detritus | Multidisciplinary Journal for Waste Resources & Residues

UPCYCLING OF BORO-ALUMINO-SILICATE PHARMACEUTICAL GLASS IN SUSTAINABLE CONSTRUCTION MATERIALS

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Article Info:
Received:
17 June 2022
Revised:
1 September 2022
Accepted:
15 September 2022
Available online:
20 September 2022

Keywords:
Alkali activation
Glass cullet
Gelation
Construction materials

ABSTRACT
The present Covid-19 emergency has dramatically increased the demand for pharmaceutical containers and the amounts of related waste. This paper aims at presenting the upcycling of discarded pharmaceutical glass into various porous ceramics, starting from the activation of fine powders suspended in weakly alkaline solutions (2.5 M NaOH/KOH). The alkaline attack determines the gelation of glass suspensions, according to hydration of glass surfaces, followed by condensation starting from 40°C ('cold consolidation'). Alkali are mostly expelled from the gel, according to the formation of water-soluble hydrated carbonates. The mutual binding of activated powders was exploited for the encapsulation of waste-derived glass (from the plasma processing of municipal solid waste) and quartz sand as coarse aggregate. Moreover, industrial mud could be used instead of water in the preparation of alkaline solutions. Depending on the formulations, products comparable to facing bricks can be obtained directly after cold consolidation or after application of low temperature (700°C) firing. In addition, selected formulations led to highly porous glass foams, to be used for thermal and acoustic insulation.

1. INTRODUCTION

Human impact on the environment and climate is nowadays an indisputable problem which undertakes public and private institutions to develop new recycle and reuse strategies based on principles of circular economy.

Glass is recyclable, by principle, indefinitely, but there are significant issues on the removal of contaminants from other materials, in cullet; contaminations may degrade the quality of glass articles from recycled material, compared to those from conventional, mineral feedstock. Discarded glasses may follow two different paths: 'closed-loop' recycling, consisting of the remelting for the obtainment of the original glass articles, and 'open-loop' recycling, when reused for a new generation of new marketable products, in a different context. The difference between economic value of the new products and manufacturing costs is a key factor: when high, open-loop recycling can be properly seen as 'upcycling' (Rincón et al., 2016). Regarding the field of building materials, glass cullet could be used as fluxing agent for clay bricks and tiles, forming liquid phase at lower temperature compared to other fluxes. On the other hand, when glass waste is reduced to fine powders, sintering processes can lead to glass foams thanks to the addition of selected additives. That results in construction materials with thermal and acoustic insulation properties (Rincón et al., 2016).

However, some shortcomings of these kinds of glass recycled materials need to be taken in account. First of all, some glasses are excluded *a priori* because of their chemical composition, including toxic elements (e.g. presence of fluorine, lead) which would be emitted in the atmosphere during sintering. Moreover, energy required to reach high temperatures somewhat undermine the ecological sustainability of thermal treatments.

Starting from these assumptions, the research was focused on pharmaceutical glass, highly overproduced during the outbreak of COVID-19, which is hardly recycled, according to the specific chemical composition (Bernardo and Scarinci, 2004). An ecological approach for the recycling of glass is the partial dissolution of boro-alumino-silicate glass fine powders in mildly basic solution of sodium and potassium hydroxides, well known as alkali activation. During this process, conducted at room temperature, dissolution of aluminosilicate components, promoted by basic nature of the solution, induces the release of 'inorganic ol-

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Detritus / Volume 20 - 2022 / pages 17-21
https://doi.org/10.31025/2611-4135/2022.15218

igomers', molecules made by few Si^{4+} and Al^{3+} ions bonded together by bridging oxygens and provided by terminal -OH groups. When this initial phase is followed by heating at low temperature (usually between 40-100°C), water release causes condensation processes that give 'zeolite like' gels. The absence of calcium limits the formation of less stable calcium silicate hydrated (C-S-H) compounds, typically observed in alkali activation of common sodalime glasses (Provis, 2014). Pharmaceutical glasses may lead by themselves monoliths comparable, in terms of density and compressive strength, to lightweight concrete and plaster of Paris. Viscous flow sintering is applied as well to consolidate cellular bodies previously developed at nearly room temperature, by intensive mechanical stirring of alkali activated glass suspensions, undergoing progressive hardening, to obtain foamed materials. This approach allows for lower firing temperatures and saving of expensive foaming agents, compared to the conventional process for glass foams (Rincón et al., 2016).

The present investigation aims at improving the sustainability of the whole building material production process, by combining different types of solid waste coming from several industrial activities. Since alkali activated glass is able to behave like a binding agent, there is the possibility to embed coarse materials in the glass matrix: three different products have been investigated for this purpose. The first case of study concerns muds coming from cutting and polishing of clay bricks, the second one is about quartz sand and the last one focused on residual of plasma gasification of urban waste. Quartz sand may be incorporated in glass-derived binder, for a new generation of mortars (Cyr et al., 2012). Plasma gasification is an alternative technology to avoid relandfilling charges and to recover energy from waste-derived gas ('syngas') as well as metals: however, a vitreous by-product remains, called Plasmastone. This waste is, nowadays, landfilled and has no other possible application (Winterstetter et al., 2015). So, the production of inorganic conglomerates with these materials was suggested for Plasmastone beneficiation.

2. MATERIALS AND METHODS

2.1 Activation with pure alkali hydroxide solution

Pharmaceutical boro-alumino-silicate glass (referred as 'BASG'; see Table 1 for chemical composition) from crushed vials, provided by the company Stevanato Group (Piombino Dese, Padova, Italy), was used as the starting material. Glass vials were first dry ball milled (Pulverisette 7 planetary ball mill, Fritsch, Idar-Oberstein, Germany) and sized to obtain particles with a diameter below 75 µm. Fine powders were later suspended in a 2.5 M aqueous solution of NaOH/KOH (ratio 1:1 wt%, reagent grade, Sigma–Aldrich, Gillingham, UK), for a solid loading of 60 wt%. The glass powders were subjected to chemical attack for 3 h, under low-speed mechanical stirring (500 rpm). After alkaline activation, the obtained suspensions of partially dissolved glass powders were cast in polystyrene moulds and cured at 40 °C for one week.

TABLE 1: Chemical composition of glass and solid waste employed in the current study (wt%).

	BASG	Plasmastone
SiO_2	72	34-37
TiO_2		0.6-0.7
Al_2O_3	7	13-15
Fe_2O_3		21-25
MnO		0.1-0.2
MgO		1-2
CaO	1	22-23
Na_2O	6	0.3-1
K_2O	2	0.3-0.5
$0P_2O_5$		0.03-0.2
B_2O_3	12	

2.2 Activation with industrial waste

As an alternative to the activation of glass described in paragraph 2.1, different modifications have been made. For the preparation of the 2.5 M alkali solution, a series of experiments involved mildly basic slurry (referred as 'mud', pH 9.5) from cutting and polishing of facing bricks (solid content ratio 60 wt%) instead of distilled water. In other selected cases, glass was used as coarser particles (< 150 µm). Both quartz sand and Plasmastone are used as embedded materials. The sand is rich in alkali oxides and in alkaline earth metals. Plasmastone was provided by Scanarc (Sweden) (Scanarc, 2017) and its chemical composition is determined by X-Ray fluorescence (reported in Table 1). Plasmastone is used as a coarse material by dry ball milling into powders between 200 µm and 420 µm. All formulations are reported in Table 2.

2.3 Characterization

The mineralogical analysis of powdered glass-ceramics was conducted by means of X-ray diffraction (XRD) (Bruker D8 Advance, Karlsruhe, Germany), using CuKα radiation, 0.15418 nm, 40 kV - 40 mA, 2θ = 10-70°, step size 0.05°, 2 s counting time. The phase identification was performed by means of the Match! ® program package (Crystal Impact GbR, Bonn, Germany), supported by data from Powder Diffraction File (PDF)-2 database (International Centre for Diffraction Data, Newtown Square, PA, USA).

Fourier-transform infrared spectroscopy (FT/IR Jasco 4200, Jasco, Japan) was performed on selected samples to determine their phase composition. Spectra were recorded in the 4000-450 cm^{-1} range, collecting an average of 64 scans with 2 cm^{-1} resolution.

Samples were subjected to boiling test (1 h in boiling water). The samples surviving the tests were cut on regular blocks and mechanically characterized by using a universal test machine (Quasar 25, Galdabini S.p.a., Cardano al Campo, Italy,) operating with a cross-speed of 0.5 mm/min. The others were first stabilized by thermal treatment, at 700 °C (1 h, 10 °C/min heating rate), then cut in cubic pieces (of about 15 mm × 15 mm × 15 mm) and subjected to compressive test. The geometrical density (ρ_{geom}) of

TABLE 2: Formulations of pastes from BASG activated with waste slurries.

Sample code	BASG wt%	Mud wt%	Water (wt% added to PG/mud)	NaOH-KOH (wt% added to PG/mud)
12071 – Unfired	90	10	22.4	12.6
12072 – Unfired	95	5	22.4	12.6
12074 – Unfired + Plasmastone	33	66 (Plasm.)	22.4	2.7
C2081 – Fired at 700°C	25	75	25	10
C2082 – Fired at 700°C	25	75	23	12
C2083 – Fired at 700°C	25	67 (+8 sand)	23	12
C20810 – Fired at 700°C	30 (coarse)	60 (+10 sand)	23	12
S15072 – Fired at 700°C (foamed)	90	10		
S15073 – Fired at 700°C (foamed)	100 (coarse)	0	22.4	12.6
S15075 – Fired at 700°C (foamed)	100	0		

the samples was determined from the weight-to-volume ratio on regular blocks, using a digital caliper and an analytical balance. The apparent and the true densities (ρapp and ρtrue) were measured by means of a gas pycnometer (Ultrapyc 3000, Anton Paar GmbH, Austria), operating with helium gas on foam block or finely milled samples, respectively. Each data point represents the average value of 4-8 individual tests.

3. RESULTS AND DISCUSSION

Preliminary experiences concerning the inherent gelation ability of pharmaceutical glass could be investigated thanks to FTIR spectroscopy. Figure 1 displays changes in the infrared spectrum of boro-alumino-silicate glass operated by activation. Unlike in previous experiments (Rincón et al., 2017) pronounced hydration bands at 3400 cm^{-1} and 1600 cm^{-1} are not visible. Interestingly, remarkable differences are found in the main band, centered at 1000-1050 cm^{-1} corresponding to tetrahedral stretching modes of Si-O bond, i.e. the 'main bonds' in the glass network.

The asymmetry of the peak in the as received condition could be due to B-O bond in BO_3 trigonal units, in turn determining a vibration at about 1200 cm^{-1}. The improved symmetry, around 1000-1050 cm^{-1}, could be due to the reduction of trigonal units and to a contribution of B-O bond in BO_4 tetrahedral units, leading to a band at about 900 cm^{-1} (El-Egili, 2003; Taveri, 2017). Such BO_4 units could be stabilized by alkali ions from the activating solution. In addition, a weak peak at about 1550 cm^{-1} is consistent with the formation of carbonates (Rincón et al., 2017). The band attributed to carbonates disappeared after boiling. On the contrary, the quite symmetric main band, at 1000-1050 cm^{-1}, remained. Such phenomenology could be due to the development of a complex, multiphasic reaction interface between glass particles. The alkaline attack likely had a multiform effect: OH- ions may have determined the cleavage of Si-O bonds, forming silanol groups, while some Na^+ and K^+ ions could be incorporated as stabilizers of BO_4 units. The persistent bonding of glass particles, after boiling, could be motivated by extensive condensation of the silanol groups (justifying the limited hydration bands), with the alkali ions not involved in BO_4 (or AlO_4) units left in other phases.

A proof of alkali extraction is given by diffraction analysis (Figure 2). The starting material was X-ray amorphous, as testified by the broad 'halo' at 2θ~15-35°; after activation, the amorphous nature was confirmed, except for weak peaks attributed to sodium hydrated carbonate (thermonatrite, $Na2CO_3 \cdot H_2O$, PDF#76-0910). After boiling, the diffraction pattern resembled that of the starting material, with complete removal of carbonate inclusions.

Glass powders, after low temperature hardening, led to compacts with a density of 1.52 ± 0.18 g/cm^3, corresponding to a porosity of ~34%, completely open (according to pycnometric analysis). Such density value, combined with the measured compressive strength of 19.8 ± 1.5 MPa, makes the compacts comparable to well established, commercial construction materials, such as plaster of Paris and lightweight concrete, as shown by Figure 3 (from the application of Ansys Granta Selector, Granta EduPack 2021).

After the analysis of boro-alumino-silicate matrix under alkali activation, different changes to original synthetic procedure have been made in order to improve the sustainability of the process using different waste materials. An initial exploration of these changes has been conduct-

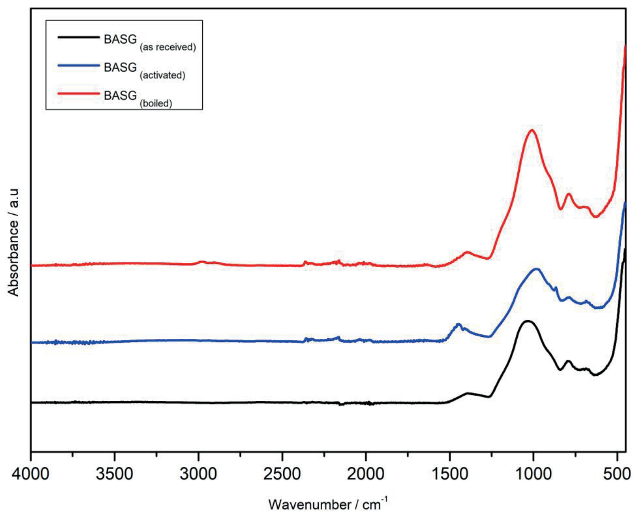

FIGURE 1: Fourier transform infrared (FTIR) analysis of boro-alumino-silicate glass in the as-received state, after activation and after boiling.

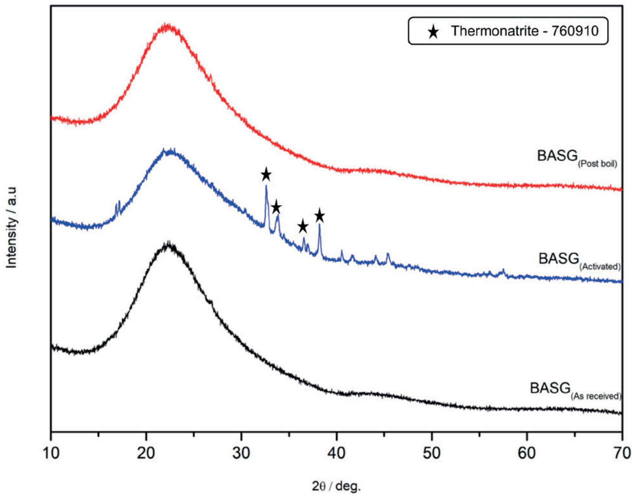

FIGURE 2: X-ray diffraction analysis of boro-alumino-silicate glass in the as-received state, after activation and after boiling.

ed with the addition of Plasmastone to the suspension, at the end of alkali activation process. The alkali activated glass matrix allows the embedding of 2/3 of total solid mass. Also in that case, obtained samples are able to resist the boiling test and show density of 1.69 ± 0.12 g/cm^3 and compressive strength of 22.4 MPa, that place them, as the previous case, in the range of some building materials (Figure 3).

Eventually, Table 1 reports the combination of alkaline solution with industrial residues from the cutting and polishing of facing bricks, by themselves representing an industrial waste. As shown by Figure 4a the activation was still successful in determining cold consolidation; dense bricks, aesthetically resembling fired bricks were finally obtained. The stability was confirmed by the boiling test, which determined some surface degradation, shown by Figure 4b. Dissolution and cracking concerned only a thin surface layer, as shown by Figure 4c. Interestingly, the strength-to-density values of the new cold consolidated materials, as shown by Figure 3, fell between the average strength-to-density values of commercial (fired) bricks.

The cold consolidation was an opportunity also for fired products. Some formulations, with much higher mud/glass ratio (see Table 1), did not yield stable gels; hardened slurries dissolved upon boiling test. These materials, however, benefited from the viscous flow sintering of glass, known to be active already at 700 °C (Bernardo and Scarinci, 2004). Sintering consolidated and stabilized the samples but did not cause a substantial densification; in fact, the viscous flow of glass could be counterbalanced by expansion, due to gasses released upon decomposition of hydrated compounds. As shown by Figure 3 the low-temperature fired materials were lighter than cold consolidated materials and commercial bricks; the strength-to-density ratio, however, remained between the average values of commercial facing bricks. The similarity was also expressed in terms of coloration (see Figure 4d).

The decomposition of hydrated compounds formed upon activation finally motivated experiments with glass-rich formulations (see Table 1). The thermal treatment determined a substantial foaming, as shown by Figure 4e. The new products, although not exhibiting strength-to-density values of materials for structural applications, were still comparable to commercial materials. More precisely,

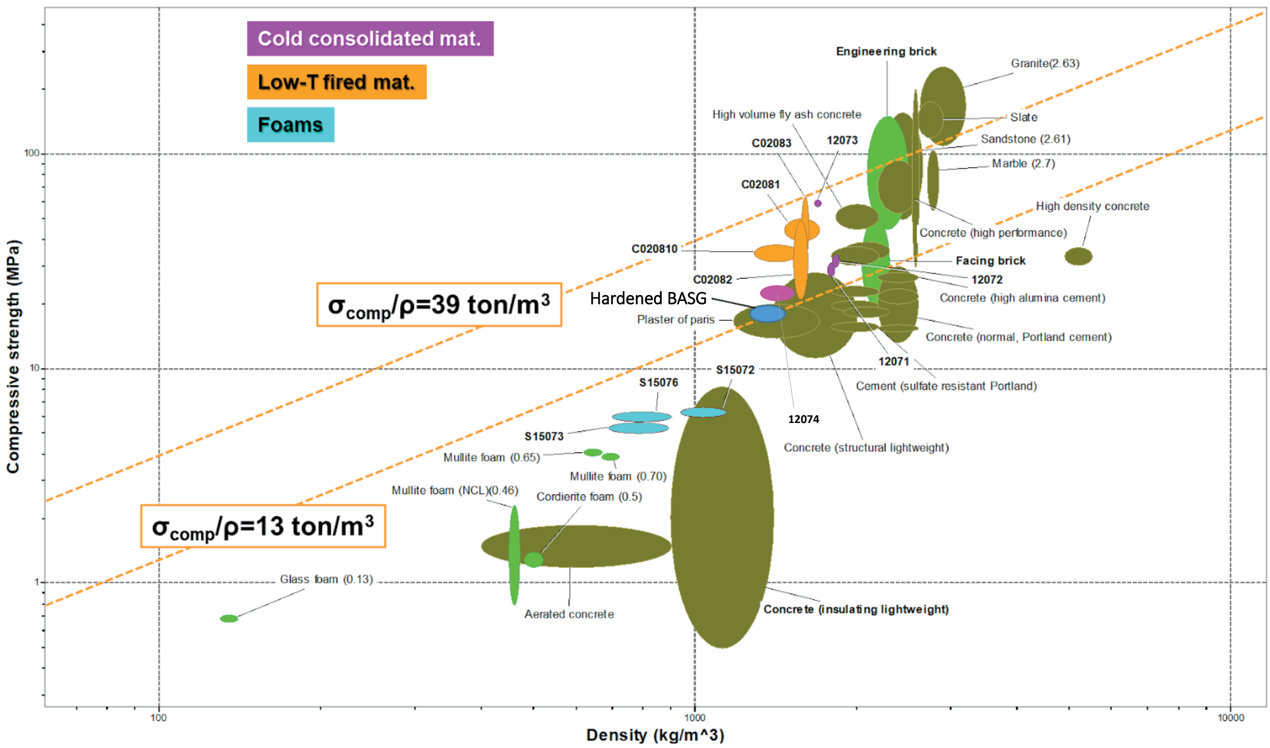

FIGURE 3: New glass-based construction materials combined with commercial products in a compressive strength/density map.

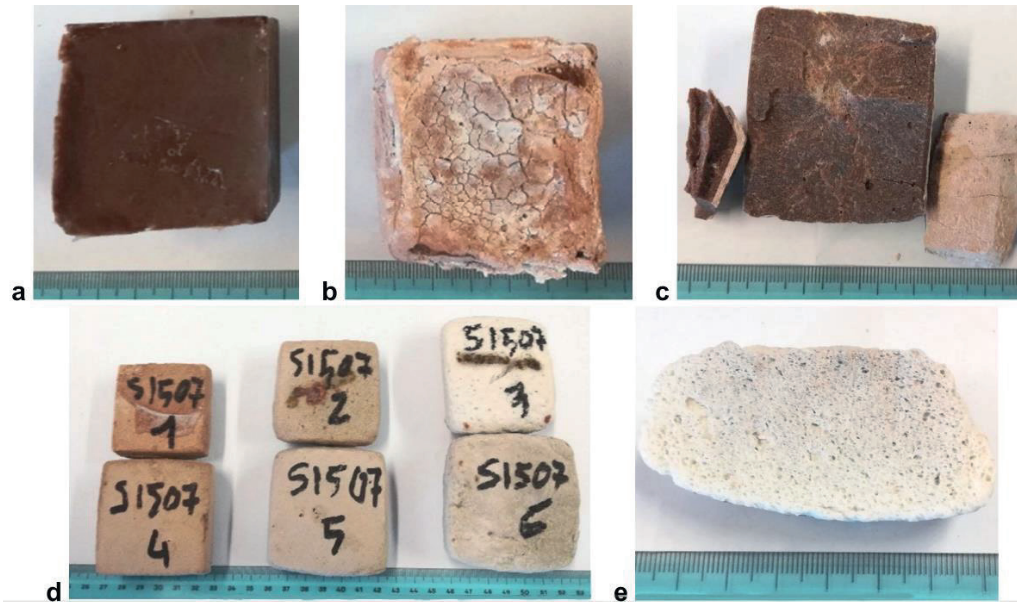

FIGURE 4: Examples of construction materials from BASG/mud mixtures: a-c) unfired product (b, c: after boiling test); d) low temperature fired materials; e) foam.

the strength-to-density was similar to that of commercial glass foams, for thermal and acoustic insulation; the compressive strength corresponds to the maximum values of denser insulating lightweight concrete. If not directly in form of panels, according to the comparison with commercial materials, the new waste-derived foams may be suggested even as lightweight aggregate.

4. CONCLUSION

Pharmaceutical glass, according to its characteristic chemical composition, is particularly promising in the perspective of alkali activation. The ‘cold consolidation’ of glass, in the applied conditions, is unprecedented and opens the way to a multitude of applications, even beyond constructions. Alkali hydroxides activate the hydration of glass surfaces, which are later subjected to condensation, in turn determining the gelation of glass suspensions. Alkali ions are only partially embedded in the gel bridging adjacent glass particles, according to their inclusion in soluble alkali hydrated carbonates. A second interesting aspect is the ability of this matrix to embed different waste without significant dropping of mechanical properties. Activating solutions based on pure distilled water may be replaced by industrial slurries, involving waste from the ceramic industry. This, besides extending the circularity of the approach (by involving different waste), has positive effects on the aesthetic appearance of products. Further perspectives could involve the embedding of wide range of other industrial waste.

ACKNOWLEDGEMENTS

The authors acknowledge the support of: national project MUR PON R&I 2014-2021 (G.T.; H.E.; E.B.); “SusPIRe” (Sustainable porous ceramics from inorganic residues) project [BIRD202134, University of Padova, Dept. of Industrial Engineering)] (E.B.); INSTM (Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali) through CaRiPLo project: 'New recycling process for the foundry sands: innovation aimed to get materials with high added value' - (F.C., E.B.).

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