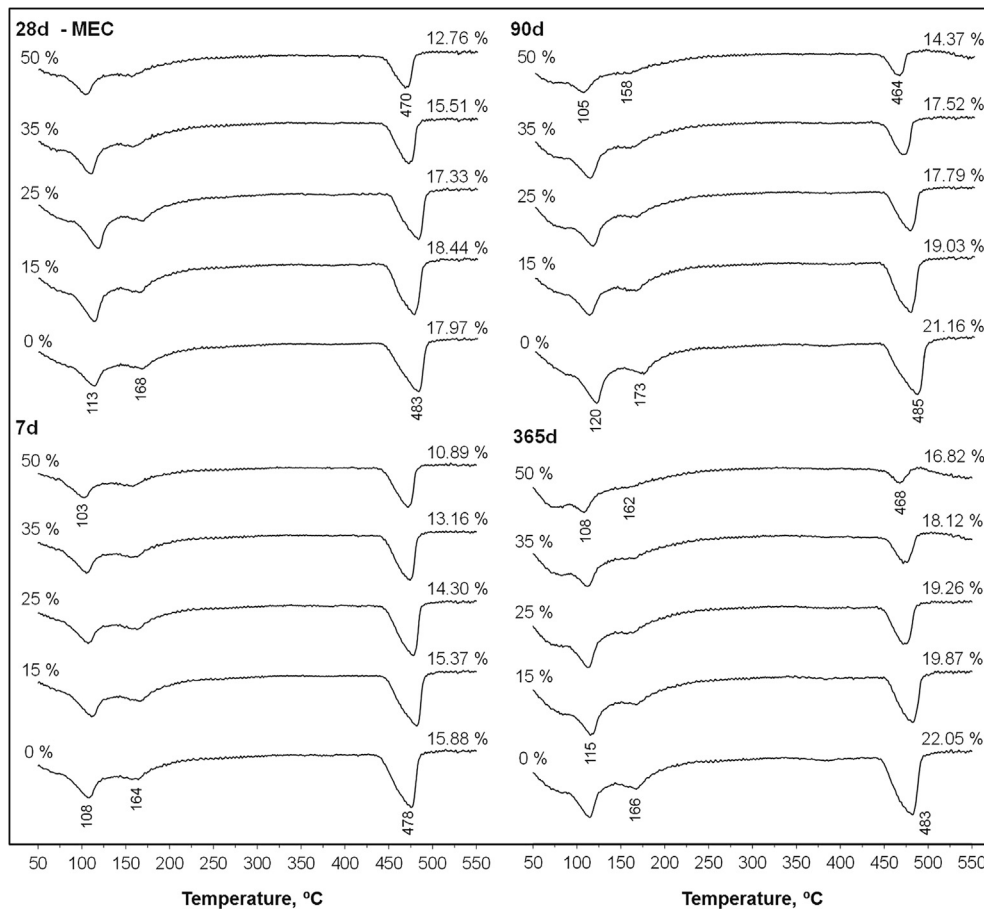

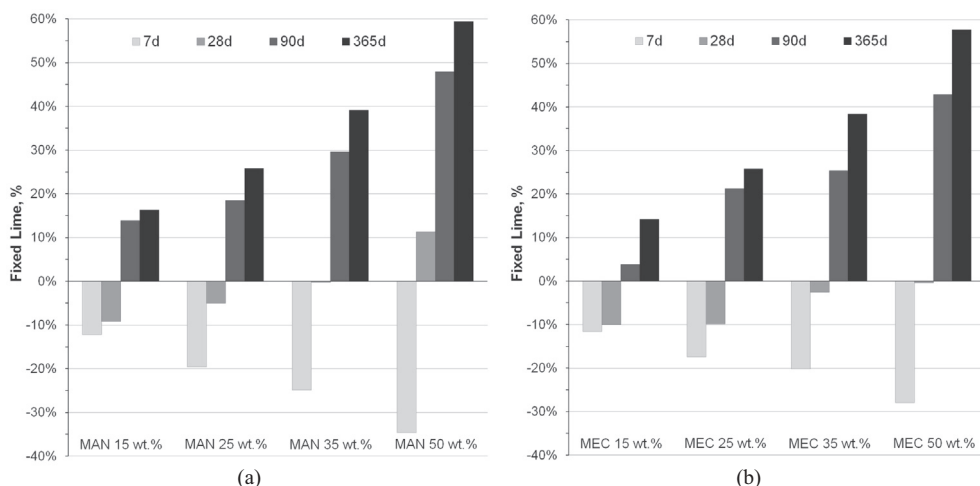**Fig. 10.** DTG curves of pastes with 0 to 50 wt% MEC glass waste, cured at 20 °C from 28 to 365 d.

Fig. 11. Percentage of fixed $Ca(OH)_2$ in pastes containing 0 to 50 wt% SFLG waste, cured at 20 °C from 28 to 365 days: a) Manual; b) Mechanical.

exhibited more negative values with higher waste contents, the results for those cured for 28 days came close to zero, or were even positive, with increasing amounts of SFLG waste. In agreement with the compressive strength results, this corroborates reduced pozzolanic activity for short curing ages (7 days, when no significant amounts of portlandite have yet been provided by PC hydration). Pozzolanic reactions started to become significant after 28 curing days, when portlandite was partially consumed by glass

waste (as evidenced in Fig. 11 by the higher FL values with increasing SFLG waste contents). The obtained results agree with those previously reviewed by Mohajerani et al. [9] and Chandra et al. [23], who observed that replacing PC with glass powder enhanced the early hydration of PC cement, and the generally large amounts of alkalis contained in glass waste also facilitate early binding gel formation. Mehta [7] and Kamali and Ghahremaninezhad [22] also noted in their studies enhanced early PC hydration in glass waste/
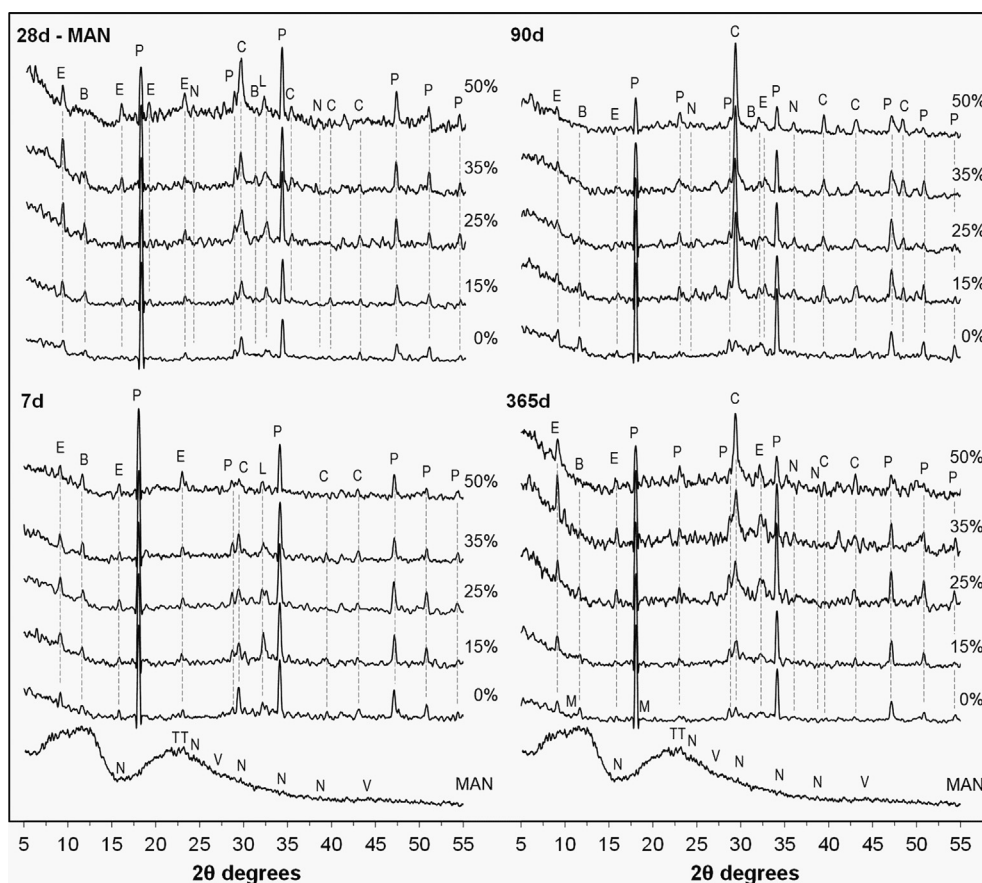

Fig. 12. XRD patterns of the SFLG waste and the blended pastes prepared with 0 to 50 wt% MAN glass, cured at 20 °C from 28 to 365 days. P, portlandite $(Ca(OH)_2)$; E, ettringite $(Ca_6Al_2(SO_4)_3(OH)_{12}·26H_2O)$; L, larnite $(\beta\text{-}Ca_2SiO_4)$; C, calcite $(CaCO_3)$; B, carboaluminate $(Ca_8Al_4O_{14}CO_2·24H_2O)$; N, natron $(Na_2CO_3·10H_2O)$; M, monosulfoaluminate $(3CaO·Al_2O_3\ CaSO_4·12H_2O)$; V, vaterite $(CaCO_3)$; T, hydrotalcite $(Mg_6Al_2CO_3(OH)_{16}\ 4(H_2O))$.

PC blended cements and pozzolanic behaviour of the waste after 28 curing days.

3.5. X-ray diffraction (XRD) studies

Figs. 12 and 13 summarise the XRD results for the 0 to 50 wt% SFLG/PC blended pastes cured at 20 °C for up to 365 days. The diffraction patterns of the milled glass waste were also plotted as a reference. No significant differences were observed among the spectra of the pastes prepared with the MAN and the MEC SFLG waste, which qualitatively exhibited the same diffraction peaks. A greater deviation from the baseline, along with greater difficulty in identifying crystalline peaks (higher noise), was observed with increasing SFLG waste contents.

In agreement with the DTG and compressive strength results, the intensity of the signals attributed to Portlandite (P, $Ca(OH)_2$, PDF #040733) generally intensified with the amount of glass waste in the samples cured for up to 28 days. This indicates that the lower PC contents in the blended pastes are compensated by the particle effect originated by the SFLG waste particles, which provides new nucleation sites that facilitate PC hydration. However, this tendency reversed after 90 curing days, and the intensity of the $Ca(OH)_2$ peaks dwindled with increasing glass contents. This corroborates the pozzolanic activity of SFLG waste as it denotes the partial consumption of the portlandite released during PC hydration. Small amounts of ettringite (E, $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$, PDF #411451), and larnite

(L, β-Ca_2SiO_4, PDF #330302) were also distinguished, the last one denoting the presence of unreacted PC.

The intensity of the signals attributed to calcite (C, $CaCO_3$, PDF #050586) diminished with SFLG addition in the pastes cured for 7 days, which was due to the dilution effect as they are attributed mainly to the presence of limestone filler in the PC composition. Conversely, after 28 curing days the intensity of the peaks due to calcite and carboaluminate $Ca_8Al_4O_{14}CO_2 \cdot 24H_2O$ (B, PDF #360129) increased with the amount of SFLG waste, which denotes higher carbonation. Chandra et al. [23], also observed in their review higher carbonation depths with rising amounts of glass when this was employed as pozzolanic admixture, whatever the type of glass used. Signals originated by sodium carbonate natron (N, $Na_2CO_3 \cdot 10H_2O$) were only identified in the 50 wt% SFLG blended pastes after 28 curing days. This is in line with the previous study by Schwarz and Neithalath [34], who observed that glass powder only releases a very small fraction of sodium ions to the solution when used as pozzolan.

After 365 curing days all pastes presented peaks due to portlandite, ettringite, calcite and carboaluminate $Ca_8Al_4O_{14}CO_2 \cdot 24H_2O$. The monosulfoaluminate $3CaO \cdot Al_2O_3$ $CaSO_4 \cdot 12H_2O$ (M, PDF #180275), originated by decomposition of ettringite, was also identified in the reference sample. Signals in the 28–30 2θ range which, according to Mejdi et al. [15], are linked to tobermorite CSH gels, were relatively wide and shifted to higher angles in the SFLG/PC blended pastes. As explained by Mejdi et al. [15], this displacement of the signals denotes higher crystallinity (lower interlayer distance) and, given that the crystallinity of
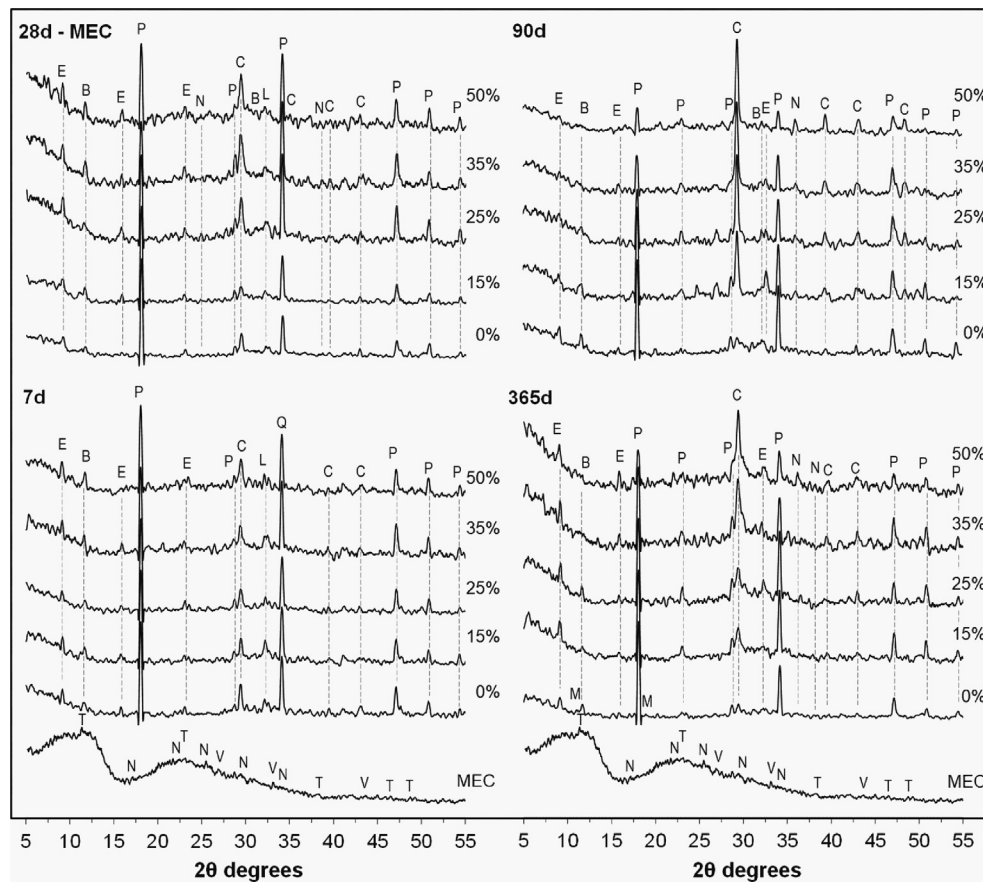

Fig. 13. XRD patterns of the SFLG waste and the blended pastes prepared with 0 to 50 wt% MEC glass, cured at 20 °C from 28 to 365 days. P, portlandite ($Ca(OH)_2$); E, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$); L, larnite ($\beta$-$Ca_2SiO_4$); C, calcite ($CaCO_3$); B, carboaluminate ($Ca_8Al_4O_{14}CO_2 \cdot 24H_2O$); N, natron ($Na_2CO_3 \cdot 10H_2O$); M, monosulfoaluminate ($3CaO \cdot Al_2O_3$ $CaSO_4 \cdot 12H_2O$); V, vaterite ($CaCO_3$); T, hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}$ $4(H_2O)$)).
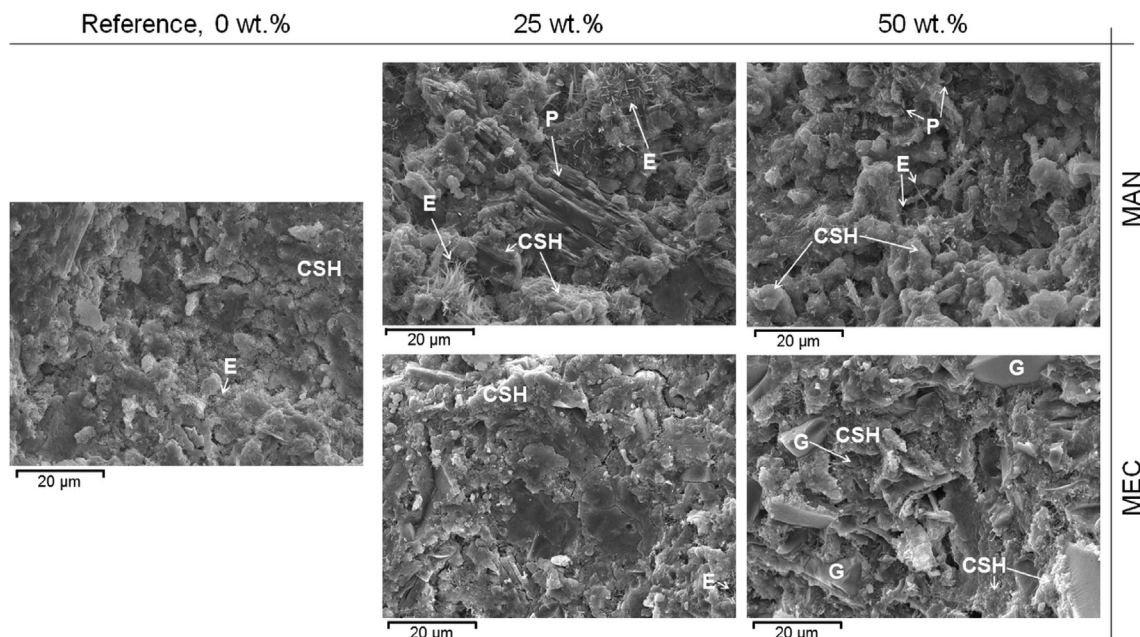
Fig. 14. Scanning electron microscope images of the reference paste and those prepared with 25 wt% and 50 wt% SFLG waste, MAN and MEC glass, cured at 20 °C for 28 d. E: Ettringite; CSH: Calcium silicate hydrate; P: Portlandite and G: SFLG waste.

CSH increases with lower Ca/Si and higher Na/Si ratios, relatively crystalline C(N)SH may form depending on the proximity of glass particles and the consequent local glass powder/portlandite proportions.

No signals attributed to heavy metals soluble salts were distinguished in any of the spectra analysed. This suggests that mercury was effectively stabilised within the cementitious matrix, since authors such as Bignozzi et al. [19] proposed the ion exchange, between calcium from the cementitious matrix and the heavy metals present as soluble salts, as the leaching mechanism. However, in order to prevent mercury leaching at the end of the useful life of the SFLG/PC blended cements developed, leaching tests will be performed in future research.

3.6. Scanning electron microscopy

Fig. 14 shows the microstructure of the reference paste and those prepared with 25 wt% and 50 wt% SFLG waste, cured at 20 °C for 28 days. The presence of the $Ca(OH)_2$ hexagonal plates and ettringite needles, previously identified by the TG and XRD analyses, was corroborated by SEM. These compounds, together with unreacted SFLG waste particles, were embedded in a binding CSH amorphous gel matrix, which was the main observed hydration product. All the pastes showed similar compactness, whatever the amount of PC replaced with SFLG waste.

4. Conclusions

This research assessed the pozzolanic activity of SFLG waste, and drew the following conclusions:

- The initial setting time hardly varied with the partial substitution of PC for the manually treated glass waste, and progressively extended with increasing amounts of the mechanically processed waste (up to 35 min longer). The FST generally prolonged with any of the SFLG waste contents (up to 60 min longer in the MEC50 paste), which prolonged the time under the plastic condition of the blended cements.

- The mortars developed with 35 wt% SFLG waste met the strength requirements established for fly ashes, as they provided strength activity indices over 75% and 85% when cured for 28 and 90 days, respectively.
- Although the SFLG/PC blended mortars obtained lower compressive strength values than the reference sample for 28 curing days, after 90 curing days the strength of the mortars containing up to 35 wt% glass waste was similar to, or even higher than, that recorded for the 100 wt% PC sample.
- The TG, XRD and SEM results confirmed the pozzolanic activity of SFLG waste, regardless of the recovery process used (manual or mechanical) as no significant differences were observed between both waste types. These studies corroborated that pozzolanic reactivity became more evident after medium-long curing ages, which gave positive fixed lime values from 28 curing days.

The present study confirms the feasibility of reusing SFLG waste as a pozzolanic admixture, with the possibility of reusing this hazardous waste as-received without washing or applying a specific treatment to remove mercury. This SFLG reutilisation route will contribute to reduce not only the volume of landfilled hazardous waste, but also the energy, natural raw materials and greenhouse gas emissions associated with PC production. If mercury is encapsulated in the binding matrix, then hazardous SFLG waste will become inert at the end of the SFLG/PC blended cement useful life. Consequently, the cementitious element can be recycled or disposed of in non-hazardous landfills. Complementary studies are currently being conducted to determine mercury leaching from SFLG/PC mortars and, although no sustainability analyses were performed in the present study, they will be the focal point of future research.

Declaration of Competing Interest

Acknowledgements

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