Materials Letters 320 (2022) 132163

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Effect of CRT glass particle size on the lead leachability of alkali-activated materials

F.J. García-Ten, M. Vicent *

Instituto de Tecnología Cerámica (ITC), Asociación de Investigación de las Industrias Cerámicas (AICE), Campus Universitario Riu Sec (UJI), Avda. de Vicent Sos Baynat s/n, 12006 Castellón, Spain

ARTICLE INFO

Keywords:
Alkali-activated materials
CRT glass
Leachability

ABSTRACT

Alkaline activation is an interesting manufacturing process from an environmental point of view as it allows the use of waste containing amorphous SiO_2 and Al_2O_3 as starting material, such as glass, bottom and fly ashes. However, the presence of heavy elements in these waste materials can limit their use since they are released during the dissolution stage and not always enter totally in the new structure formed. In this work, the feasibility of using glass from Cathode Ray Tubes (CRT) with a high particle size to reduce lead leaching has been studied.

1. Introduction

Alkali-activated materials are prepared by mixing an aluminosilicate with an alkaline activator following by a curing stage at low temperature, resulting an "aluminosilicate network" which is composed by cold-setting binders. Several materials (including fly ashes and different type of glasses) display this reactivity due to their glassy phase content, rich in silica and alumina [1].

One of the European Union policies is related to waste and it aims to contribute to the circular economy by extracting high-quality resources from waste as much as possible [2].

With the progressive analogic switch-off officially completed for EU country members in 2012, a progressive increase in the amount of TV and computer monitors with Cathode Ray Tubes (CRT) landfilling is expected due to the replacement by flat panel displays. Last data for EU-27 shows a value of the collected amount of CRT devices of 450,000 ton in 2015 (55% accounts for CRT glass: 247,500 ton). Both panel and funnel CRT glass contains lead which is concentrated in the Pb_2O_3 layer applied to these devices to block the X-rays [3].

The recycling of CRT waste in alkali-activated products would reduce the waste disposal in Europe. However, there is scarce literature focusing on it (only 7 recent contributions were found, 2 referenced in this paper) [4,5] and, in addition, none of these papers deal with how to decrease the lead content in the leachate of alkali-activated materials prepared from CRT glass.

In this work, fly ash and CRT glasses have been used as starting materials to obtain alkali-activated materials. First, waste materials were characterised, then specimens were prepared for determining the technological properties such as mechanical strength, compacity and open porosity. Leachability of Pb was conducted to ensure that the final product fulfils the criteria to be classified as inert or non-dangerous.

2. Materials and methods

2.1. Materials

Fly ash (FA) from a coal power plant and two CRT glasses, panel (PG) and funnel (FG), were used as waste materials. These wastes were milled and/or sieved to reach a particle size of less than 200 µm prior to its characterisation. The alkaline solution, with a SiO_2/Na_2O weight ratio of 0.2, was made up of 85% of NaOH 10 M and 15% of sodium silicate (25.5–28.5 wt% SiO_2 and 7.5–8.5 wt% Na_2O).

2.2. Waste characterisation

Waste materials were chemically characterised by Wavelength Dispersive X-Ray Fluorescence in a spectrometer (Axios, PANalytical, The Netherlands). Moreover, the rejection fraction at 63 µm of the powders was determined by wet sieving to obtain information related to particle size distribution (PSD).

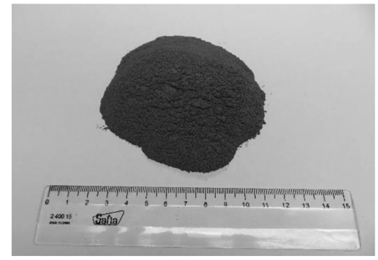
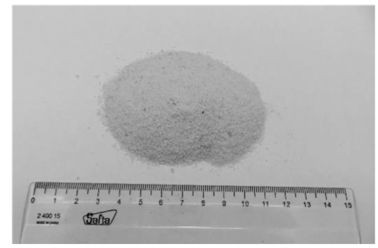
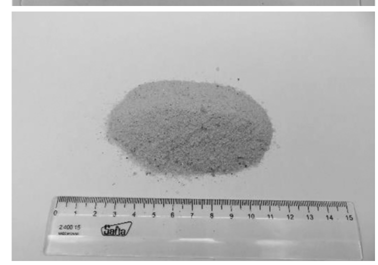
2.3. Compositions tested and specimen's characterisation

Two series of compositions were prepared, the first one with 100% of

* Corresponding author.
E-mail address: monica.vicent@itc.uji.es (M. Vicent).

https://doi.org/10.1016/j.matlet.2022.132163
Received 1 October 2021; Received in revised form 15 February 2022; Accepted 26 March 2022
Available online 28 March 2022

Table 1
As-received waste materials.

Waste	Ref.	Origin	Classification LER Code	Aspect
Fly ash	FA	Asturias (Spain)	Non-hazardous 10 01 02	
CRT panel glass	PG	Albacete (Spain)	Non-hazardous 19 12 05	
CRT funnel glass	FG	Albacete (Spain)	Hazardous 19 12 11*	

each waste and the second made up to 90% of FA and 10% of each CRT glass. Each composition was mixed with the activating solution at a different liquid/solid (L/S) ratio to obtain a granulate suitable for the shaping. After the mixing, prismatic steel moulds (40 × 40 × 80 mm) were filled and levelled with the granulate and then the material was pressed at 1.0 MPa (manometric pressure). Later, the specimens were cured at 85 °C and 95% relative humidity for 20 h and after that they were maintained during 24 h at room conditions before characterisation. The tests conducted were as follows:

- Bulk density, determined by the mercury immersion method.
- Compressive strength, conducted in a mechanical testing machine (RetroLine, ZwickRoell, Germany) at a constant load speed of 2400 N/s. 10 specimens of each sample were tested.
- Water absorption, calculated by measuring the weight gain undergone by the specimens after being subjected to a vacuum pressure of 91 kPa for 30 min and subsequently immersed in water for a period of 15 min.
- Leaching test, carried out according to the standard UNE-EN 12457-2:2003. The lead was determined on the liquid fractions of the samples by means of flame atomic absorption, using a spectrophotometer (Aanalyst 400, Perkin Elmer, USA).

3. Results and discussion

3.1. Waste characterisation

Table 1 shows reference, origin, LER code as well as the aspect of the as-received waste materials. Fly ash was a fine grey powder and was mainly composed by spherical particles. It is classified as a non-hazardous waste material. CRT glasses were composed by irregular shaped fragments, transparent in colour with some black spots (note that PG has fewer black spots than FG, possibly due to the lower amount of lead). While PG is classified as a non-hazardous, FG is a hazardous (marked in the table with an asterisk) waste due to its higher lead content.

Table 2
Waste materials characterisation.

Oxide content (%)	FA	PG	FG
SiO_2	53.9	60.2	52.8
Al_2O_3	26.0	2.64	2.79
Fe_2O_3	6.01	0.05	0.07
CaO	5.32	0.46	3.00
MgO	1.73	0.36	1.56
SO_3	0.45	—	—
K_2O	2.38	6.35	7.77
Na_2O	0.36	8.13	6.47
P_2O_5	0.69	—	—
MnO	0.06	—	—
TiO_2	1.3	0.23	0.08
ZnO	—	—	0.14
BaO	—	8.89	1.90
SrO	—	9.25	1.57
ZrO_2	—	2.03	0.26
PbO	—	0.84	21.1
*LoI	1.68	0.57	0.52
Rejection fraction at 63 μm (%)	23.3	60.5	79.4

*LoI: loss on ignition at 1000 °C.

Table 2 shows the chemical composition and the rejection fraction at 63 μm of every waste. The main oxide detected in all waste materials was SiO_2, followed by Al_2O_3 in the case of FA. The presence of Fe_2O_3 was also relevant in FA. In the case of CRT glasses, apart from SiO_2, Na_2O was detected as it is a flux in glass production. In addition, it is remarkable the high PbO content in both CRT glasses, particularly in FG.

Table 3
Bulk density, compressive strength, water absorption and Pb leachate values for every composition and target Pb values for landfilling waste materials (Guideline specified in Article 16 of Council Decision of 2003/33/EC and Annex II of Directive 1999/31/EC).

Composition (d < 200 μm)	L/S ratio	Molar ratios composition		Bulk density (g/cm^3)	Compressive strength (MPa)	Water absorption (%)	Pb in the leachate (mg/kg)
		SiO_2/Na_2O	SiO_2/Al_2O_3				
100FA	0.35	7.4	3.6	1.55 ± 0.03	24 ± 1	15 ± 2	—
100PG	0.25	4.7	39.3	2.07 ± 0.03	21 ± 2	3.4 ± 1.1**	228
100FG	0.20	5.2	32.6	1.80 ± 0.03	9.0 ± 0.9	Soluble	6090

Type of waste	**Maximum Pb content (mg/kg)**
Inert waste	0.5
Non-hazardous waste	10
Hazardous waste	50

** Partially soluble.

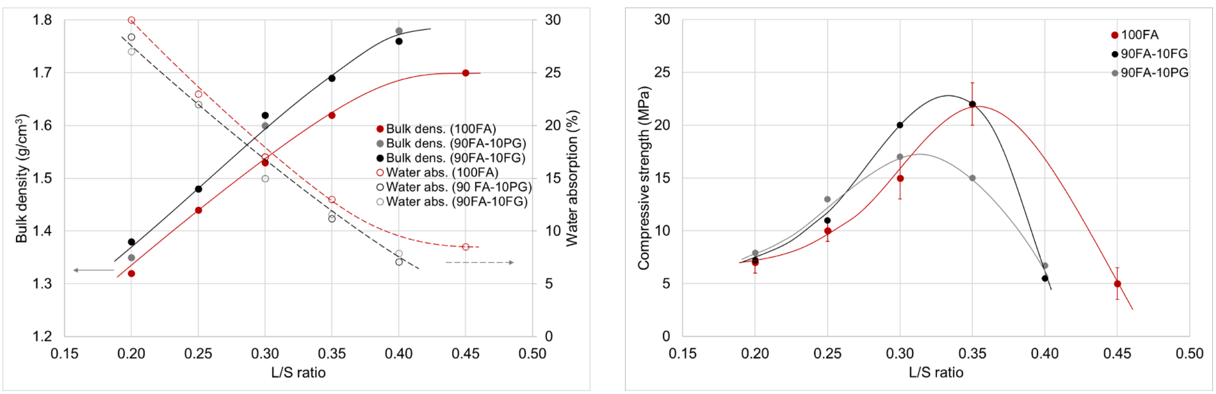


Fig. 1. Bulk density, water absorption (left) and compressive strength (right) versus L/S ratio.

3.2. *Specimen characterisation*

Table 3 shows the results for the compositions made up 100% of each waste. The L/S ratio for composition FA was 0.35 and for both glasses 0.25 (PG) and 0.20 (FG). These differences are probably related to the different particle packing of each waste, being the waste with the lowest particle packing (FA) the one that requires the higher amount of alkaline solution to form a granulate. As particle packing is related to the width of the PSD [6], this last characteristic was assessed by determining the content of coarser particles (rejection fraction at 63 μm), as usually the higher the content of coarser particles the wider the PSD. Results shows that the content of coarser particles in both CRT wastes is higher than that of FA, what point out that particle packing is the reason for the differences in the L/S required for each waste.

The influence of particle packing can also be observed in the bulk density and water absorption values, in which specimens FA provided the lowest value of bulk density and the highest of water absorption. In the case of specimens PG and FG a high solubility during the water absorption tests was appreciated leading to deformed specimens, particularly for FG specimens in which it was not even possible to determine the water absorption.

Regarding compressive strength, it was observed that the values obtained with FA and PG specimens were similar and close to 20 MPa. The value for FG specimens decreased drastically due to its poor stability in water damaged the specimens.

Pb leachate from PG and FG specimens was high for the samples prepared with both glasses being classified the specimens as hazardous. To use both waste in alkali-activated products it is necessary to reduce the Pb leaching under the limits and to increase its stability in water. For this, it was decided to increase the particle size of both glasses up to sizes below 2.0 mm. In this way CRT glasses were used as fillers with the additional advantage of a good reactivity at the surface of the glass particles with the alkaline solution.

Specimens prepared with compositions made up 90% of FA and 10% of both CRT glasses (d < 2 mm) were prepared and characterised. Fig. 1 shows the evolution of bulk density, water absorption (left) and compressive strength (right) with the L/S ratio. Composition FA was included as reference. For the 3 compositions, when the L/S ratio increased higher values of the bulk density and lower water absorption were observed because of the higher reactivity (more gel formed). Specimens with both CRT glasses provided higher bulk density and lower water absorption values respect to FA. This difference can be attributed to the improvement of the particle packing of FA specimens when coarser CRT glass particles were added to the mixture due to the increase of the width of the PSD.

Regarding the compressive strength, each composition showed a maximum at a different L/S ratio. The increase of L/S ratio has positive effects on the strength since the higher reactivity and more sodium and silicon are located in the network of the alkali-activated material. After the maximum, strength decreases due to an excess of the amount of silica required [7]. While specimens FA and FA-10FG provided similar values of the maximum compressive strength, specimens with PG showed a lower value of this property.

Finally, data on Pb in the leachate showed a dramatically decrease (<1 mg/kg and 1.9 mg/kg for the compositions with 10% of PG and FG, respectively), due to the reduction of CRT glass in the specimens (10%) and to the lower reactivity of CRT glasses when their particle size increase.

4. Conclusions

Materials obtained from CRT glasses have high solubility in water, which together with the presence of lead produce an excessive leaching of lead and cannot be used as the only starting materials for obtaining alkali-activated materials. However, mixing these wastes with FA to increase the alumina proportion together with an increase in their particle size provide stable materials, with good mechanical properties and very low lead solubility, which can be an alternative to the disposal of this type of glasses.

CRediT authorship contribution statement

F.J. García-Ten: Conceptualisation, Writing – review & editing, Supervision. **M. Vicent:** Investigation, Writing – original draft, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work has been carried out thanks to LIFE HYPOBRICK project funded by the European Union Environment and Climate Action Programme LIFE 2014-2020 (reference: LIFE18 CCM/ES/001114). It is also supported by the Valencian Business Competitiveness Institute (Instituto Valenciano de Competitividad Empresarial, IVACE) of the Generalitat Valenciana.

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