Chelating agent treatment on leaded residuals from glass separated urban collection to be used in cement mortars

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Abstract

A mild chelating agent treatment was performed on the residuals of the sorting processes of separately collected urban glass, which is currently landfilled. This fraction, that represents about the 10 wt.% of the overall collected glass, has a very heterogeneous composition and contains relatively high amounts of lead and barium and consequently cannot be used to produce new glass containers. This contaminated material shows, when used as fine aggregate in Portland Cement based composites, an expansive behaviour due to the alkali silica reactions. The expansion can only be partially reduced by using finely ground soda lime glass, showing pozzolanic activity. However, after the chelating agent treatment, because of heavy atoms surface depletion, the synergic effect of pozzolan addition leads to a suppressed expansion, thus allowing the use of waste in the formulation of cement composites.

Keywords: glass waste, separated urban collection, lead glass, aggregates for building materials, chelating agent treatment, ASR

Introduction

In 2015 in Italy the recycled packaging glass from urban collection increased by 2.9% compared to the previous year. An overall quantity of more than 1,660,000 tonnes of glass containers were collected, reaching a recycling rate of 70.9%, but at the same time 164,000 tonnes of waste materials wrongly conferred to glass separate collection were disposed of in landfill with European Waste Catalogue (EWC) code 191205 [1].

Among the "false friends" of packaging glass there are crystal items (containing at least 25 wt.% of lead oxide), ceramics (including porcelain), Pyrex (borosilicate glass), light bulbs, neon tubes, mirrors, television and computer monitors (like cathode ray tubes (CRTs) and liquid crystal displays (LCDs)) and other inert materials, which can be wrongly considered like easily assimilated to packaging glass, while they are indeed contaminating materials.

In order to remove such contaminants, the recycling system employs sophisticated optical selectors, which cannot however reach a 100% efficiency. This procedure results therefore in the loss and dumping of soda-lime glass fragments otherwise recyclable to produce new packaging items.

A statistical survey carried out in Italy in 2015 on a sample of 1016 people highlighted that, among the interviewed, the 31.5% introduces crystal items in the packaging glass separated collection, 15.9% Pyrex glass, 11.9% light bulbs, 8.3% ceramic items, 4.1% neon tubes and 2.2% CRTs. In general, the 43.7% of the interviewed introduces at least one among these materials in the glass separated collection: crystals, light bulbs, neon tubes, CRTs, ceramics, Pyrex. Although this value is decreasing compared to the past (58.6% in 2010) thanks to the better information of the citizens about the collection programs, the percentage of erroneous transfers is still high. Up to now, this heterogeneous waste material, containing both glass fragments and pollutants, finds no possible application and is sent to dumping [2].

On the other side, glass recycling aimed at replacing fine natural aggregates in cementitious composites is a rather consolidated and environmentally positive practice [3-8]. While soda-lime glass derived from packaging shows a limited reactivity towards alkali silica reaction (ASR), mostly depending on its colour, i.e. cromophore ions present in the network [9-10], glass of different origin, having a more complex chemical composition and usually containing heavy metals like lead, barium and strontium may exhibit strong expanding behaviour [11-14].

The other possible use of separately collected glass in construction and building materials is as supplementary cementing material (SCM), taking advantage of its possible pozzolanic activity [15-19]. This practice, however, implies a more energy-consuming milling process to reduce particles size to the microns range and allows to recycle a lower amount of waste in the composites. In the present study, following previous researches concerning the use of wastes in concretes [20-22], the possibility of recycling this discarded fraction as fine aggregates in mortars was investigated.

Polluted waste glass from urban collection was used as received and after a chemical treatment based on nitrolotriacetic acid (NTA) chelating agent, able to modify its surface chemical composition subtracting heavy atoms as lead and barium. This treatment was developed in other previous works on waste CRT funnel glass (PbO=12-25 wt.%) and, compared to other leaching methods present in literature [23-26], it offers several advantages, including: low temperature (70-80 °C), low time of reaction (1 h), preservation of the glassy nature of the material and the possibility of regenerating the spent NTA solution recovering the extracted lead as pure lead sulphide [27-28].

The absence of deleterious expanding behaviours, as well as the mechanical properties of derived composites were investigated. Since one of the possible remedies to ASR is the addition of a pozzolanic fraction to the binder [29-30], the effect of pulverized flint soda-lime glass was also tested.

Experimental

Materials

Glass waste: crashed residuals of glass waste (hereafter described as GW) were kindly supplied by CoReVe (Consortium for Glass Recycling, Italy). Visually, the as-received material appeared extremely heterogeneous, with clear presence of several fragments of ceramics (especially porcelain), garden pebbles, mirrors and light bulbs between the glass grains. As the study is aimed at evaluating the performance of this waste material as a whole, the contaminants, although coarse, were not removed.

In order to define the average chemical composition of the material, considered its high heterogeneity, a representative sample of 1 kg was collected by quartering. This sample was remelted at 1450°C in electric oven and quenched at room temperature to get a homogeneous glassy bulk, which was then grounded into pieces and analysed by energy-dispersive spectrometer EDS (microanalyzer Inca-350, Oxford Instruments) in different areas of its surfaces. The average chemical composition is reported in Table 1, compared to that of a typical packaging glass [31].

Table 1

The as-received GW was dry-ground in a laboratory ball mill to get particles between 0.075 and 2.00 mm (Figure 1), with size distribution close to that of normalized sand [32].

Figure 2 shows the morphology of the crashed material detected by means of scanning electron microscopy SEM (ESEM, Quanta-200 Fei, Oxford Instruments).

Fig. 1

Fig. 2

Cement: Type 1 52.5 Portland cement (Italcementi, Bergamo (Italy) with a Na_2O amount of 0.47 wt.% was used.

Supplementary Cementing Material: white (flint) fine sized soda-lime glass was used to substitute a 25 wt.% of Type I 52.5 Portland cement. The powder (having size distribution of: 10 % volume < 1.5 μm, 50% volume < 9.5 μm and 90% volume < 48 μm) had previously shown pozzolanic behavior [15].

Aggregate: Normalised silica sand conforming to the EN 196-1 Standard [32] was used.

Chelating agent: Nitrilotriacetic acid disodium salt (NTA), ≥ 99% purity, provided by Sigma Aldrich was used. NTA solution of 0.1 M concentration was prepared keeping pH fixed at 10 by means of ammonium hydroxide–ammonium chloride buffer solution.

Glass waste treatment

After the milling process, the GW underwent a chelating agent treatment to extract lead and other heavy metals like barium from its surface. GW was sealed in containers with NTA solution (solid/liquid weight ratio = 1/10), and treatment was performed at 80°C for 1 h. Conditions were chosen by a previous work of

screening of different chelating agents [27]. After treatment, GW was separated from NTA solution by filtration and washed with distilled water. The cleaned glass was collected and dried in oven at 110°C overnight.

In order to detect the effectiveness of the treatment on this particular kind of waste, the 0.5-1 mm particle size fraction (which represents about the 30 wt.% of the total GW aggregate, as reported in Fig. 1), underwent leaching tests at pH 5 and at the natural pH of water/glass equilibrium. Both NTA-treated and NTA-untreated samples were investigated.

During the tests, the samples were kept in stirring for 48 h at room temperature, with solid/liquid weight ratio of 1/10. Concerning pH 5, this was kept constant (+/- 0.2) for the whole duration of the test. Control was achieved automatically by adding appropriate volumes of acid (HNO_3 0.1 M) varying from 0.05 mL to over 1 ml. The natural pH of water/glass equilibrium resulted close to 7, always remaining in the range 6-7. This pH, slightly higher than that of distilled water (5.5-6), can be explained by the release of Na^+ ions from the glassy sample, which has a typical soda-lime nature. Lead concentration in eluates from leaching tests was determined by FA-AAS analysis (Perkin Elmer AAnalyst 400).

Mortars preparation

Mortars were mixed by substituting a 25 wt.% of natural siliceous sand by NTA-treated or NTA-untreated GW. The water/binder ratio was 0.5, and the binder/aggregate ratio was 1.00/3.00 for samples to be submitted to mechanical tests and 0.47 w/b and 1.00/2.25 b/a for samples submitted to ASR expansion test. Table 2 reports the mix design of all the investigated mortars and their relevant denomination, which will be used afterwards in the text. Mixing procedures followed the instruction of EN 196 [32].

Table 2

Instruments and methods

Expansion test: alkali silica reactivity was evaluated according to the procedure described by ASTM C1260 [33], i.e. curing in moisture saturated conditions for one day, one day at 80°C in water and subsequent storage at 80 °C in a 1 N solution of sodium hydroxide. Indeed, for samples containing the pozzolan binder a longer initial curing period (28 days) was applied. The test was repeated on three samples.

Mechanical test: Mechanical tests on all samples were performed at room temperature and R.H. 50 ± 10 % by means of 200 kN Volpert Amsler equipment with a 50 mm/min displacement rate. The test was repeated on six samples.

Microstructure: analyses were performed by means of a Quanta (FEI) scanning electron microscope equipped with an EDS X-ray detector. Specimens' surfaces were coated by graphite. Accelerating voltage of 20 kV was applied during measurements.

Results and discussion

Leaching tests at controlled pH

Figure 3 shows the results of leaching tests of GW and TRGW with 0.5-1 mm particle size. Pb leached at the natural pH of water/glass equilibrium is generally low (about 0.05 mg/g for GW and 0.02 mg/g for TRGW), with a positive effect of NTA treatment, which halved the release. The effect of the chelating agent treatment is even more appreciable at pH 5: Pb released passed from about 0.23 mg/g to 0.05 mg/g after the treatment with NTA. These results confirm the effectiveness of the Pb removal treatment.

Fig. 3

Expansion test

Figure 4 reports the expansion (1M NaOH solution, 80°C) of mortar samples formulated with NTA-untreated GW containing Type I cement and soda-lime milled glass. As can be seen, the expansion values are largely above the limits (0.1 – 0.2 %) defined by the standards to ensure a safe behaviour of the aggregates in the composites.

Fig. 4

Figures 5 and 6 show at different magnification the effect of alkali of the recycled glass aggregates.

Fig. 5

Fig. 6

The morphology of the expansive products is similar to those found in natural reacting aggregates or to those present in mortars modified by separated recycled waste glass [14]. The chemical compositions, derived from the EDS analysis of the gels, reveals in almost all cases that the expanding gels are close to aggregates containing heavy atoms, either Ba or Pb, disclosing that the reacting particles must derive either from crystal décor items or WEEE equipments. Indeed, especially for glass containing PbO up to about 50 wt.%, like CRT glass (percentage around 20 wt.%), Pb behaves like a network modifier: it decreases the number of bonds between the $[SiO_4]^{4-}$ tetrahedra and consequently weakens the glass resistance towards dissolution [34]. Considered a typical composition of CRT funnel glass [15], this results in a possibly increase of glass solubility and a corresponding release of alkaline cations (Na^+, K^+) into the cement matrix.

The use of pozzolanic binders, at least at this percentage, although decreasing the expanding extent is unable to allow a safe use of the wastes in cementitious composites.

Fig. 7

Figure 7 shows the expansion test results of treated aggregates. Although the expansion is reduced compared to that of untreated glass waste (probably due to lead depletion from the surface), only in the presence of the pozzolan fraction the acceptable limit for the expansion is obtained. Figure 8 shows the fracture surfaces of samples TRGW-SCM(CaNa) after expansion tests. The absence of reacted products, as well as the sharp unreacted surfaces of the waste aggregate confirms the suppression of the expanding reactions.

Fig. 8

Mechanical test

Figure 9 shows the compressive strength of the mortars at 90 days of curing at 20 ±1 °C and 60 ±10 % R.H.. The mechanical properties of mortars containing treated and untreated aggregates (GW-CEM and TRGW-CEM) are almost equal to those of the reference specimen. In mortars containing the SCM binder the slight reduction (about 13%) is related to the slow rate of the pozzolanic reaction as confirmed by sample Ref-SCM(CaNa).

Fig. 9

Conclusions

Wastes deriving from the selection of separately collected glass represent a complex environmental problem as to what concerns their recycling opportunities. In this paper, it was proved that it is possible to use them as fine aggregates in cementitious composites performing a mild chelating agent treatment and exploiting the synergic activity of pozzolanic fraction. Indeed, the pozzolanic fraction is obtained from milled soda-lime glass thus providing a further possibility to recycle cullets surplus.

Advantages concern the preservation of a natural raw material (pure silica sand) and the exploitation of a waste material that otherwise would be landfilled.

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Figures

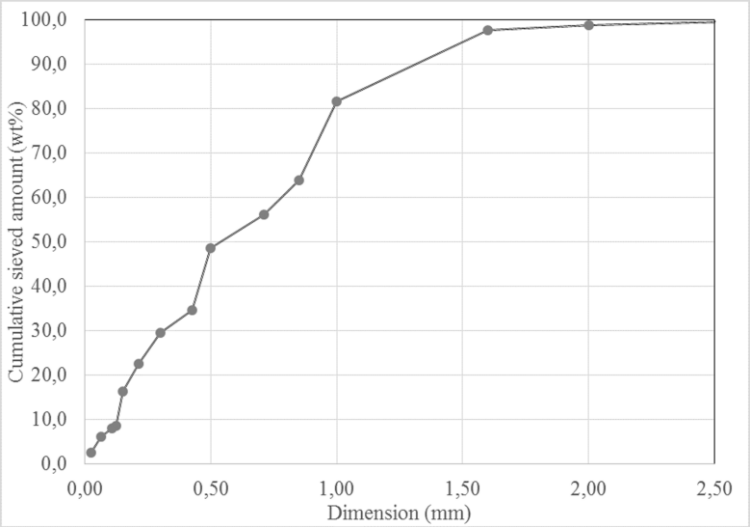


Fig. 1

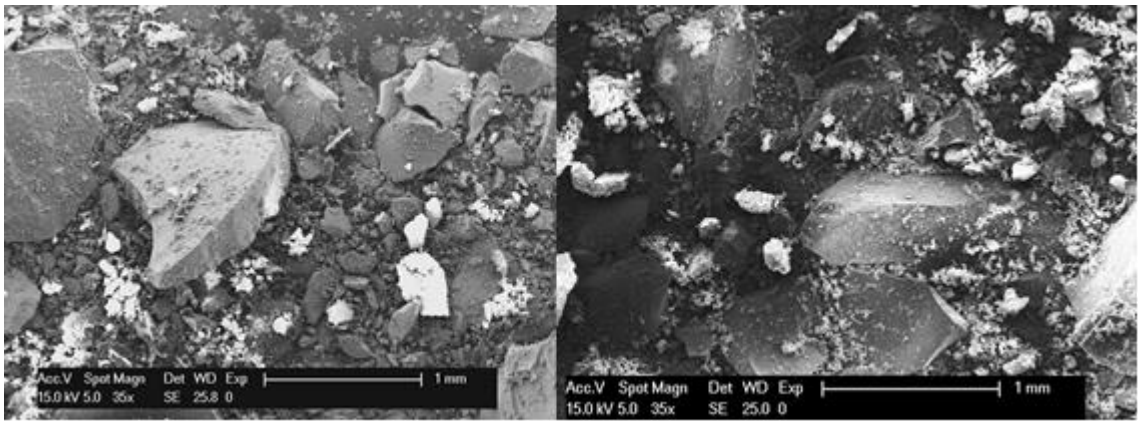


Fig. 2

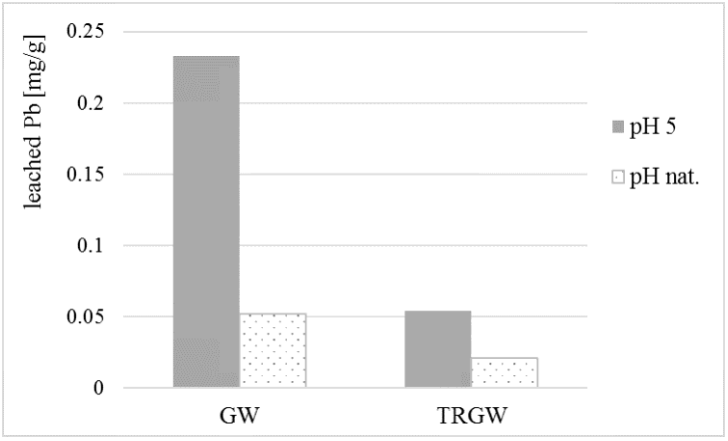
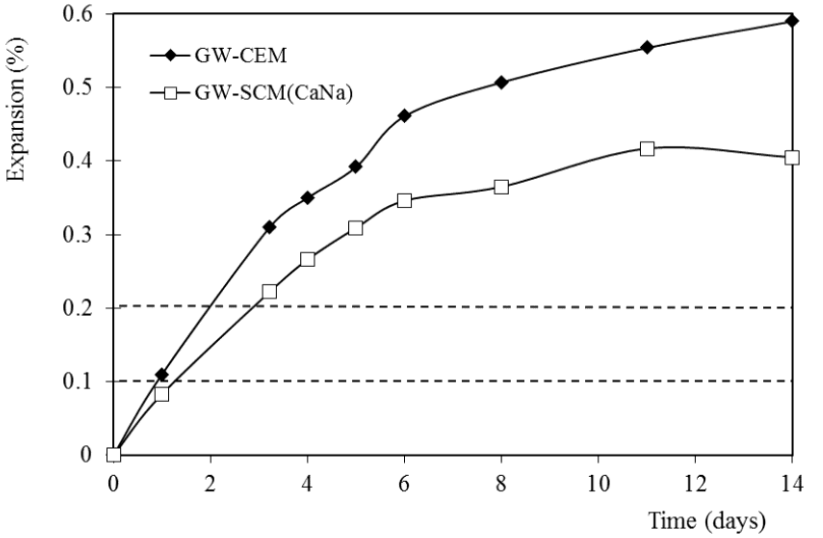


Fig. 3



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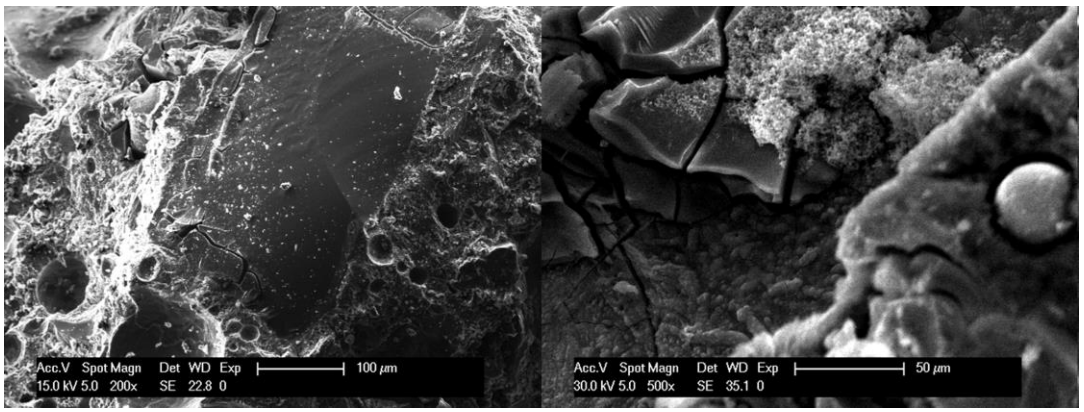

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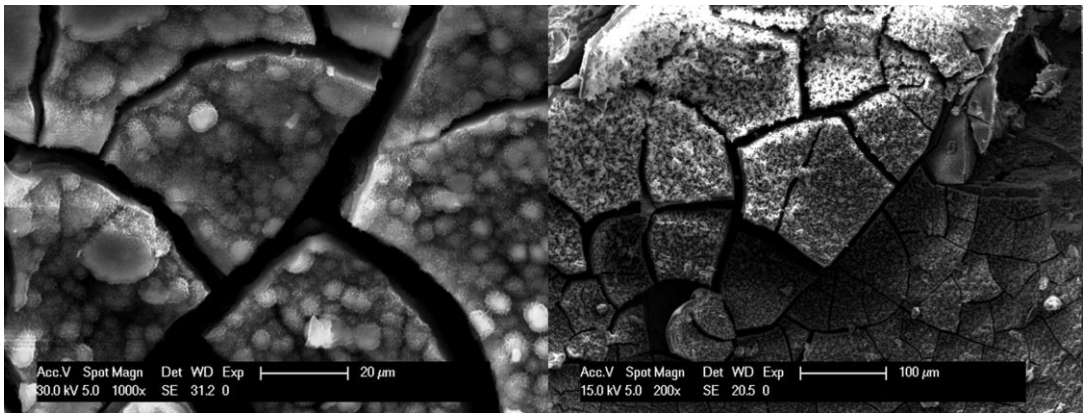

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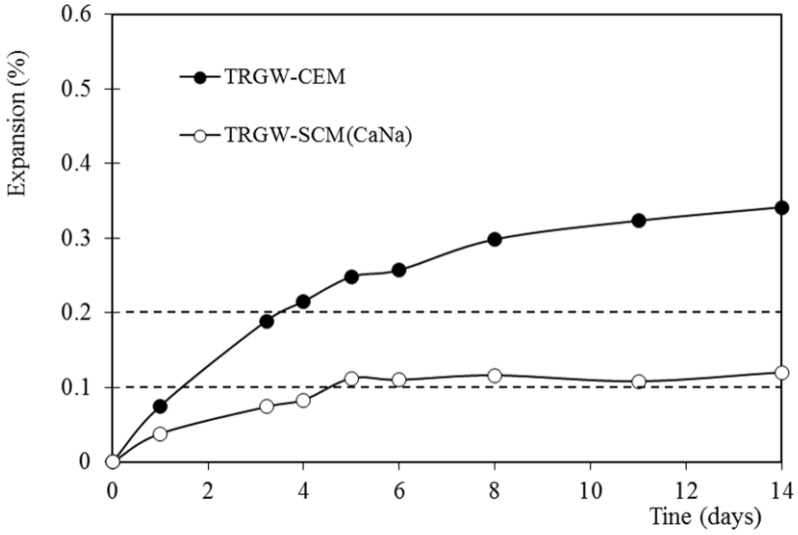

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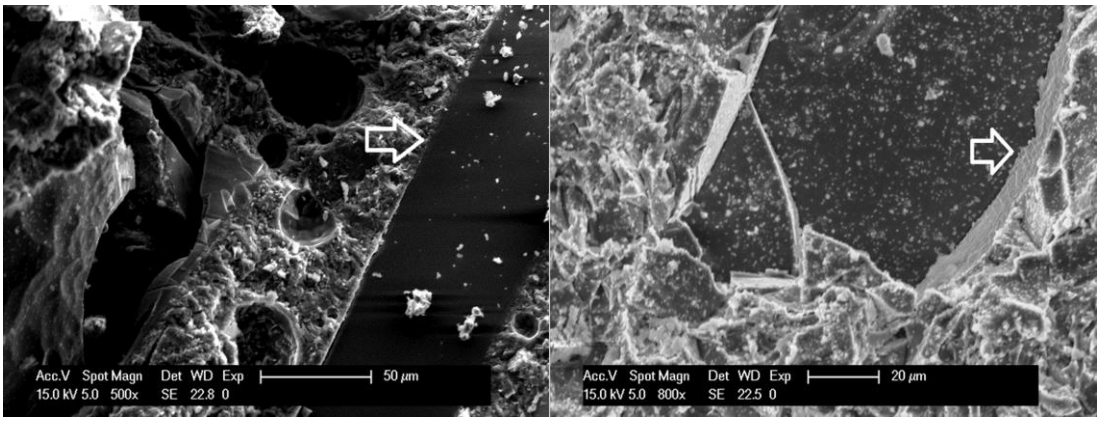

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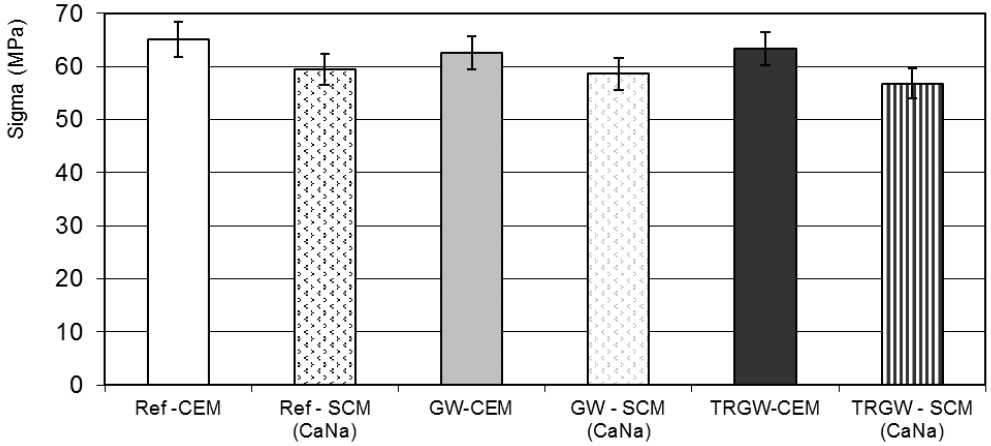

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320 **Fig. 9**
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Captions

Fig. 1 Size distribution of glass waste

Fig. 2 Morphology of the glass waste used as fine aggregate

Fig. 3 Pb released [mg/g] from GW and TRGW glass sample with 0.5-1 mm particle size

Fig. 4 Expansion of GW-CEM and GW-SCM(CaNa) in a 1 M solution of NaOH at 80°C

Fig. 5 ASR products after accelerated test at 80°C in untreated GW-CEM

Fig. 6 ASR products after the accelerated test at 80 °C in GW- SCM(CaNa)

Fig. 7 Expansion of TRGW samples in a 1 M solution of NaOH at 80°C

Fig. 8 Microstructure of TRGW-SCM(CaNa) after expansion test

Fig. 9 Mechanical properties (compression) of the investigated mortars after 90 days of curing.

Tables

Table 1 Average chemical composition of GW glass grains (elements) compared to that of a typical packaging glass (Pack. Glass)

	O	Na	Mg	Al	Si	K	Ca	Ba	Pb
GW wt.%	43-54	5-7	0-1	0-1	29-31	4-5	3-4	0-2	5-6
Pack. Glass wt.%	36-55	7-12	0-2	0-2	32-35	0-3	6-10	/	/

Table 2 Composition and labelling of all investigated samples

Mortar sample	Natural sand (g)	Untreated GW (g)	Treated GW (g)	Cement (g)	SCM (g)
Ref	1350	-	-	450/600	-
GW-CEM	923	337	-	450/600	-
GW-SCM(CaNa)	923	337	-	338/450	112/150
TRGW-CEM	923	-	337	450/600	-
TRGW-SCM(CaNa)	923	-	337	338/	112/150

GW = glass waste TRGW= treated glass waste SCM(CaNa) = Powdered soda-lime glass