

CLOCKS project

CLOsing the loop: building Circular sKillS on the entire value chain

CIRCULAR SUMMER SCHOOL ON RAW MATERIALS

R4
Recycling
Remanufacturing
Recovery
Refurbishment

July 17th, 2023

Glass Recycling: Contradictions & Opportunities for New Sustainable Construction Materials

Enrico Bernardo

Department of Industrial Engineering,University of Padova, Italy

in cooperation with FunGlass – Centre for Functional and Surface Functionalized Glass, Alexander Dubček University of Trenčín, Trenčín, Slovakia

800 1222·2022 ANNI

UNIVERSITÀ DEGLI STUDI DI PADOVA

DIPARTIMENTO DI INGEGNERIA INDUSTRIALE

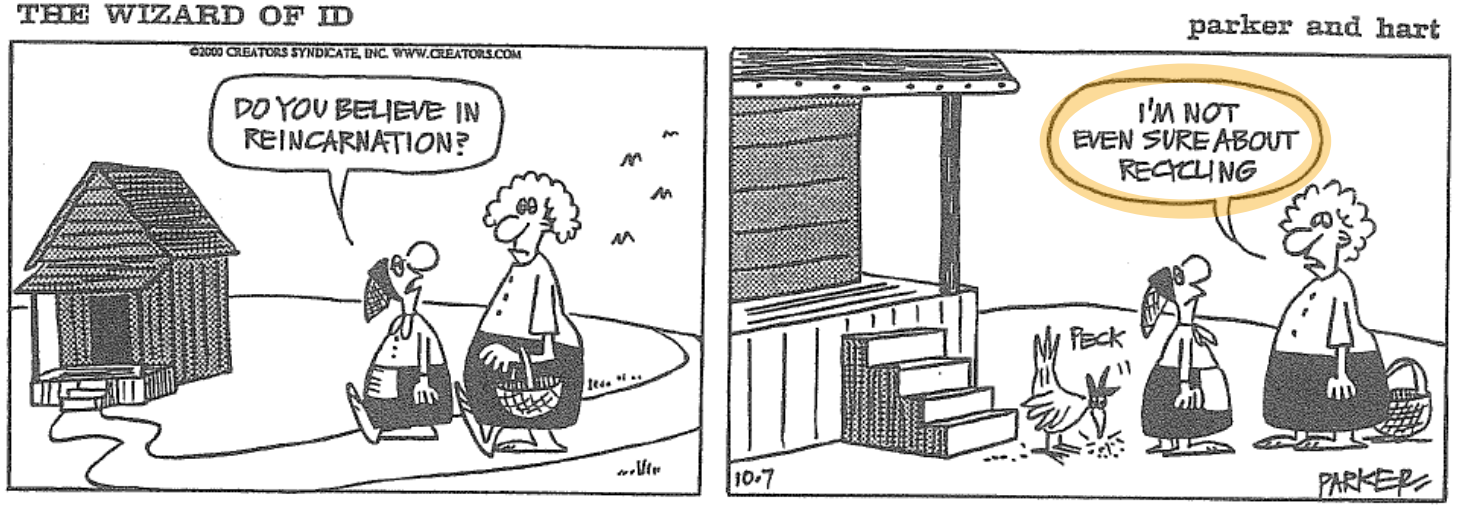
CERAM GLASS RESEARCH GROUP

FunGlass
Centre for Functional and Surface Functionalized Glass

European Commission | Horizon 2020 European Union funding for Research & Innovation

Fundamental questions

What are we going to recycle?
How can we recycle?



Used by permission of Johnny Hart and Creators Syndicate, Inc.

- **Personal duty: enhancing (open-loop) glass recycling and recycling of inorganic residues by means of glass**
- **Fundamental problem: environmental and economic sustainability of technologies for the development of new glass-based products**

→ Answer #1: minimize cost/energy for new products

→ Answer #2: new products for specific applications in order to express added value

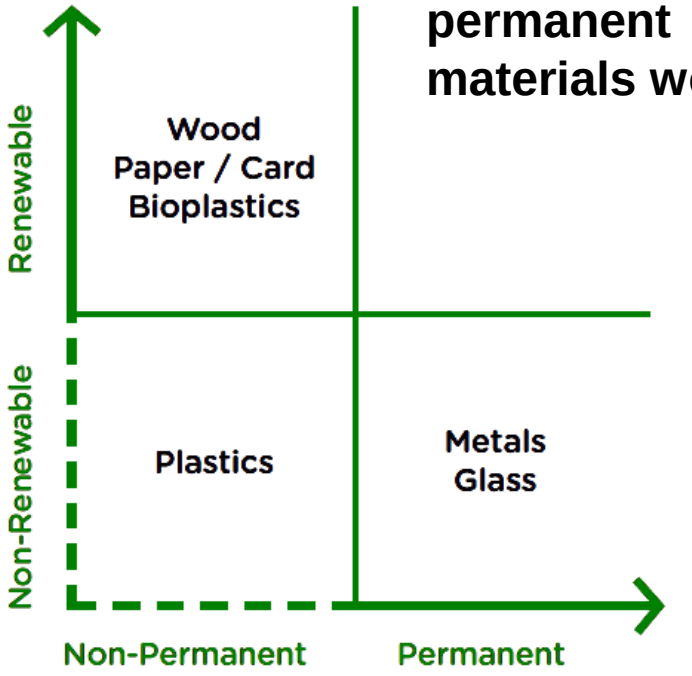
Introduction

Glass proposed as 'permanent' material
Is it true? Please mind 'quality' as key word

Materials in general can be classified as renewable or non-renewable or as permanent or non-permanent.

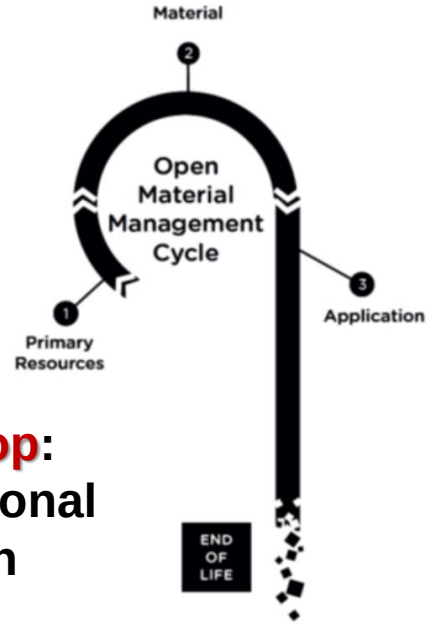
Renewable materials such as wood, paper/card or bio plastics are made from natural resources that can be re-built by biological processes.

Permanent materials are classified as materials that once produced can be recycled or reused without the loss of quality, regardless of how often the material is recycled.



Closed loop: how permanent materials work





Open loop: conventional approach

Courtesy Prof. Paolo Colombo, University of Padova

Is glass really 100% recyclable?

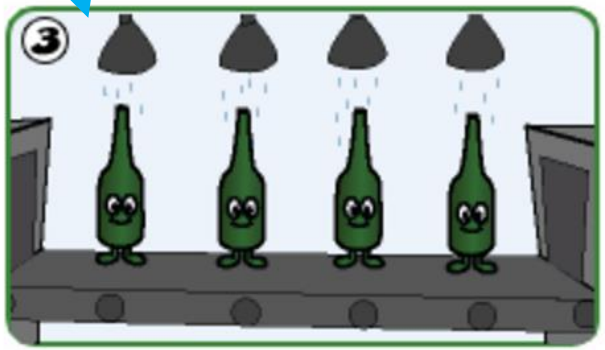
What's the common idea about glass recycling?
Some examples, also from school times…



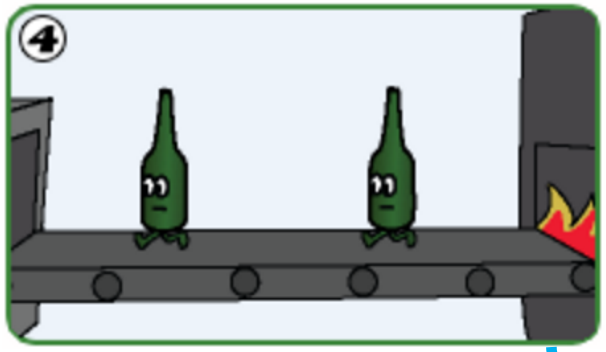
The consumer throws glass into a recycle bin.



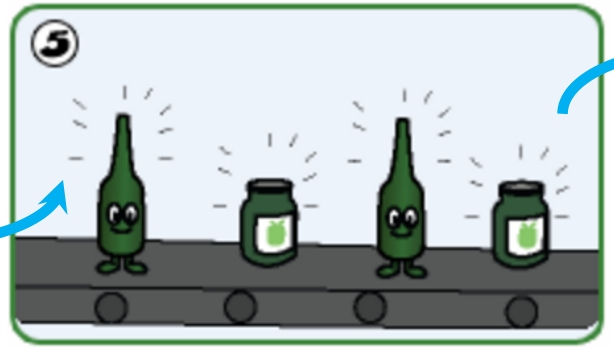
Glass is taken from the bin and taken to a glass treatment plant.



The glass is sorted by colour and washed to remove any impurities.



The glass is then crushed and melted, then moulded into new products such as bottles and jars. Or it may be used for alternative purposes such as brick manufacture or decorative uses.



The glass is then sent back to the shops ready to be used again.

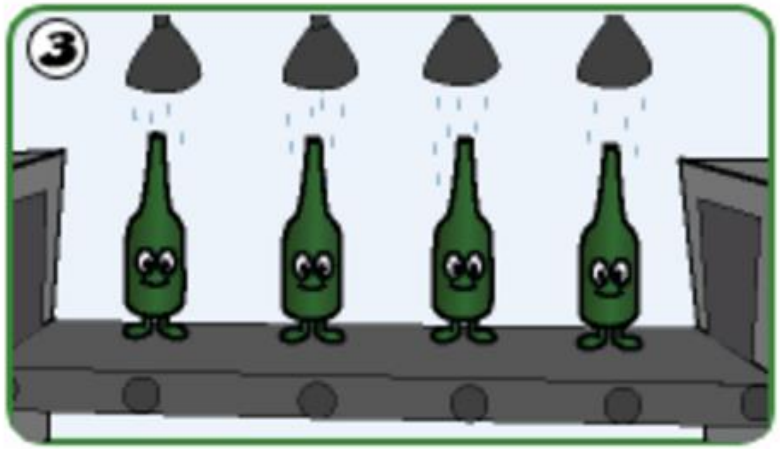


Glass does not degrade through the recycling process, so it can be recycled again and again.

Taken from http://www.recycling-guide.org.uk/science-glass.html

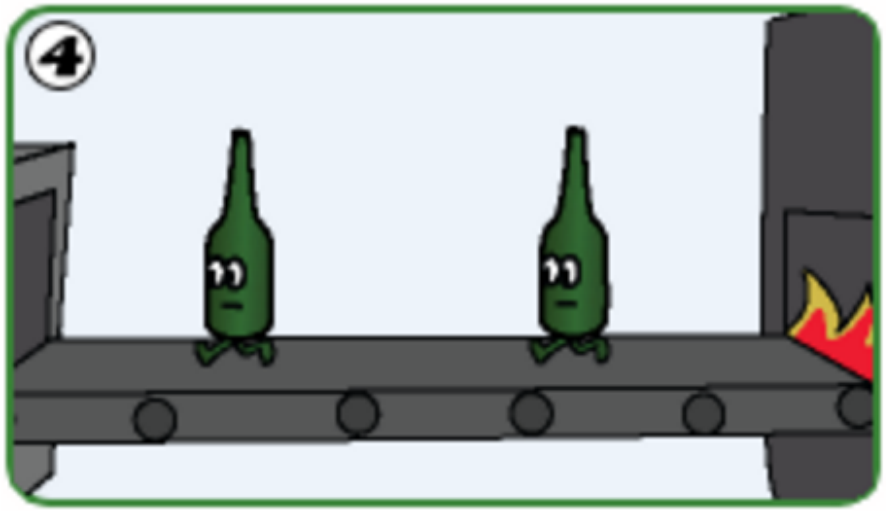
Is glass really 100% recyclable?

What's the common idea about glass recycling?
Some examples, also from school times…



The glass is sorted by colour and washed to remove any impurities.

Not trivial!



The glass is then crushed and melted, then moulded into new products such as bottles and jars. Or it may be used for alternative purposes such as brick manufacture or decorative uses.

Not the only option

Pretty reductive

Is glass really 100% recyclable?

What's the common idea about glass recycling?
Some examples, also from school times…



Glass does not degrade through the recycling process, so it can be recycled again and again.

Not always true



'Stone' in glass bottle
[http://monofrax.com/services/]

Big troubles in case of unsuccesful removal of impurities

This talk: aimed at presenting opportunities and challenges of glass recycling in its multiple aspects

Talk divided in two sections, standing for:

1. **Closed-loop actions**: full circularity intended as **Refurbishment**, **Remanufacturing** and **Recycling** → preservation of functionality (discarded material from a product of a first generation used to "create" a product of a second generation)

- **Refurbishment**: minimized actions on the product of first generation
- **Remanufacturing**: application of some form of restoration
- **Recycling**: waste used as **raw material** for new product, after 'disruptive' actions = **remelting (& reshaping)**

2. **Open-loop actions**: *circularity in a wider sense*, based on the concept of **Recovery** → definition of new products, completely different from the original ones

- **Waste glass as raw material for new articles: focus on energy savings** → sintering as key word
- **Downcycling**: definition of product of lower value
- **Upcycling**: challenging operations, defining products with higher value compared to that of the feedstock

Refurbishment

Reuse of glass containers

Minimized operations (cleaning, refilling, recapping)

B. Simon et al. / Journal of Cleaner Production 112 (2016) 238–248

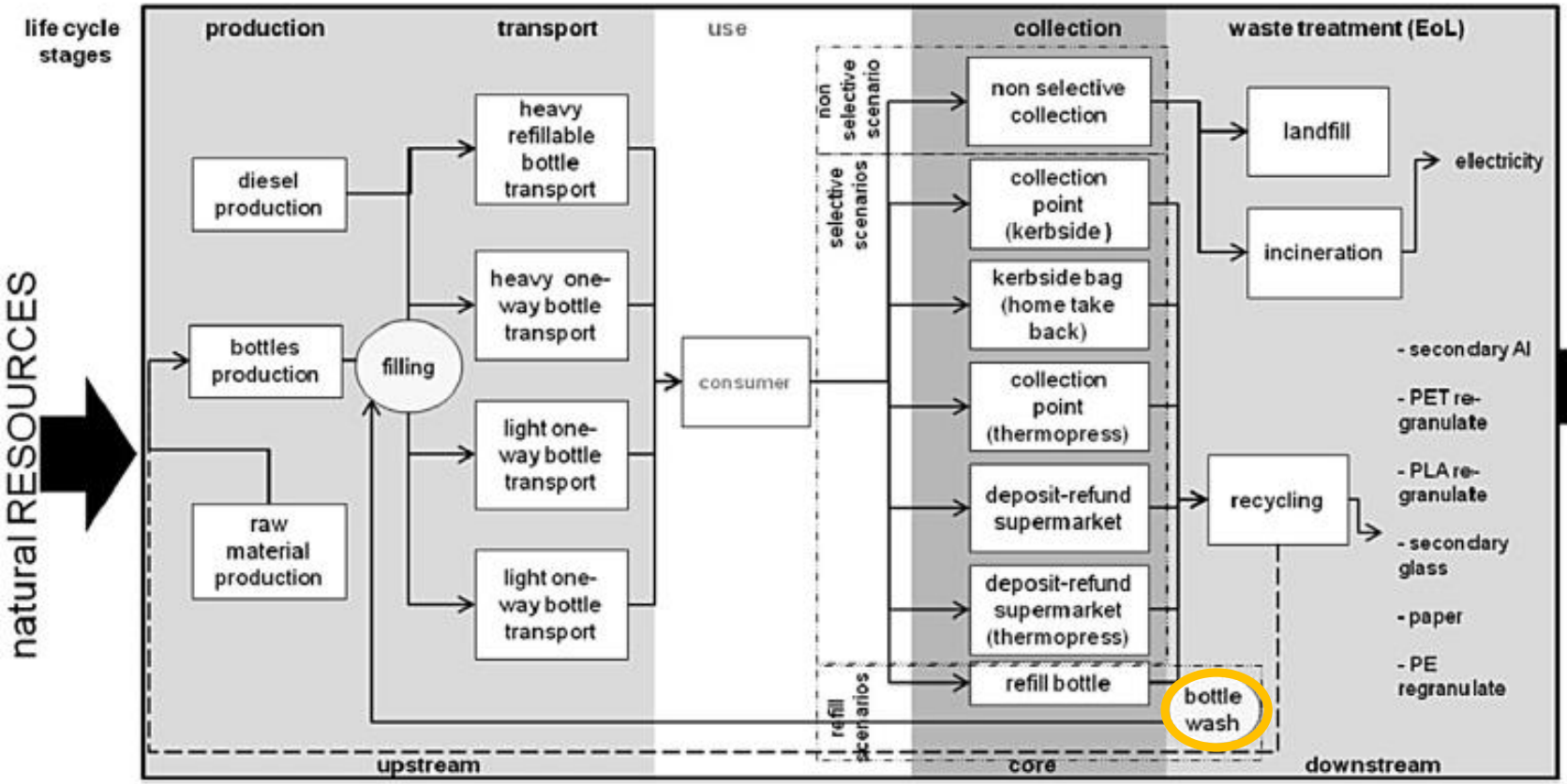


Fig. 1. Schematic description of investigated system boundaries (life cycle phases are shown on the top).

Several studies on 'washing' as alternative to 'recycling'

Not trivial, since many variables are involved → difficulty in modelling

Journal of Cleaner Production 112 (2016) 238–248
Contents lists available at ScienceDirect
Journal of Cleaner Production
journal homepage: www.elsevier.com/locate/jclepro

Life cycle impact assessment of beverage packaging systems: focus on the collection of post-consumer bottles

Bálint Simon [a, *], Mourad Ben Amor [b], Rita Földényi [a]
[a] University of Pannonia, Institute of Earth and Environmental Sciences, Egyetem u. 10, H-8200 Veszprém, Hungary
[b] Université de Sherbrooke, Department of Civil Engineering, 2500, boul. de l'université, Sherbrooke, Qc J1K 2R, Canada

Refurbishment

Reuse of glass containers

Minimized operations (cleaning, refilling, recapping)

Table 3
Overview of kg CO_2-equivalent emissions during the whole life cycle of packaging materials (1000 L volume) considering the sub-systems (The "*potential credit*" means the potentially avoidable CO_2-Eq. emissions by using the secondary material instead of primaries).

		Al 0.33	Al 0.5	PET 0.5	PET 1.0	PET 1.5	PET 2.0	PLA 1.5	Carton 1.0	GL 0.33	GL 0.5
Production I	(on-site production)	535.8	449.5	325.8	173.2	135.6	173.2	73.7	63.6	573.7	582.9
Production II	(external production)	538.1	451.4	328.5	175.6	137.8	175.4	66.6	65.2	582.3	607.4
Distribution		46.4	45.9	46.2	46.0	45.8	45.8	45.8	45.8	65.5	61.8
Waste collection	deposit-refund (supermarket)	1.1	0.9	1.5	1.1	0.8	0.7	0.7	0.8	19.2	21.7
	kerbside bag	0.5	0.5	1.2	1.1	1.1	1.1	1.1	0.4	2.3	2.8
	coll. point (kerbside)	1.2	1.1	2.8	2.7	2.6	2.6	2.6	1.4	13.8	11.0
	col. point (tpress)	n.a.	n.a.	10.6	5.5	3.7	2.8	3.7	n.a.	n.a.	n.a.
	s.market (tpress)	n.a.	n.a.	6.1	3.3	2.2	1.5	2.2	n.a.	n.a.	n.a.
	w/o selectiv collection	6.9	5.8	8.7	6.5	4.4	4.8	4.4	4.7	143.4	113.6
Waste treatment	*recycling (potential credit)*	*444.3*	*374.2*	*156.6*	*85.4*	*66.4*	*86.9*	*37.0*	*42.9*	*538.6*	*426.6*
	recycling	18.3	15.4	5.9	3.2	2.1	3.3	2.1	25.1	107.0	84.7
	landfill	588.5	495.6	736.7	555.9	374.7	555.9	370.2	401.8	12,176.0	9644.0
	incineration	585.8	493.4	733.4	553.3	373.0	553.3	368.5	400.0	12,120.0	9600.0

- **Aluminum and glass containers implying higher environmental demands** compared to plastic containers
- Recycling gives a remarkable **end-of-life credit** (saving of raw materials in secondary production)
- **Recycling has a low impact by itself** (numbers to be verified)

Journal of Cleaner Production 112 (2016) 238–248
Contents lists available at ScienceDirect
Journal of Cleaner Production
journal homepage: www.elsevier.com/locate/jclepro

Life cycle impact assessment of beverage packaging systems: focus on the collection of post-consumer bottles

Bálint Simon [a, *], Mourad Ben Amor [b], Rita Földényi [a]
[a] University of Pannonia, Institute of Earth and Environmental Sciences, Egyetem u. 10, H-8200 Veszprém, Hungary
[b] Université de Sherbrooke, Department of Civil Engineering, 2500, boul. de l'université, Sherbrooke, Qc J1K 2R, Canada

Refurbishment

Reuse of glass containers

Minimized operations (cleaning, refilling, recapping)

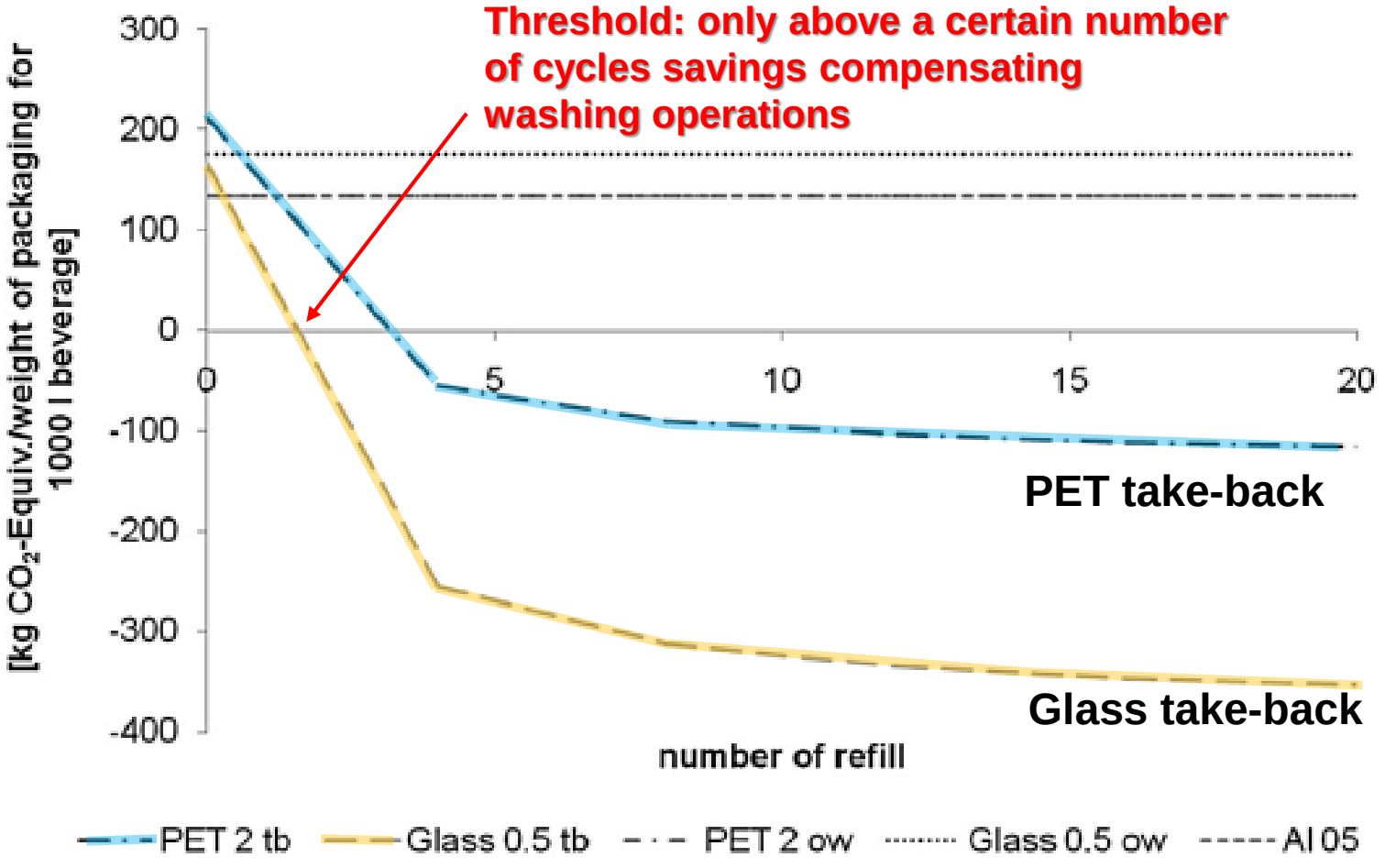


Fig. 5. GHG emissions variations as a function of the numbers of refilling (for acronyms see Table 1, ow = one-way bottle, tb = refill bottle/take back/).

Refilling of containers calculated as particularly useful

Saving of big amounts of production energy (bigger saving with glass, compared to PET)

- **Attention to the plateau: after a certain number of cycles, the number of damaged/lost containers becomes relevant**
- **Refilling to be encouraged (money-back on return)**

Journal of Cleaner Production 112 (2016) 238–248
Contents lists available at ScienceDirect
Journal of Cleaner Production
journal homepage: www.elsevier.com/locate/jclepro

Life cycle impact assessment of beverage packaging systems: focus on the collection of post-consumer bottles

Bálint Simon [a, *], Mourad Ben Amor [b], Rita Földényi [a]
[a] University of Pannonia, Institute of Earth and Environmental Sciences, Egyetem u. 10, H-8200 Veszprém, Hungary
[b] Université de Sherbrooke, Department of Civil Engineering, 2500, boul. de l'université, Sherbrooke, Qc J1K 2R, Canada

Remanufacturing

Refilling determines some degradation (contact between container)
Some form of restoration applicable

Enhancing the lubrication

Issue of glass container technology:

- **Hot end coating (SnO_2-based coating on hot containers, 'along' primary production)**

e.g. butyl-tin-chloride sprayed at 550-450 °C, used to seal microcracks
[https://www.bohemichemicals.com/products/hot-end-coating/index.html]

- **Cold end coating ('wax'-based coating on cold containers): it may be applied both to 'virgin' and 'used (washed)' container**

Useful to 'mask' microcracks and reduce mutual wear

Extra material (organic-based) obviously with an extra environmental impact (low compared to remelting)



https://www.arkema.com/global/en/resources/post/recycled-and-returnable-a-futur-for-glass-bottles/

Up to 50 cycles of use

As for returnable bottles, Arkema works with local bottlers (brewers, producers of mineral water, carbonated or non-alcoholic) by offering them two complementary glass protection ranges that considerably improve the appearance and the extension of returnable bottles life cycle.

- The **Kercoat®** covering delays the appearance of fissures and white scratches; used after every wash, it can extend the use of a bottle to 50 cycles, compared to 20 traditionally.
- And **Opticoat®** emulsion reduces the appearance of fissures and marks, which makes the containers more attractive.

"The two solutions can be used either separately or together, depending on the individual bottler's strategy", says Ines Khalfallah. Like the Petropolis group, number three in the Brazilian market, which opted in 2019 to apply the Opticoat® solution to its Premium range, showing that it is possible to improve the user experience by making bottles look almost new, even as part of a economic and sustainable drive by preventing (re) throwing away scratched bottles.

What is the difference between "recycling" and "revalorizing" a glass bottle?

Recycling as remelting

Impact on energy and CO_2 emissions

Attention to «embodied energy» and «embodied CO_2»

Fundamental environmental burdens of production

- **Embodied energy (H_m)** = energy to be committed for the preparation of 1 kg (unit mass) of usable material
- **Embodied CO_2** = carbon dioxide amount to be emitted for the preparation of 1 kg (unit mass) of usable material

Energy committed to activate chemical reactions, but also dissipated e.g. in fumes escaping from furnaces

«Historical data», subject to variations, depending on processing conditions

Examples of CO_2 reduction:

- **electric-driven thermal processes (no more fumes from combustion)**
- **hydrogen-fueled thermal processes (nominally C-free fumes)**

Embodied energy and CO_2 sensitive to recycling, e.g.

$$H_{m\ recycled} = H_m^* = H_m \cdot (1-R) + H_r \cdot R \quad [J/kg_{product}]$$

Where R is the recycled fraction, H_r=embodied energy for material after recycling

Recycling as remelting

Impact on energy and CO_2 emissions

The glass paradox: big question of quality of recycling

Material	Recycled fraction in current supply(1) (%)	Embodied energy, virgin material (MJ/kg)	Embodied energy, recycled material (MJ/kg)	Ratio of recycled to virgin energies (%)
Aluminum	36	210	26	12
Steel	42	26.5	7.3	27
Copper	42	58	13.5	23
Lead	72	27	7.4	27
PET	21	85	39	46
PP	5	74	50	67
Glass	24	10.5	8.2	78
Paper	72	45	20	44

Extremely convenient

Quite low!

Relatively high!

M.F. Ashby, "Materials and the Environment – Eco-informed Material Choice", Elsevier, Oxford (UK), 2013

Glass: energy and CO_2 to be spent to get from used material the same degree of quality achieved with natural raw materials

Purification of cullet is a demanding step

Recycling as remelting

Impact on energy and CO_2 emissions

The glass paradox: big question of quality of recycling

Material	Recycled fraction in current supply(1) (%)	Embodied energy, virgin material (MJ/kg)	Embodied energy, recycled material (MJ/kg)	Ratio of recycled to virgin energies (%)
Aluminum	36	210	26	12
Steel	42	26.5	7.3	27
Copper	42	58	13.5	23
Lead	72	27	7.4	27
PET	21	85	39	46
PP	5	74	50	67
Glass	24	10.5	8.2	78
Paper	72	45	20	44

Positive evolution in recent years
[Italy with recycling rate (76,6% in 2021)* above EU average]
Separation of cullet remains challenging

*** CoReVe** (Consorzio Recupero Vetro) - ***https://coreve.it/coreve-nel-2021-continuano-a-crescere-la-raccolta-e-il-riciclo-del-vetro/***

Recycling as remelting

Impact on energy and CO_2 emissions

Attention: CO_2 not only from energy generation

Prototype composition of glass containers

Oxides	SL glass
SiO_2	71.6
Al_2O_3	1.0
Na_2O	13.5
K_2O	0.4
MgO	3.9
CaO	9.0
B_2O_3	
Fe_2O_3	0.1
TiO_2	
SrO	
others	0.5

Typically from carbonate minerals: CO_2 emitted from decomposition



Current trend: engineering of glass formulation to minimize the input of C-containing (and C-yielding, upon melting) minerals and *lowering processing T*

LionGlass (Prof. J. Mauro, Penn State)

Researchers at Penn State University, USA, have created a new family of glass compositions, called LionGlass, that will help lower energy costs and extend tank lifetimes.

LionGlass is a new family of glass chemistry developed by a team of glass researchers at Penn State University.

LionGlass is meant to replace soda lime silicate glass — the common glass used on everyday items including windows, jars and drinking glasses.

The makers of LionGlass say it can help lead to more sustainable form of glass manufacturing.

https://www.glass-international.com/news/lionglass-to-help-extend-glass-manufacturing-furnace-lifetimes

Challenging aspects:

- Each processing step, on glass, depends on viscosity/T (same as common glass?)
- Equivalence in properties to be assessed
- Revision of equipments needed

Recycling as remelting

Impact on energy and CO_2 emissions

Attention: CO_2 not only from energy generation

Prototype composition of glass containers

Oxides	SL glass
SiO_2	71.6
Al_2O_3	1.0
Na_2O	13.5
K_2O	0.4
MgO	3.9
CaO	9.0
B_2O_3	
Fe_2O_3	0.1
TiO_2	
SrO	
others	0.5

Typically from carbonate minerals: CO_2 emitted from decomposition



Current trend: engineering of glass formulation to minimize the input of C-containing (and C-yielding, upon melting) minerals and *lowering processing T*

LionGlass (Prof. J. Mauro, Penn State)

Researchers at Penn State University, USA, have created a new family of glass compositions, called LionGlass, that will help lower energy costs and extend tank lifetimes.

LionGlass is a new family of glass chemistry developed by a team of glass researchers at Penn State University.

LionGlass is meant to replace soda lime silicate glass — the common glass used on everyday items including windows, jars and drinking glasses.

The makers of LionGlass say it can help lead to more sustainable form of glass manufacturing.

https://www.glass-international.com/news/lionglass-to-help-extend-glass-manufacturing-furnace-lifetimes

Recycled material melts without CO_2 emission, keeps the properties, keeps the implants…

Challenging aspects:

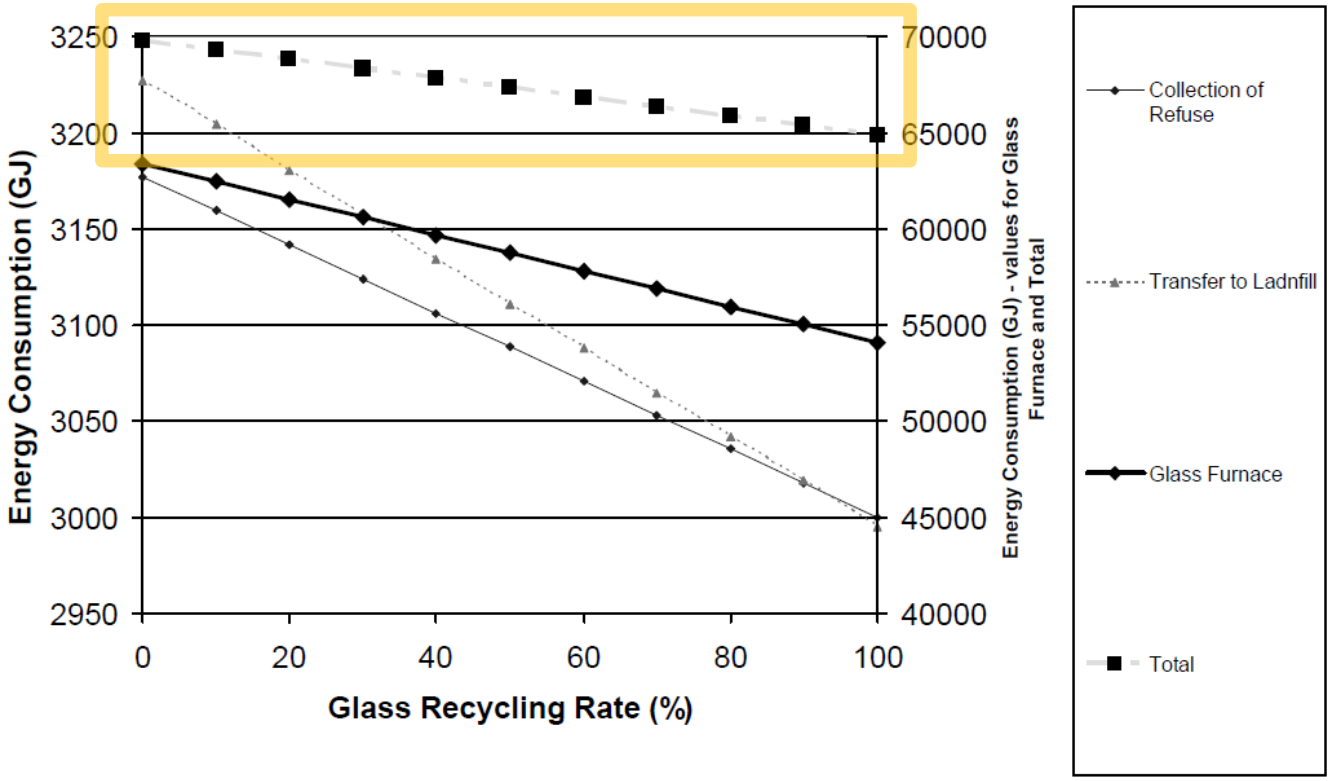
- Each processing step, on glass, depends on viscosity/T (same as common glass?)
- Equivalence in properties to be assessed
- Revision of equipments needed

Recycling as remelting

Very promising aspects
Attention to the boundary conditions

Savings with recycled material

- **Raw materials**
- **Heat for reactions to occur** - **Heat lost from flue gasses** in turn developed from decomposition of raw materials
- **Costs for waste management**



ELSEVIER
Available online at www.sciencedirect.com
SCIENCE DIRECT®
Ecological Modelling 174 (2004) 175–189
ECOLOGICAL MODELLING
www.elsevier.com/locate/ecolmodel

Analysis of energy footprints associated with recycling of glass and plastic—case studies for industrial ecology

V. Krivtsov[a,*], P.A. Wäger[b], P. Dacombe[a], P.W. Gilgen[b], S. Heaven[a], L.M. Hilty[b], C.J. Banks[a]

Not new: studies dating back to nearly 20 years ago

Lacking focus on the quality of products

Cullet = recycled glass, remelted (T in the order of 1500 °C)

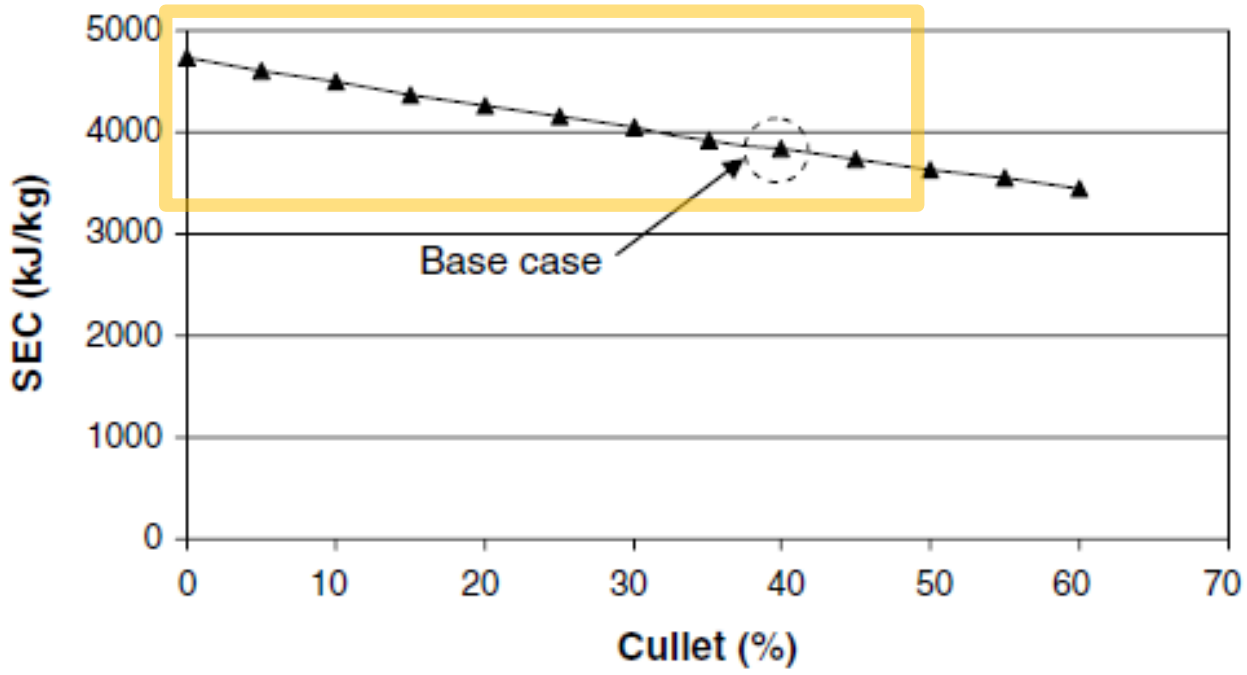


Fig. 18. Effect of cullet percentage on specific energy consumption.

ELSEVIER

Available online at www.sciencedirect.com
ScienceDirect
Energy Conversion and Management 48 (2007) 2718–2738

Energy Conversion & Management
www.elsevier.com/locate/enconman

Model based energy benchmarking for glass furnace

Vishal Sardeshpande, U.N. Gaitonde, Rangan Banerjee *

Department of Energy Systems Engineering, Indian Institute of Technology Bombay, Mumbai 400 076, India

Received 31 August 2006; accepted 12 April 2007
Available online 19 June 2007

Just to cite another: many papers available
Many models applied

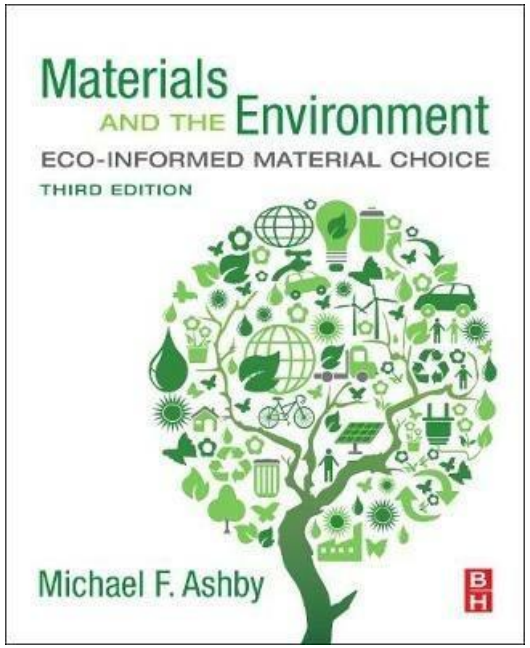
Weakness: glass cullet as 'perfect glass'

Cullet has some important quality issues

Let's evaluate more comprehensive approaches…

Eco-Audits

Inventory of energy spent or CO_2 emitted in several phases
Useful to understand the most critical aspects

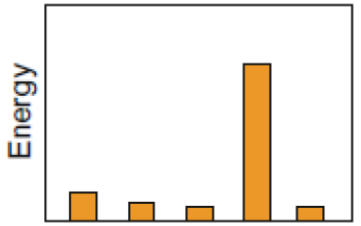


Pioneering work from Prof. M.F. Ashby (University of Cambridge, UK)

1. Eco-audit

Assess energy/CO_2 over life

Materials
Manufacturing
Transportation
Use
Disposal



More properly, re-design

2. Design

Materials
Minimize
- Mass of part
- Embodied energy
- CO_2/kg

Manufacturing
Minimize
- Process energy
- Process CO_2/kg

Transportation
Minimize
- Mass
- Distance moved
- Energy mode of transport

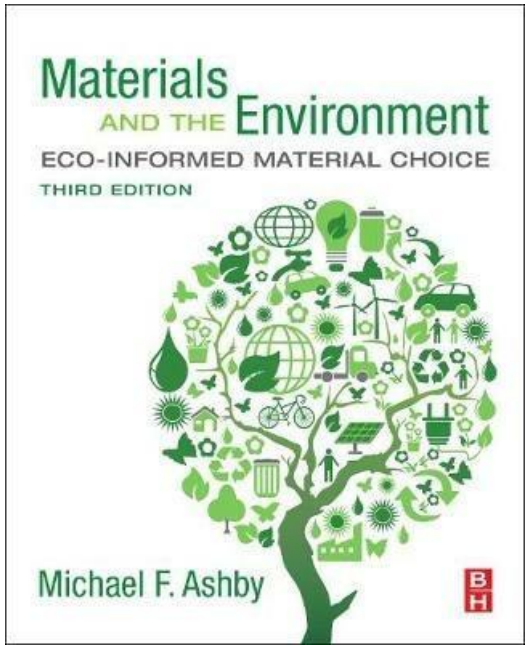
Use
Minimize
- Mass
- Thermal loss
- Electrical loss

Disposal
Select
- Nontoxic materials
- Recyclable materials

MFA '11

Eco-Audits

Case study: 100 bottle, carrying each 1 L water
Materials as part of a more complex problem



Pioneering work from Prof. M.F. Ashby (University of Cambridge, UK)

Example of inputs for CES (Cambridge Engineering Selector) [ANSYS-Granta] software



- 1 litre PET bottle with PP cap
- Blow molded
- Filled in France, transported 550 km to UK
- Refrigerated for 2 days, then drunk

Product name: *PET bottle*

Compare with... | Clear | Open | Save

Number	Name	Material	Process	Mass (kg)	End of life
100	Bottles	PET	Molding	0.04	Recycle
100	Caps	Polyprop	Molding	0.001	Landfill
100	Water			1.0	

Transport

Stage 1	14 tonne truck	550 km

Use - refrigeration

Fossil to electric	0.12 kW	2 days	24 hrs/day

Survey charts

Full report

GRANTA TEACHING RESOURCES

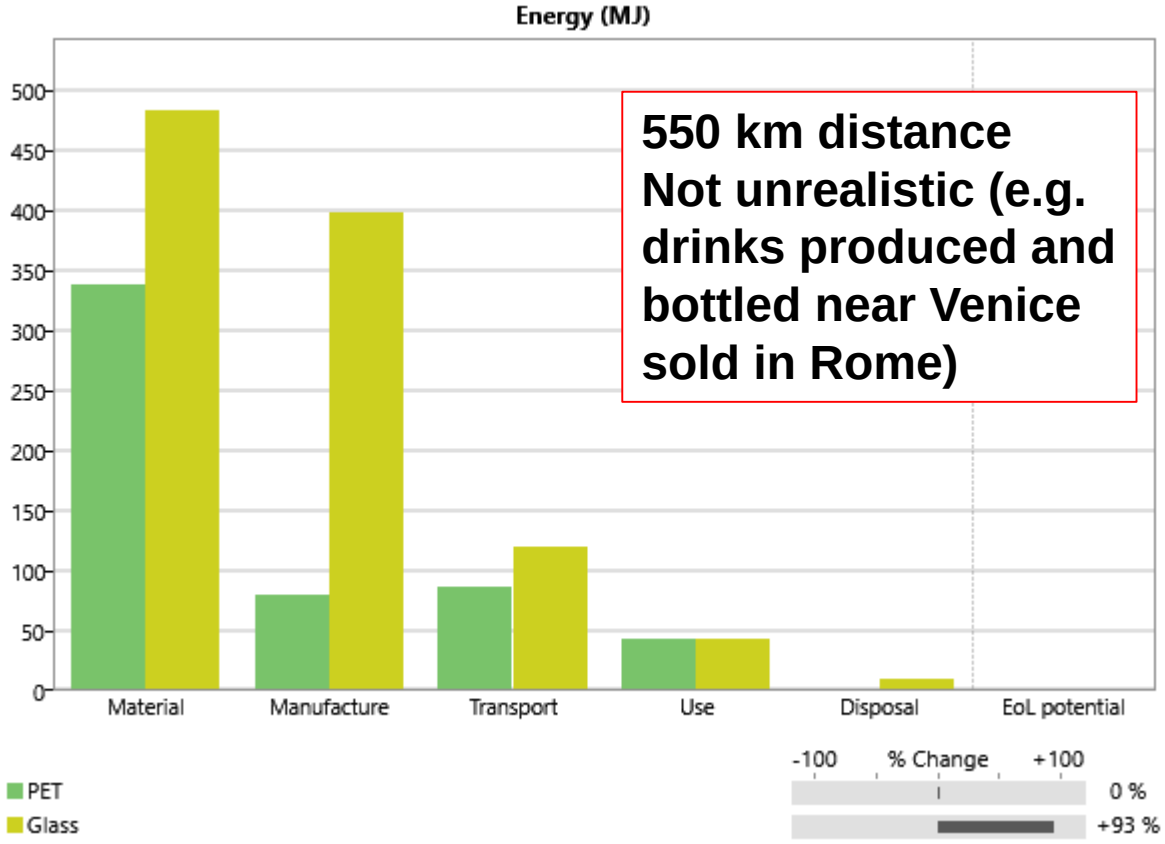
Mike Ashby, 2013

www.grantadesign.com/education/resources

Eco-Audits of containers

Comparison between PET and soda-lime glass

Surprising facts

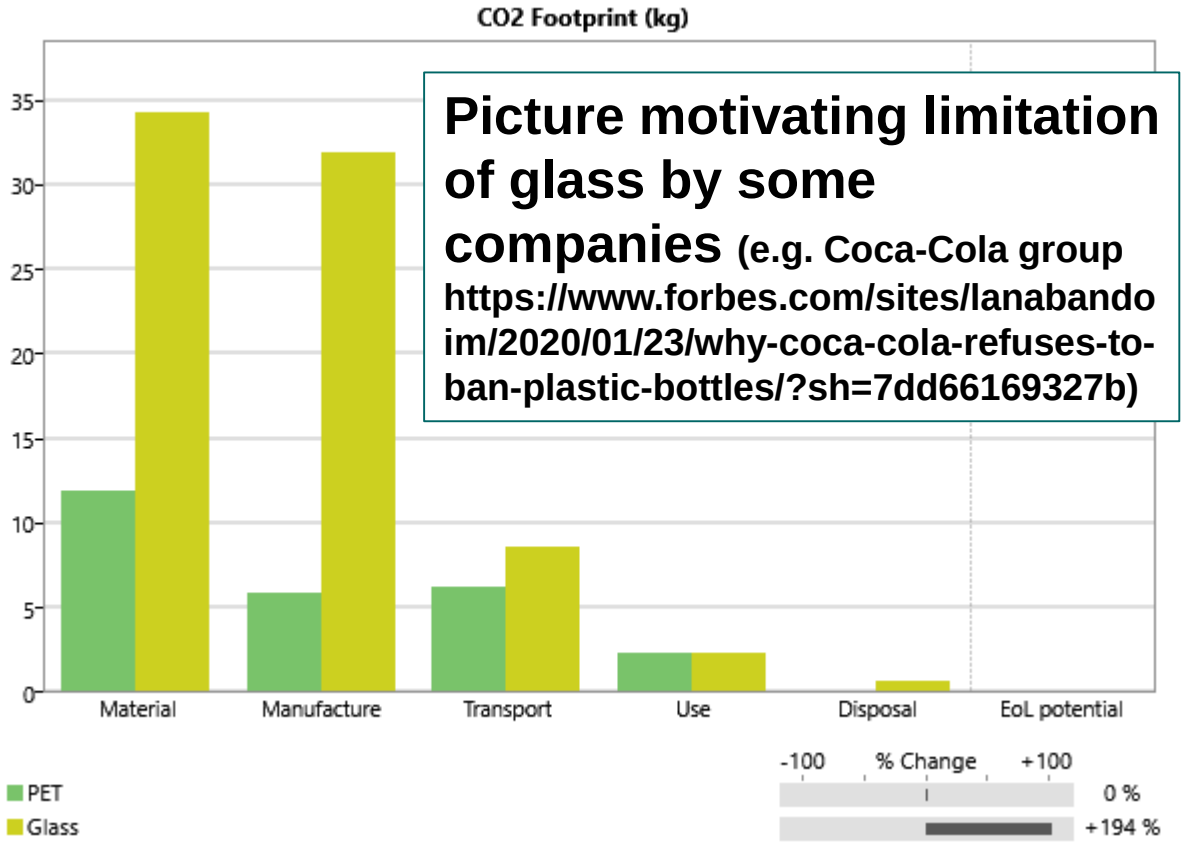


550 km distance
Not unrealistic (e.g. drinks produced and bottled near Venice sold in Rome)

***Bad news*: Glass has a much lower embodied energy compared to PET, but the '*amount per unit product*' is much higher**

Worst scenario, virgin feedstock, landfilling

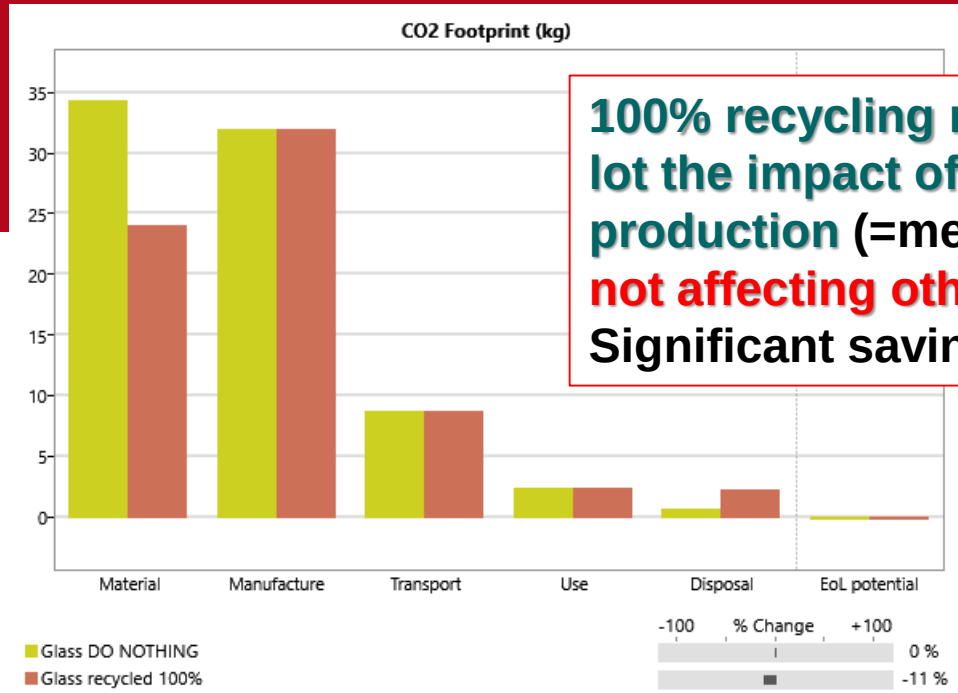
PET container: 0.04 kg/L
Glass container: 0.45 kg/L



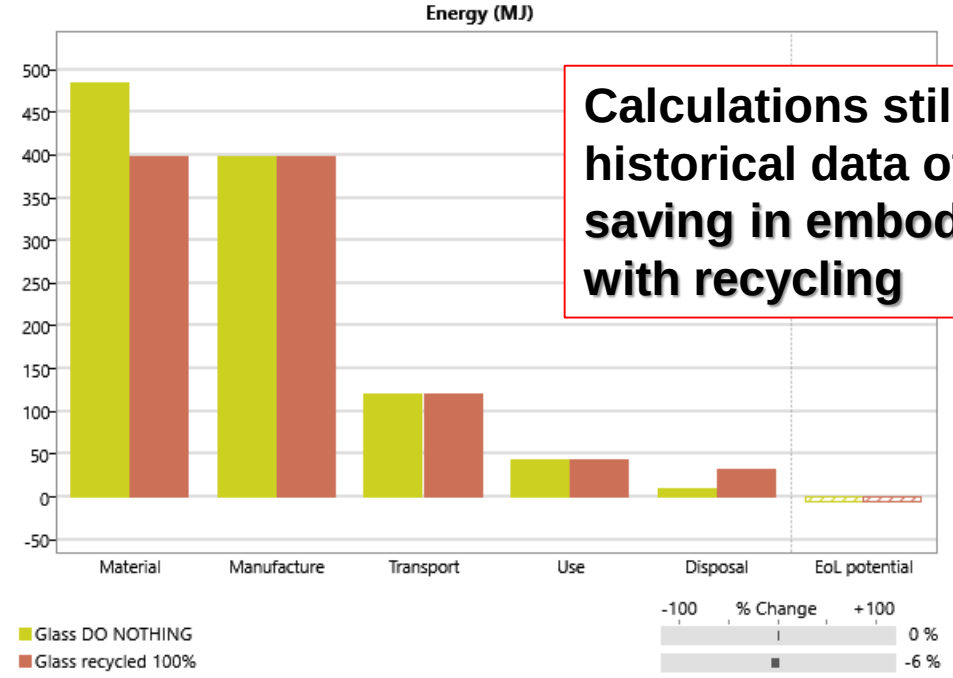
Picture motivating limitation of glass by some companies (e.g. Coca-Cola group https://www.forbes.com/sites/lanabandoim/2020/01/23/why-coca-cola-refuses-to-ban-plastic-bottles/?sh=7dd66169327b)

Eco-Audits of containers

Comparison between PET and soda-lime glass
Surprising facts

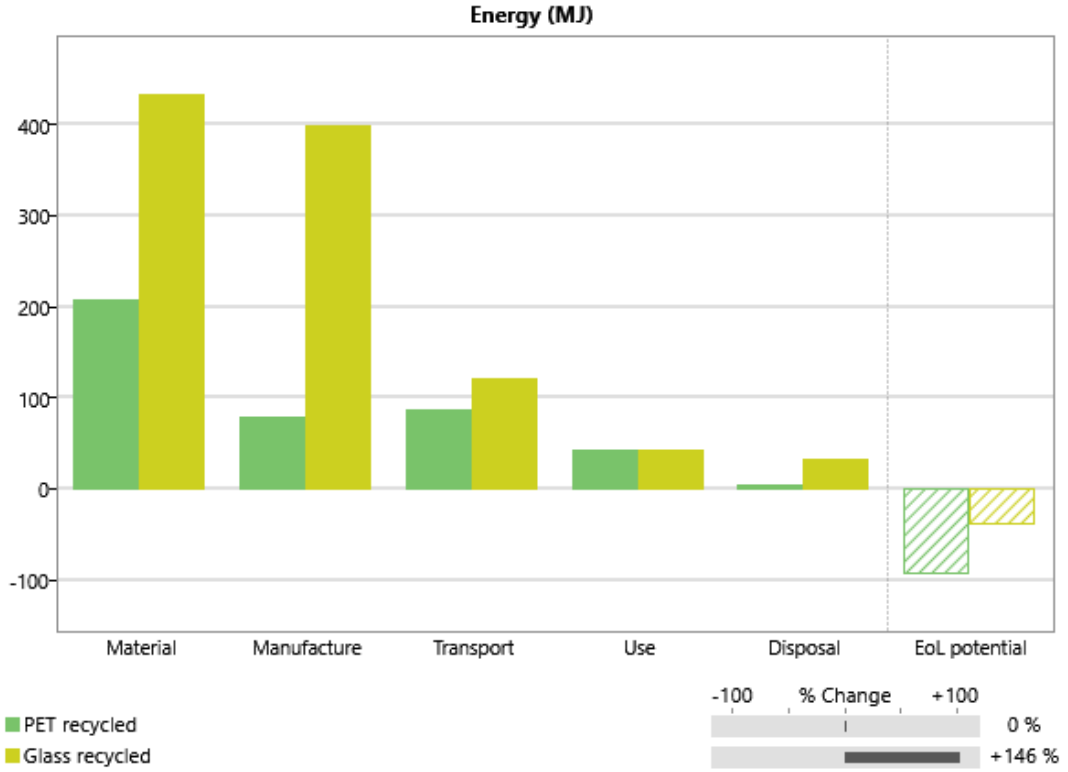


100% recycling reducing a lot the impact of primary production (=melting) but not affecting other aspects
Significant savings, anyway



Calculations still based on historical data of limited saving in embodied energy with recycling

Hard comparison with other materials, e.g. with the same recycled amount of 60%...



Glass always interesting in terms of preservation of quality of contained liquid, but a weakness is evident… the mass

Mass of containers

Attention to combination of properties
Glass indeed possessing an unfavorable combination

Stress / Failure stress

$$\sigma = \frac{p \cdot R}{t} \leq \sigma_f$$

Pressurized container: ***to avoid failure***

Strong materials enabling ***thin containers***

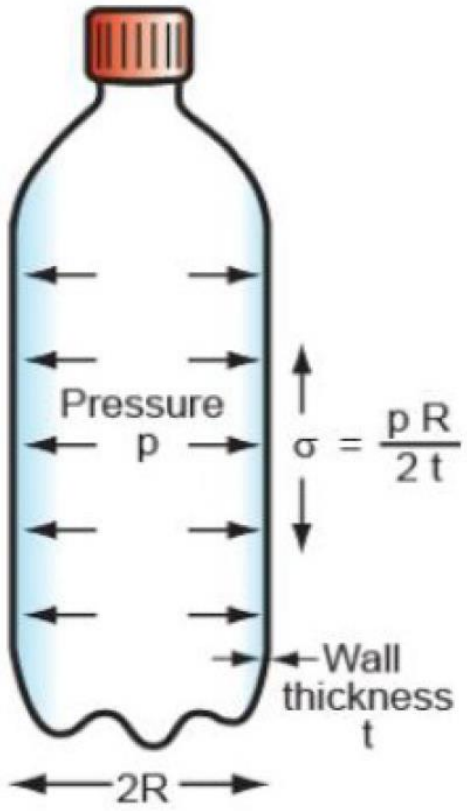
$$t \geq \frac{p \cdot R}{\sigma_f} = FS_t \cdot \frac{1}{\sigma_f}$$

Thickness *[factor of structure]*

Mass = m = t · Area · ρ **[ρ=density]**

$$m_{Area} = t \cdot \rho \geq FS_t \cdot \frac{1}{\sigma_f} \cdot \rho$$

Mass minimized by ↑ $I = \sigma_f / \rho$ *[materials selection index for mass]*



In general, mass mimimized by
↑ **$I = (\sigma_f)^n/\rho$** **[n≤1]**

Glass **not favoured** by:

- Extreme brittleness (=sensitivity to defects), implying **low max design stress σ_f**
- Not particularly low density

Current research: stronger glass objects, by control of defects upon molding
→ Reduced thickness
→ Reduced mass

Real embodied energy

Energy should take into account the amount of material needed

Another paradox: low nominal embodied energy, quite high absolute number

Overall energy per unit area [J/kg] Mass per unit area

$$H_{TOT} = H_m \cdot \rho \cdot t = FS \cdot \frac{H_m \cdot \rho}{\sigma_f} \quad [J]$$

Analogous trend for CO_2

In general, energy mimimized by

↑ $I' = (\sigma_f)^n/(\rho \cdot H_m)$ $[n \leq 1]$

[materials selection index for overall energy expense]

Recommendations:

- **Maximize strength, to minimize mass (=amount of material involved)**
- **Minimize embodied energy, by a more efficient recycling (=H_m* instead of H_m, when maximizing R & minimizing H_r)**

Treatment useful to **understand in full circular approaches**: having **a low H_m is meaningless if the strength is limited** [case of many natural-derived, renewable materials] – **Recycling is a real advantage if $H_m^*/H_m << 1$ and strength is preserved**

Mass of containers

Attention to combination of properties
Technology improvements

A lighter way to enjoy glass



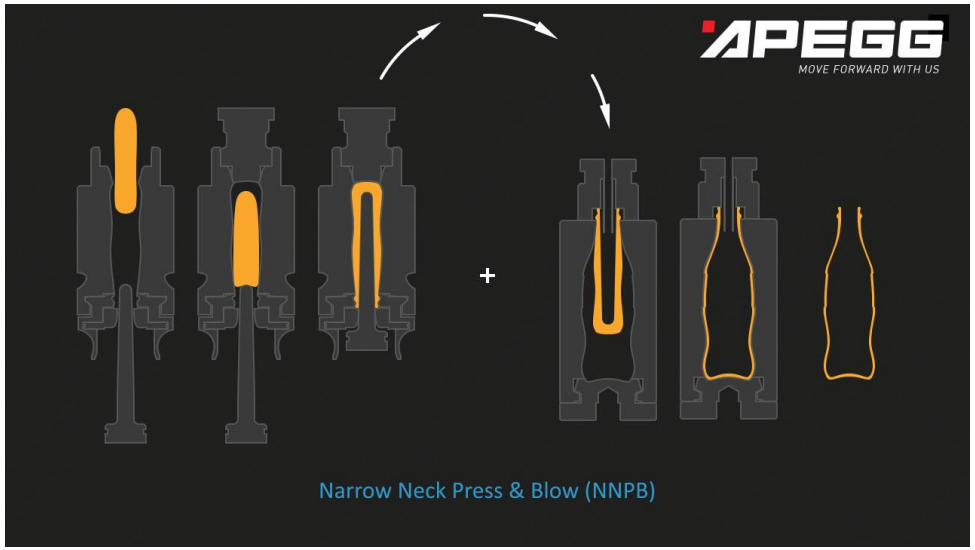
Clear weight reduction. Thanks to new manufacturing techniques, lightweight glass weighs significantly less:

	Conventional glass	Lightweight glass	Weight reduction
Beer bottle A, 330 ml	205 g	185 g	20 g
Beer bottle B, 330 ml	200 g	175 g	25 g
Beer bottle C, 330 ml	190 g	160 g	30 g
Wine bottle, 250 ml	204 g	180 g	24 g
Wine bottle, 750 ml	400 g	350 g	50 g
Wine bottle, 1000 ml	500 g	420 g	80 g
Glass jar, 720 ml	300 g	280 g	20 g
Spice jar, 99 ml	127 g	116 g	11 g
Glass jar, 3400 ml	1100 g	1050 g	50 g

vetropack

Mass of containers

Attention to combination of properties
Technology improvements



https://glassopenbook.com/services/id600005

Narrow-neck Press&Blow: actually close to the traditional process for containers with large neck

Production technology

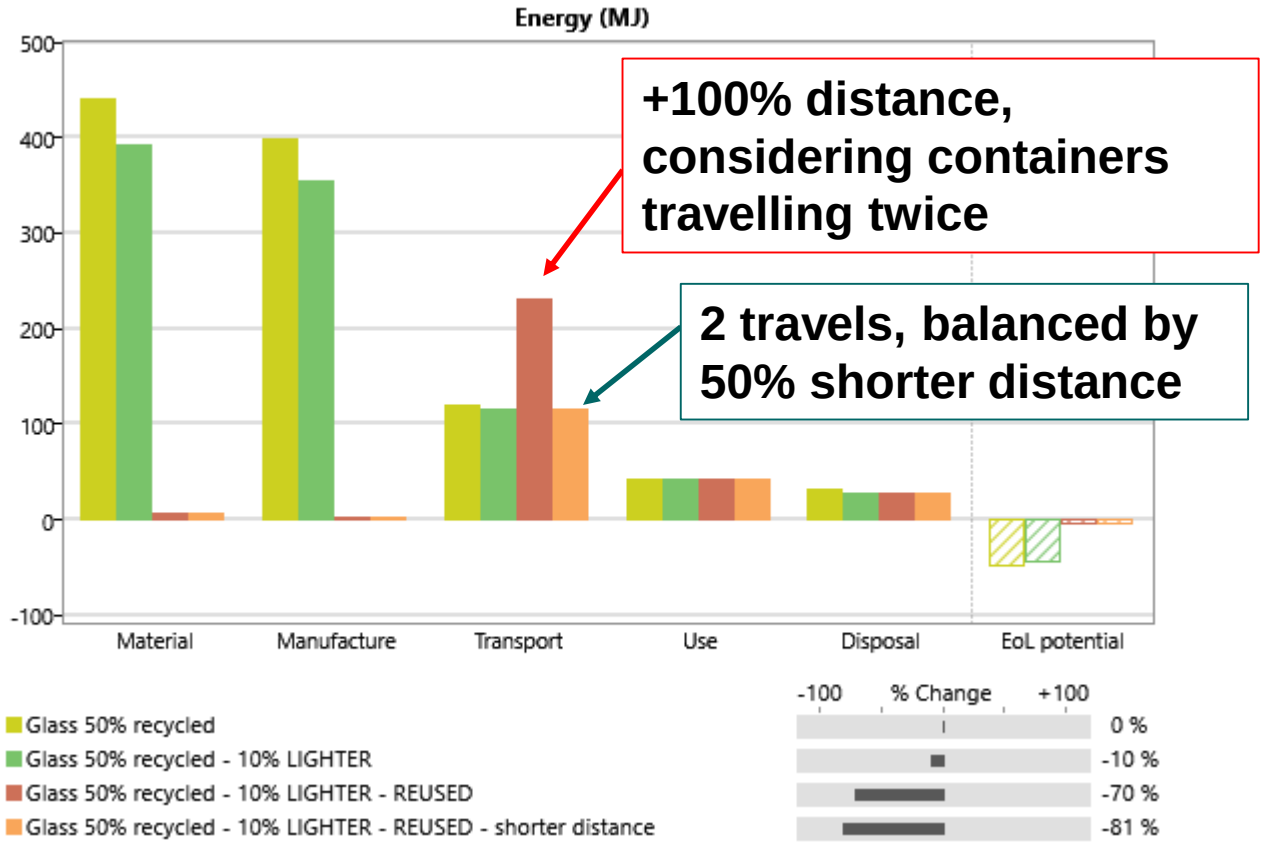
The manufacture of lightweight glass has been made possible by changes in the production process. Instead of the traditional blow-and-blow process, the narrow neck press and blow process is now used: to ensure that the thicknesses of the sides of a glass container are both as uniform as possible and at the same time thinner, a plunger is pressed into the liquid glass in the blank mould.



The narrow neck press and blow process (right) allows the production of both uniform and thinner glass containers.

Synergies for sustainability

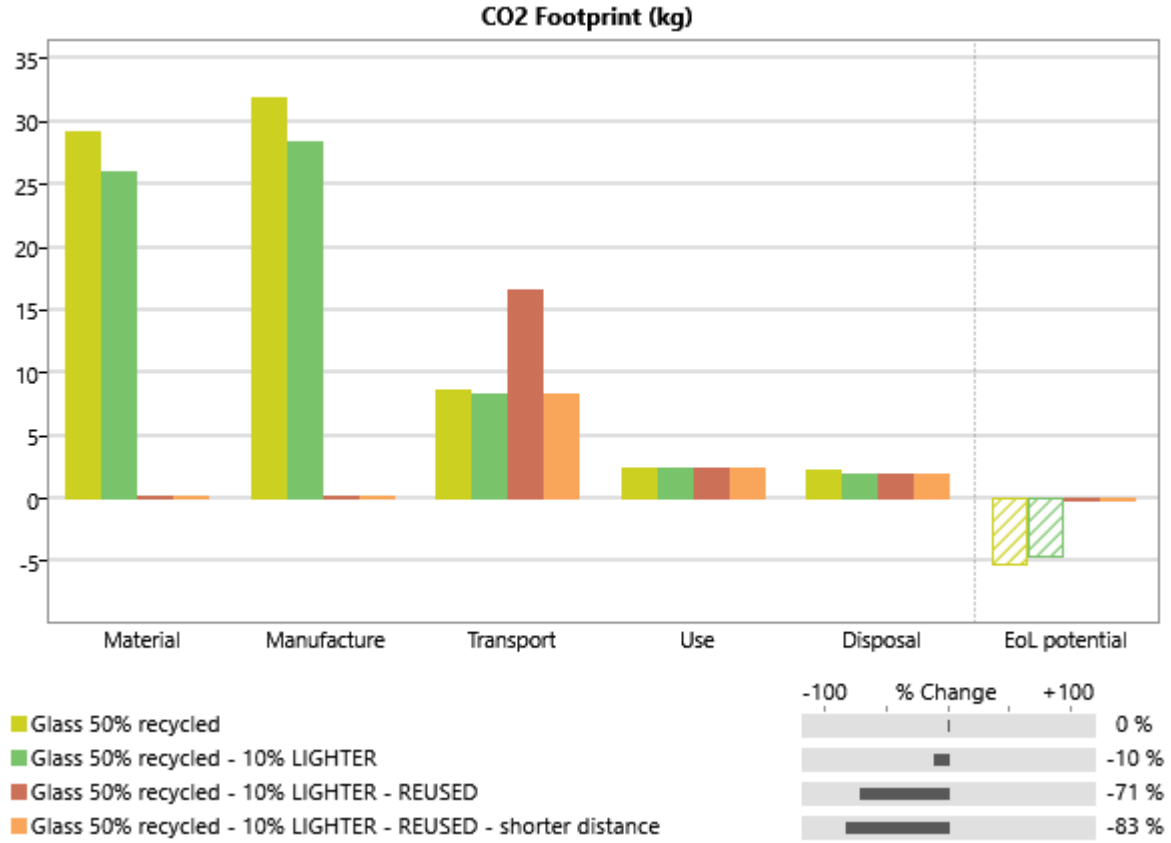
Let's go back to the concept of refilling
A single action is not enough



+100% distance, considering containers travelling twice

2 travels, balanced by 50% shorter distance

10% lighter bottles, 10% lower emissions and energy expenses



- **Reuse confirmed as very convenient: really big savings**

(to be encouraged: deposit refund policy)

- **Distances still having a big, surprising impact**

Recycling as remelting

Impact on energy and CO_2 emissions

Attention to «embodied energy» and «embodied CO_2»

Fundamental environmental burdens of production

- Embodied energy (H_m) = energy to be committed for the preparation of 1 kg (unit mass) of usable material
- Embodied CO_2 = carbon dioxide amount to be emitted for the preparation of 1 kg (unit mass) of usable material

En … dissipated e.g. in fumes escaping fro…

«H… …cessing conditions Ex…

- … combustion)
- … umes)

Em…

Mind the difficulty in coupling actions

- **Increasing R, risk of lower quality → weaker glass, more material needed**
- **Increasing the purity of recycled materials allows higher R, but enhances H_r**
- **Trade-off as current 'hot topic' for glass technologists**

R to be enhanced

H_r to be reduced

$$H_{m\ recycled} = H_m^* = H_m \cdot (1-R) + H_r \cdot R$$

Where R is the recycled fraction, H_r=embodied energy for material after recycling

Measures to enhance efficiency

First of all, glass is not a single material: sorting needed
Many glass compositions available: some examples

- **Nearly all of the commercial tonnage of glass consists of oxide compositions**
- **By far the largest percentage of these are silica-based**
- **This includes both commodity glass products as well as highly specialized applications of glass**
- **Soda-lime compositions dominant, but… i) not comprising all oxide glasses ii) having some variations depending on application**

Courtesy Prof. Paolo Colombo, University of Padova

Table 1-1: Commercial Glass Compositions (wt.% oxides)

<--- Oxide	Vitreous Silica	"Float" Window	Bottle or Container	Bulb & Tubing	Lime Tableware	T_2-Glass fiber "wool"	Laboratory Glassware Pyrex Type	Pharmaceutical container	Borosilicate Crown	Lead "Crystal"	Electronic Sealing	Glass Halogen Lamp	Liquid Crystal Display Sheet	Glass-Ceramic "Corningware"	E-Glass (fiber-reinforced plastics)	Optical Flint
SiO_2	100.0	73.0	74.0	73.6	74.0	59.0	81.0	72.0	69.6	59.6	3.0	60.0	59.2	69.7	53.2	49.8
Al_2O_3	..	0.1	2.0	1.0	0.5	4.5	2.0	5.0	..	..	11.0	14.3	16.7	17.8	14.5	0.1
B_2O_3	..	..	..	..	..	3.5	12.5	11.0	10.9	..	12.0	..	7.3	..	9.2	..
Li_2O	..	..	..	..	..	..	..	..	..	..	..	..	..	2.8	..	..
Na_2O	..	13.7	14.3	15.5	17.5	11.0	4.5	8.0	8.4	3.3	..	..	..	0.4	..	1.2
K_2O	..	0.1	0.6	0.6	..	0.5	..	1.0	8.4	10.9	..	Tr	..	0.2	1.0	8.2
MgO	..	3.8	3.7	3.6	..	5.5	..	..	..	..	..	..	1.0	2.6	4.4	..
CaO	..	8.8	5.4	5.2	7.5	16.0	..	1.0	..	1.3	..	7.0	4.0	..	17.4	..
SrO	..	..	..	..	..	..	..	..	..	..	..	..	1.8	..	..	..
BaO	..	..	..	..	..	..	..	2.0	2.5	..	..	18.3	9.6	..	..	13.4
ZnO	..	..	..	..	..	..	..	..	..	..	..	..	..	1.0	..	8.0
PbO	..	..	..	..	..	..	..	..	..	24.4	74.0	..	..	..	..	18.7
TiO_2	..	..	..	..	..	..	..	..	..	..	..	..	..	4.7	..	..
ZrO_2	..	..	..	..	..	..	..	..	..	..	..	..	..	0.1	..	..
As_2O_5	..	..	Tr	Tr	..	..	..	..	0.3	0.5	..	..	0.4	0.6	..	0.5
SO_3	..	0.5	Tr	0.5	0.5	..	..	..	..	..	..	0.3	..	..	..	..

Measures to enhance efficiency

First of all, glass is not a single material: sorting needed
Many glass compositions available: some examples

- **The compositions of ancient glasses are not very different from those of modern glasses**
- **Limitations in the purity → unwanted colors**
- **There have been several factors that have contributed to the development of the composition of glass, including trade policies, taxes, availability of raw materials**

Glass Compositions

Glass[†]	Oxide content (wt%)							
	SiO_2	B_2O_3	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3
(1) Egypt, 1500 BC[‡]	67.8		16.08	2.08	3.8	2.89	3.22	0.92
(2) Palestine, 4th Century	70.5		15.7	0.8	8.7	0.6	2.7	0.4
(3) Sudan, 3rd century	64.2		15.9	2.65	10.2	2.73	2.06	2.3
(4) Italy, 9th–10th centuries	77.8		6.4	8.7	2.1	0.7	2.2	0.8
(5) Container glass, 1980	73.0		13.7	0.4	10.6	0.3	1.8	
(6) 1:1:6 soda–lime–silica	75.3		13.0		11.7			
(7) Faraday ''heavy glass''[‡]	10.6	15.6						
(8) ''Jena Standard Glass''[‡]	67.2	2.0	14.0		7.0		2.5	
(9) Schott thermometer glass	72.0	12.0	11.0				5.0	
(10) Schott utensil glass	73.7	6.2	6.6			5.5	3.3	
(11) Schott Welsbach chimney[‡]	75.8	15.2	4.0					
(12) Nonex[‡]	73.0	16.5	4.25					
(13) Pyrex	80.5	12.9	3.8	0.4			2.2	
(14) E-glass, typical	54.0	10.0			17.5	4.5	14.0	

[†](1) Morey,[5] Table I-1 (10); (2) Brill,[20] Jalame glass, (low potassium, high sodium); (3) Brill,[21a] Sedeinga tomb glass, (high potassium, high magnesium); (4) Brill,[21b] Frattesina glass, (mixed alkali); (5) Ryder and Poole[43]; (6) by calculation; (7) Faraday;[37] (8) Hovestadt,[40] Jena glass 16^{III}, 1884; (9) Hovestadt,[40] p. 246, Jena glass 59^{III}, 1889, ''ideal thermometer glass''; (10) Steiner,[42] p. 172, Jena glass 202^{III}, 1893, recalculated from batch; (11) Steiner,[42] p. 172, Auer von Welsbach gas light chimney, Jena glass 276^{III}, 1895, recalculated from batch; (12) Corning code 7720; (13) Corning code 7740, Morey;[5] (14) Aubourg and Wolf,[46] typical composition, can vary, depending upon manufacturer and materials. [‡]Glass contains other oxides: (1) 0.54% Mn_2O_3, 1.51% CuO, and 1.0% SO_3; (7) 70% PbO; (8) 7.0% ZnO; (11) 4.0% Sb_2O_3 and 0.9% As_2O_3; (12) 6.25% PbO.

Courtesy Prof. Paolo Colombo, University of Padova

Measures to enhance efficiency

First of all, glass is not a single material: sorting needed

Many glass compositions available: some examples

Modo di fare la fritta di Cristallo, altrimenti detto bollito. **Cap. II.**

Quando si vuole fare un cristallo bello, e di tutta perfettione, veggasi di havere Tarso bianchissimo. A Murano usano quocoli del Tesino, pietra abbondante nel fiume Tesino. Il tarso adunque è una specie di marmo duro e bianchissimo che in Toscana fa a piè della Verucola di Pisa, a Seraveza, e a Massa di Carrara, e in nel fiume Arno sopra, e sotto Firenze, e in altri luoghi ancora è pietra assai nota e conosciuta, si avverta di havere di quella sorte di Tarso, che è bianchissimo, che non habbia vene nere, ne giallognole in forma di ruggine, ma che sia candido e puro. Avvertendo che ogni pietra che con l'acciaiolo, o vero fucile, fa fuoco, e atta a vetrificare e a fare il vetro e cristallo e tutte quelle pietre che non fanno fuoco con acciaiolo, o fucile come sopra non vetrificano mai; il che serva per avviso per poter conoscere le pietre che possono trasmutarsi in vetro da quelle che non si possono trasmutare.

Antonio Neri. L'arte vetraria (1612)

DELL'ARTE
VETRARIA
DI PRETE ANTONIO NERI
LIBRO PRIMO.

A cauar il ſale del Poluerino Rocchetta, e Soda, con il quale ſi fà la fritta del Criſtallo, detto Bollito, fondamento dell'Arte Vetraria, con vn nuouo, e ſecreto modo. Cap. I.

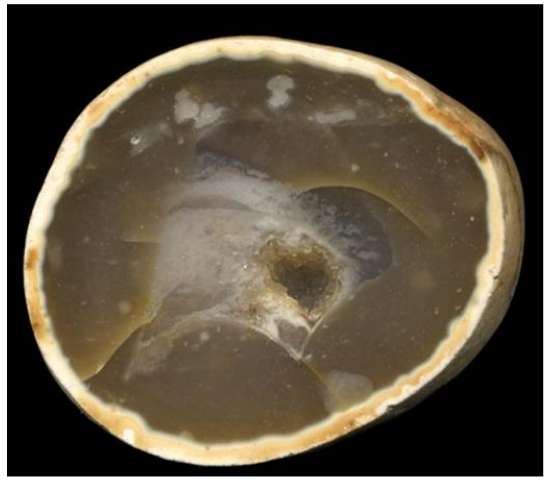
IL Poluerino, ò Roc chetta, che viene di Leuante, e Soria, è cenere di certa erba che quiui è abbondante: non è dubbio alcuno, che fà il Sale più bianco aſſai, che non fà la Soda di Spagna, e però quãdo ſi vuol fare vn chriſtallo di tutta perfettione, e bellezza ſi faccia con il ſale cauato dal Poluerino, ò Rocchetta di Leuante; perche la Soda di Spagna, come più graſſa, ſe bene dà più ſali, tutta via il Criſtallo fatto con il ſuo ſale ſempre

THE
Art of Glaſs,
WHEREIN
Are ſhown the wayes to make and colour Glaſs, Paſtes, Enamels, Lakes, and other Curioſities.

Written in *Italian* by *Antonio Neri*, and Tranſlated into *Engliſh*, with ſome Obſervations on the Author.

Whereunto is added an account of the Glaſs Drops, made by the Royal Society, meeting at *Greſham College*.

English translation (1662)



Flint nodule

	Egyptian 15th Cent. BC	Roman 1st Cent. AD	European 13th Cent. AD	Syrian 14th Cent. AD	Modern
Silica, SiO_2	65	68	53	70	73
Soda, Na_2O	20	16	3	12	16
Potash, K_2O	2	0.5	17	2	0.5
Lime, CaO	4	8	12	10	5
Magnesia, MgO	4	0.5	7	3	3
Batch Materials	plant ash quartz	natron sand	wood ash sand/quartz	plant ash sand/quartz	synthetic components

Courtesy
Prof. Paolo Colombo,
University of Padova

Measures to enhance efficiency

Hidden list of operations
Issue of waste collection systems



Collection in containers



Manual control



Crushing and sieving



Removal of ferrous metals



Removal of ceramics and stones



Removal with vacuum (paper)



Removal of non ferrous metals

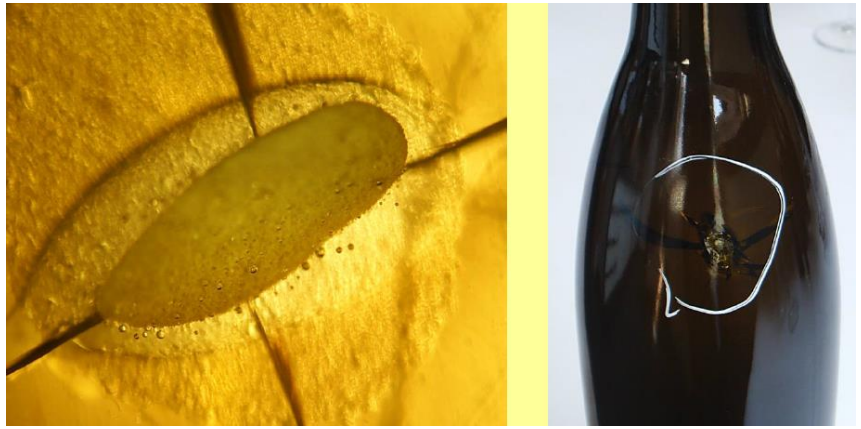


Removal of ceramics and stones



Final manual control

Crushed glass = cullet
Not actually 'for free' raw material: all operations express embodied energy/CO_2



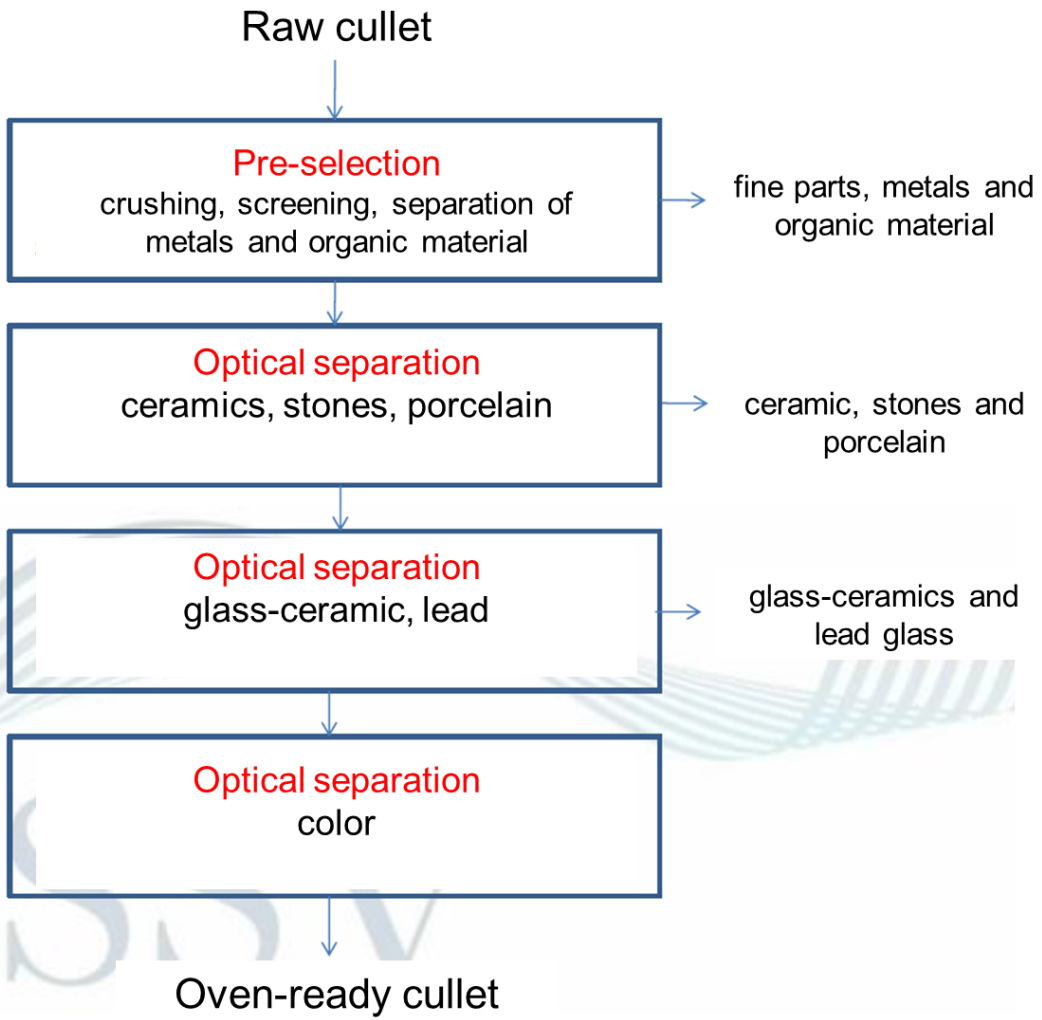
Examples of 'stones' (ceramic parts, not solubilized upon remelting)

Courtesy
Prof. Paolo Colombo,
University of Padova

Separation from heterogeneities

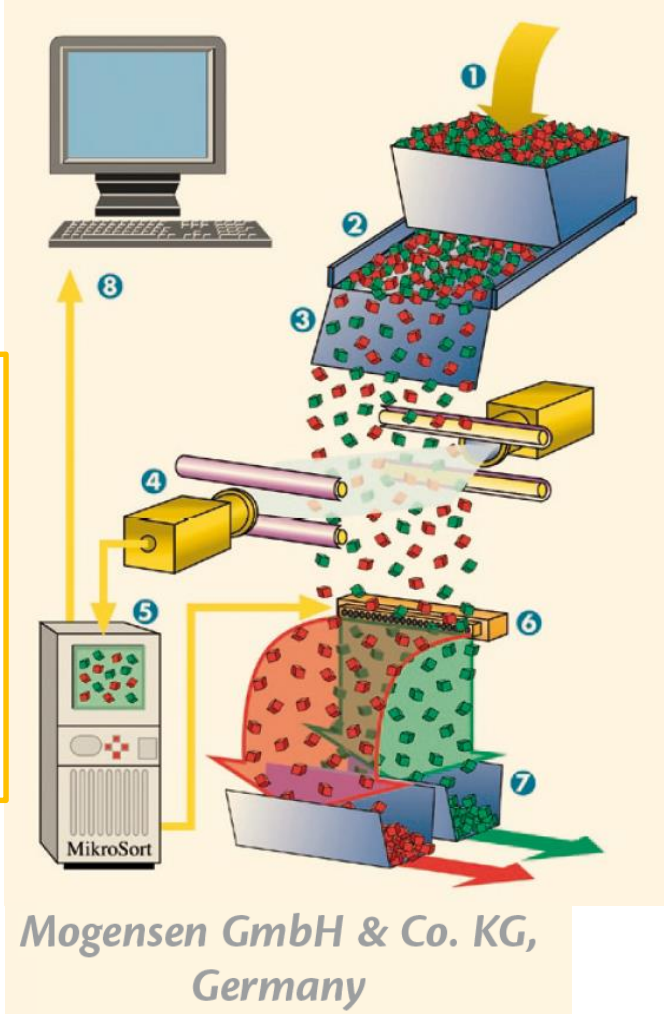
Classical solutions, to eliminate metal and polymer contaminations
Separation of ceramic inclusions more challenging

TREATMENT PLANT



Metals separated by means of magnets/eddy currents

Basic optical selection
Visible light
Selection by colour or transparency /opacity

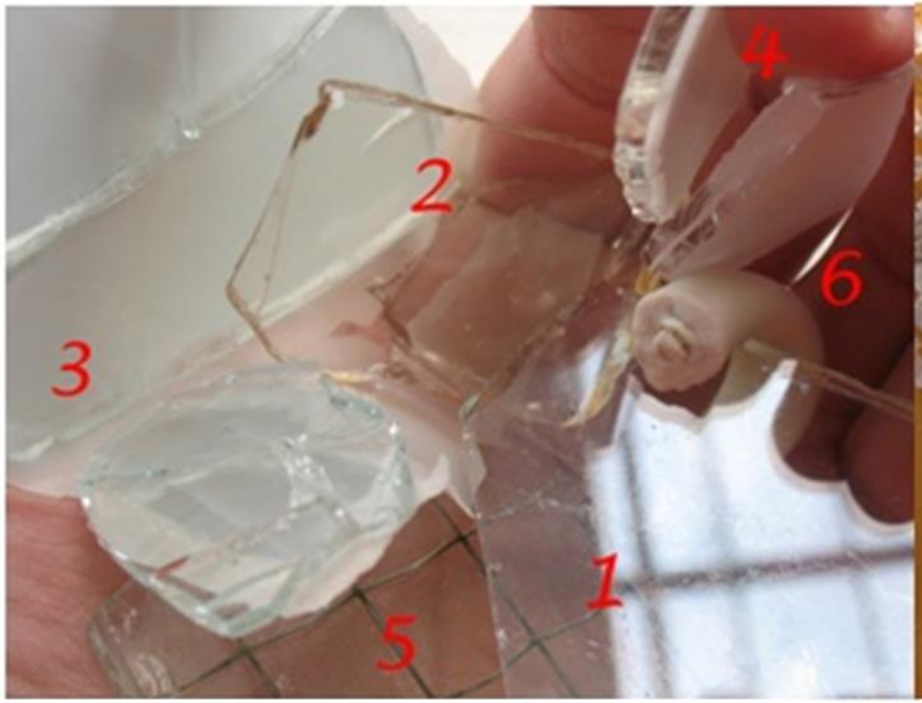


Courtesy
Stazione Sperimentale del Vetro, Venice
Prof. Paolo Colombo, University of Padova

https://www.allgaier-process-technology.com/en/Company/Brands/Mogensen/

Difficulties in colour sorting

Colourless glasses of dramatically different compositions
Some contaminations are particularly undesirable (e.g. PbO)



Comparison between glass and ceramic

1) Float glass panel
2) Glass-ceramic
3) Laminated glass
4) Opal glass
5) Wired glass
6) Ceramic cup handle



Ground flat glass

Courtesy
Prof. Paolo Colombo,
University of Padova



Crystal glass

'White' glass does not correspond to a specific composition

'Crystal glass' = 'dangerous' for its PbO content
Presence of lead glass in waste is still high
→ continuous increase of Pb content in manufactured glass
→ issue for export (EU lead % accepted < 200 ppm; USA < 100 ppm) → wine export issues

Compositional sorting

Acceptance of material within quite strict compositional ranges
Enabled separation from ceramics and 'not desired' glasses

A glass may be identified and separated from other waste according to specific emissions

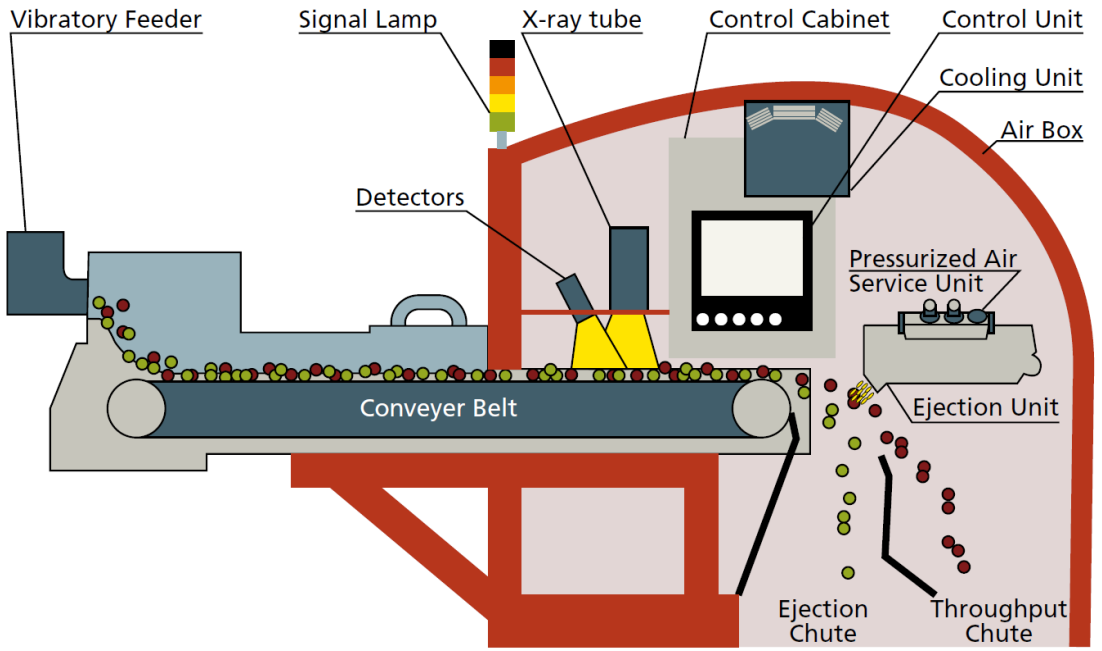
E.g. Soda-lime may be detected from intensity (absolute and relative) of signals from Si, Na and Ca

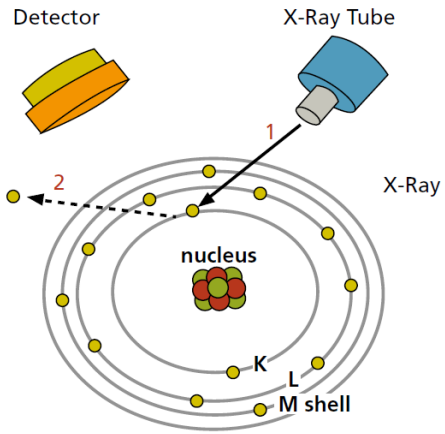
11	22.99
Na	0.97
Sodium	
Kα	1.040

20	40.08
Ca	1.54
Calcium	
Kα	3.692
Lα	0.341

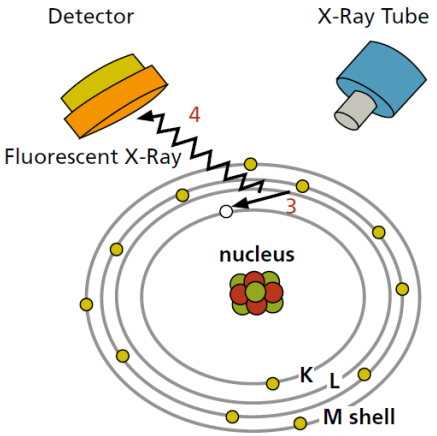
14	28.09
Si	2.33
Silicon	
Kα	1.740







Excitation



X-Ray emission

Successful application to the removal of lead glass and glass-ceramics
It should be extended

https://redwave.com
https://www.bruker.com

Compositional sorting

Acceptance of material within quite strict compositional ranges
Enabled separation from ceramics and 'not desired' glasses

REDWAVE sorting machines for glass sorting

Redwave (Graz, Austria)
https://redwave.com

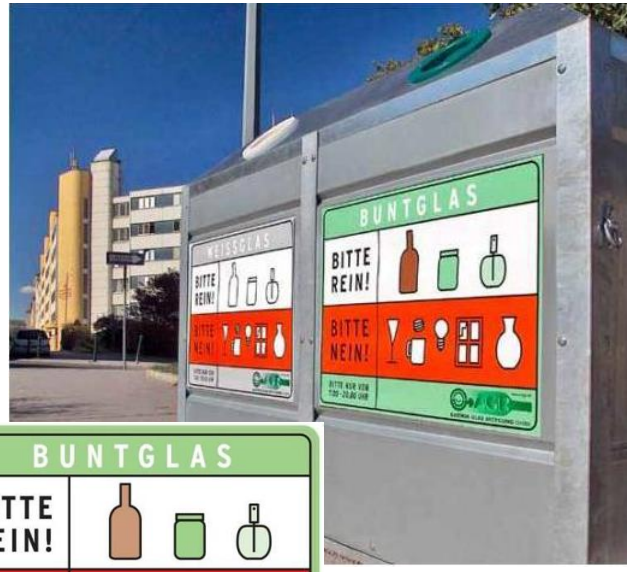
Sorting task	Technology	Model
Deposition of		
> Ceramics, stones, porcelain (KSP)	Camera with transmitted light	REDWAVE CX / CXF / CXP
> Metal (iron and non-ferrous)	All metal sensor	REDWAVE +/M
> Lead glass	X-ray fluorescence	REDWAVE XRF-G
> Glass ceramic	X-ray fluorescence	REDWAVE XRF-G
> Plastics, acrylic glass, laminated glass	Near infrared spectroscopy	REDWAVE NIR
> Color sorting	Camera with transmitted light	REDWAVE CX / CXF /CXP
Other sorting tasks		
Processing of picture tube glass	X-ray fluorescence	REDWAVE XRF-G
Monitoring of the incoming material and / or quality control of the finished product	Sample Analysing System	REDWAVE *mate*

Good practices

Separation promoted directly by customers
Simplification of overall chain (lower costs), with difficulties









Big problem: glass type not marked on products as in the case of polymer families









Observation: what about 'not accepted' glass?

Source: Report (2012)

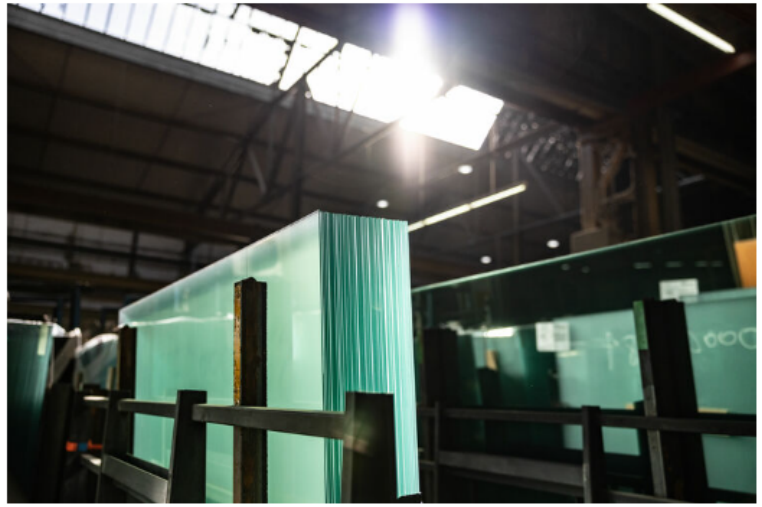
ACR+

FEVE
The European Container Glass Federation

Good practices
Focus on the same article
Enhanced control of chemistry

04/25/22 | Ingolstadt | Company

Pilot project started: Faulty car glass to be turned into new windowpanes for the Audi Q4 e-tron



- One-year pilot operation of glass recycling: joint project between Audi, Reiling, Saint-Gobain Glass, and Saint-Gobain Sekurit started in January
- Feasibility of a glass cycle for car windows: research on recycling methods, quality, and process reliability
- Recycled plate glass is intended to be used for car windows in the Audi Q4 e-tron series

Download PDF (159 KB) Facebook Twitter LinkedIn

Faulty car windows often go in the recycling bin when the cracked part cannot be fixed. A closed material circuit does not yet exist for damaged car glass. This is where Audi and its partner companies Reiling Glas Recycling, Saint-Gobain Glass, and Saint-Gobain Sekurit are now doing pioneering work as part of a joint pilot project. The partner companies want to turn the damaged auto glass into recyclable material for model production and have drawn up a multi-stage process for that purpose: using an innovative recycling process, the car windows are first broken into small pieces. Then all the non-glass impurities like glue residue are eliminated. The resulting glass granulate is melted down and turned into new plate glass. That plate glass is then turned into a new car window. If this pilot is successful, the windows that are produced this way will be used in models in the Audi Q4 e-tron series in the future.

https://www.audi-mediacenter.com/en/press-releases/pilot-project-started-faulty-car-glass-to-be-turned-into-new-windowpanes-for-the-audi-q4-e-tron-14618

Interesting approach

Old automotive glass → New automotive glass

Composition of glass kept constant

Challenges remain in the separation of glass from polymer sheets, in windshields (laminated glass)

Good for clear glass parts, serigraphed parts (dark) nearly unrecyclable [glass enamel on base glass]



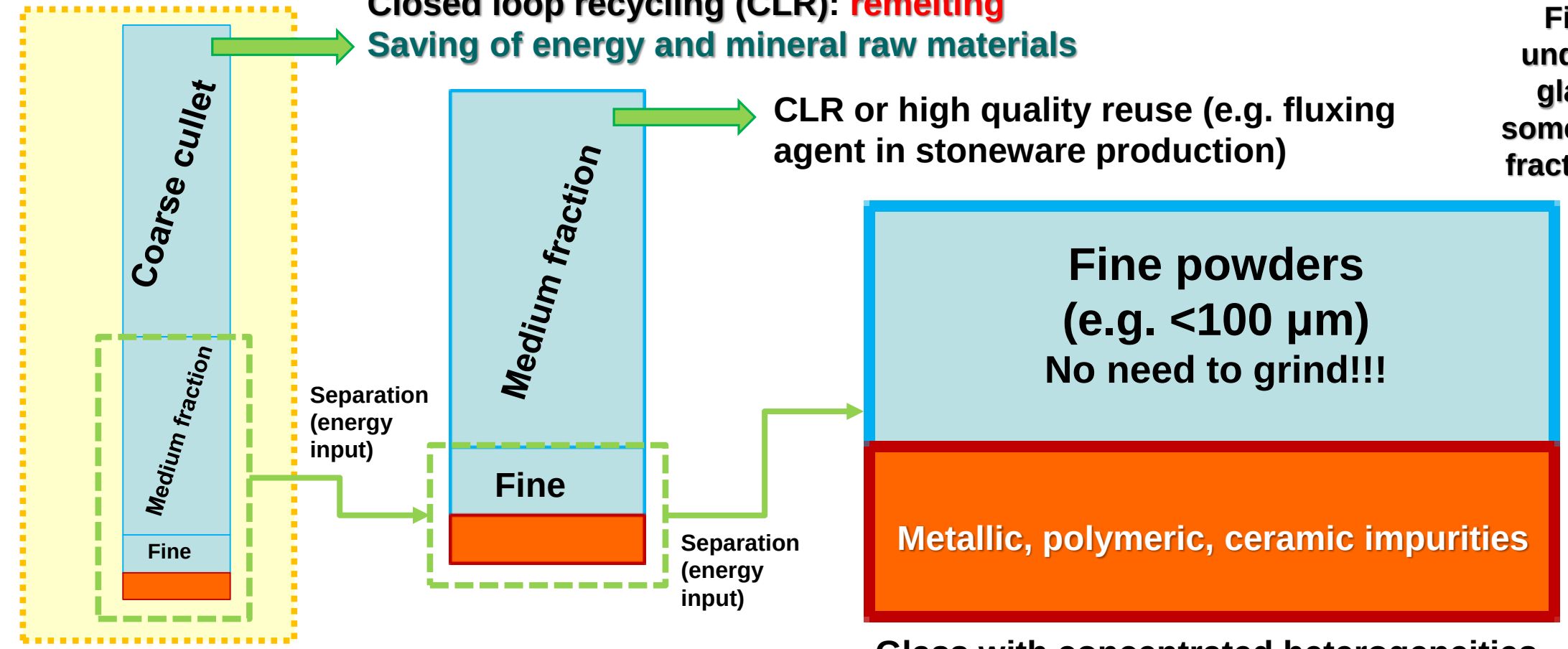
https://www.dealerautoglassaz.net/auto-glass-phoenix-blog/every-wonder-what-windshields-are-made-of/

Remaining issues in recycling any glass

Crushing of articles as starting point

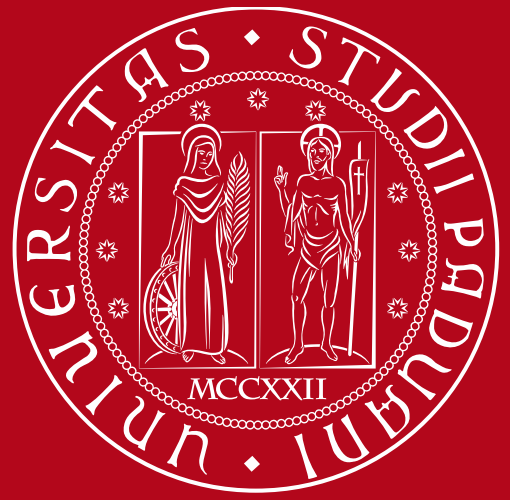
Even if the composition is uniform, no 100% recycling

Recycling of 'non-sodalime' glass: an open issue



1222 • 2022

800 ANNI



Università degli Studi di Padova

Enhanced glass recycling: key facts

Open Loop Recycling as further option
Definition of glass-based construction materials

- **Strict recycling means remelting for regeneration of original articles**, with the same quality standards [Closed Loop Recycling]
- **Open loop recycling (OLR) involves any operation in which 'recovered' glass is part of the raw materials** → new products, of different value
- OLR comprises technologies in which glass is a minor component (e.g. additive in formulation of traditional ceramics)
- Challenge of **upcycling**: **definition of products of high economic value comprising the maximum amount of recovered glass**
- **Foams** as fundamental benchmark as construction materials: 1. active in thermal and acoustic insulation; 2. highly durable (not combustible!); 3. maximizing the content of glass
- Room for optimization: i) process with low sensitivity to impurities (e.g. involving fractions not used in other recycling operations); ii) reduction of **materials** (=additives) and **energy** (=firing) inputs
- Alternative inspiration: **Geopolymers** (=**'unfired' ceramics**)→room for glass

Waste glass

Any discarded fraction rich in glass
Reuse as 'historical' mission of the group

ELSEVIER
Available online at www.sciencedirect.com
SCIENCE DIRECT®
Current Opinion in Solid State and Materials Science 7 (2003) 225–239
Current Opinion in Solid State & Materials Science

Discarded fractions: important forms of inorganic waste

Inertization and reuse of waste materials by vitrification and fabrication of glass-based products

P. Colombo [a,b,*], G. Brusatin [c], E. Bernardo [c], G. Scarinci [c]

[a] Department of Materials Science and Applied Chemistry, University of Bologna, viale Risorgimento 2, 40136 Bologna, Italy
[b] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16801, USA
[c] Department of Mechanical Engineering, Materials Sector, University of Padova, via Marzolo 9, 35131 Padova, Italy

Received 6 June 2003; accepted 11 August 2003

Abstract

Vitrification is widely accepted as the most safe process for treating hazardous wastes and converting them into leach-resistant materials. In this paper a review of the current and emerging waste vitrification technologies is reported. Analysis of different methods of vitrification, according to physical state and composition of the waste, can offer a guideline for process selection. Moreover, the most recent studies on vitrification of various types of industrial and civil wastes and their further transformation in useful marketable products are presented and discussed.
© 2003 Elsevier Ltd. All rights reserved.

Attention to definition of 'glass-based' (=enjoying key features of glass nature)

Big differences among products, in terms of degree of exploitation

1. **Products with glass as supplementary component**
   - ***Flux*** **in stoneware production (10wt%)**
   - ***Supplementary cementitious component*** **(pozzolanic material, see SiO_2) [saving cement, not replacing it!]**

Interesting for the huge production volumes

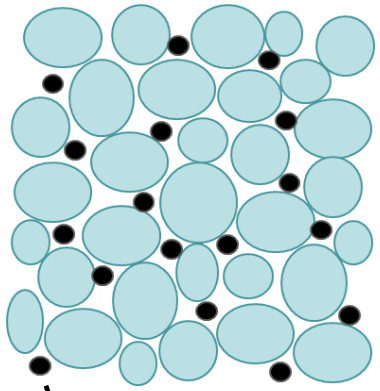
2. Products almost entirely based on glass

Case study: glass foams

Fundamental examples of sintering of glass (no remelting)

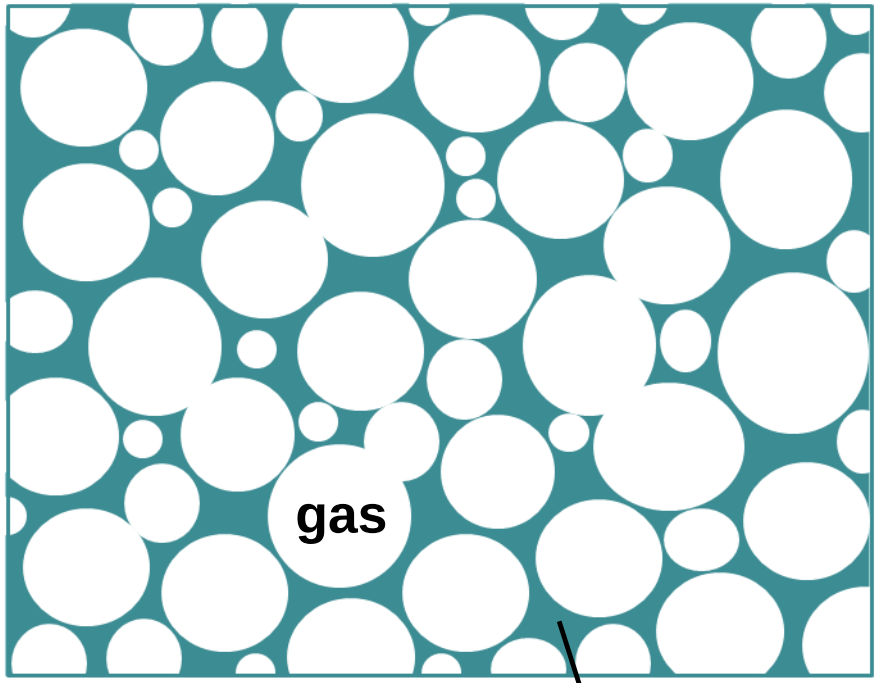
Exploiting glass softening

Mix of fine glass particles and foaming agent



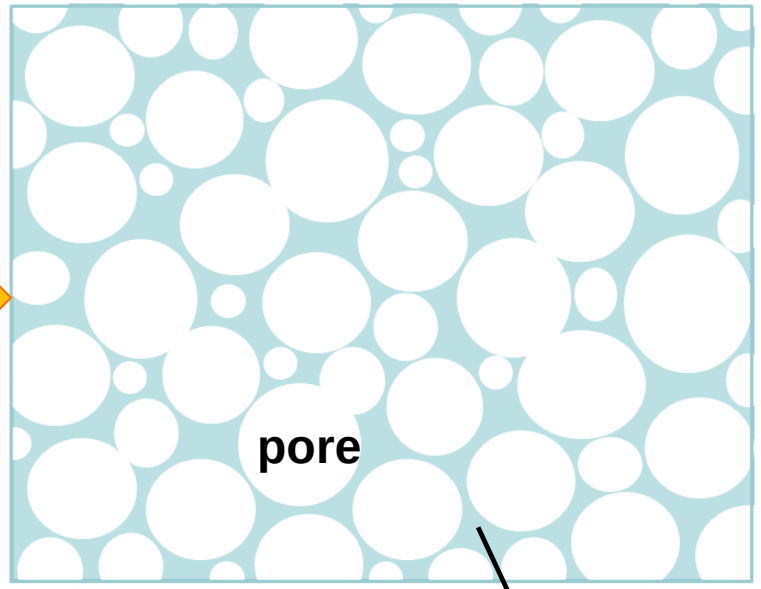
Additive releasing gas according to decomposition or oxidation reactions

Sintering @ 850-950 °C



Mass of softened glass
(High viscosity liquid)

Back to RT



Matrix of solid glass

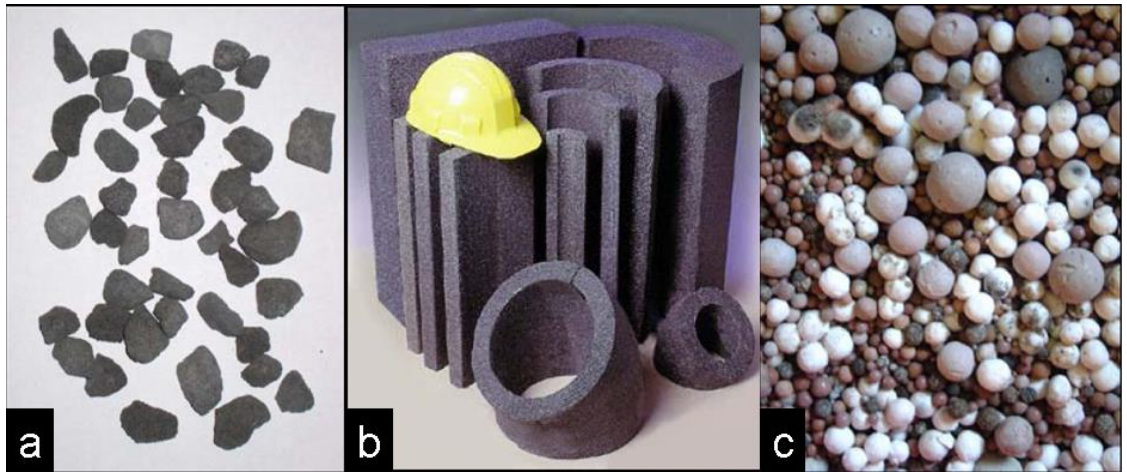
Glass foam (cellular glass)

Glass recycling key facts

Closed Loop Recycling vs. Open Loop Recycling
Definition of glass-based construction materials

- **High porosity (>>80%)**, mostly closed pores separated by thin walls
- Lightweight material (ρ=**0.13-0.30 g/cm^3**), but quite strong **(crushing strength>1 MPa)** and thermally insulating (λ**<0.1 W/mK**);
- **Fireproof (and generally very stable, chemically)** – no gas release, no decay of mechanical properties in case of fire (e.g. WW II, used in ships and submarines)
- Produced in loose blocks (20-25 mm), **panels**, or pellets (10-15 mm).

From: J. Hurley, Glass research and development final report: a UK market survey for foam glass. (WRAP, The Waste and Resources Action Programme, 2003)



Please visit https://www.foamglas.com





Glass recycling key facts

Closed Loop Recycling vs. Open Loop Recycling
Definition of glass-based construction materials

Scarinci, G., Brusatin, G. and Bernardo, E. (2005) Glass Foams, in Cellular Ceramics: Structure, Manufacturing, Properties and Applications (eds M. Scheffler and P. Colombo), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG. doi: 10.1002/3527606696.ch2g

Table 2 Typical properties of commercial glass foam products

http://onlinelibrary.wiley.com/doi/10.1002/3527606696.ch2g/summary

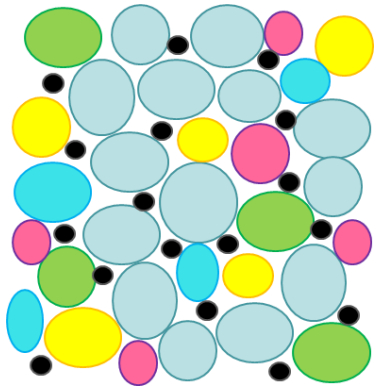
Density	0.1–0.3 g cm^{-3}
Porosity	85–95 %
Crushing strength	0.4–6 MPa
Flexural strength	0.3–1 MPa
Flexural modulus of elasticity	0.6–1.5 GPa
Coefficient of thermal expansion	8.9×10^{-6} K^{-1}
Thermal conductivity	0.04–0.08 W m^{-1} K^{-1}
Specific heat	0.84 kJ kg^{-1} K^{-1}
Thermal diffusivity at 0 °C	$(3.5–4.9) \times 10^{-7}$ m^2 s^{-1}
Sound transmission loss at normal frequency	28 dB/100 mm

Case study: glass foams

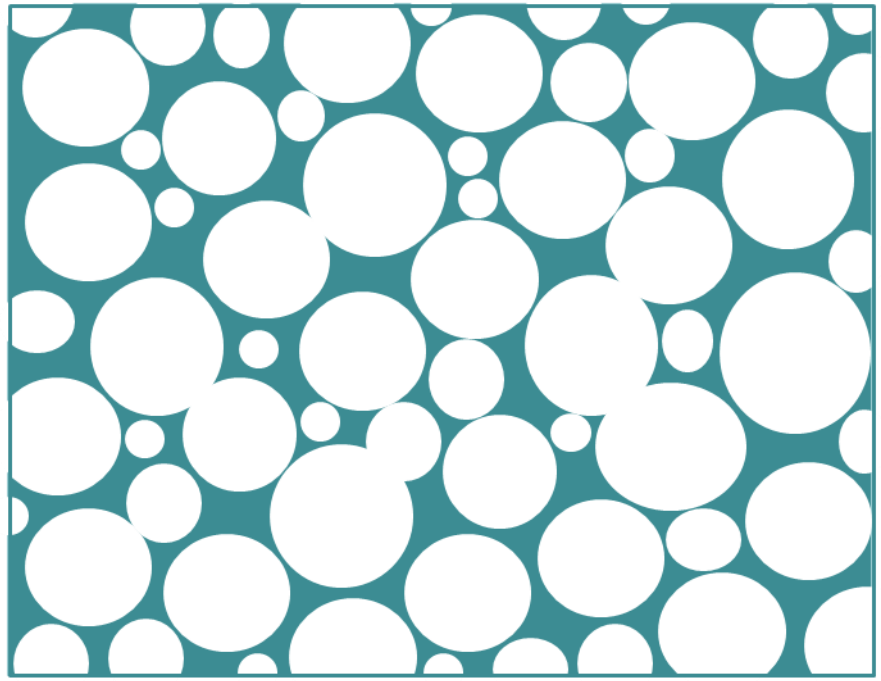
Fundamental examples of sintering of glass (no remelting)

Trying with glass mixtures…

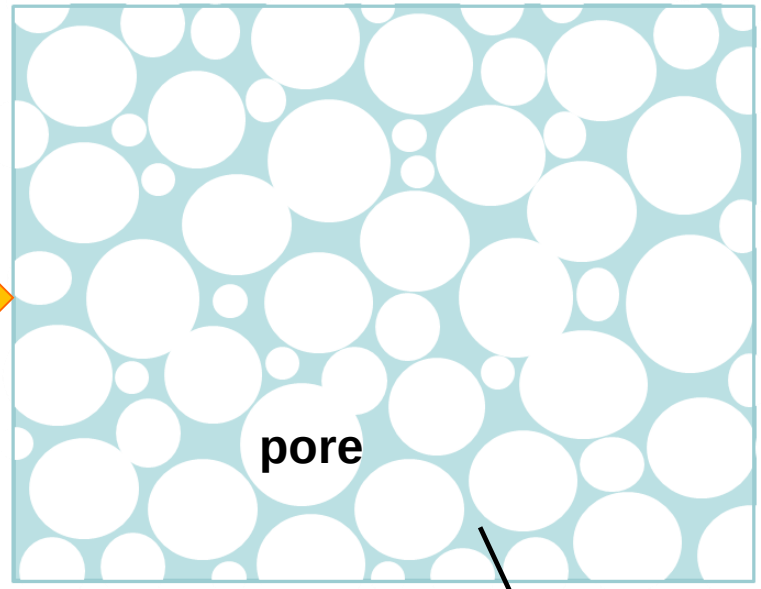
Sintering @ 850-950 °C



Mixed glass and
foaming agent



Back to RT



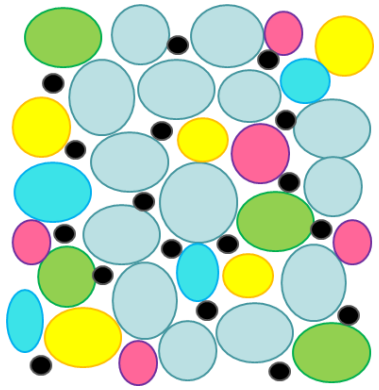
Matrix of solid glass

Glass foam
(cellular glass)

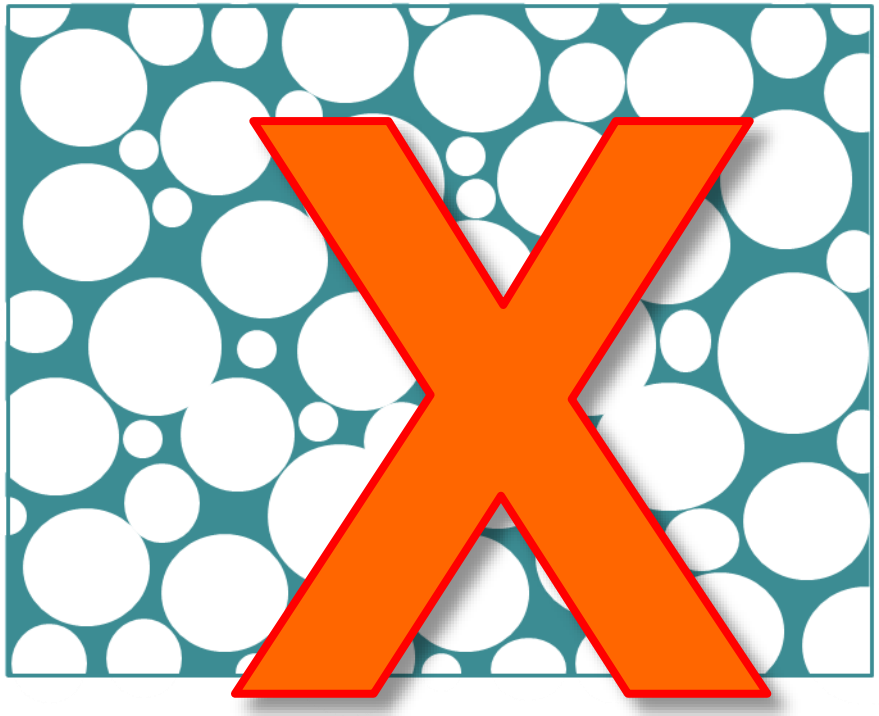
Case study: glass foams

Fundamental examples of sintering of glass (no remelting)
Trying with glass mixtures…very challenging

Sintering @ 850-950 °C



Mixed glass and foaming agent



Problem of homogeneity



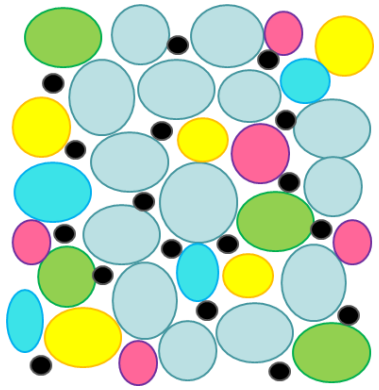


Cooperation wit Sasil, Biella, Italy (2018-19)

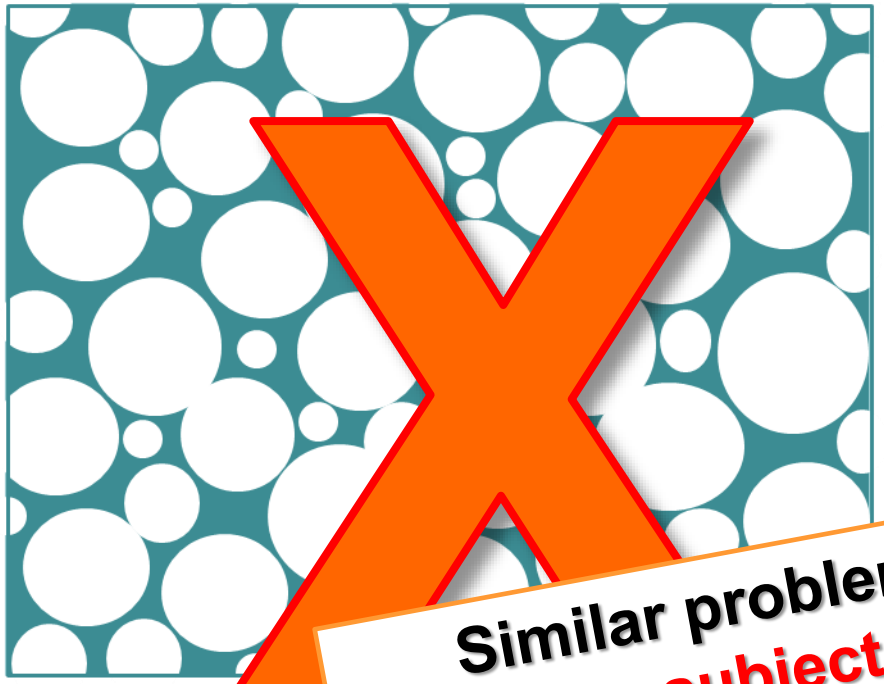
Case study: glass foams

Fundamental examples of sintering of glass (no remelting)
Trying with glass mixtures…very challengin

Sintering @ 850-950 °C



Mixed glass and
foaming agent







Problem

Similar problems with single glasses, subject to crystallization (sinter-crystallization)

Cooperation wit Sasil, Biella, Italy (2018-19)

Alternative approach: non-fired products

Geopolymers from extensive use of glass

Collaboration with Prof. A.R. Boccaccini (University of Erlangen, Germany)

Key points of Geopolymers

- Condensation of **alumino-silicate hydrated 'oligomers'** [poly-sialates]
- Oligomers from **alkali activation of alumino-silicate compounds** [dissolution in alkali or alkali-silicate aq. solutions]
- Stable structures [e.g. resisting boiling tests] for (amorphous or semi-crystalline) **zeolite-like structures**: [SiO_4] tetraedra mixed with [AlO_4] tetrahedra
- **[AlO_4] tetrahedra stabilized by alkali ions**

Construction and Building Materials 188 (2018) 1077–1084

Contents lists available at ScienceDirect

Construction and Building Materials

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

Extensive reuse of soda-lime waste glass in fly ash-based geopolymers

N. Toniolo [a], A. Rincón [b], J.A. Roether [c], P. Ercole [d], E. Bernardo [b,*], A.R. Boccaccini [a,*]

[a] Institute of Biomaterials, Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Cauerstraße 6, 91058 Erlangen, Germany
[b] Department of Industrial Engineering, University of Padova, Via Marzolo 9, Italy
[c] Institute of Polymer Materials, University of Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany
[d] Sasil S.p.a, Regione Dosso, 13862 Brusnengo, BI, Italy

Research carried out in the framework of European Community's H2020 MSCA-ITN 'CoACH-ETN', g.a. #642557
http://www.coach-etn.eu/

European Training Network

Chemical composition of raw materials (wt%) determined by XRF.

wt%	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3	TiO_2
FA	54.36	24.84	0.83	3.03	2.56	2.06	8.28	1.07
SLG	70.5	3.2	12	1	10	2.3	0.42	0.07

Idea: Avoiding alkali silicates

- **Useful in enhancing the SiO_2/Al_2O_3 ratio**
- **Expensive**, since they imply a preliminary **melting stage (and dissolution → 'water glass')**

First attempts to non-fired products

Geopolymers from extensive use of glass

Collaboration with Prof. A.R. Boccaccini (University of Erlangen, Germany)

Stabilization of heavy metals

Element (ppm)	As	Cd	Cr	Cu	Mo	Pb	Se	Zn
6S5M	0.174	0.007	0.0251	0.11	0.363	0.1	0.038	<0.203
6S8M	0.134	0.004	0.0101	0.115	0.143	0.078	0.048	<0.203
FA	<0.049	<0.002	0.467	0.028	0.898	<0.047	0.022	<0.2
SLG	<0.049	0.001	0.043	0.036	0.007	0.018	0.018	0.088
Inert material	0.5	0.04	0.5	2	0.5	0.5	0.1	4
Non-hazardous material	2	1	10	50	10	10	0.5	50

Mixtures designed to lead to:

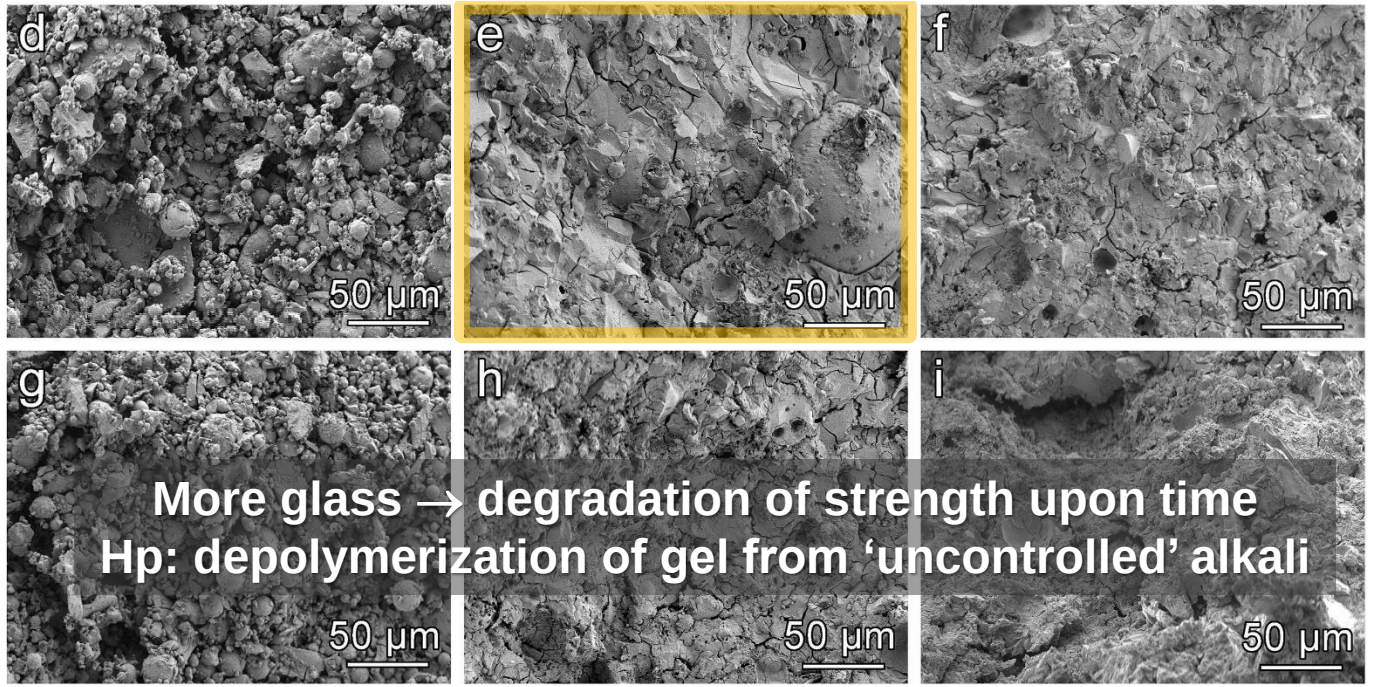
SiO_2/Al_2O_3 = 5 → FA/SLG = 76/24

SiO_2/Al_2O_3 = 6 → FA/SLG = 64/36

SiO_2/Al_2O_3 = 7 → FA/SLG = 54/46

Best: evidence of reaction, higher compaction (density 1.93 ± 0.01 g/cm³, porosity 17 vol%)

Stable compressive strength (>45 MPa, after 7 and 28 days)



First attempts to non-fired products

Geopolymers from extensive use of glass

Collaboration with Prof. A.R. Boccaccini (University of Erlangen, Germany)

Stabilization of heavy metals

Element (ppm)	As	Cd	Cr	Cu	Mo	Pb	Se	Zn
6S5M	0.174	0.007	0.0251	0.11	0.363	0.1	0.038	<0.203
6S8M	0.134	0.004	0.0101	0.115	0.143	0.078	0.048	<0.203
FA	<0.049	<0.002	0.467	0.028	0.898	<0.047	0.022	<0.2
SLG	<0.049	0.001	0.043	0.036	0.007	0.018	0.018	0.088
Inert material	0.5	0.04	0.5	2	0.5	0.5		
Non-hazardous material	2	1	10	50	10			0

Success, but… high molarity alkaline solutions applied

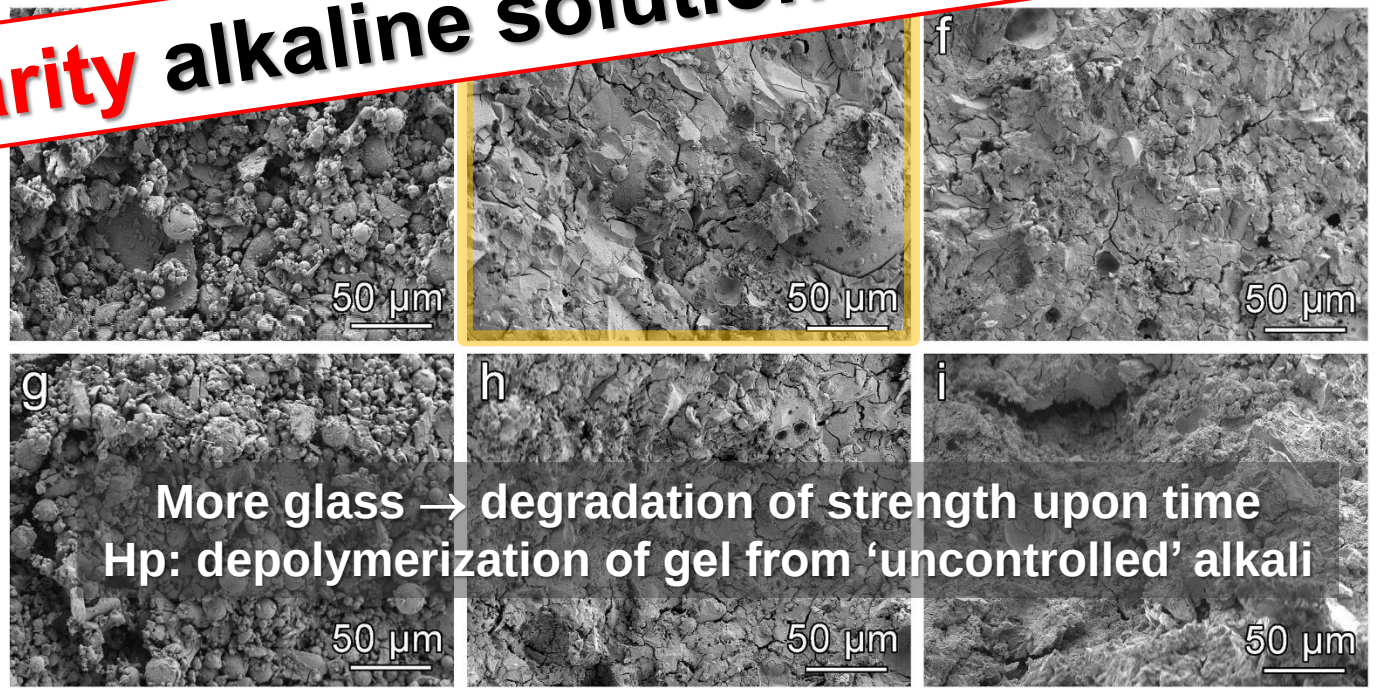
Mixtures designed to lead to:

SiO_2/Al_2O_3 = 6 → FA/SLG = 64/36

SiO_2/Al_2O_3 = 7 → FA/SLG = 54/46

Best: evidence of reaction, higher compaction (density 1.93 ± 0.01 g/cm³, porosity 17 vol%)

Stable compressive strength (>45 MPa, after 7 and 28 days)



First attempts to non-fired products

Geopolymers from extensive use of glass

Collaboration with Prof. A.R. Boccaccini (University of Erlangen, Germany)

Stabilization of heavy metals

Element (ppm)	As	Cd	Cr	Cu	Mo	Pb	Se	Zn
6S5M	0.174	0.007	0.0251	0.11	0.363	0.1	0.038	<0.203
6S8M	0.134	0.004	0.0101	0.115	0.143	0.078	0.048	<0.203
FA	<0.049	<0.002	0.467	0.028	0.898	<0.047	0.022	<0.2
SLG	<0.049	0.001	0.043	0.036	0.007	0.018	0.018	0.088
Inert material	0.5	0.04	0.5	2	0.5	0.5		
Non-hazardous material	2	1	10	50	10			0

Success, but… high molarity alkaline solutions applied

Mixtures designed to lead to:

SiO_2/Al_2O_3 = 6 → FA/SLG = 64/36

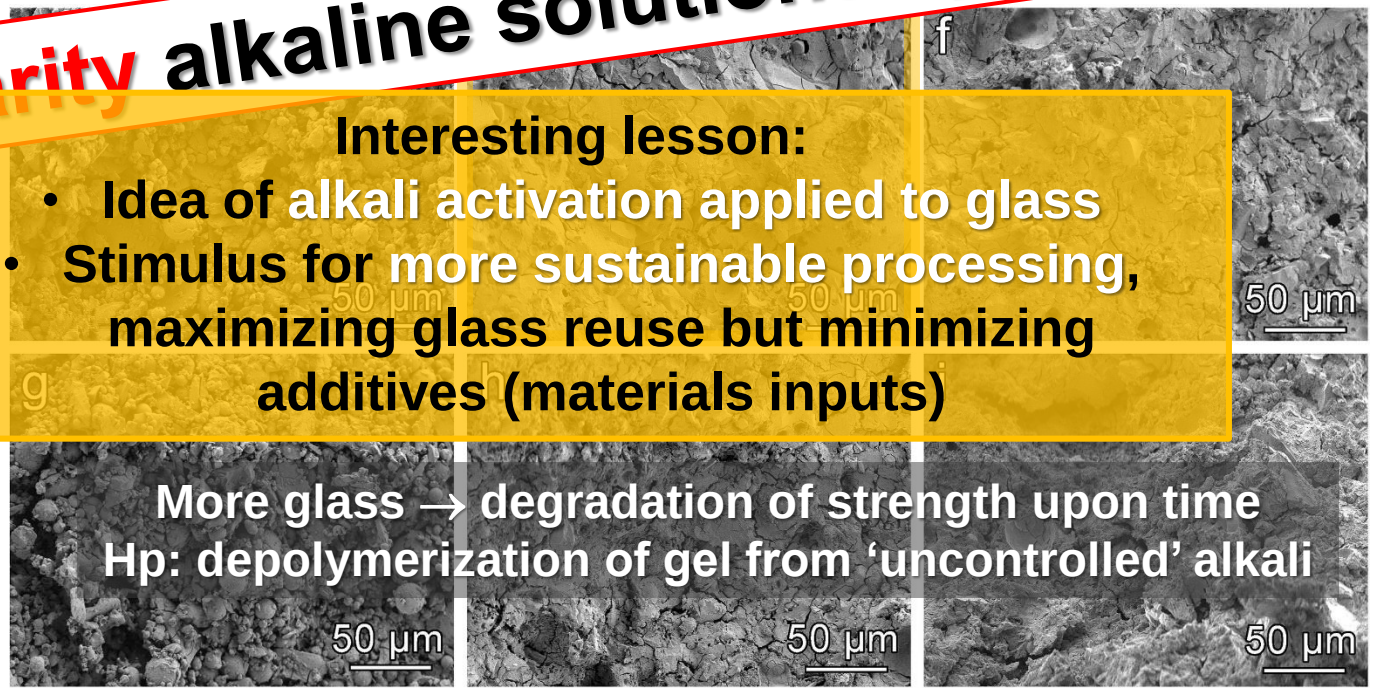
SiO_2/Al_2O_3 = 7 → FA/SLG = 54/46

Best: evidence of reaction, higher compaction (density 1.93 ± 0.01 g/cm³, porosity 17 vol%)

Stable compressive strength (>45 MPa, after 7 and 28 days)

Interesting lesson:

- **Idea of alkali activation applied to glass**
- **Stimulus for more sustainable processing, maximizing glass reuse but minimizing additives (materials inputs)**



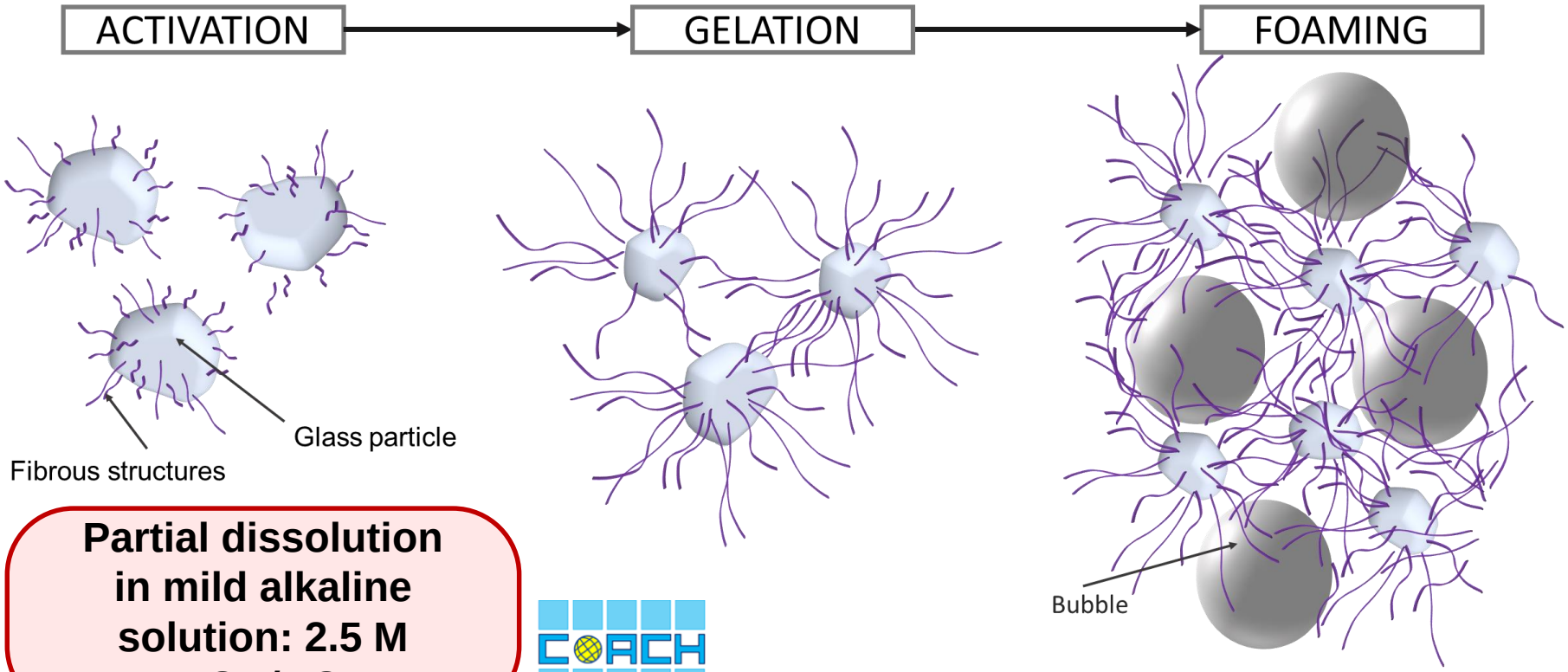
More glass → degradation of strength upon time

Hp: depolymerization of gel from 'uncontrolled' alkali

‘Mild’ activation: at first, a processing step

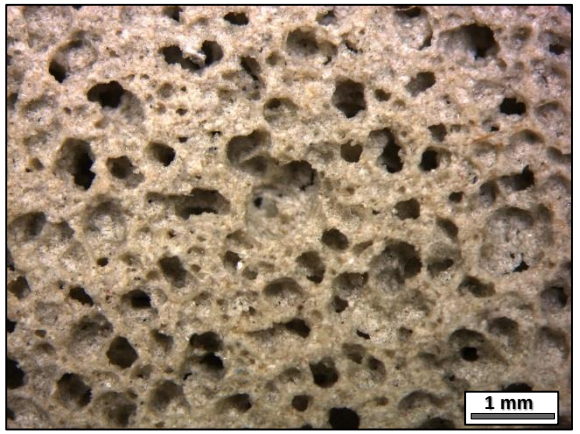
Glass foams form low T firing of ‘green’ foams

Green foams from mechanical foaming of alkali-activated glass suspensions

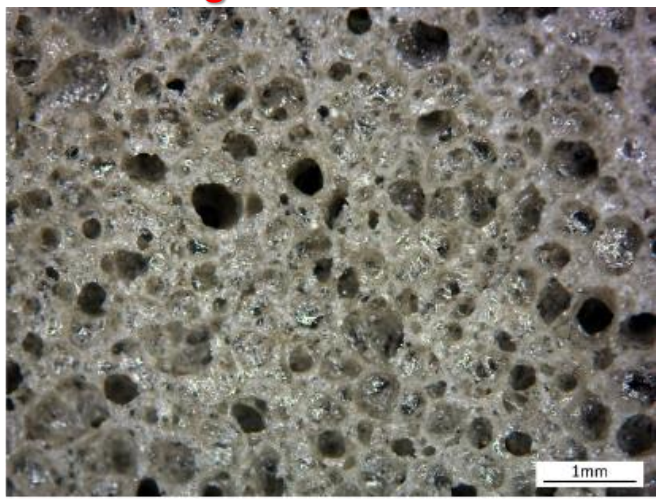


Partial dissolution in mild alkaline solution: 2.5 M NaOH/KOH

‘Green foam’ (room T)



After firing at 700 °C



Soda-lime glass: glass prone to the formation of gels from C-S-H (calcium silicate hydrated compounds)

Other glasses: gels with different chemistry → Challenges & Opportunities

Extension beyond waste

Wollastonite-Diopside glass-ceramic system
Activation even with 1 M NaOH solution

COACH European Training Network

	WDP
SiO_2	51.7 wt%
P_2O_5	2.5
CaO	32.1
MgO	11.5
Na_2O	2.2

- Dissolution (only 3 hours)

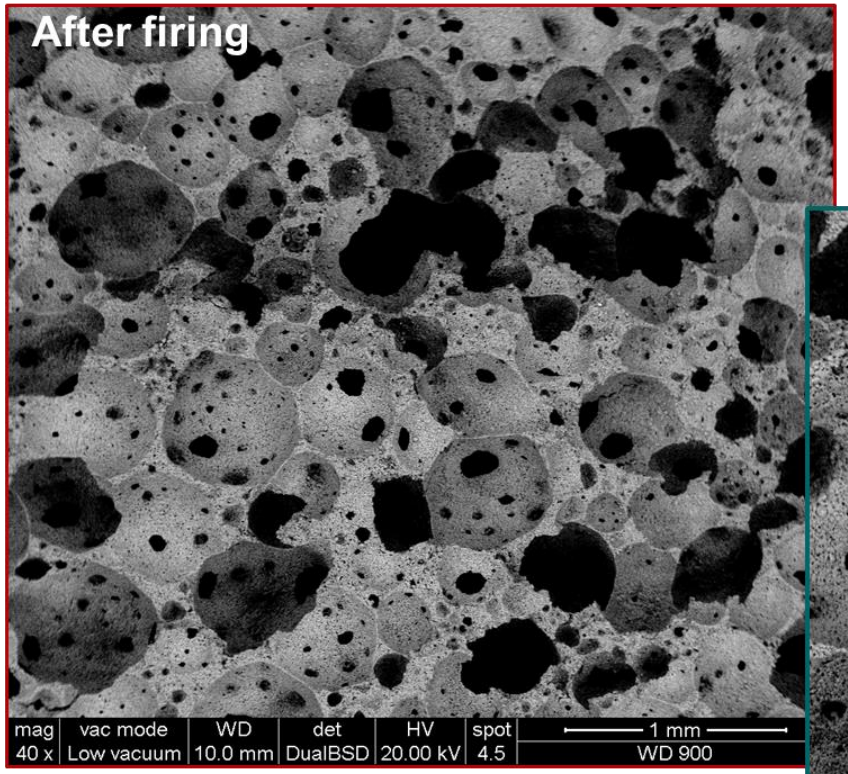
Solid loading (fine powders, <63 µm): 60-65 wt%
alkali conc. 1 M NaOH]

No curing step

- Foaming with Triton X-100
- Firing at 900-1000 °C, 1h

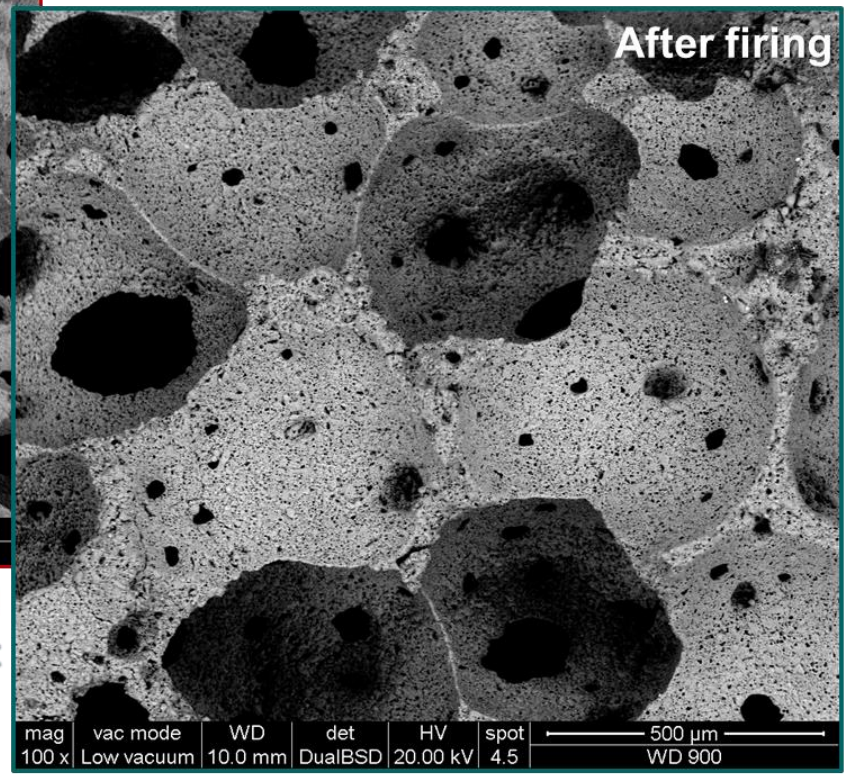
Wollastonite ($CaSiO_3$) – Diopside ($CaMgSi_2O_6$) system

Powders <40 µm



After firing: open macro-porosity

Wide openings (>100 µm) [a recognized minimum threshold value for effective tissue ingrowth and vascularization]



Micro-porosity at cell walls: good for cell attachment

Jones&Hench, Factors affecting the structure and properties of bioactive foam scaffolds for tissue engineering, J. Biomed. Mater. Res. Part B: App. Biomater. 68 (2004) 36

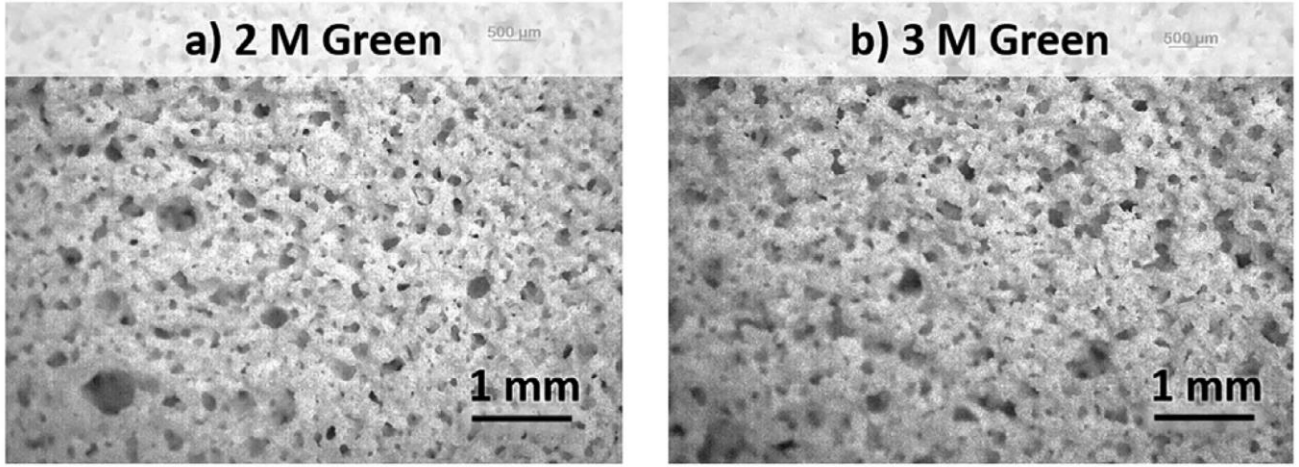
Lesson: crystallization occurring with sintering, AFTER foaming

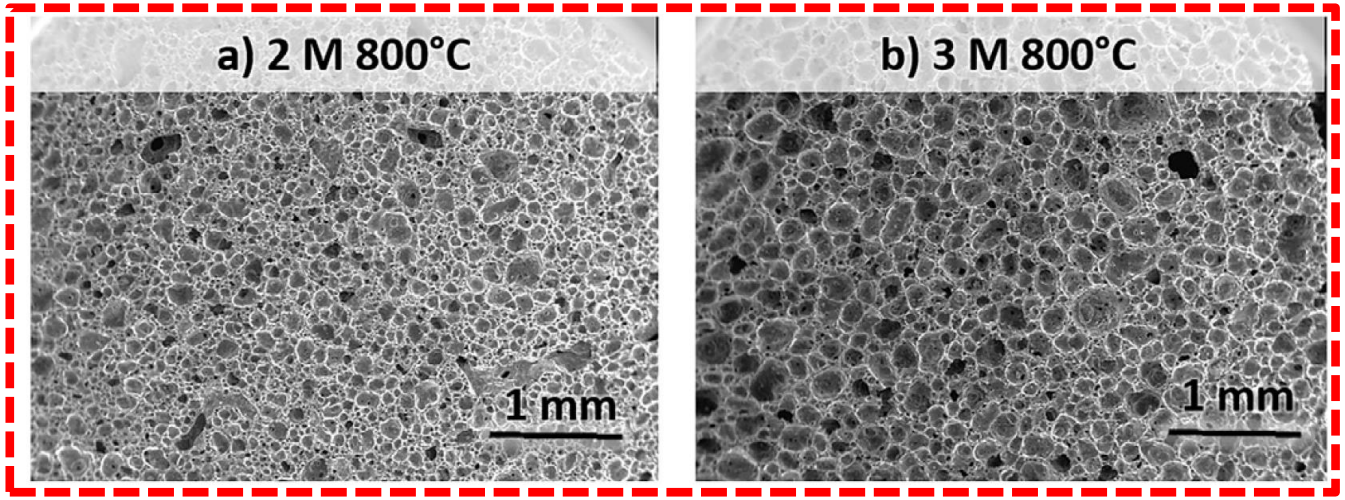
Extension to other waste glass

Glass for fibres: subject to crystallization

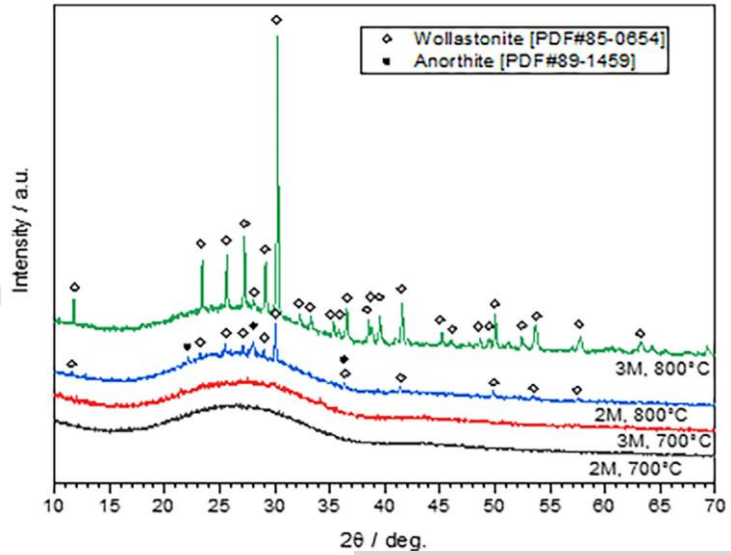
New process exploiting crystallization just as reinforcement option

Residues from glass fibre production: Johns Mansville (Trnava, Slovakia): 55.2 wt% SiO_2 - 14.3 Al_2O_3 - 22.8 CaO - 0.6 MgO - 4.4B_2O_3 - 0.4 Na_2O - 0.7 K_2O





Glass sinter-crystallization AFTER low T foaming: great homogeneity, high specific strength 83% porosity, >8 MPa compressive strength



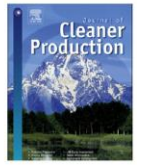
Powders <60 µm

Journal of Cleaner Production 278 (2021) 123985

Contents lists available at ScienceDirect

Journal of Cleaner Production

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



Up-cycling of 'unrecyclable' glasses in glass-based foams by weak alkali-activation, gel casting and low-temperature sintering

Durgaprasad D. Ramteke [a], Miroslava Hujova [a], Jozef Kraxner [a, b], Dušan Galusek [a, b], Acacio Rincón Romero [c], Roberto Falcone [d], Enrico Bernardo [c, *]

[a] FunGlass – Centre for Functional and Surface Functionalized Glass, Alexander Dubček University of Trenčín, Študentská 2, 911 50, Trenčín, Slovakia
[b] Joint Glass Centre of the IIC SAS, TnUAD, and FChFT STU, Študentská 2, 911 50, Trenčín, Slovakia
[c] Department of Industrial Engineering, University of Padova, Via Marzolo 9, Padova, 35131, Italy
[d] Stazione Sperimentale Del Vetro, Via Briati 10 - Murano, Venice, 30141, Italy

FunGlass

Main collaborators: Dr D. Ramteke, Dr. M. Hujova

Extension to waste-derived glasses

Solution to the difficult overlapping of conventional foaming and sinter-crystallization

New process: sinter-crystallization of 'green' foams as an opportunity

Some glasses are formed by melting inorganic waste → convenient if exploited for some new products

- ***Waste-derived glass (vitrification of MSWI bottom ash) successfully converted into foams***

Oxide (wt%)	Vitrified bottom ash (VBA)
SiO_2	51.7
Al_2O_3	10.9
CaO	16.2
Na_2O	6.9
Fe_2O_3	5.8
MgO	4.1
K_2O	1.6
TiO_2	0.7
BaO	0.2
ZnO	0.2
MnO	0.1
Others	Balance

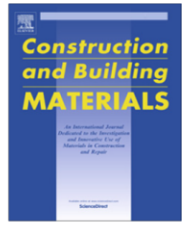
Main collaborator: Prof M. Salvo (Politecnico di Torino)

Construction and Building Materials 192 (2018) 133–140

Contents lists available at ScienceDirect

Construction and Building Materials

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



Up-cycling of vitrified bottom ash from MSWI into glass-ceramic foams by means of 'inorganic gel casting' and sinter-crystallization

Acacio Rincon Romero [a], Milena Salvo [b], Enrico Bernardo [a,*]

[a] Department of Industrial Engineering, University of Padova, Italy
[b] Department of Applied Science and Technology, Politecnico di Torino, Turin, Italy

Extension to waste-derived glasses

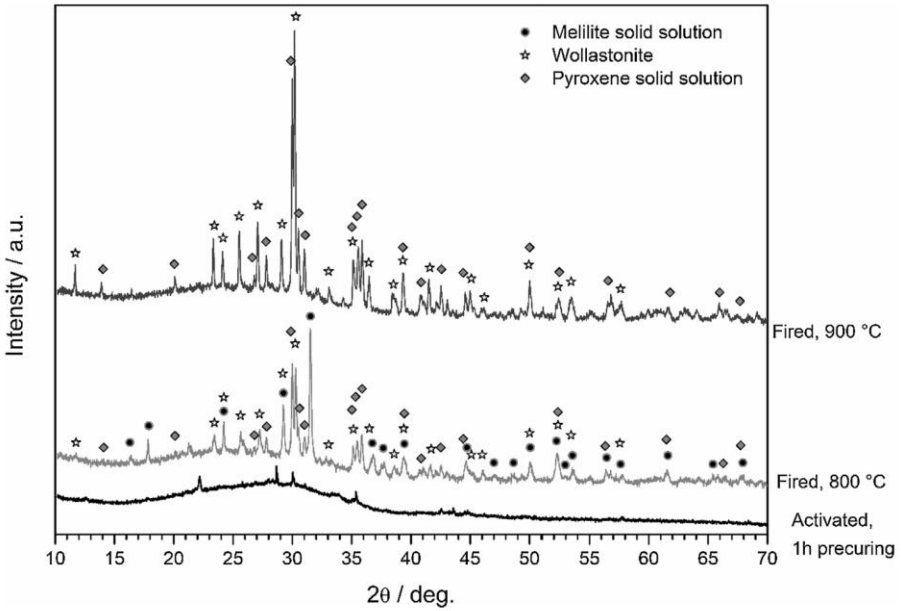
Solution to the difficult overlapping of conventional foaming and sinter-crystallization

New process: sinter-crystallization of 'green' foams as an opportunity

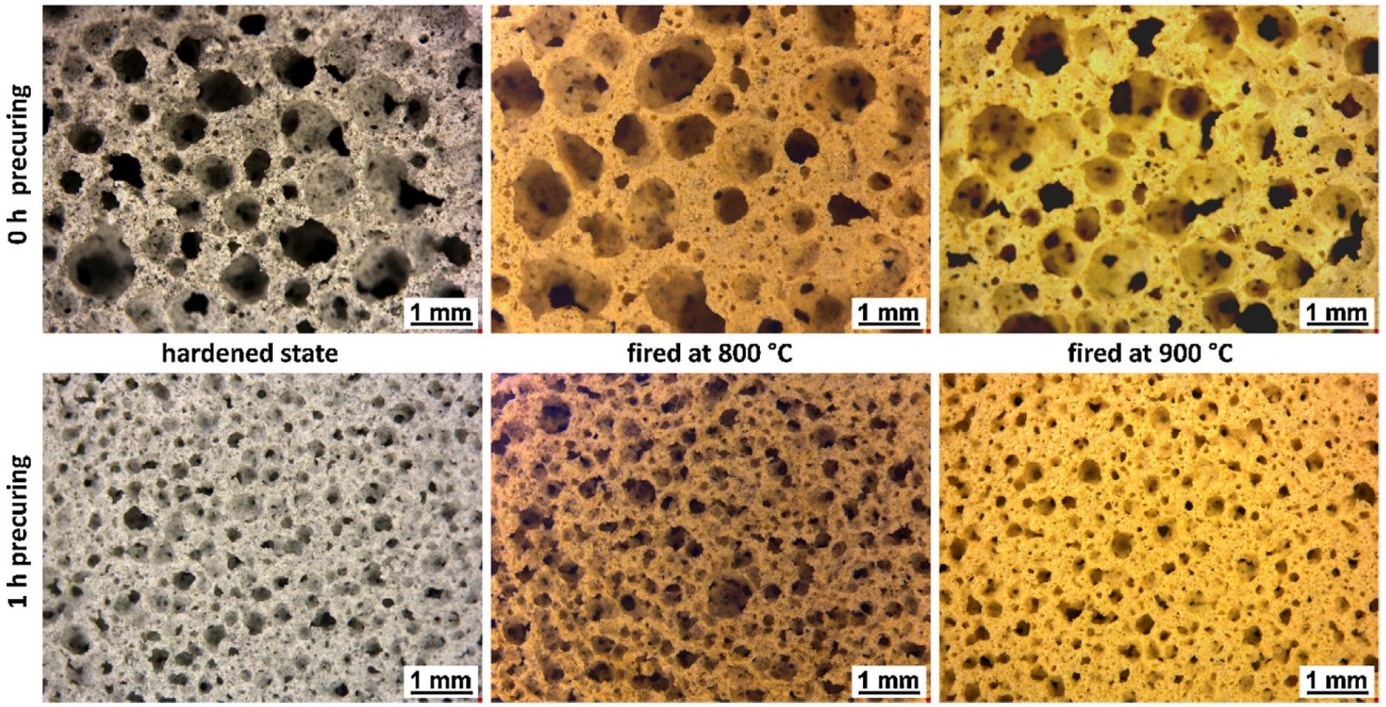
Some glasses are formed by melting inorganic waste → convenient if exploited for some new products

- ***Waste-derived glass (vitrification of MSWI bottom ash) successfully converted into foams***

~80 % porosity,
Crushing strength >6 MPa
[excellent strength-to-density]



A. Rincon Romero et al. / Construction and Building Materials 192 (2018) 133–140



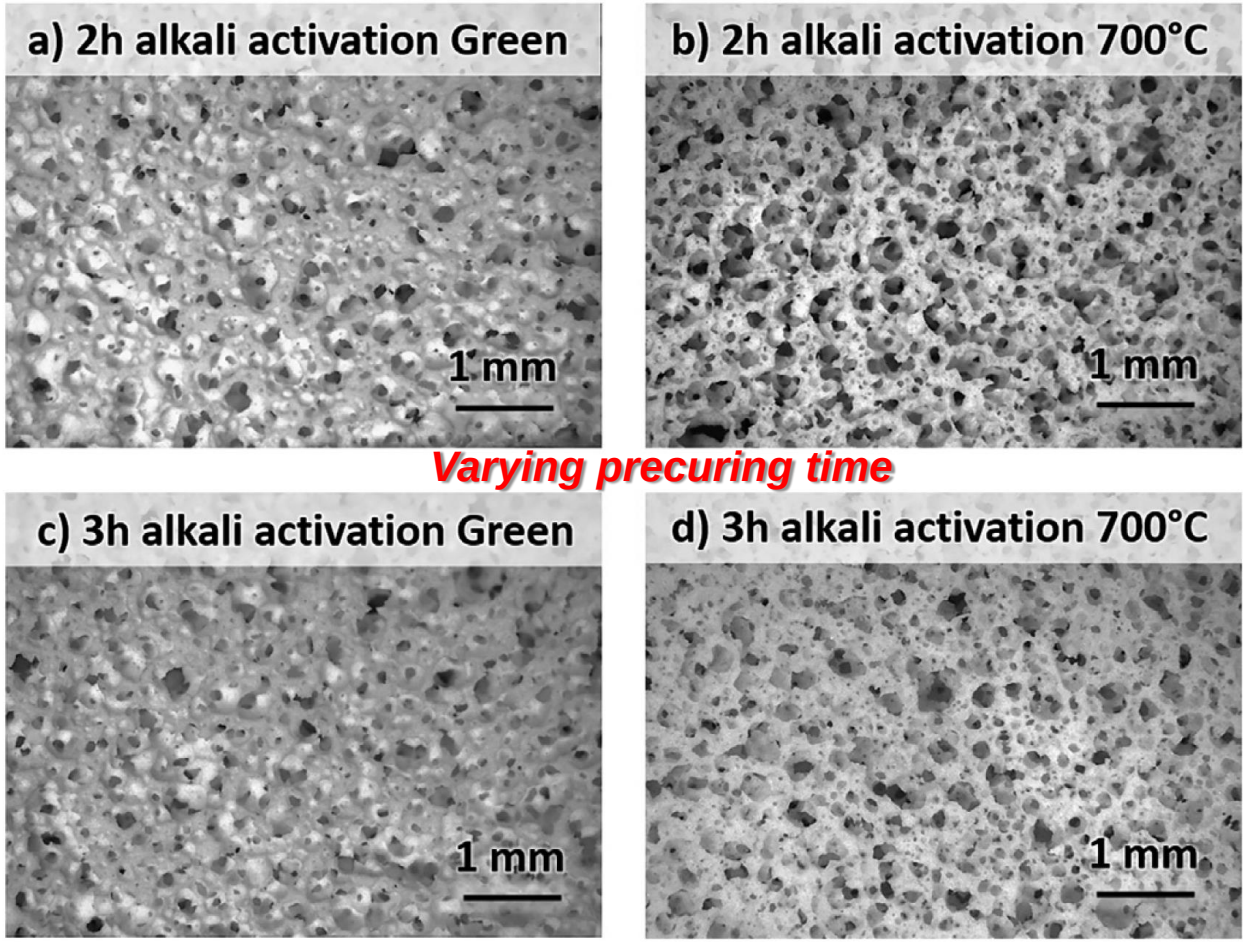
Heavy metals kept stabilized (limited leaching)

Extension to other waste glass

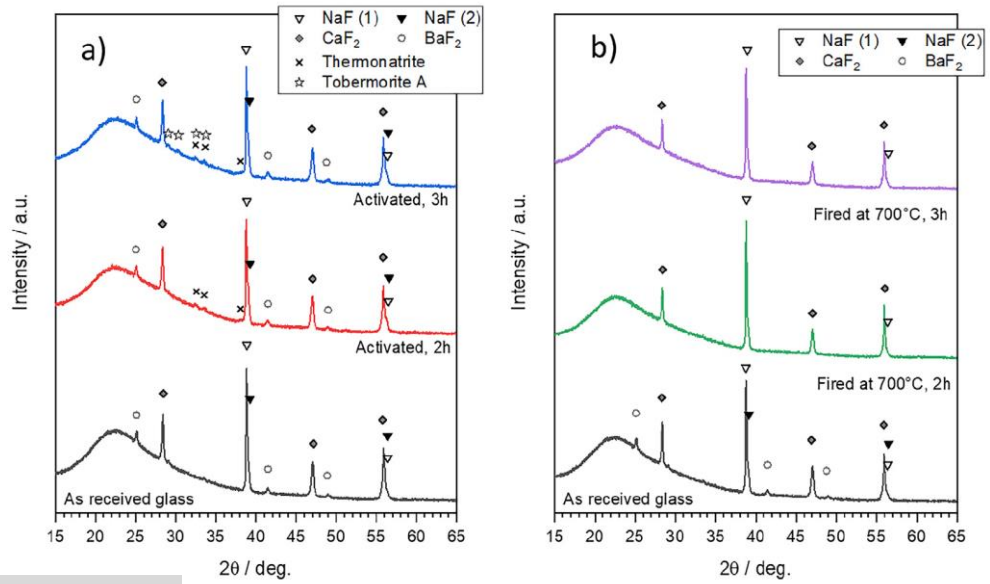
Opal glass: subject to fluorine evolution

New process keeping fluorine content unchanged

Residues from opal glass production: ARC Intl. (Arques, France): 72 wt% SiO_2 – 8 Al_2O_3 – 2 CaO – 2 BaO – 12 Na_2O - 1.5 K_2O – 5 F_2



3h
2.5 M NaOH attack



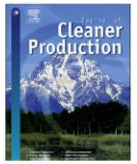
Powders <60 µm

Journal of Cleaner Production 278 (2021) 123985

Contents lists available at ScienceDirect

Journal of Cleaner Production

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



Up-cycling of 'unrecyclable' glasses in glass-based foams by weak alkali-activation, gel casting and low-temperature sintering

Durgaprasad D. Ramteke [a], Miroslava Hujova [a], Jozef Kraxner [a, b], Dušan Galusek [a, b], Acacio Rincón Romero [c], Roberto Falcone [d], Enrico Bernardo [c, *]

[a] FunGlass – Centre for Functional and Surface Functionalized Glass, Alexander Dubček University of Trenčín, Študentská 2, 911 50, Trenčín, Slovakia
[b] Joint Glass Centre of the IIC SAS, TnUAD, and FChFT STU, Študentská 2, 911 50, Trenčín, Slovakia
[c] Department of Industrial Engineering, University of Padova, Via Marzolo 9, Padova, 35131, Italy
[d] Stazione Sperimentale Del Vetro, Via Briati 10 - Murano, Venice, 30141, Italy

Unrecyclable glasses: a key example

Some glasses cannot be recycled at all

Strict requirements on chemical purity favour 'virgin' raw materials

Data in wt%

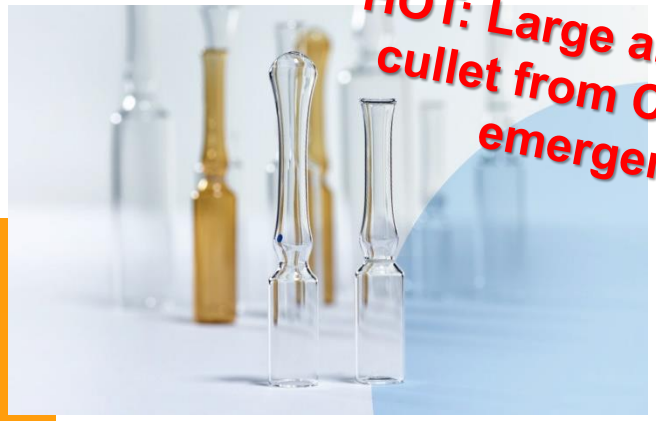
Oxides	SL glass	BS glass
SiO_2	71.6	72
Al_2O_3	1.0	7
Na_2O	13.5	6
K_2O	0.4	2
MgO	3.9	
CaO	9.0	1
B_2O_3		12
Fe_2O_3	0.1	
TiO_2		
SrO		
others	0.5	
L.O.I.		

SL: Partially unrecyclable (highly contaminated fractions)

BS: Hardly recyclable in closed loop mode

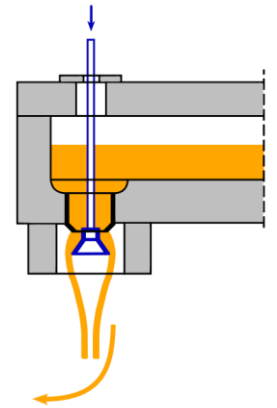
Images and glass cullet courtesy of Stevanato Group (Padova, Italy)





HOT: Large amounts of cullet from COVID-19 emergency

[https://www.stevanatogroup.com/]



True recycling unfeasible according to:

- **Strict control of chemical composition and quality**
- **Industrial approach: glass pre-formed in form of tubes in one plant [Danner process] later transformed in another plant → cullet hardly transported to primary manufacturer**

Glass foams from pharmaceutical glass

Mechanical foaming of alkali activated suspensions
Structural modifications with activation compounds

materials

MDPI

Article

Extension of the 'Inorganic Gel Casting' Process to the Manufacturing of Boro-Alumino-Silicate Glass Foams

COACH
European Training Network

Dissolution
- 4 hours

NaOH or NaOH/KOH conc.
- 2.5M

Solid loading
- 68 wt%

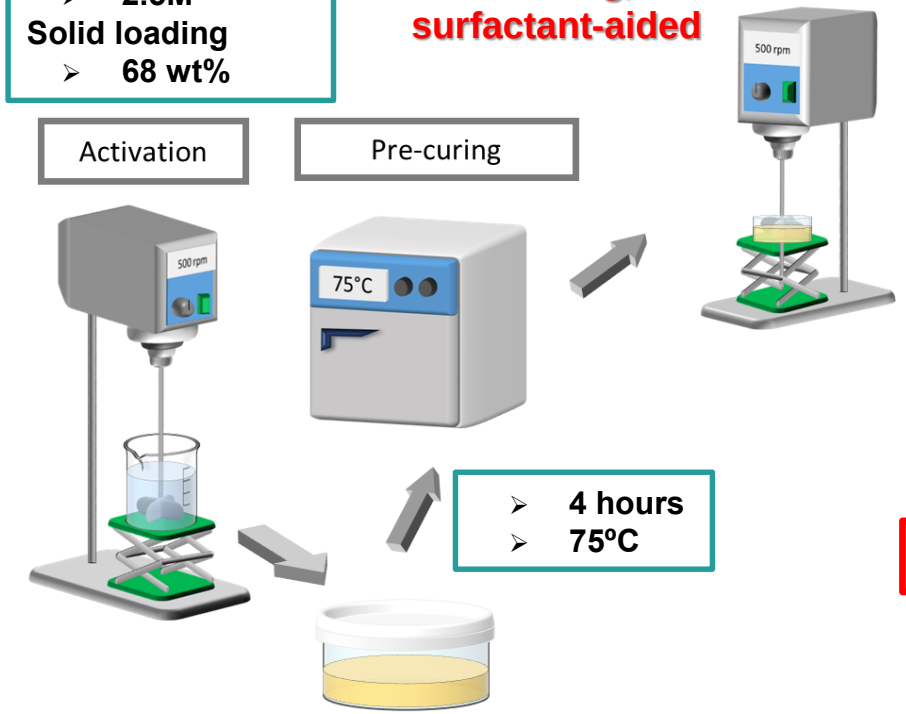
Activation

Pre-curing

Mechanical foaming, surfactant-aided

Foaming

Triton-X100, 4wt%



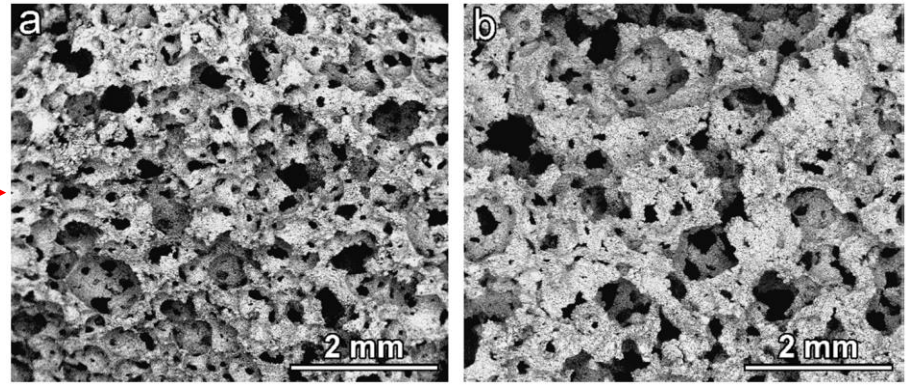
- 28 hours
- 75°C

Curing

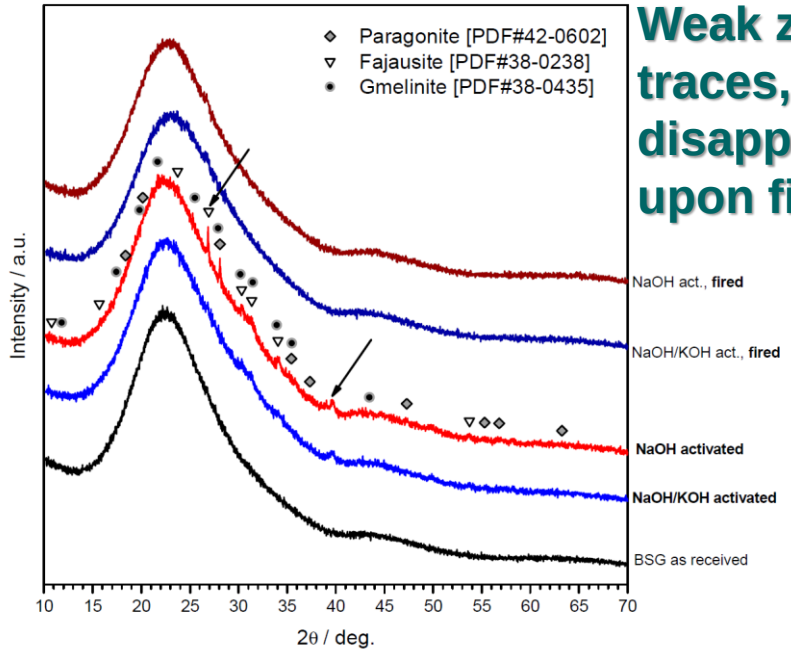
- 4 hours
- 75°C

Green foam

Particles bound by surface gel



NaOH **NaOH/KOH** (50mol%-50mol%)



Weak zeolite traces, disappearing upon firing

Glass foams from pharmaceutical glass

Mechanical foaming of alkali activated suspensions
Structural modifications with activation compounds

materials

MDPI

Article

Extension of the 'Inorganic Gel Casting' Process to the Manufacturing of Boro-Alumino-Silicate Glass Foams

COACH European Training Network

Dissolution
- 4 hours

NaOH or NaOH/KOH conc.
- 2.5M

Solid loading
- 68 wt%

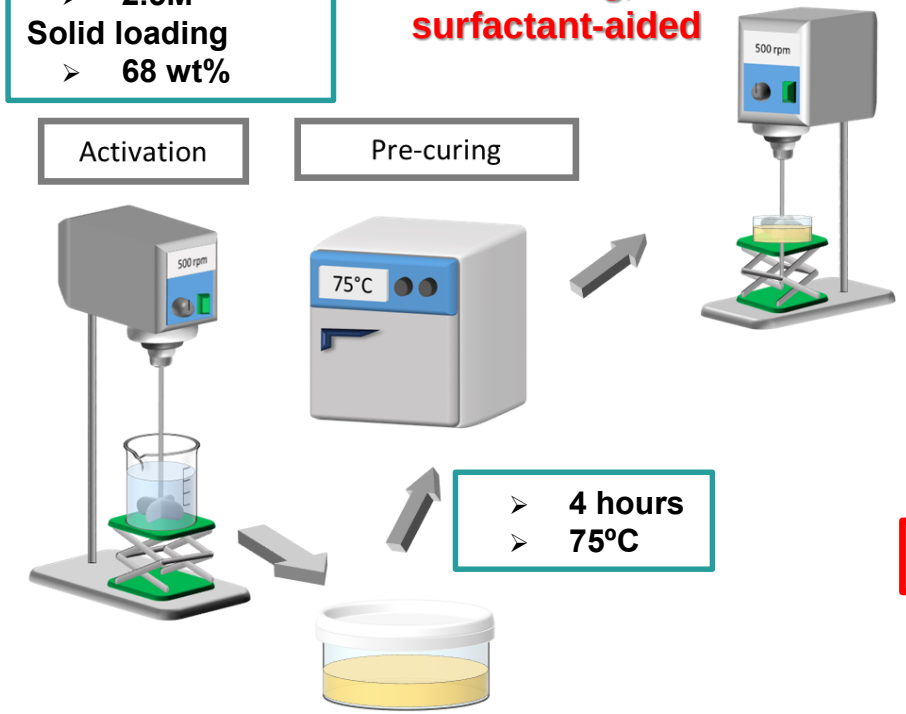
Activation

Pre-curing

Mechanical foaming, surfactant-aided

Foaming

Triton-X100, 4wt%

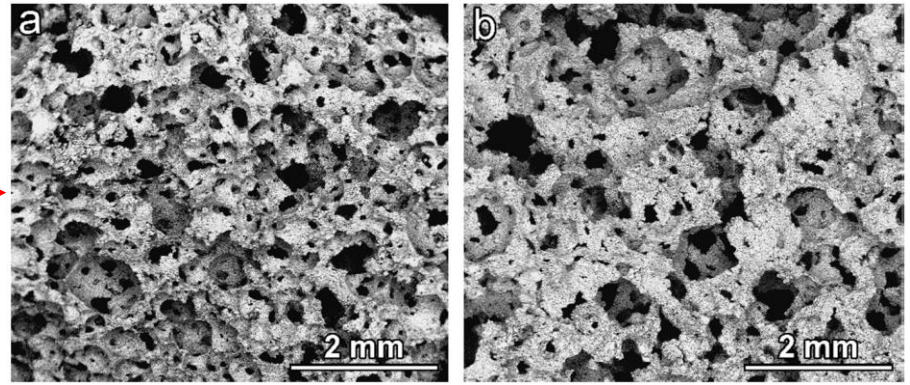


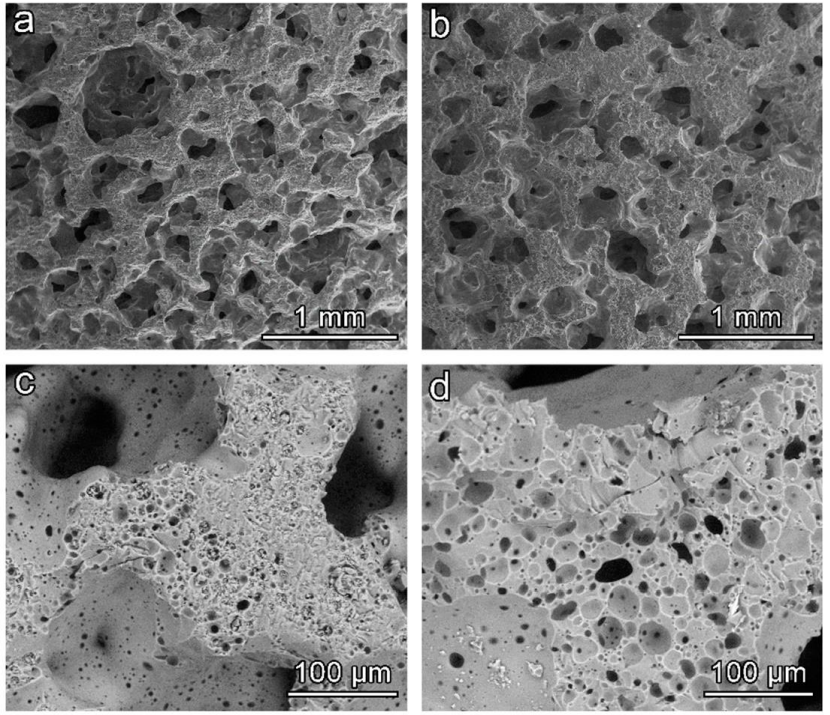
- 4 hours
- 75°C

- 28 hours
- 75°C

Curing

Green foam





Fired at 700°C

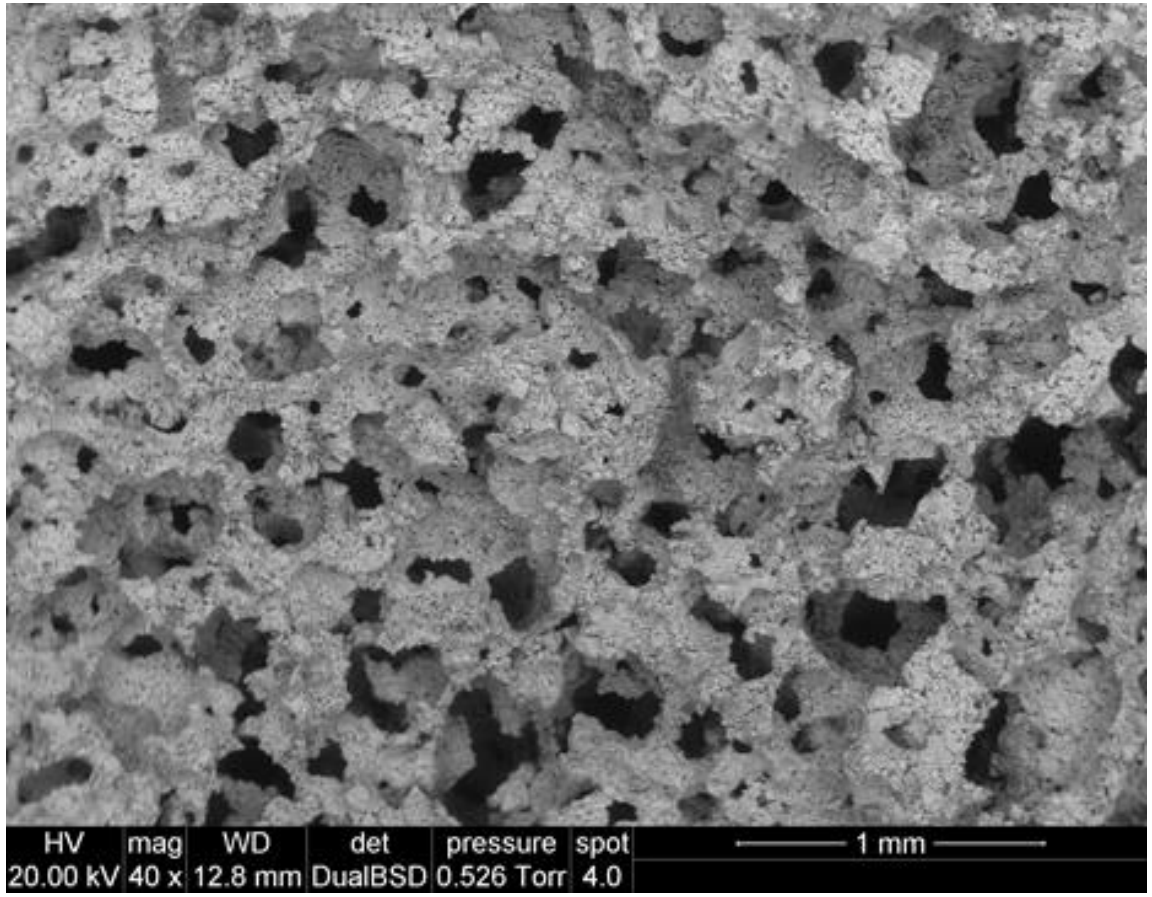
T_g +150°C

Updated foams: activation with NaOH/KOH

Enhancing sustainability

Reducing the firing temperature: tests at only 650 °C

Surfactant	4
Firing T (°C)	650
ρ_{geom} (g/cm^3)	0.70 ± 0.03
$\rho_{apparent}$ (g/cm^3)	2.17 ± 0.05
ρ_{true} (g/cm^3)	2.36 ± 0.05
Total porosity (%)	70.3
Open porosity (%)	67.7
Closed porosity (%)	2.6
σ_{comp} (MPa)	3.9 ± 0.1
σ_{bend} (MPa)	~ 120



$$\sigma_{comp} = \sigma_{bend\ sol\ phase} \cdot 0.2 \cdot (\rho_{rel})^{1.5}$$

$\sigma_{bend\ sol\ phase}$ ~120 MPa

Firing tests @650 °C: below dilatometric softening

Reduced viscous flow, compared to previous foams

FunGlass

But…
the strength-to-density remains excellent (see Gibson&Ashby model for open-celled foams)

Binding by thermal transformation of gel between particles?

Updated foams: activation with NaOH/KOH

Enhancing sustainability …something more?

materials

MDPI

Article

Upcycling of Pharmaceutical Glass into Highly Porous Ceramics: From Foams to Membranes

Akansha Mehta [1,2,*], Khaoula Karbouche [3], Jozef Kraxner [1], Hamada Elsayed [2,4], Dušan Galusek [1,5] and Enrico Bernardo [2]

1 FunGlass—Centre for Functional and Surface Functionalized Glass, Alexander Dubček University of Trenčín, 91150 Trenčín, Slovakia; jozef.kraxner@tnuni.sk (J.K.); dusan.galusek@tnuni.sk (D.G.)
2 Department of Industrial Engineering, Università degli Studi di Padova, 35131 Padova, Italy; hamada.elsayed@unipd.it (H.E.); enrico.bernardo@unipd.it (E.B.)
3 École Polytechnique de Constantine, Constantine 25000, Algeria; ibtissam48@yahoo.fr
4 Refractories, Ceramics and Building Materials Department, National Research Centre, Cairo 12622, Egypt
5 Joint Glass Centre of the IIC SAS, TnU AD and FChFT STU, 91150 Trenčín, Slovakia
* Correspondence: akansha.akansha@tnuni.sk

FunGlass

Pharmaceutical glass actually represents a great opportunity for studies beyond foams

Some unexpected potential to be expressed: FunGlass discovery (Dr. Akansha Mehta, Mr. Mokhtar Mahmoud)

Alkali activation decoupled from foaming → 'weak' alkali activation for cold consolidation of glass

No foaming: highlighting low T binding

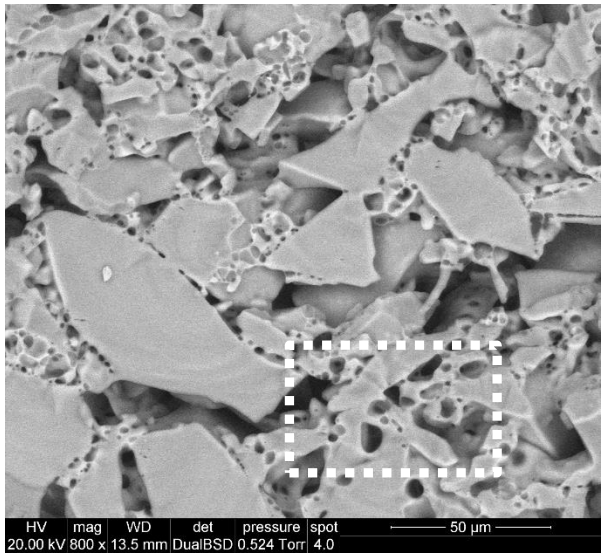
Enhanced strength with no firing

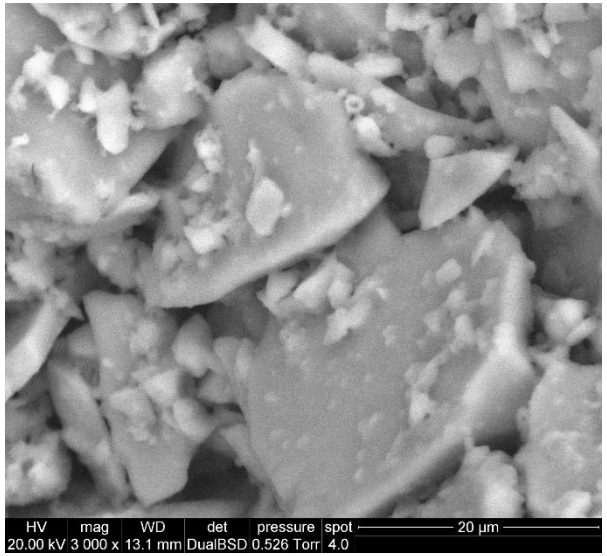
Attention to binding phase: active also without thermal treatment

Surfactant	4			- (no foaming)		
Firing T (°C)	650	550	green	650	550	green
ρ_{geom} (g/cm^3)	0.70 ± 0.03	0.54 ± 0.02	0.58 ± 0.03	1.49 ± 0.05	1.41 ± 0.04	1.43 ± 0.10
$\rho_{apparent}$ (g/cm^3)	2.17 ± 0.05	2.35 ± 0.05	2.31 ± 0.05	2.01 ± 0.05	2.19 ± 0.05	2.33 ± 0.05
ρ_{true} (g/cm^3)	2.36 ± 0.05	2.37 ± 0.05	2.36 ± 0.05	2.35 ± 0.05	2.36 ± 0.05	2.38 ± 0.05
Total porosity (%)	70.3	77.2	75.4	36.5	40.2	38.7
Open porosity (%)	67.7	77.0	74.9	25.9	35.6	38.3
Closed porosity (%)	2.6	0.2	0.5	10.6	4.6	0.4
σ_{comp} (MPa)	3.9 ± 0.1	0.8 ± 0.1	0.5 ± 0.1	19.4 ± 0.1	16.4 ± 0.1	19.4 ± 0.1
σ_{bend} (MPa)	~ 120	~ 35	~ 20			

Fired at 550°C

No flow of glass, just transformation of gel into porous extra glass phase



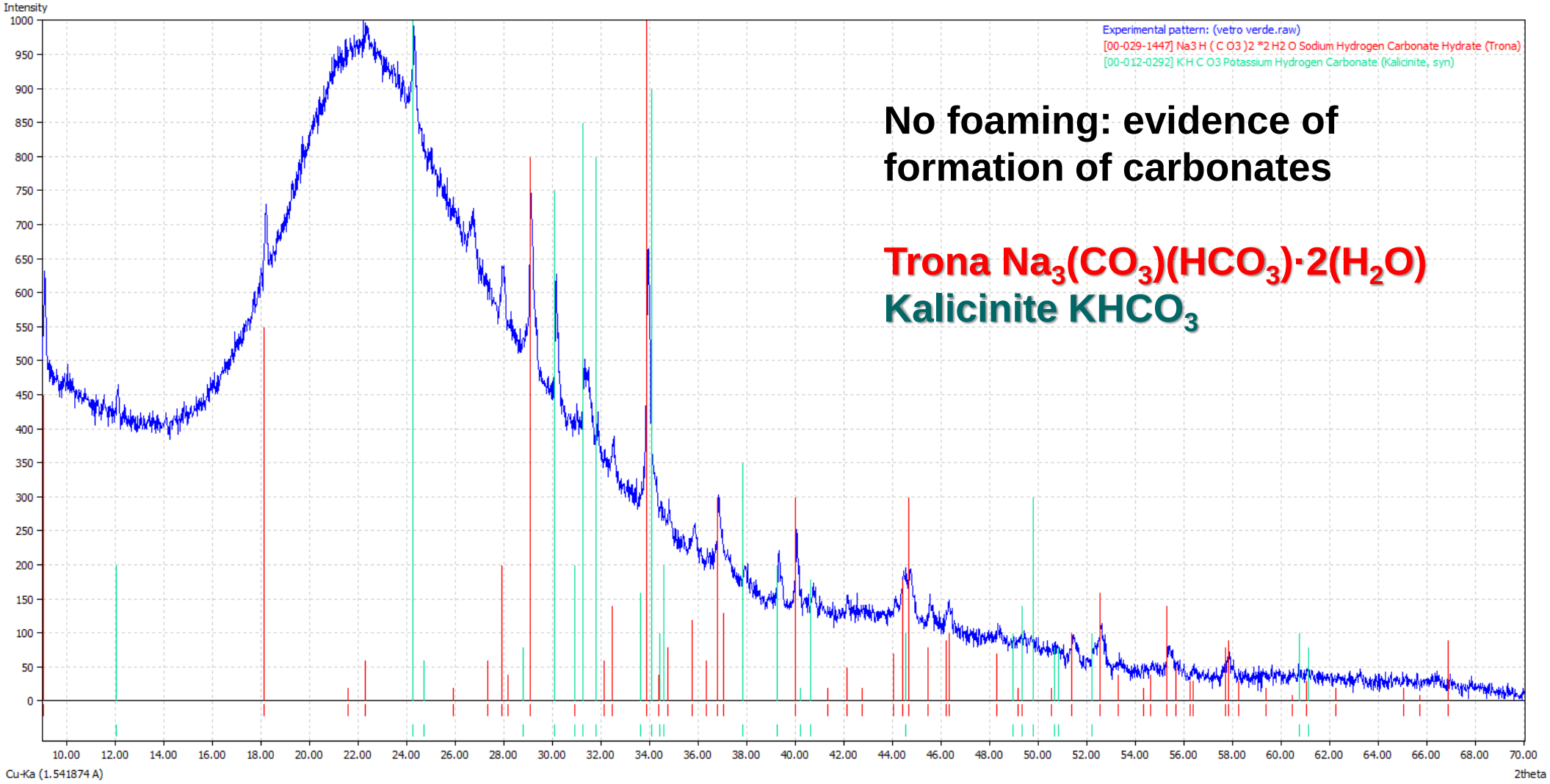


Green, unfoamed Gel binding particles

Surprisingly strong material: 'cold consolidated'

Unfired dried suspension: mineralogy

Attention to new phases
Are they responsible for gelation?



No foaming: evidence of formation of carbonates

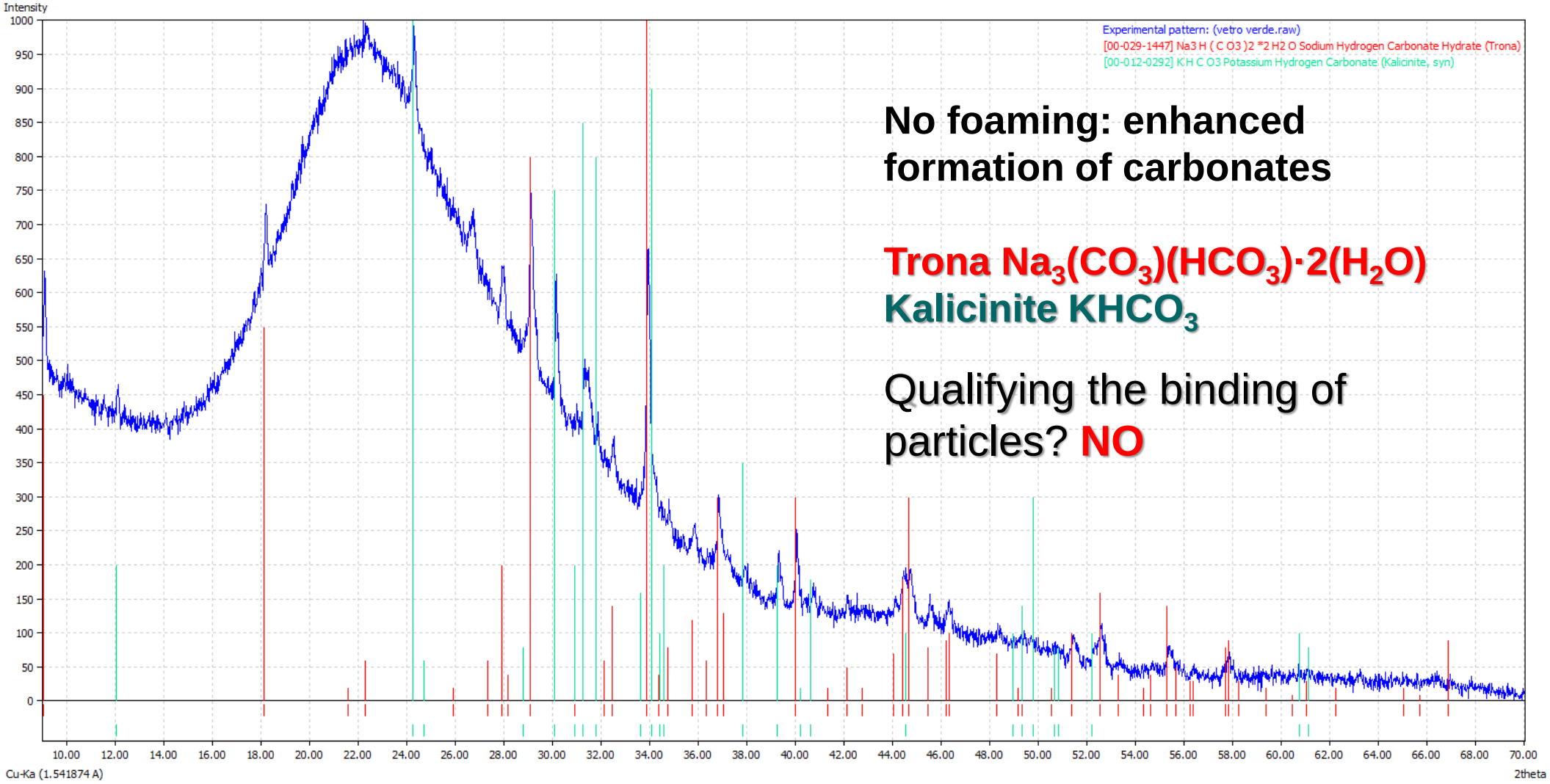
Trona $Na_3(CO_3)(HCO_3)\cdot 2(H_2O)$

Kalicinite $KHCO_3$

Unfired dried suspension: mineralogy

Attention to new phases

Are they responsible for gelation? NO



No foaming: enhanced formation of carbonates

Trona $Na_3(CO_3)(HCO_3)\cdot 2(H_2O)$

Kalicinite $KHCO_3$

Qualifying the binding of particles? **NO**

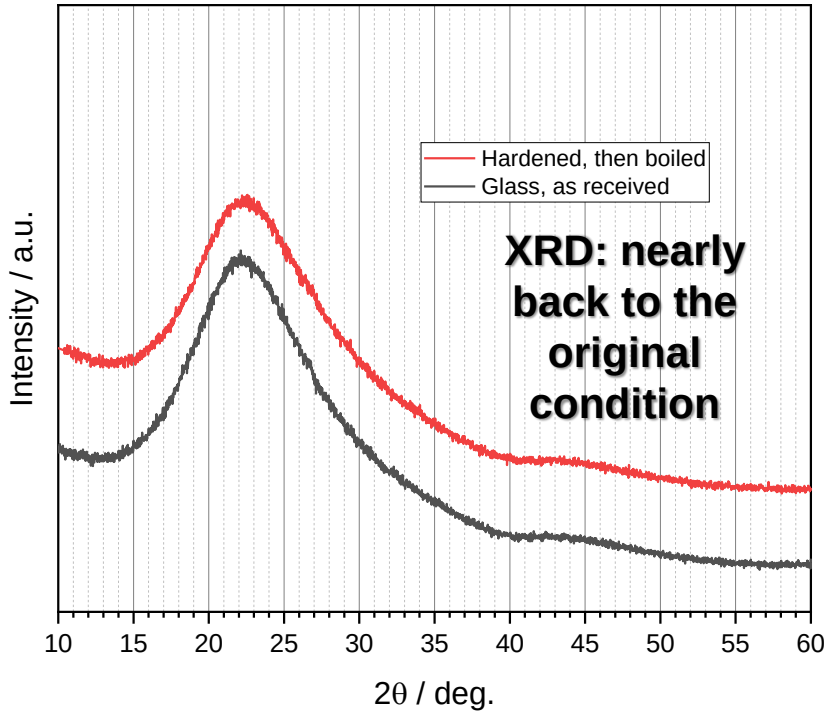
Unfired dried suspension: boiling

Hypothesis of selective dissolution: 2 interparticle phases

Alkali-rich phase removed, no dismantling of binding phase: strong bonds!

Surfactant	4			- (no foaming)			
Firing T (°C)	650	550	green	650	550	green	green, after boiling
ρ_{geom} (g/cm^3)	0.70 ± 0.03	0.54 ± 0.02	0.58 ± 0.03	1.49 ± 0.05	1.41 ± 0.04	1.43 ± 0.10	1.32 ± 0.10
$\rho_{apparent}$ (g/cm^3)	2.17 ± 0.05	2.35 ± 0.05	2.31 ± 0.05	2.01 ± 0.05	2.19 ± 0.05	2.33 ± 0.05	2.31 ± 0.05
ρ_{true} (g/cm^3)	2.36 ± 0.05	2.37 ± 0.05	2.36 ± 0.05	2.35 ± 0.05	2.36 ± 0.05	2.38 ± 0.05	2.37 ± 0.05
Total porosity (%)	70.3	77.2	75.4	36.5	40.2	38.7	42.5
Open porosity (%)	67.7	77.0	74.9	25.9	35.6	38.3	42.5
Closed porosity (%)	2.6	0.2	0.5	10.6	4.6	0.4	0
σ_{comp} (MPa)	3.9 ± 0.1	0.8 ± 0.1	0.5 ± 0.1	19.4 ± 0.1	16.4 ± 0.1	19.4 ± 0.1	21.3 ± 0.1
σ_{bend} (MPa)	~ 120	~ 35	~ 20				

10 min in boiling water: no dissolution: still strong blocks (10 mm diam, 5 mm height)



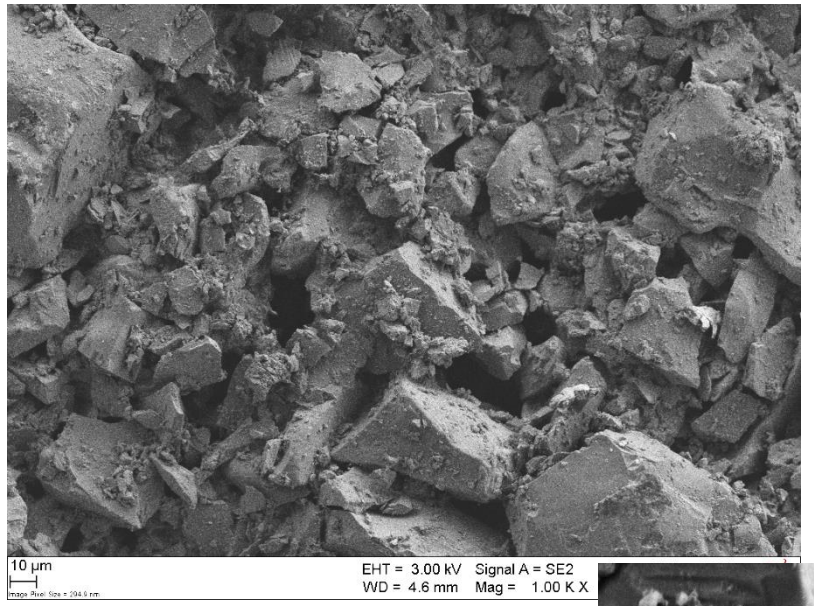
Hydrated carbonates leaving: possibility of alkali recovery?

Unfired dried suspension: boiling

Alkali-rich phase removed, no dismantling of binding phase

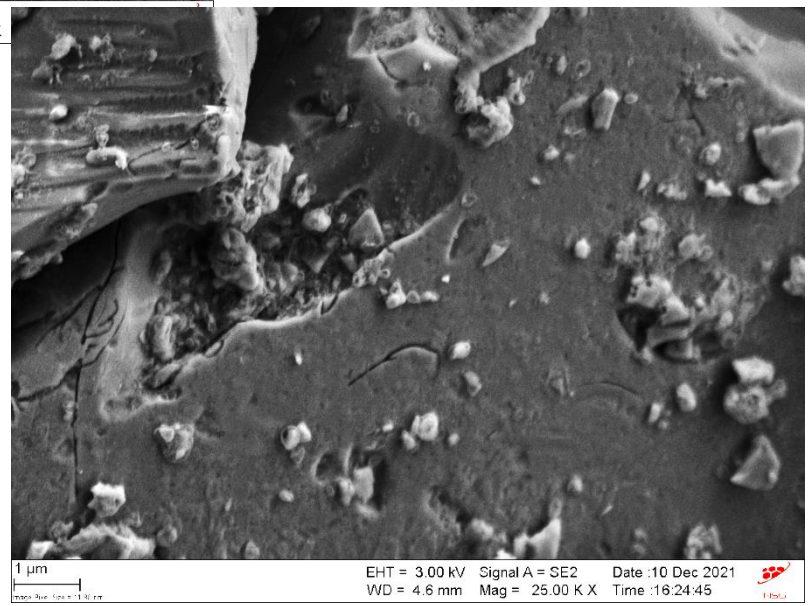
Confirmation by SEM: binding of particles by means of thin surface layers

Surfactant	- (no foaming)			
Firing T (°C)	650	550	green	green, after boiling
ρ_{geom} (g/cm^3)	1.49 ± 0.05	1.41 ± 0.04	1.43 ± 0.10	1.32 ± 0.10
$\rho_{apparent}$ (g/cm^3)	2.01 ± 0.05	2.19 ± 0.05	2.33 ± 0.05	2.31 ± 0.05
ρ_{true} (g/cm^3)	2.35 ± 0.05	2.36 ± 0.05	2.38 ± 0.05	2.37 ± 0.05
Total porosity (%)	36.5	40.2	38.7	42.5
Open porosity (%)	25.9	35.6	38.3	42.5
Closed porosity (%)	10.6	4.6	0.4	0
σ_{comp} (MPa)	19.4 ± 0.1	16.4 ± 0.1	19.4 ± 0.1	21.3 ± 0.1
σ_{bend} (MPa)				



Powders still bound by gel

Interesting texturing of glass surfaces

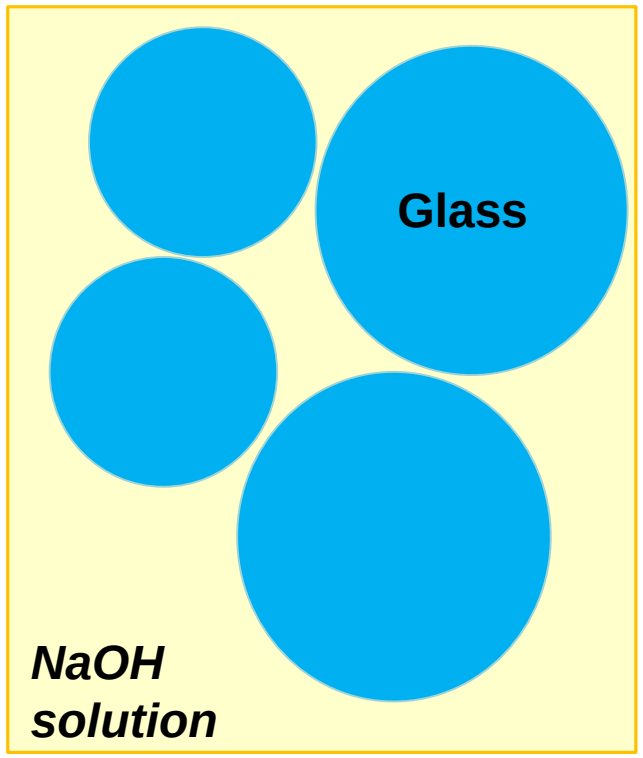


Hint for a new generation of unfired glass-based materials for *structural* and… *functional applications*

Possible mechanism

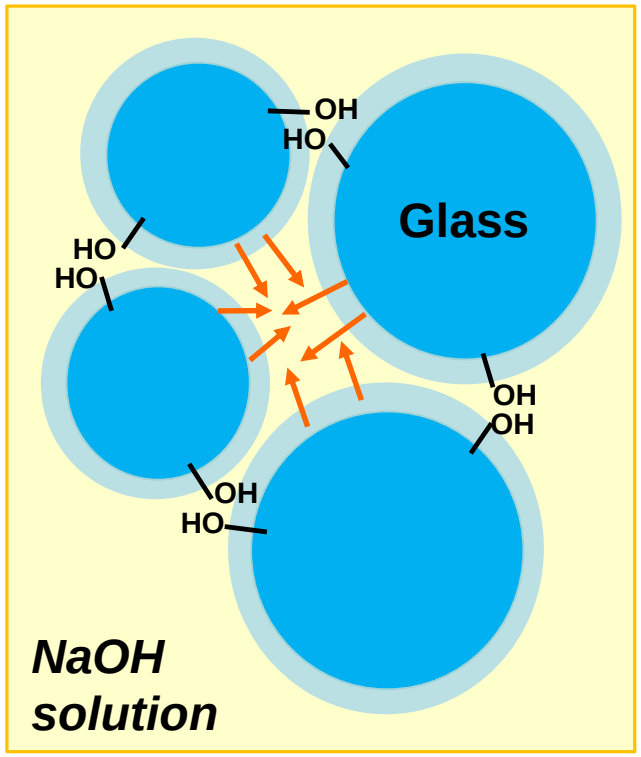
Cold consolidation by 'mild' alkali attack

Ongoing studies (e.g. NMR) to confirm [key difficulty: thin reaction layer]

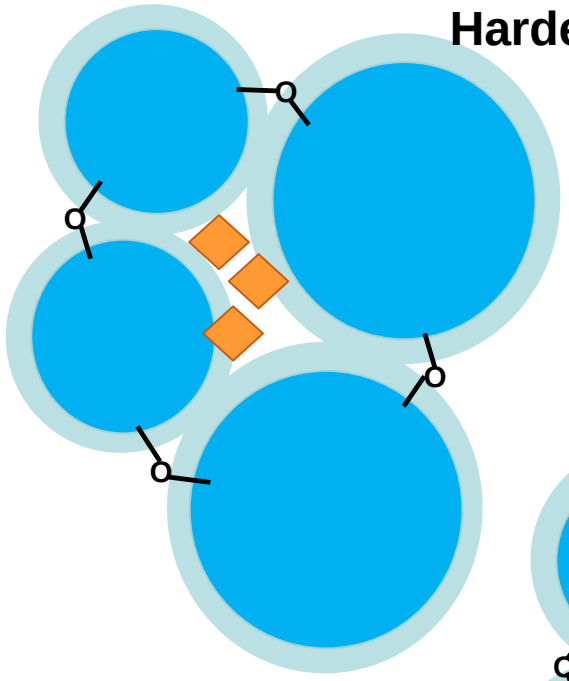


1. Alkaline attack

2. Formation of hydrated layers and release of glass components in solution

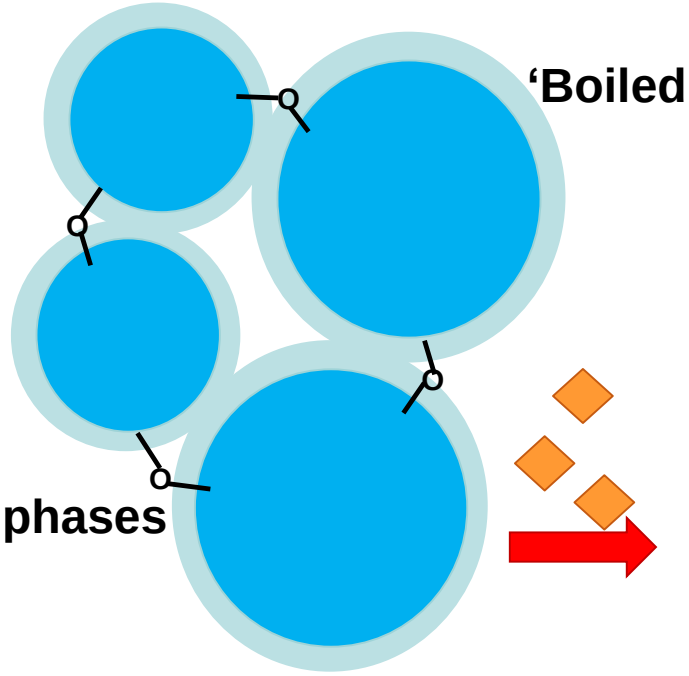


Hardened (dried)



3. Condensation reactions at hydrated layers, formation of secondary phases (also by interaction with atmosphere)

'Boiled'



4. Boiling
Removal of secondary soluble phases

Ongoing cooperation with
Prof. S. Ashbrook, Dr. D. Lawson, Univ. St Andrews UK

Extension #1: structural application

Combination with other waste
Unfired…and LT fired

Cooperation with Terreal San Marco (Noale, Venice - Italy)
Use of 'industrial water' and mud from polishing of clay bricks

TERREAL SANMARCO pica

Low mud formulations: stability even after boiling test, no firing
Firing as option for 'unstable products', but applicable also to others

BSG=PG ('pharmaceutical glass')

Table 1. Formulations of pastes from PG activated with waste slurries

Sample code	BSG wt%	Mud wt%	Water (wt% added to PG/mud)	NaOH (wt% added to PG/mud)
12071 – Unfired	90	10	22.4	12.6
12072 – Unfired	95	5	22.4	12.6
12074 – Unfired (+11.7% Na_2SiO_3)	90	10	11.7	11.7
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		

'unstable'

Main collaborator: Ms Giulia Tameni

Structural application

Combination with other waste

Unfired samples… or low temperature firing







Unfired products (‘Cold-consolidated’) Boro-alumino-silicate glass + ‘mud’

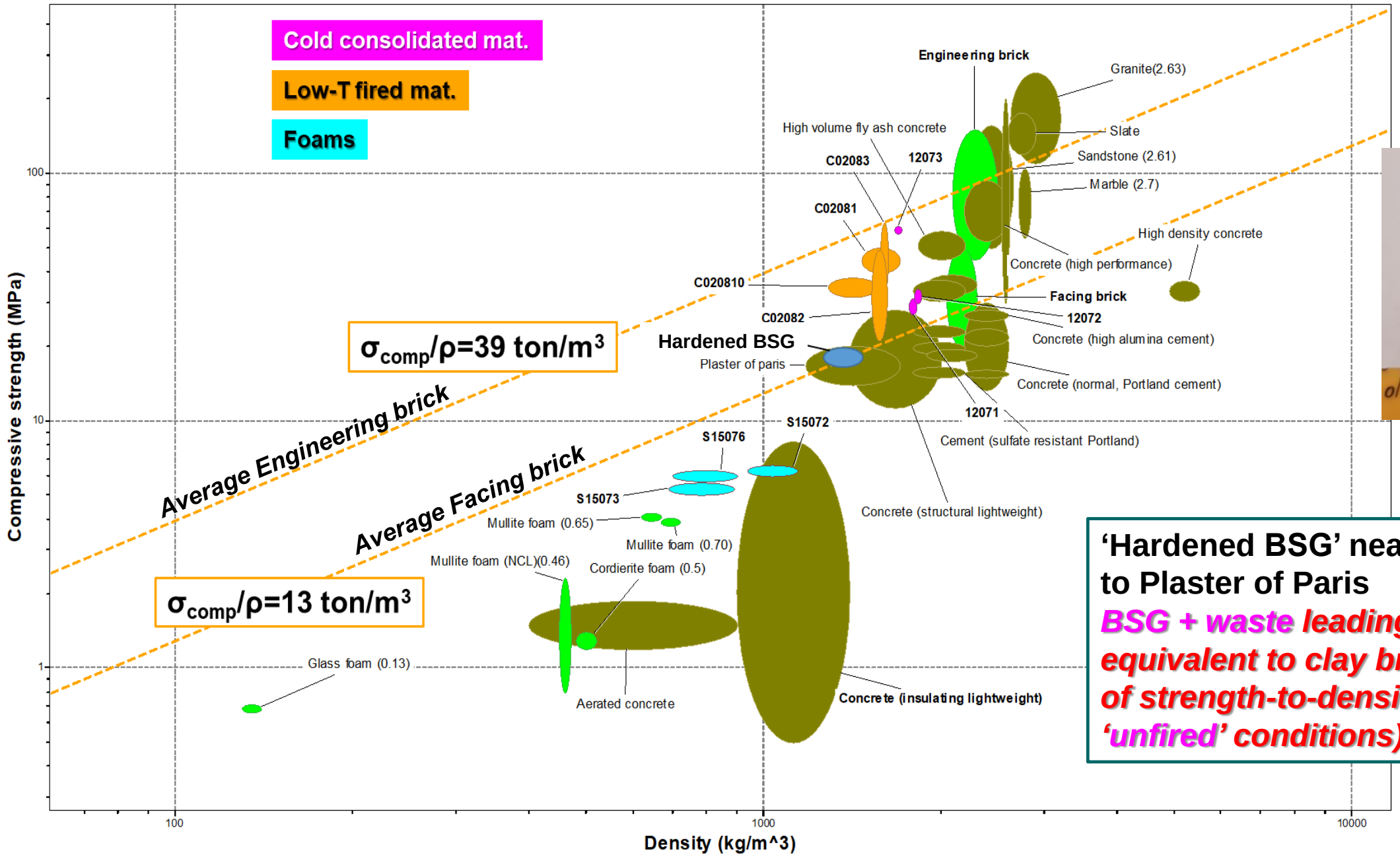
Fired products Activation useful for casting and low T firing





Foamed products (again!) ‘2nd life’ of glass-rich unfired products

Summary
Ashby's plot





'Unfired brick'

'Hardened BSG' nearly equivalent to Plaster of Paris

BSG + waste leading to products equivalent to clay bricks in terms of strength-to-density (also in 'unfired' conditions)

Cooperation with INSTM (National Institute for Science and Technology of Materials): recovery of used foundry sand from Lombardy region

Use of 'industrial waste' → Incapsulation of foundy sand as inert
→ Glass powder deriving from plasma processing of municipal waste 'Plasmastone' (secondary option)



Plasmastone







Three different types of foundry sands

Sample code	Ratio PG/inert [wt%/wt%]	Molarity (NaOH/KOH)	Name of inert	Temperature of mixing [°C]	Density [g·cm^{-1}]	Compressive strength [MPa]
CONG1	1:3	2.5	Plasmastone	20	1.90±0.2	7.7±2.2
CONG2	1:3	2.5	11-A	20	1.72±0.06	7.1±1.8
CONG3	1:3	2.5	11-A	40	1.84±0.12	7.8±3.2
CONG4	1:1	5	26-A	20	1.51±0.11	3.8±0.4
CONG5	1:1	5	26-A	40	1.20±0.11	6.2±2.6
CONG6	1:3	5	31-A	40	1.42±0.09	3.4±2.8
CONG7	1:2	5	31-A	40	1.62±0.06	9.3±5.6

Table 3: Samples obtained by incorportation of foundry sand or Plasmastone in PG matrix

Main collaborator:
Mr Francesco Cammelli

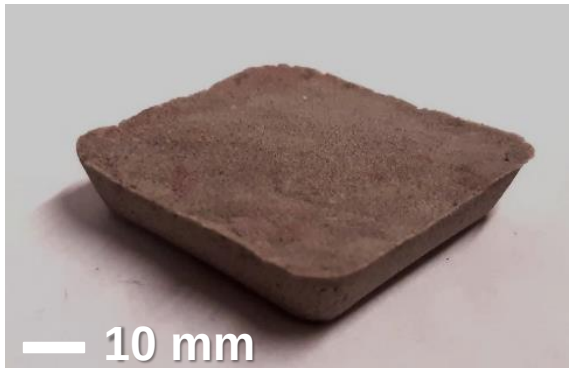
Extension #2

Combination with other waste
Application in 'waste-derived concrete'

Cooperation with INSTM (National Institute for Science and Technology of Materials): recovery of used foundry sand from Lombardy region

Use of 'industrial waste' → Incapsulation of foundy sand as inert

→ Glass powder deriving from plasma processing of municipal waste 'Plasmastone' (secondary option)



Sand in BSG-derived matrix

Sample code	Ratio PG/inert [wt%/wt%]	Molarity (NaOH/KOH)	Name of inert	Temperature of mixing [°C]	Density [g·cm^{-1}]	Compressive strength [MPa]
CONG1	1:3	2.5	Plasmastone	20	1.90±0.2	7.7±2.2
CONG2	1:3	2.5	11-A	20	1.72±0.06	7.1±1.8
CONG3	1:3	2.5	11-A	40	1.84±0.12	7.8±3.2
CONG4	1:1	5	26-A	20	1.51±0.11	3.8±0.4
CONG5	1:1	5	26-A	40	1.20±0.11	6.2±2.6
CONG6	1:3	5	31-A	40	1.42±0.09	3.4±2.8
CONG7	1:2	5	31-A	40	1.62±0.06	9.3±5.6

Table 3: Samples obtained by incorportation of foundry sand or Plasmastone in PG matrix

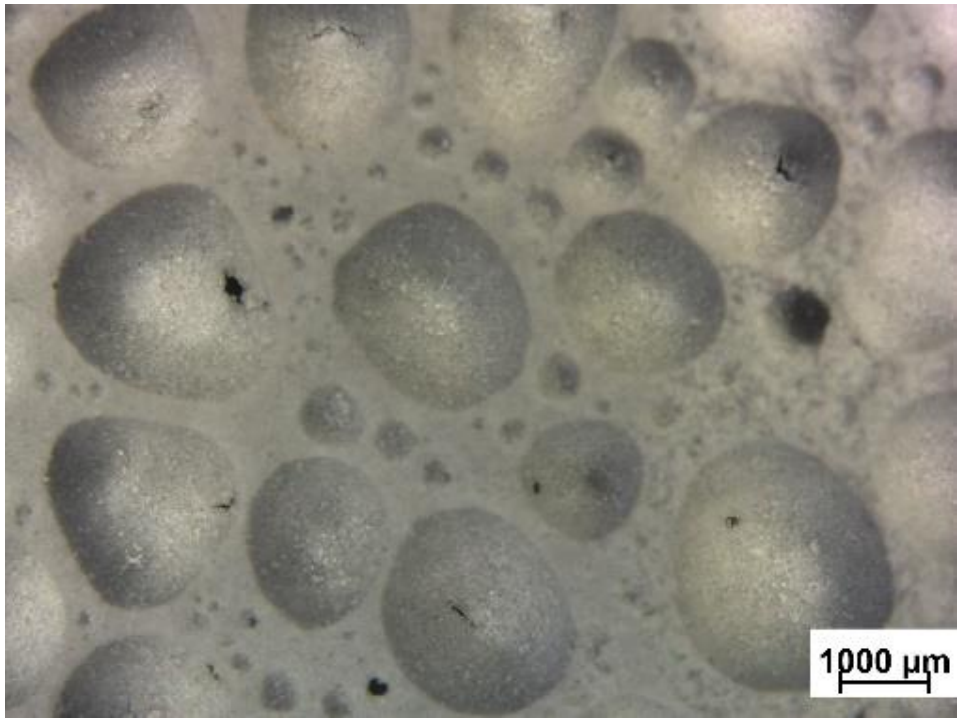
Extension #3

Back to glass foams (current studies)
Unfired foams: gas release during drying step

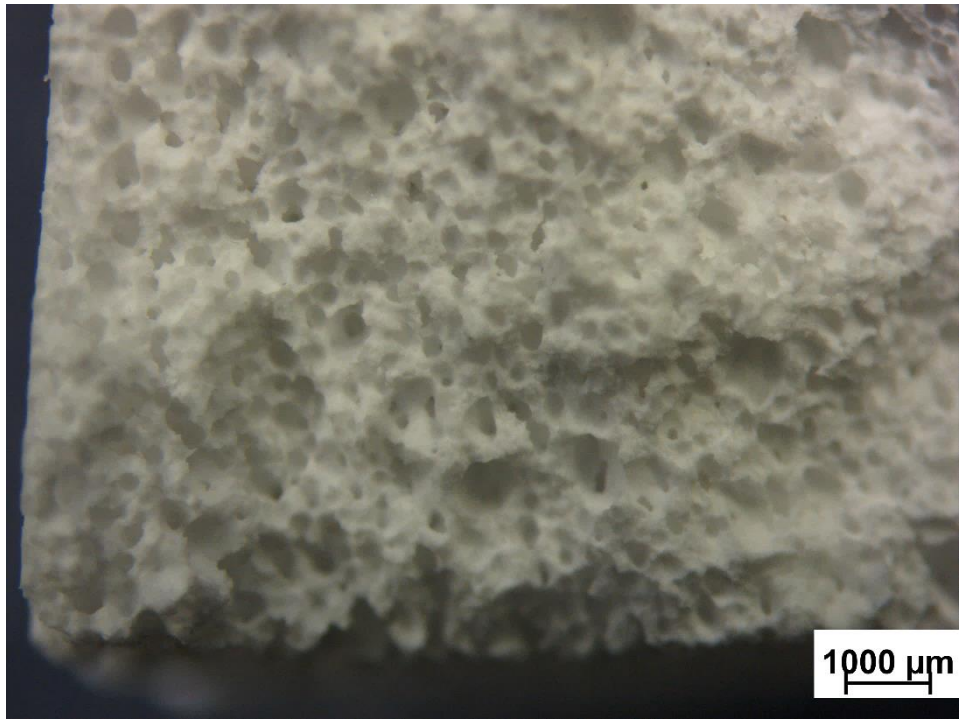
Activation of BSG with

1. Sodium perborate (SPB, $NaBO_3 \cdot 4H_2O$, 1 wt% on glass content) ['FOAM1']

2. SPB + Sodium dodecyl sulfate (SDS, $CH_3(CH_2)_{11}SO_4Na$, 1 wt% on glass content)



FOAM1 obtained starting from BSG

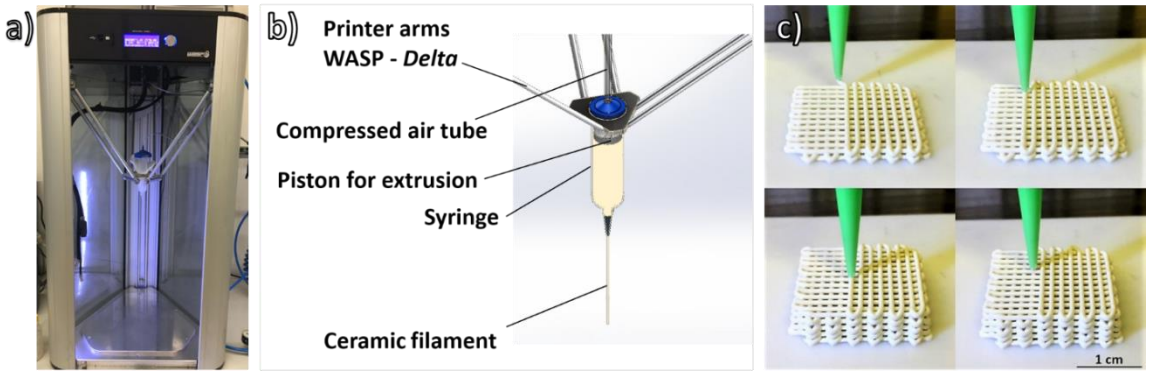


FOAM1 + SDS obtained starting from BSG: enhanced homogeneity

Much less surfactant: unfired foams surviving boiling test!

Beyond constructions: AM of functional composites

Perspective of organic-free direct ink writing of glass powders
Determination of photocatalytic scaffolds



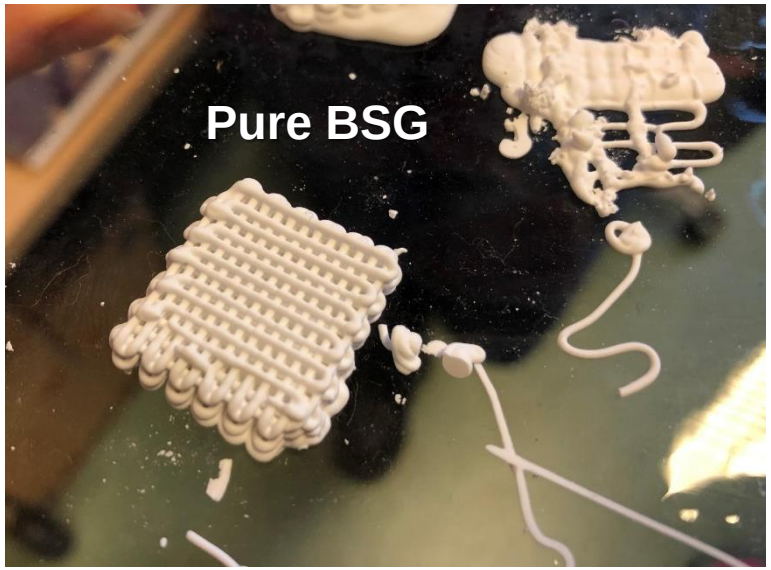
Delta printer (Turbo 20x40, Wasp, Massa Lombarda, Italy) Extrusion process was through a conical nozzle (Nordson EFD, Westlake, Ohio) of 0.8 mm diameter

- **Activation with 2.5M NaOH**
- **Solid loading: 65 wt%**
- **Printing repeated with:**

a. TiO_2 nanoparticles (anatase, ~21 nm, Evonik Degussa GmbH, Germany**) - added to starting suspension [10 wt% compared to BSG amount]**

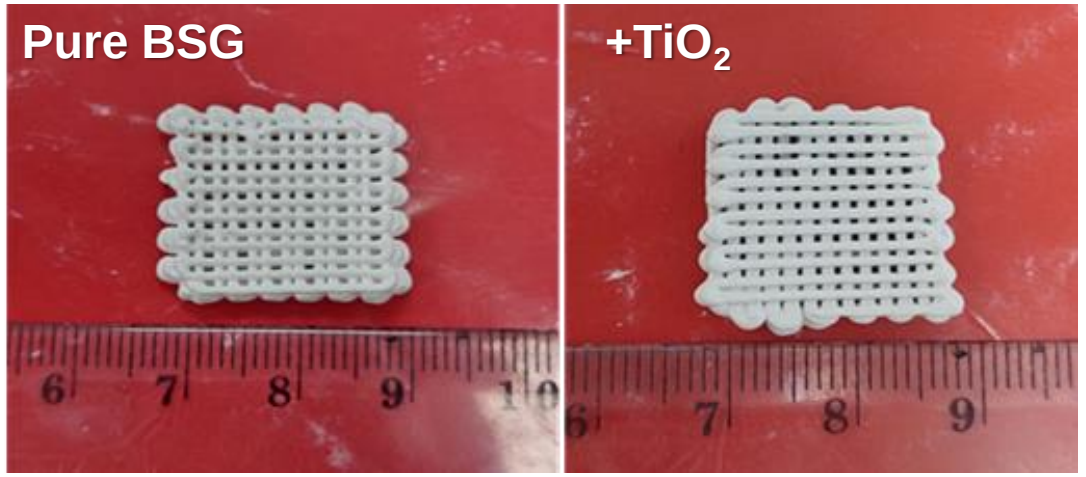
→ ***Reduced sagging in z direction***

→ ***Introduction of functional phase***



Mixing (3h) + curing 3h + extrusion

NO ORGANIC



FunGlass

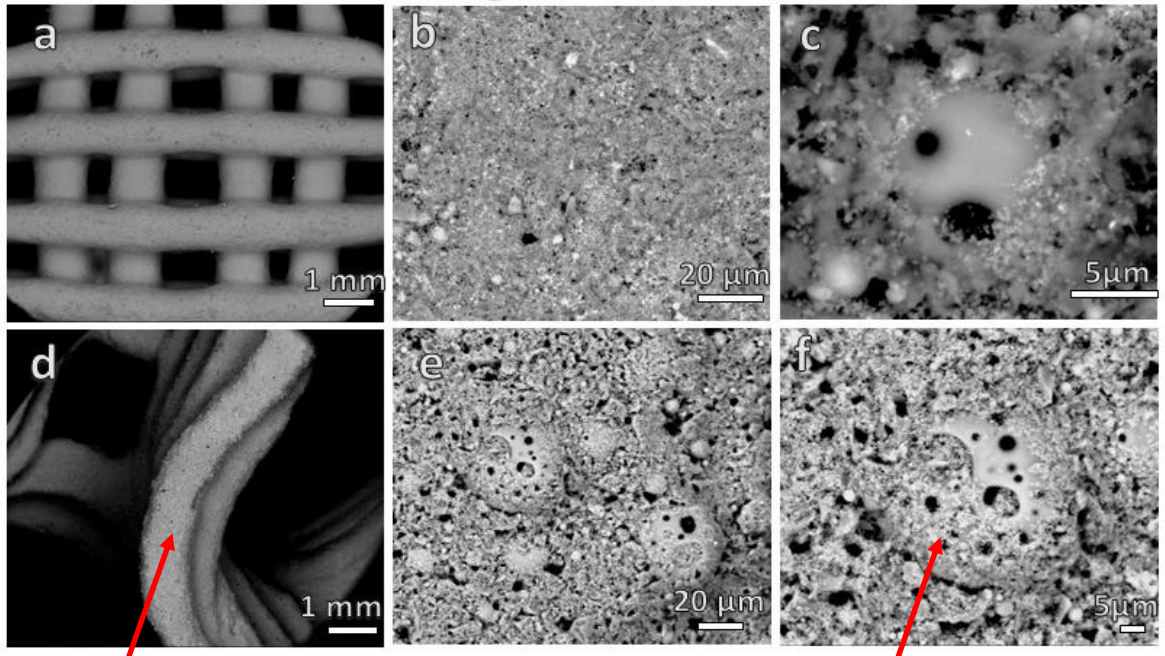
Main collaborator: Mr Mokhtar Mahmoud

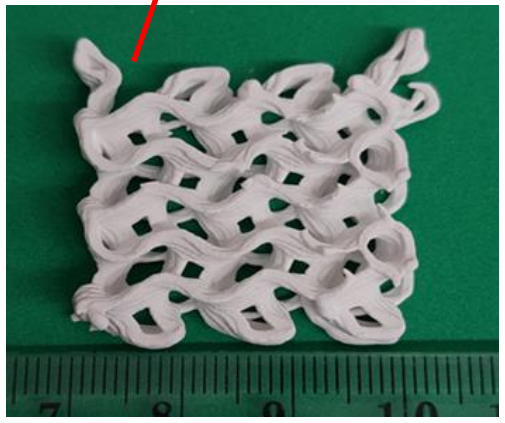
Beyond constructions: AM of functional composites

Perspective of organic-free direct ink writing of glass powders
Determination of photocatalytic scaffolds

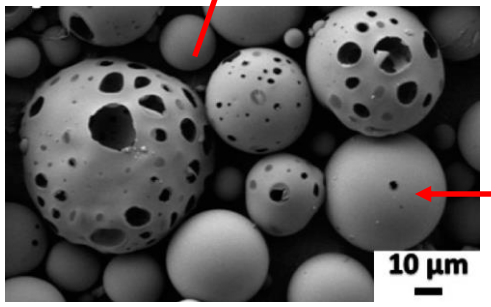
Reticulated scaffold

Limited sagging, complete integration of fillers





Gyroid scaffold



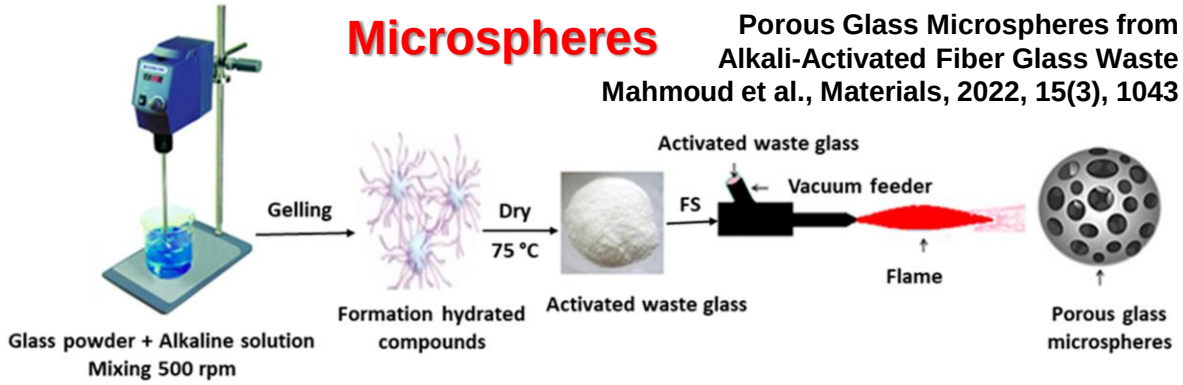
- **Activation with 2.5M NaOH**
- **Solid loading: 65 wt%**
- **Printing repeated with**

a. TiO_2 nanoparticles (anatase, ~21 nm, Evonik Degussa GmbH, Germany) **- added to starting suspension [10-20 wt% compared to BSG amount]**

b. Glass microspheres (from alkali activated fibre glass powders, dried & fired with methane torch) - added to starting suspension [20-30 wt% replacing BSG amount]

Microspheres

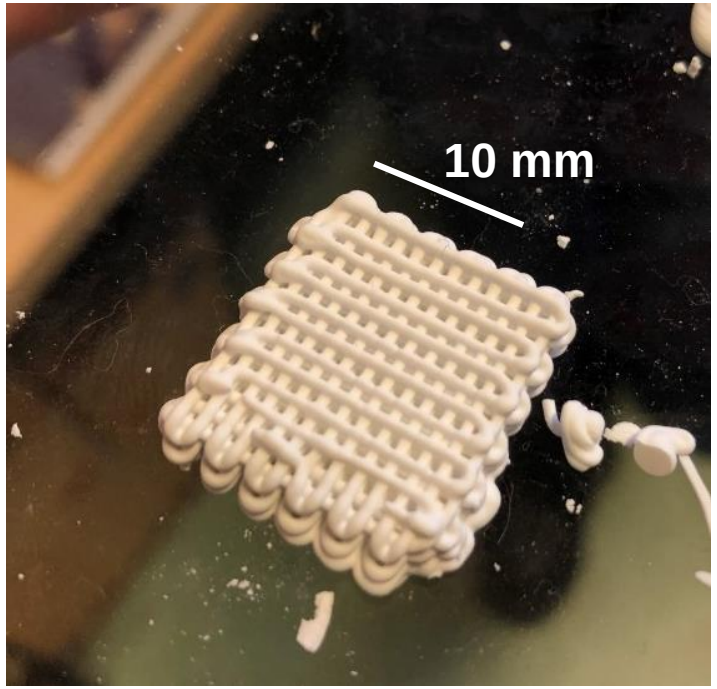
Porous Glass Microspheres from Alkali-Activated Fiber Glass Waste
Mahmoud et al., Materials, 2022, 15(3), 1043

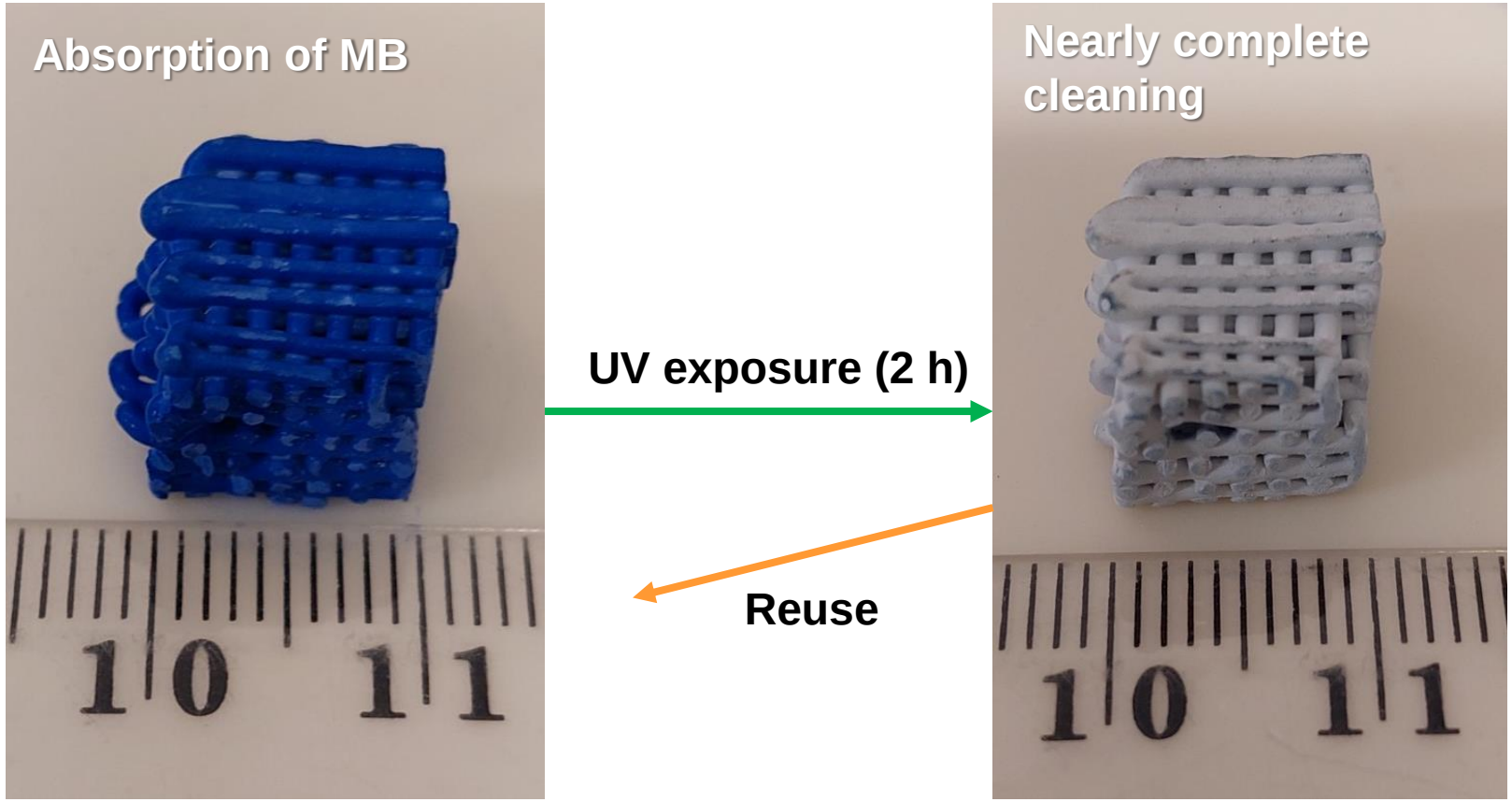


‘Static’ test

Immersion in MB solution first, UV after UV exposure [Hg lamp, λ=366 nm, P=125 W] as cleaning step

Functional additive-manufactured (unfired) composites

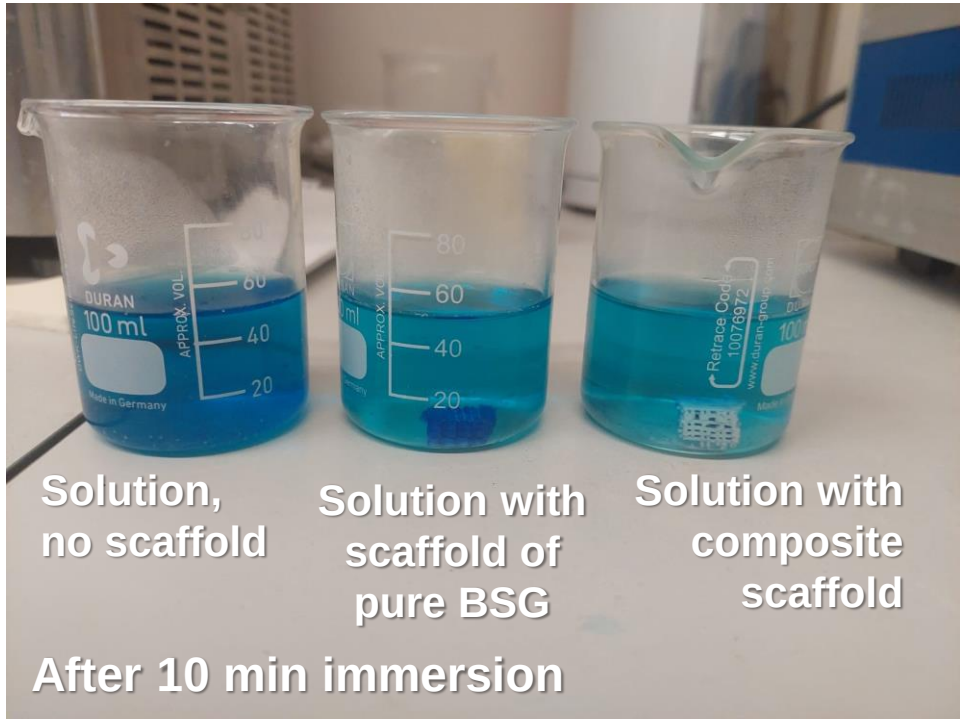




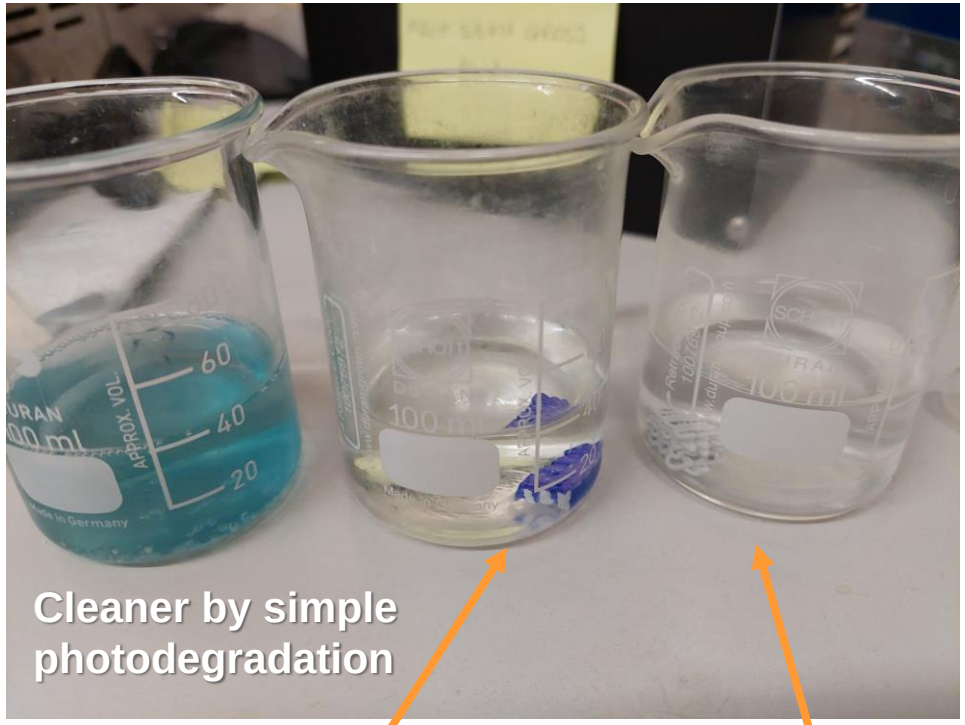
Printing method: DIW
Composition: Pharmaceutical Glass + 20 wt%TiO_2
Methylene Blue Concentration: 10 mg/L
30 min immersion

'Dynamic ' test

Immersion in MB solution first, UV with scaffold immersed
More evident photocatalytic effect



UV exposure (2 h)



Clean, by photodegradation + absorption

Clean, by photodegradation + absorption + catalysis

Extended tests

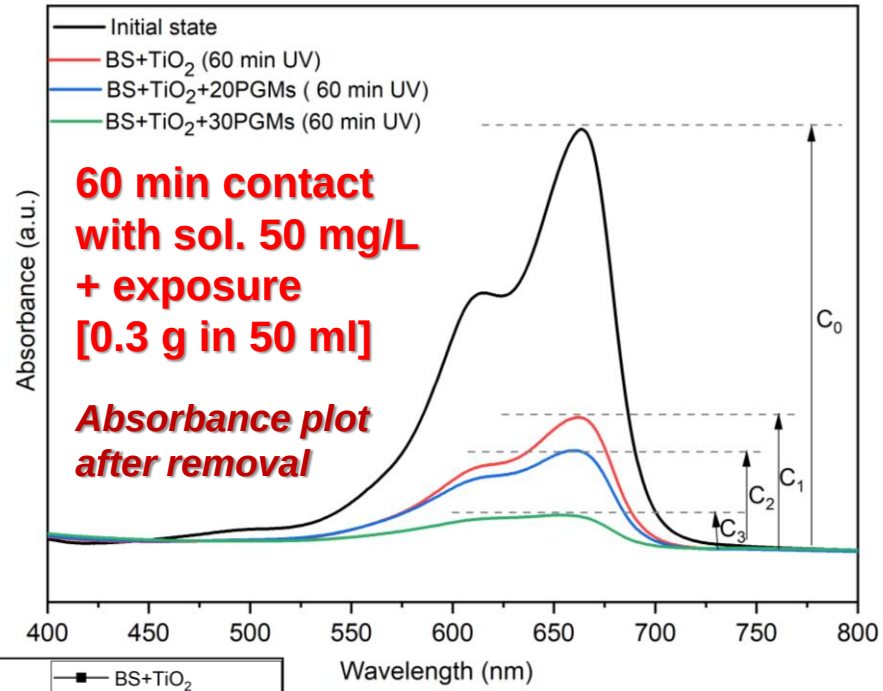
Microspheres leading to lighter and…stronger scaffolds
Improvements also in photocatalytic effect

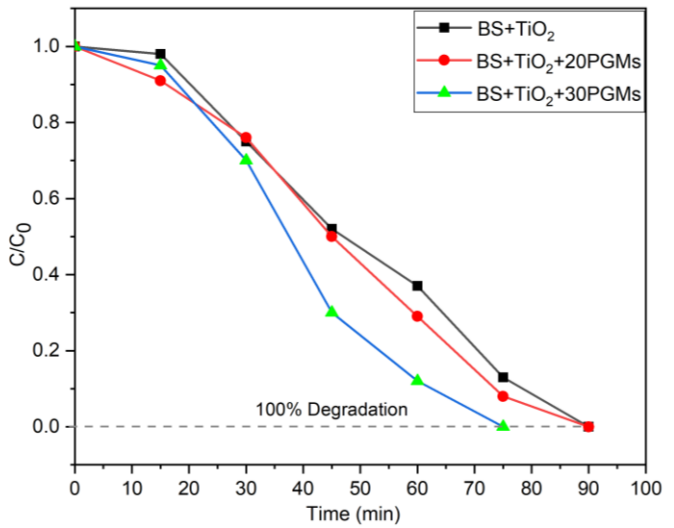
Samples	ρ_{geom} (g/cm³)	ρ_{app} (g/cm³)	ρ_{true} (g/cm³)	Total porosity, P (%)	Open porosity OP (%)	Closed porosity CP (%)	Compressive strength (MPa)
BSG +TiO_2	0.97 ±0.01	2.73 ±0.06	2.86 ±0.06	65 ± 1	64 ± 1	1 ± 1	0.3 ± 0.1
BSG+TiO_2 +20PGMs	0.91 ±0.01	2.70 ±0.04	2.81 ±0.04	67 ± 1	66 ± 1	1 ± 1	1.2 ± 0.2
BSG+TiO_2 +30PGMs	0.77 ±0.02	2.71 ±0.03	2.77 ±0.03	72 ± 1	71 ± 1	1 ± 1	1.5 ± 0.2

$$\sigma_{comp} = \sigma_{bend\ sol\ phase} \cdot 0.2 \cdot (\rho_{rel})^{1.5}$$

$\sigma_{bend\ sol\ phase} \sim 50$ MPa

Still to be analyzed in full: glass microspheres
(Ca alumino-silicate glass) probably offering stronger gels
All samples surviving water boiling testing





Enhanced porosity with glass microspheres likely increasing the absorption

Confirming the strong bonding

Study of porous cold-consolidated block as membranes for inorganic waste

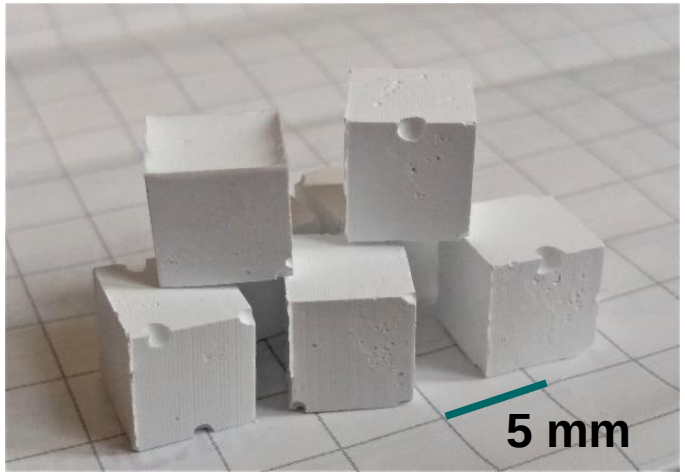
Deposition depending on (acidic) pH values

- **Pharmaceutical boro-alumino-silicate glass cullet: particle size < 75 μm.**
- **Alkali activator: NaOH-KOH, 2.5 M (50mol%:50mol%)**
- **Solid to liquid ratio: 60:40**
- **Curing temperature: 40 °C, 14 days.**
- **Open container**

Wt(%)	C	O	Na	Al	Si	K	Ca
BSG	10.46	50.02	**13.95**	2.15	18.55	**4.04**	0.79
BSG-w	-	51.25	**6.03**	4.02	35.94	**1.56**	1.2

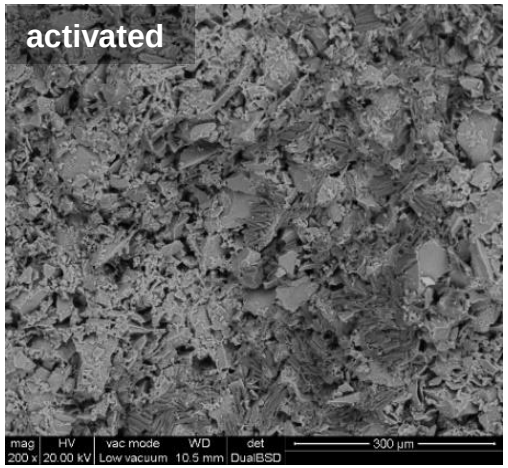
EDS

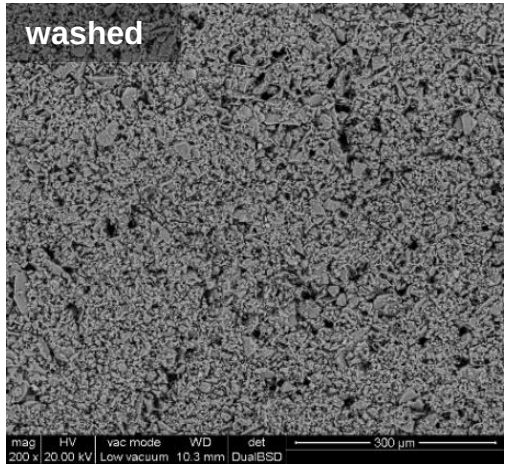
The BSG was shaped in the form of cubic castings: surviving even at pH=2

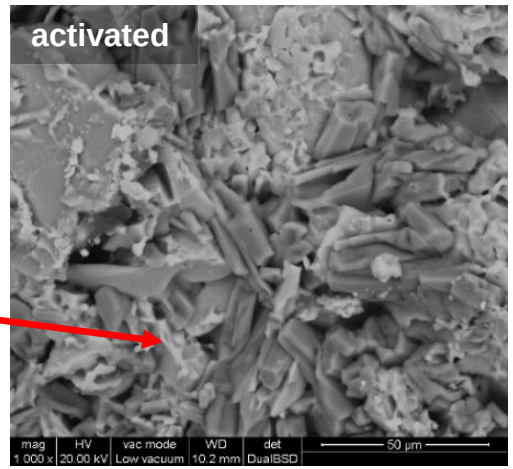


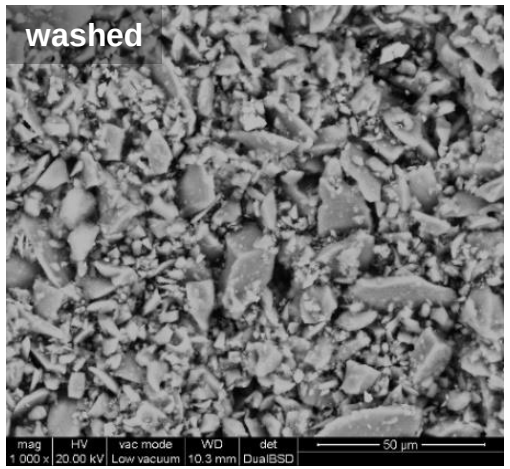
Washing: application of boiling test

Alkali carbonates leaving







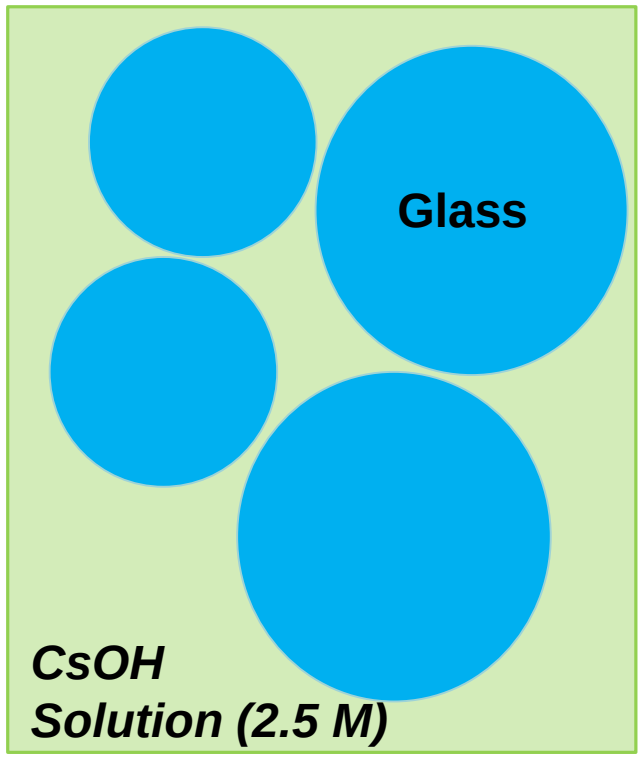


FunGlass

Main collaborator: Dr Diana Carolina Lago

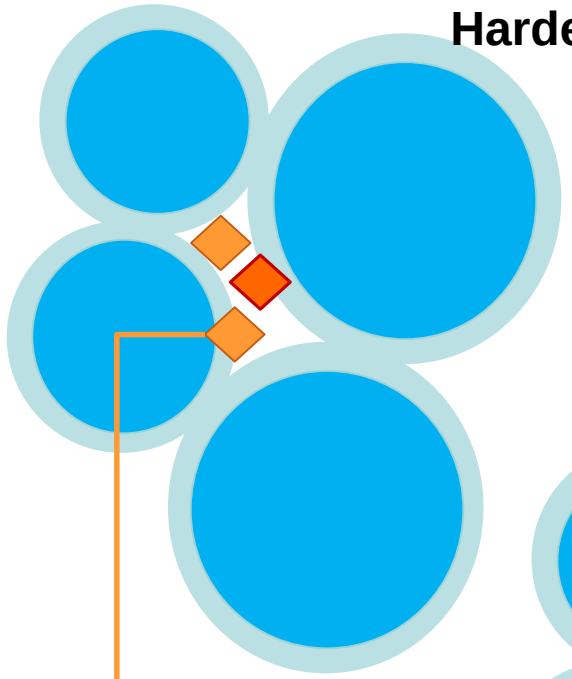
Beyond NaOH: CsOH (latest tests)

Prototype of nuclear waste of difficult stabilization
Confirming the overall mechanism



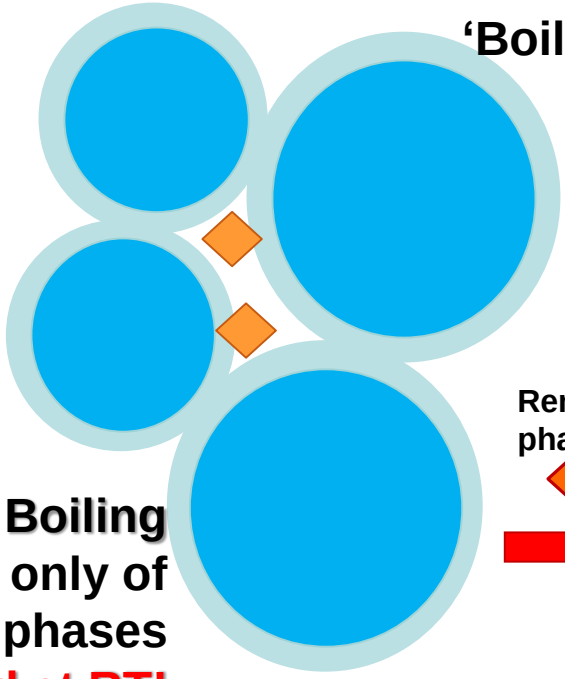
1. Alkaline attack

Pollucite developed by collecting SiO_4, AlO_4 and BO_4 from the solution (the latter stabilized by Cs^+ ions)



Hardened (dried)

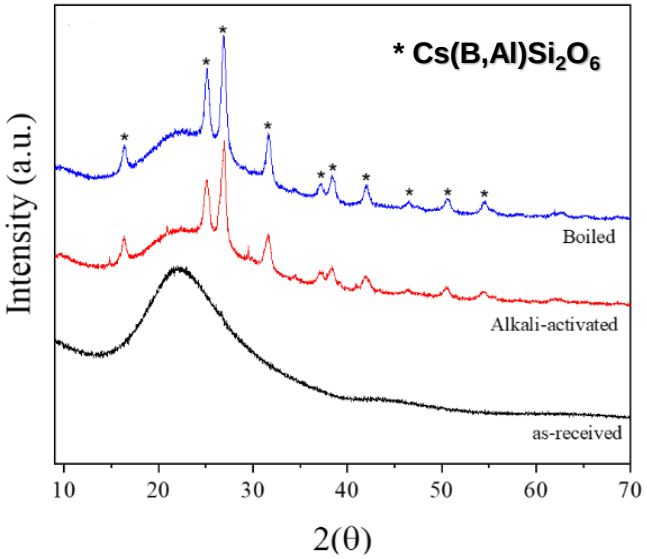
2. Formation of multiple secondary phases:
Cs_2CO_3 (water soluble)
+ pollucite solid solution [framework structure]
$Cs(B,Al)Si_2O_6$

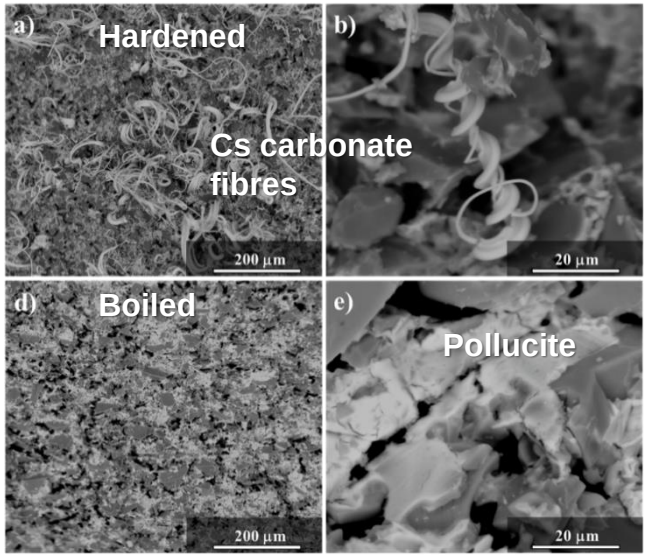


'Boiled'

3. Boiling
Removal only of secondary soluble phases
Some Cs immobilized at RT!

Removed phase

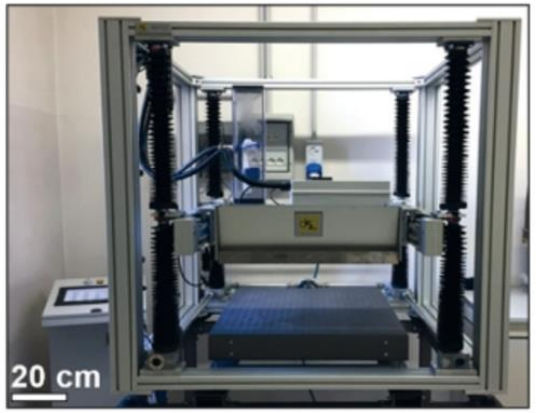




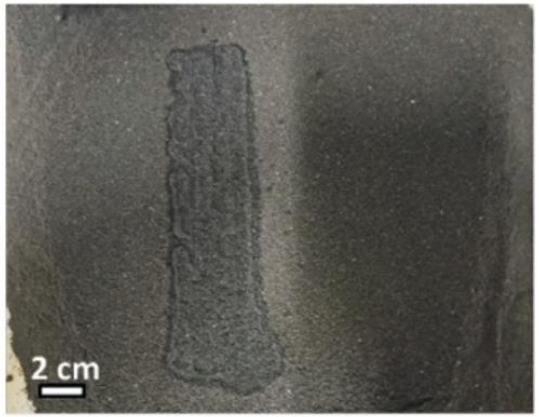
Final stabilization by sintering

Extended AM technologies (ongoing studies)

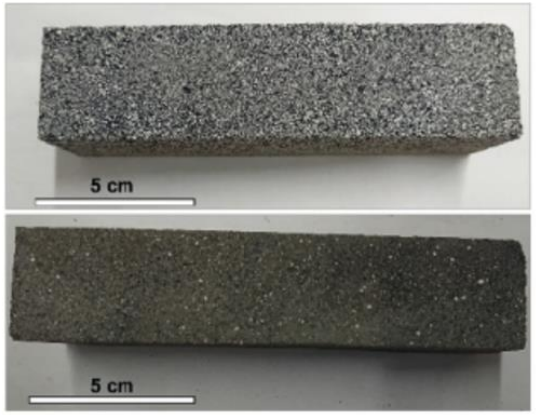
Large scale additive manufacturing: ink-jet printing
Powder beds injected with alkaline solution



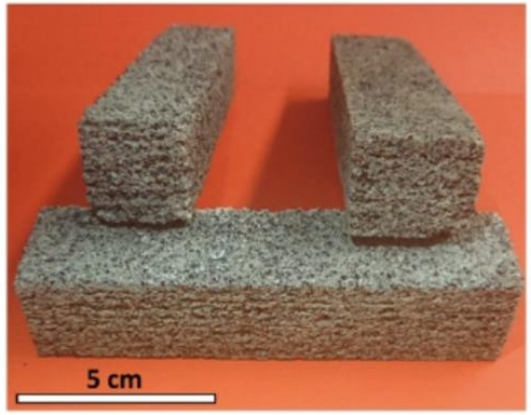
The printer



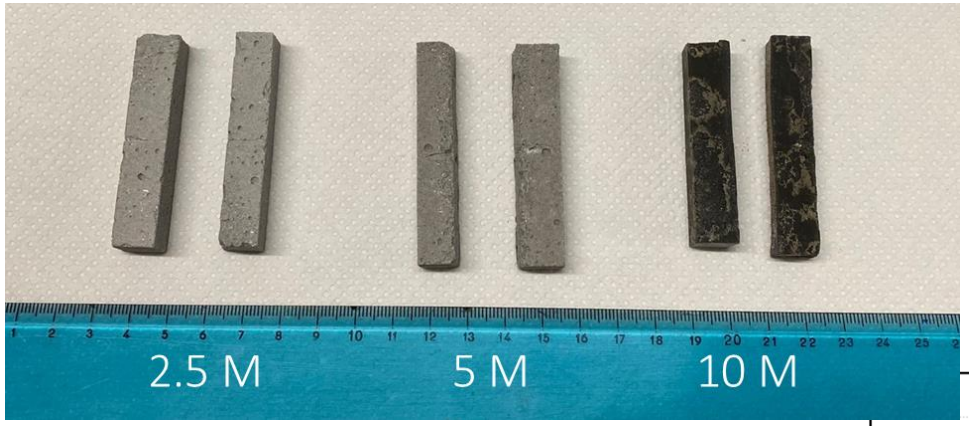
The powder bed



Slag-based printed parts

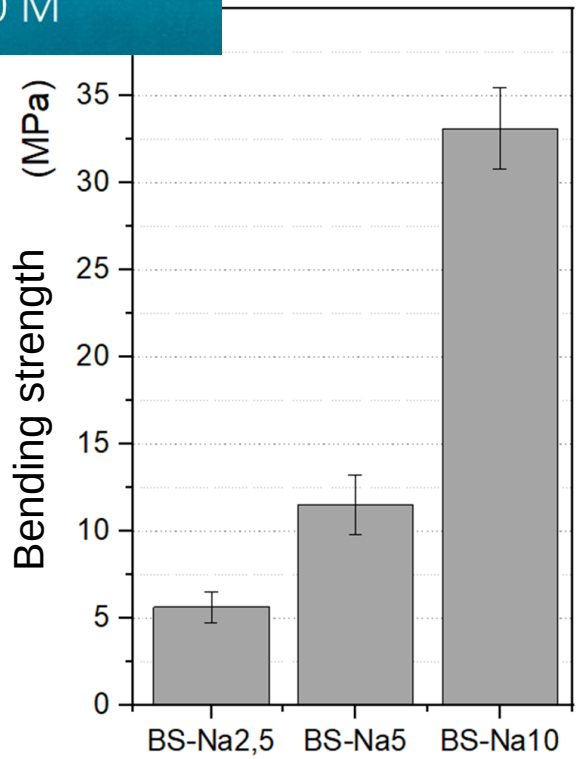


Cooperation with Prof. P. Colombo, Prof. H. Elsayed and Dr F. Gobbin



First tests with discarded pharmaceutical glass (coarse fraction, including some metal fractions)

Different glass/solution interaction: update of molarity



Beyond BSG

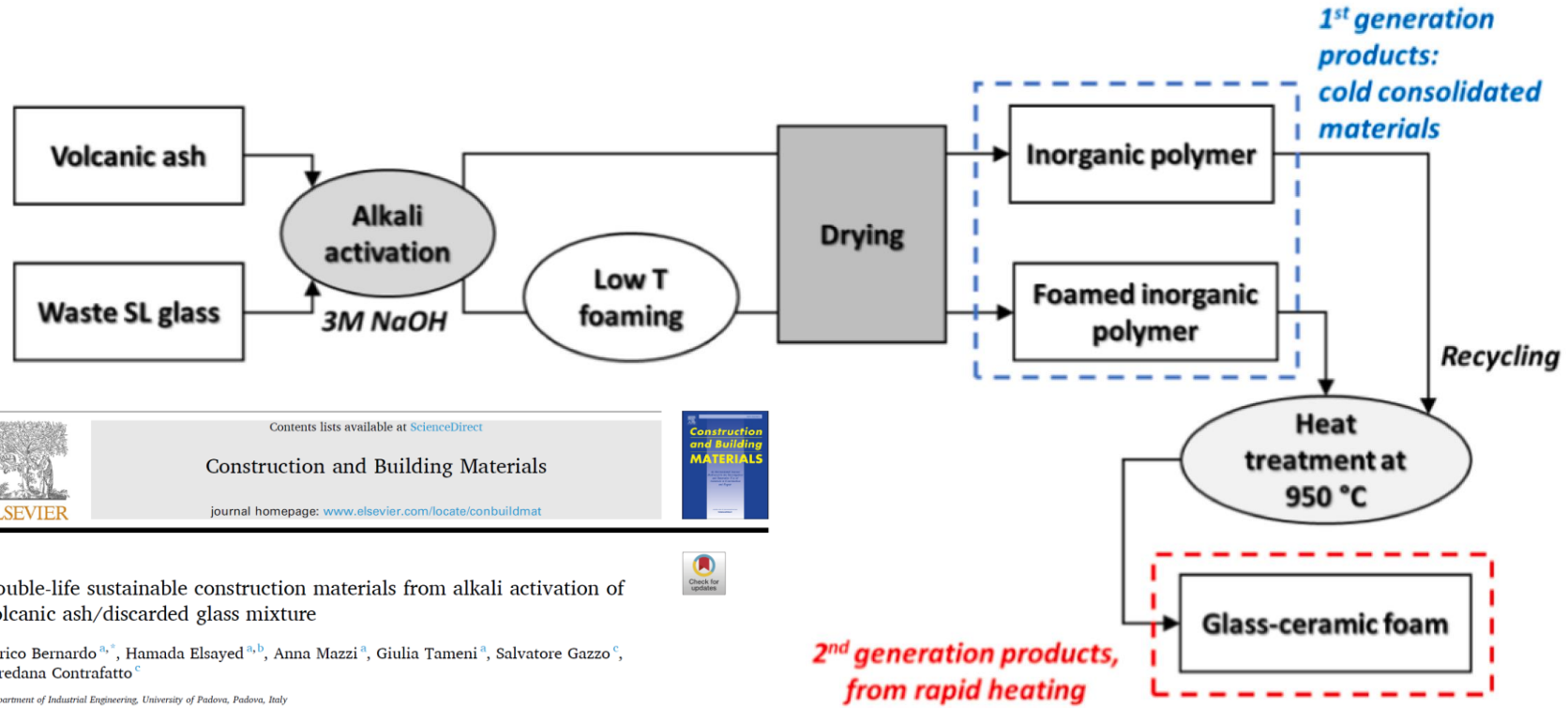
Soda-lime glass combined with volcanic ash (Mt Etna)
Ash providing Al_2O_3

Chemical analysis (oxide contents in wt%) of volcanic ash (V) and cullet (G).

	V	G
SiO_2	46.8	71.7
TiO_2	1.9	0.1
Al_2O_3	16.0	0.7
Fe_2O_3	11.9	0.1
MgO	6.3	3.3
CaO	9.8	10.1
Na_2O	2.8	13.2
K_2O	1.8	0.1
SO_3	0.3	0.2
Other	2.4	0.5

Cooperation with Prof. Loredana Contrafatto
Dept. of Civil Engineering and Architecture, University of Catania, Italy

Concept of 'double-life' ('inherently recyclable') materials



Contents lists available at ScienceDirect
Construction and Building Materials
journal homepage: www.elsevier.com/locate/conbuildmat

Double-life sustainable construction materials from alkali activation of volcanic ash/discarded glass mixture

Enrico Bernardo [a,*], Hamada Elsayed [a,b], Anna Mazzi [a], Giulia Tameni [a], Salvatore Gazzo [c], Loredana Contrafatto [c]

[a] Department of Industrial Engineering, University of Padova, Padova, Italy
[b] Refractories, Ceramics and Building Materials Department, National Research Centre, 12622 Cairo, Egypt
[c] Department of Civil Engineering and Architecture, University of Catania, Catania, Italy

Formulations and hardening

Very simple processing
Suitable locally: use of soda-lime residues

50 wt% Etna ashes (milled and sieved < 75 µm) + **50 wt% soda-lime glass** powders (Savel CS60 type: fine powders, residue from the refinement of container glass)

- **Casting in 3 M NaOH solution**, within moulds [100 g of powder mix (50 g Etna ashes + 50 g soda-lime glass) / 42-39 ml of solution] meaning **'water'/solid ratio from 0.42 to 0.35**
- **Mechanical stirring at 400 rpm for 30 min + sonication 3 min**
- **Curing performed at 75 °C for 72 hours**.



Casting Moulds covered by PE film



After curing

Formulations and hardening

Very simple processing
Evidences of interaction

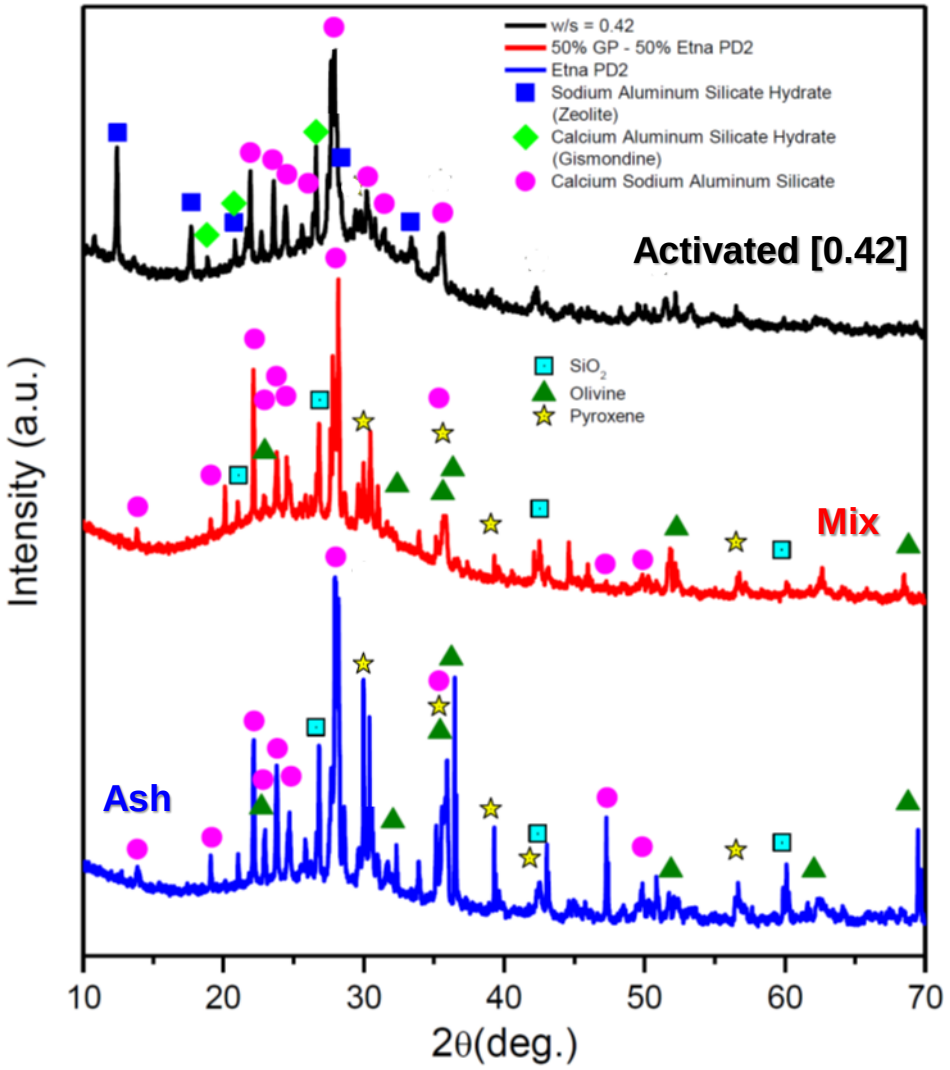
50 wt% Etna ashes (milled and sieved < 75 μm) + **50 wt% soda-lime glass** powders (Savel CS60 type: fine powders, residue from the refinement of container glass)

- **Casting in 3 M NaOH solution**, within moulds [100 g of powder mix (50 g Etna ashes + 50 g soda-lime glass) / 42-39 ml of solution] meaning **'water'/solid ratio from 0.42 to 0.35**
- **Mechanical stirring at 400 rpm for 30 min + sonication 3 min**
- **Curing performed at 75 °C for 72 hours**.

Activation leading to reduction of silicate-related peaks (chain silicates as more reactive)

2θ upshift of amorphous halo [typical of AAMs]

Evidence of (Ca- and Na-based) zeolite formation

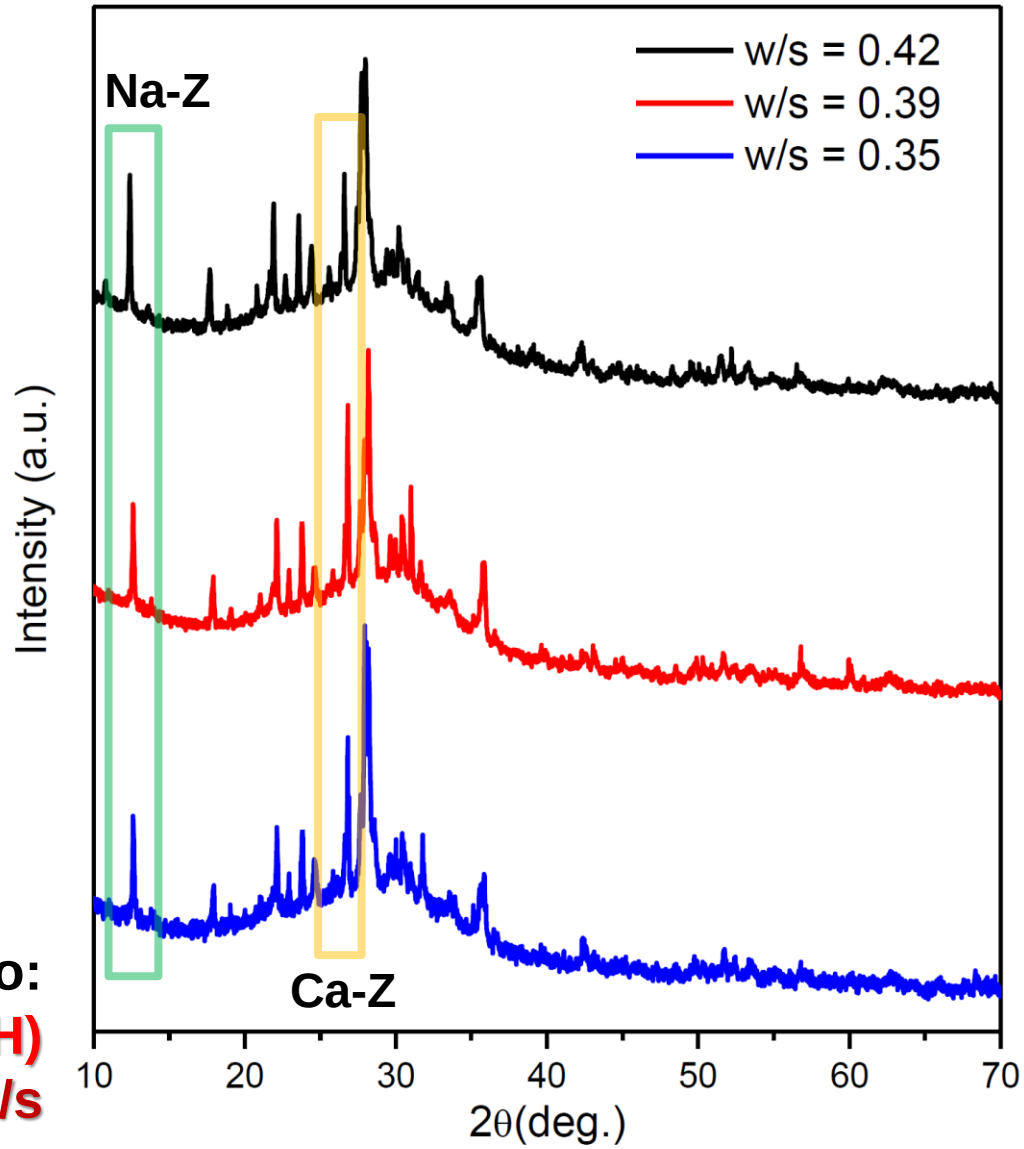


Formulations and hardening

Very simple processing
Evidences of interaction

50 wt% Etna ashes (milled and sieved < 75 μm) + **50 wt% soda-lime glass** powders (Savel CS60 type: fine powders, residue from the refinement of container glass)

- **Casting in 3 M NaOH solution**, within moulds [100 g of powder mix (50 g Etna ashes + 50 g soda-lime glass) / 42-39 ml of solution] meaning **'water'/solid ratio from 0.42 to 0.35**
- **Mechanical stirring at 400 rpm for 30 min + sonication 3 min**
- **Curing performed at 75 °C for 72 hours**.



Some variations in Ca- and Na- with w/s ratio:

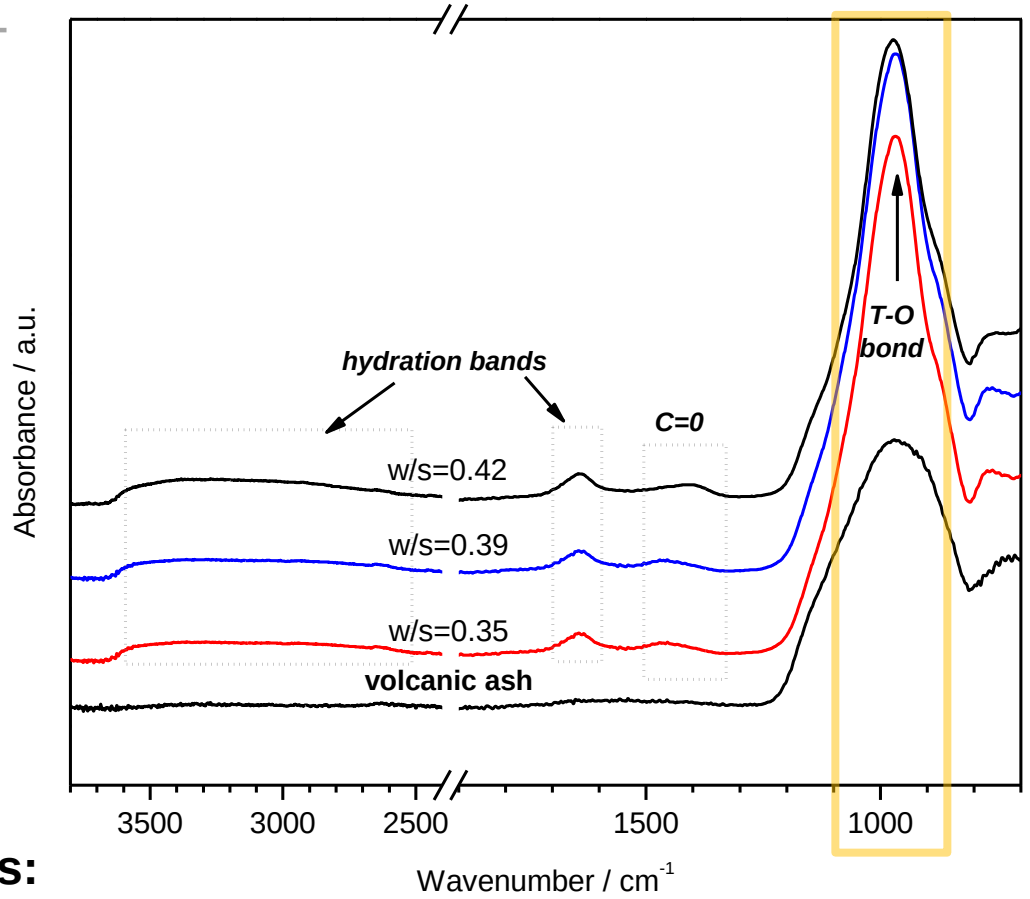
- **Na zeolite favoured at high w/s (more liq→more NaOH)**
- **Ca zeolite favoured at low w/s**

Formulations and hardening

Very simple processing
Evidences of interaction

50 wt% Etna ashes (milled and sieved < 75 μm) + **50 wt% soda-lime glass** powders (Savel CS60 type: fine powders, residue from the refinement of container glass)

- **Casting in 3 M NaOH solution**, within moulds [100 g of powder mix (50 g Etna ashes + 50 g soda-lime glass) / 42-39 ml of solution] meaning **'water'/solid ratio from 0.42 to 0.35**
- **Mechanical stirring at 400 rpm for 30 min + sonication 3 min**
- **Curing performed at 75 °C for 72 hours**.



Confirmations from IR bands:

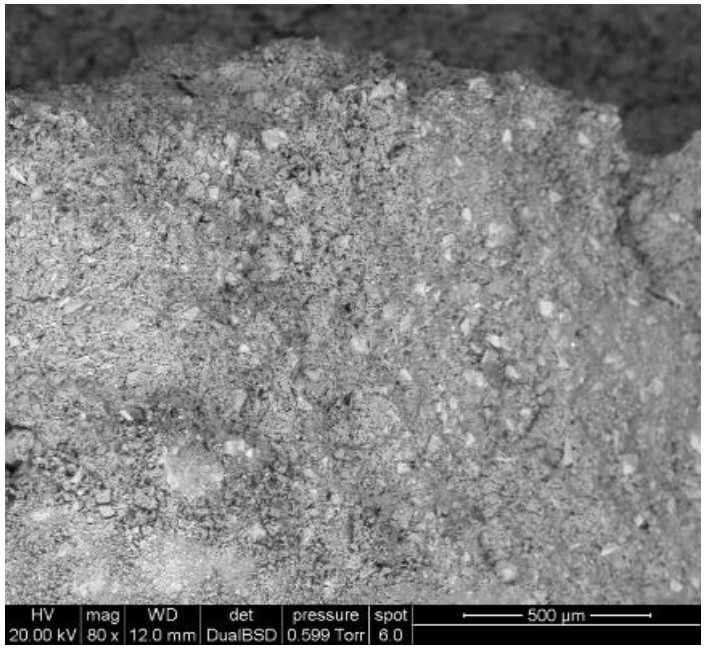
- **Hydration (at high wavenumber)**
- **Crystal phases with framework structure (1000 cm^{-1}) as dominant: old (feldspar) and new (zeolites)**
- **Limited carbonation**

Characterization of bricks

Binder-only formulations

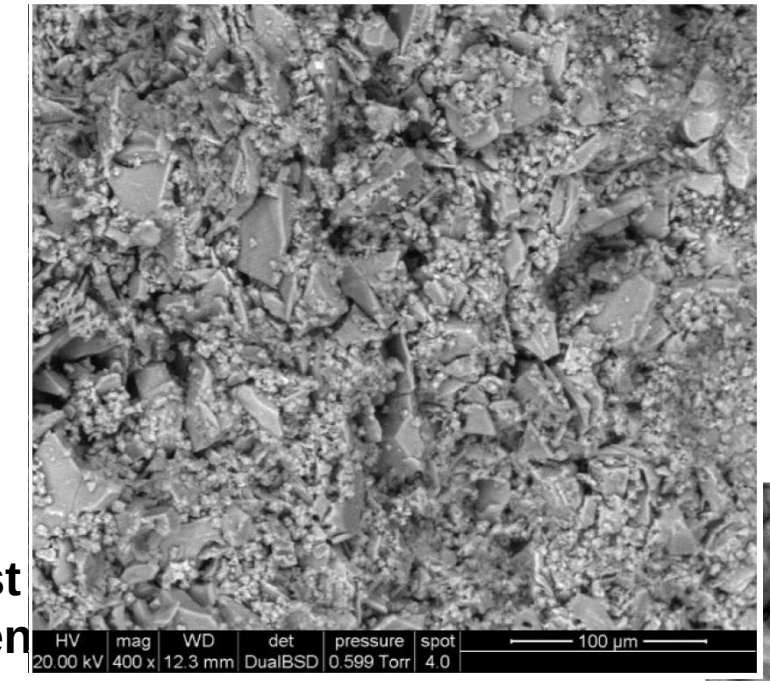
Significant residual porosity, but excellent integrity

	w/s		
	0.42	0.39	0.35
ρ_{geom} [g/cm^3]	1.54 ± 0.02	1.52 ± 0.03	1.62 ± 0.01
φ_{total} [%]	36.08 ± 0.01	38.18 ± 0.01	31.65 ± 0.01
φ_{open} [%]	35.54 ± 0.01	37.45 ± 0.01	29.27 ± 0.01
φ_{close} [%]	0.54 ± 0.01	0.70 ± 0.01	2.38 ± 0.01

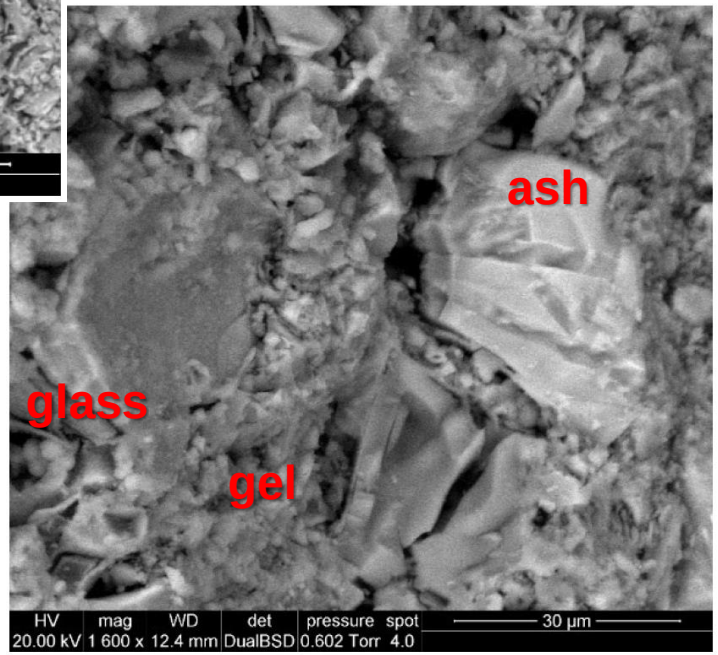


High residual porosity, almost completely open
No microcracks

w/s = 0.42
activated



Newly developed gel binding unreacted material

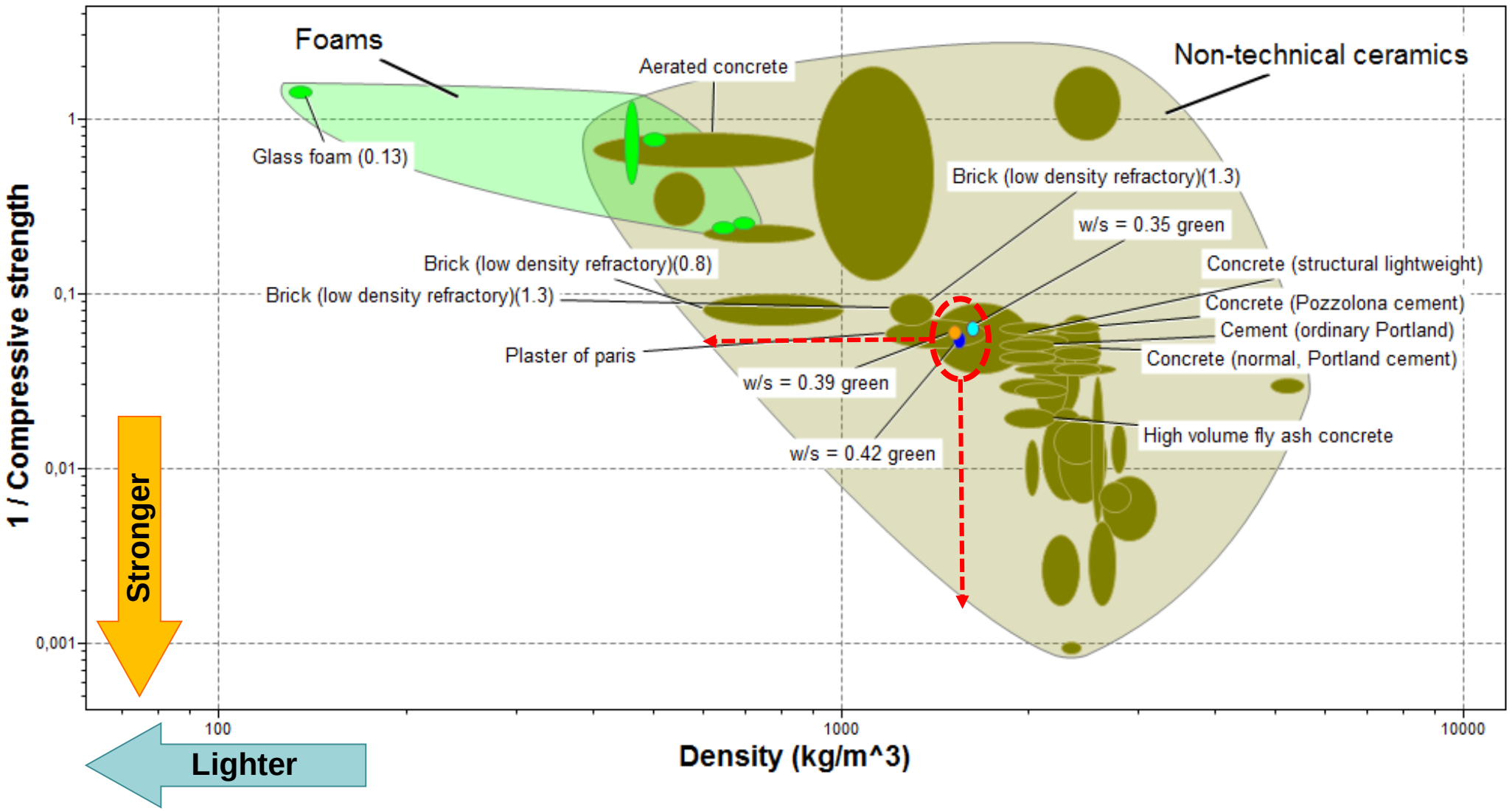


Gel resisting to boiling test (2h in boiling water, with no disintegration of samples)

Characterization of bricks

Comparison with other structural materials

Strength/density trade-off analysis



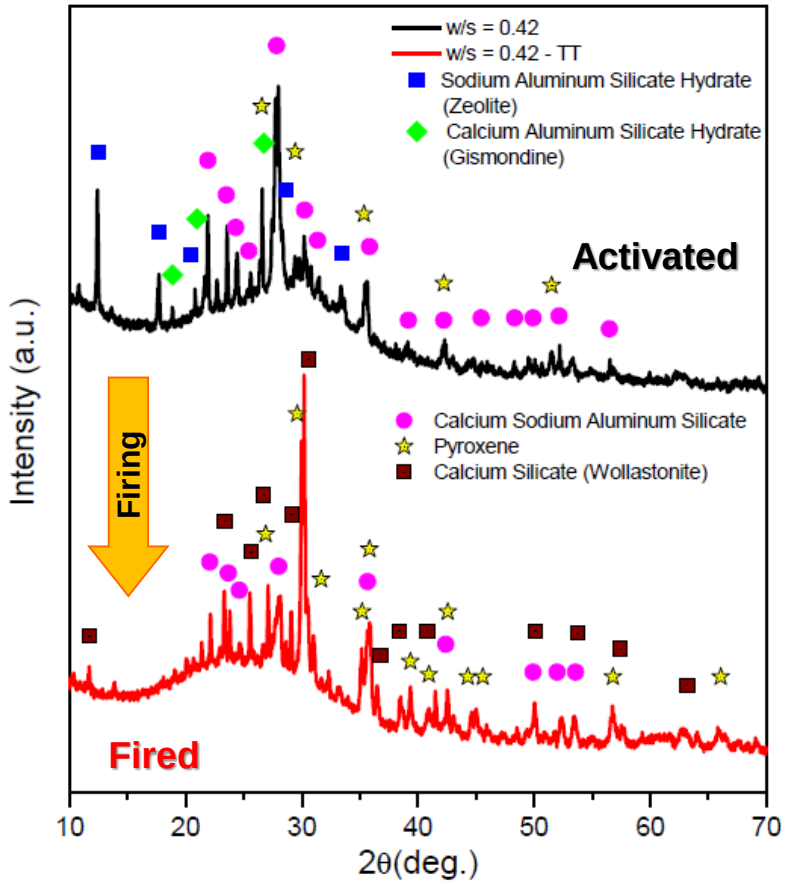
Data and chart from Ansys Granta Selector (CES) software package

Favourable trade-off ***('nothing stronger with the same density')***

Overlapping with structural lightweight concrete confirmed

2nd life: heating at 950 °C

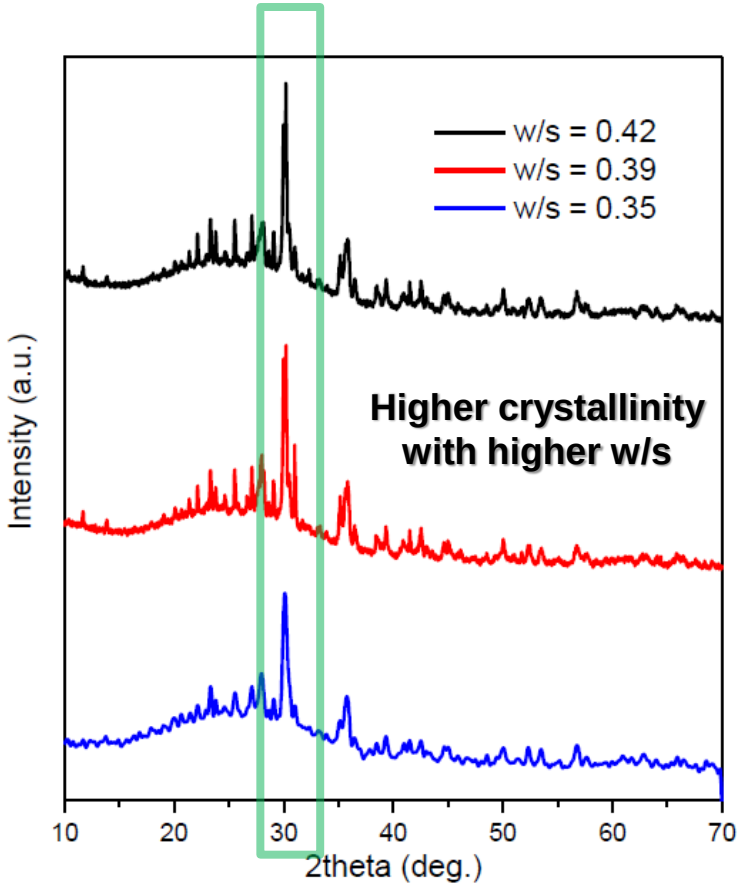
Direct insertion at firing T, 15 min holding time
Transformation into glass-ceramic foams



- **Decomposition of zeolites as possible foaming contribution**
- **Plagioclase dissolved**
- **Pyroxene reformed**

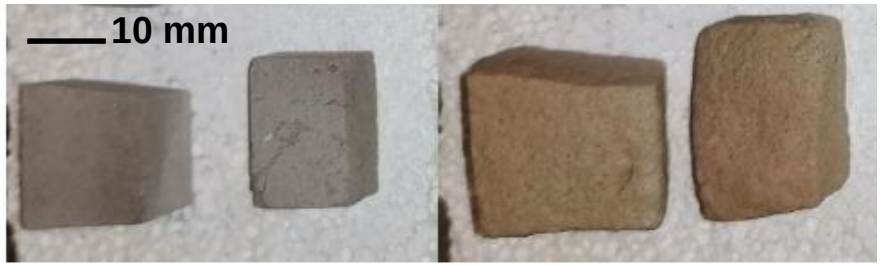
New main phase: wollastonite ($CaSiO_3$)→*proof of mixing with (Al-poor) soda-lime*

Most of Al_2O_3 in glassy phase



	w/s		
	0.42	**0.39**	**0.35**
ρ_{geom} [g/cm³]	0.68 ± 0.01	0.72 ± 0.03	0.75 ± 0.02
φ_{total} [%]	74.48 ± 0.01	72.43 ± 0.01	72.13 ± 0.01
φ_{open} [%]	71.59 ± 0.01	64.80 ± 0.01	63.04 ± 0.01
φ_{close} [%]	2.89 ± 0.01	7.64 ± 0.01	9.09 ± 0.01

	w/s		
	0.42	**0.39**	**0.35**
σ_c [MPa]	4.32 ± 0.48	4.50 ± 0.47	4.57 ± 0.57

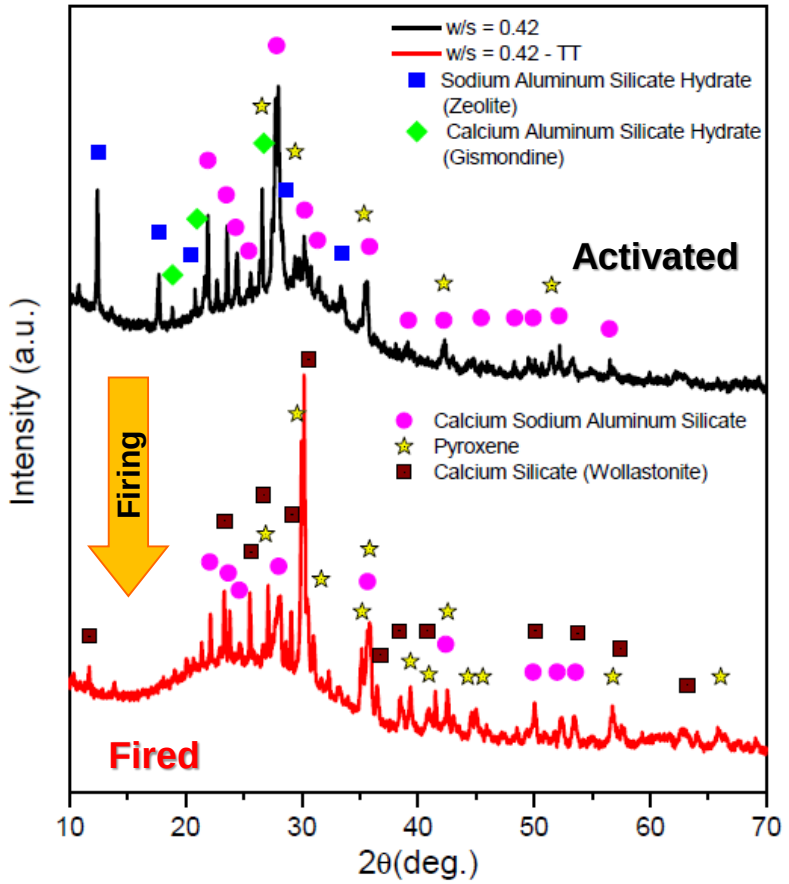


w/s = 0.42 activated after TT

Samples cut from fragments recovered from previous tests

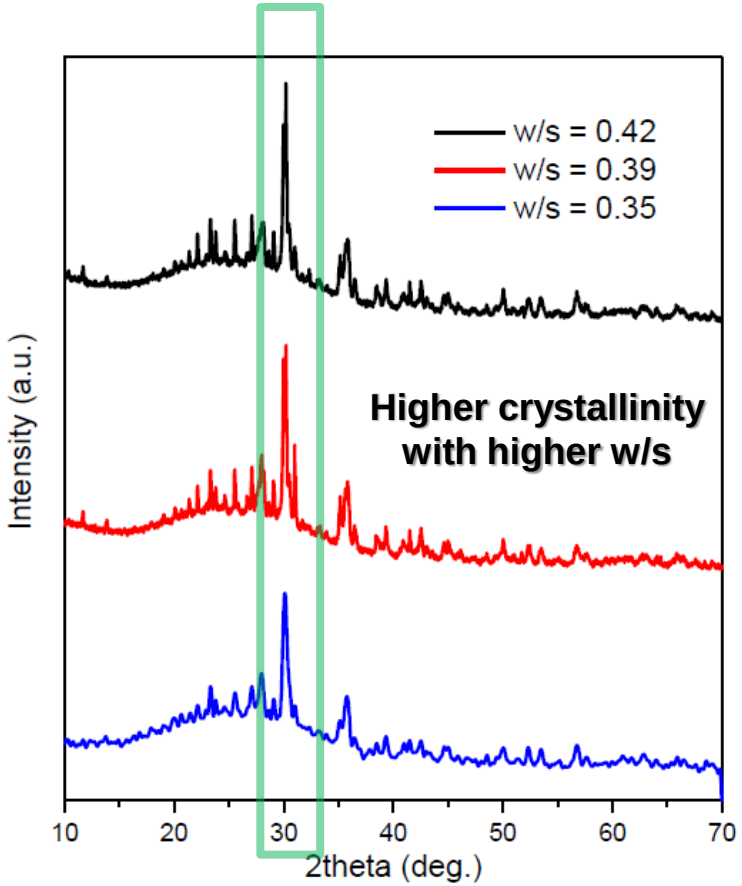
2nd life: heating at 950 °C

Direct insertion at firing T, 15 min holding time
Transformation into glass-ceramic foams



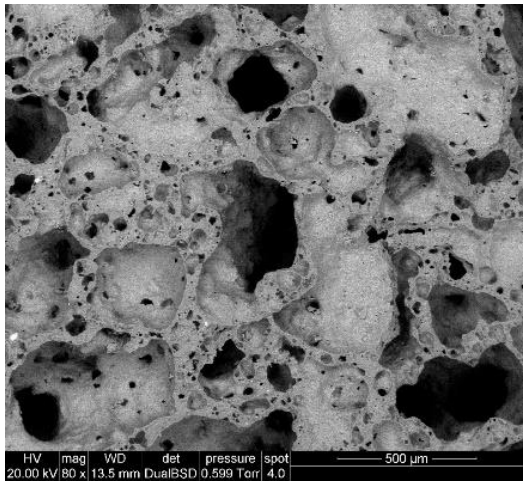
- **Decomposition of zeolites as possible foaming contribution**
- **Plagioclase dissolved**
- **Pyroxene reformed**

New main phase: wollastonite ($CaSiO_3$)→proof of mixing with (Al-poor) soda-lime
Most of Al_2O_3 in glassy phase



	w/s		
	0.42	**0.39**	**0.35**
ρ_{geom} [g/cm³]	0.68 ± 0.01	0.72 ± 0.03	0.75 ± 0.02
φ_{total} [%]	74.48 ± 0.01	72.43 ± 0.01	72.13 ± 0.01
φ_{open} [%]	71.59 ± 0.01	64.80 ± 0.01	63.04 ± 0.01
φ_{close} [%]	2.89 ± 0.01	7.64 ± 0.01	9.09 ± 0.01

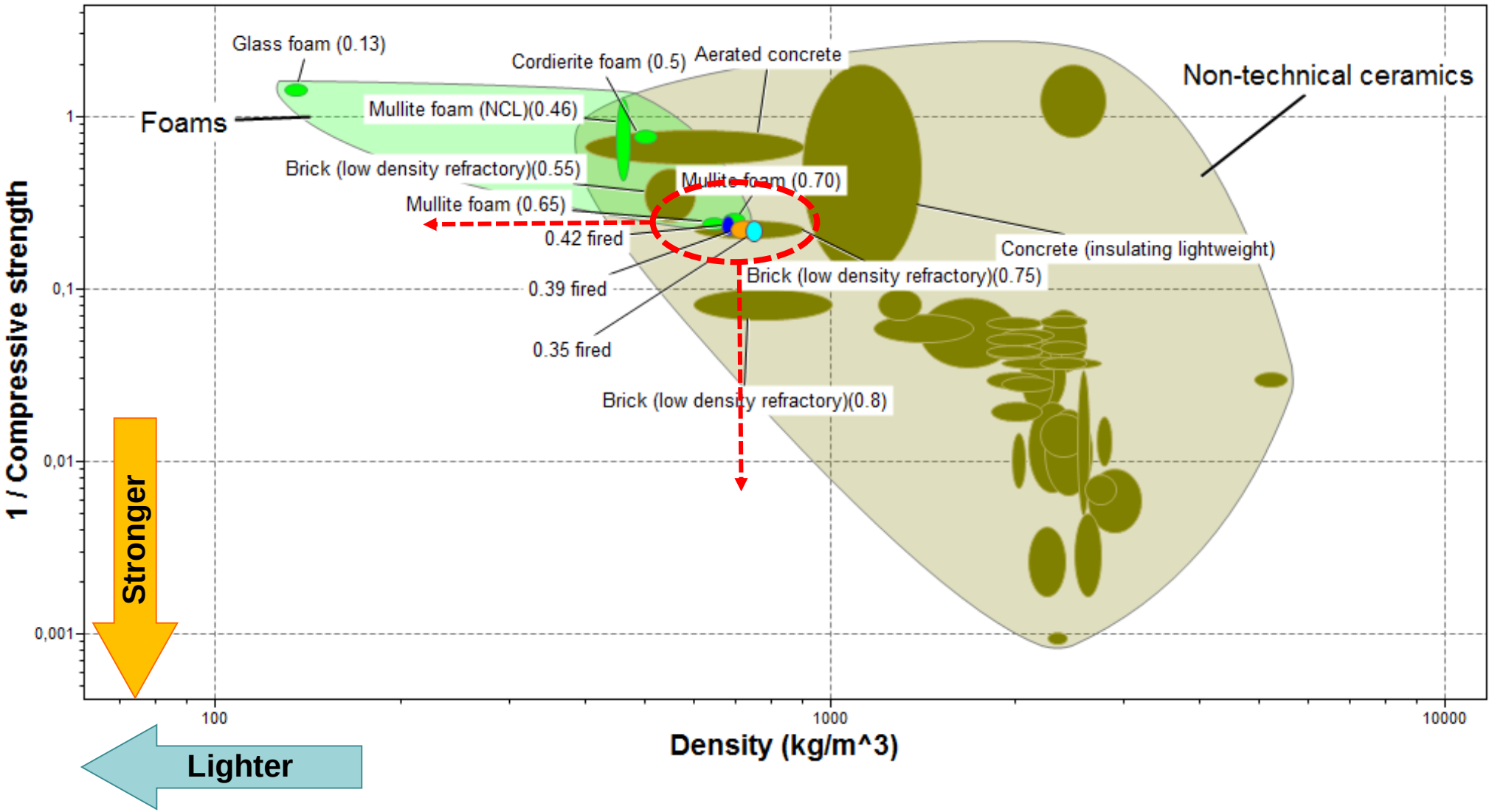
	w/s		
	0.42	**0.39**	**0.35**
σ_c [MPa]	4.32 ± 0.48	4.50 ± 0.47	4.57 ± 0.57



Validation of 'upcycled' binders

Comparison with other structural materials

Strength/density trade-off analysis



Data and chart from Ansys Granta Selector (CES) software package

Still favourable strength/density trade-off

Lighter but as strong as lightweight concrete

Possible hybridation: foams as lightweight aggregates

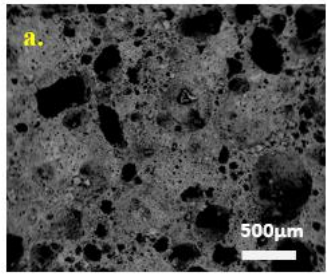
Inorganic polymers from waste fibre glass (ongoing)

Possible inclusion of dismantled AZS refractory (up to 20 wt%)

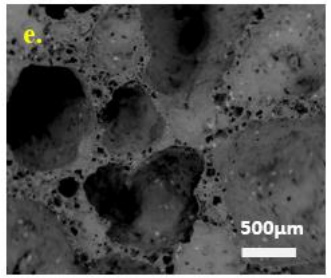
Quite successful unfired products + transformation into porous GCs

Fast activation:
10 min mixing
+ 24 h drying at 60 °C
(L(S=0.4)

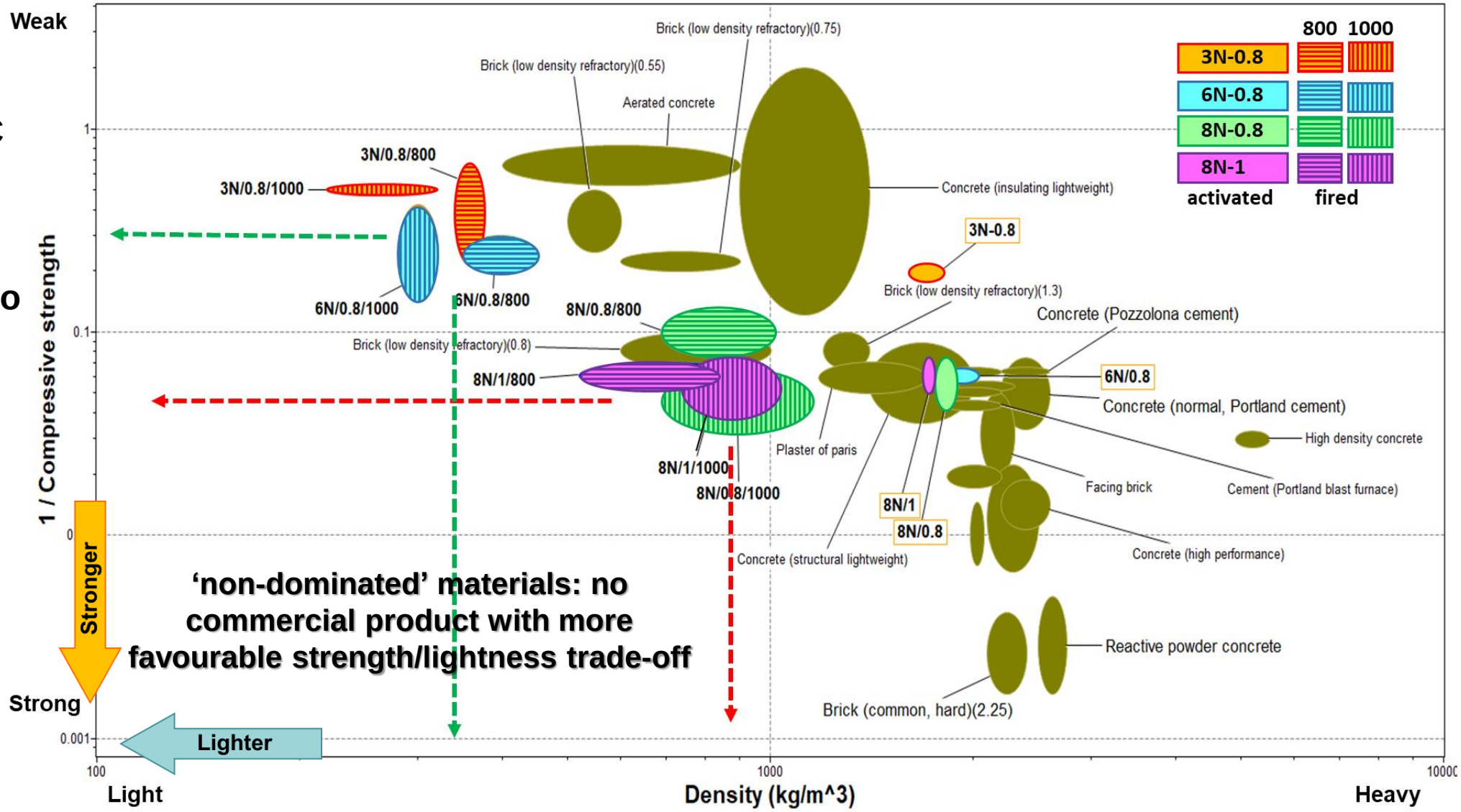
- **Stable IPs**
- **Transformation into GCs by heating**



Fired at 800°C



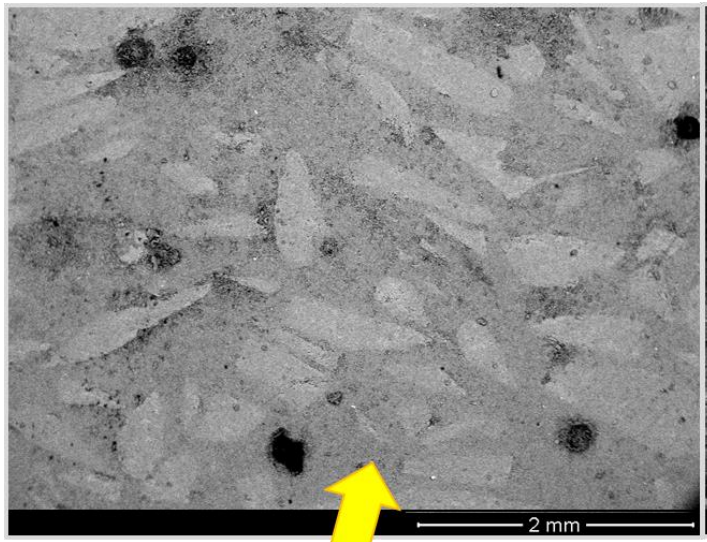
Fired at 1000°C

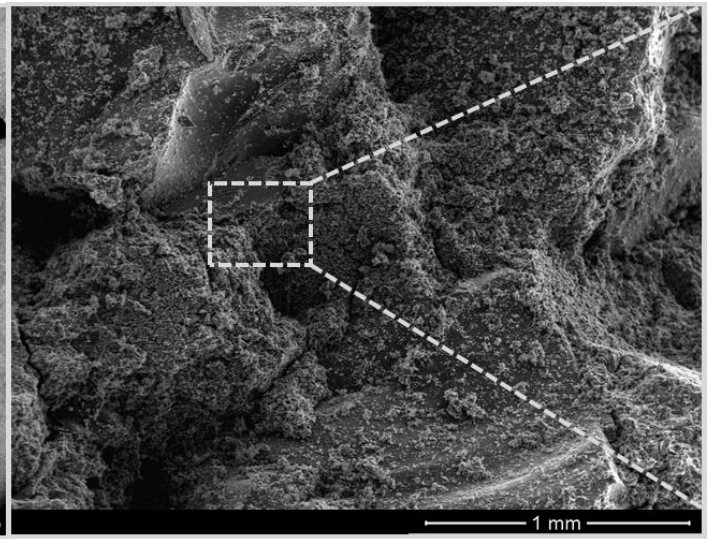


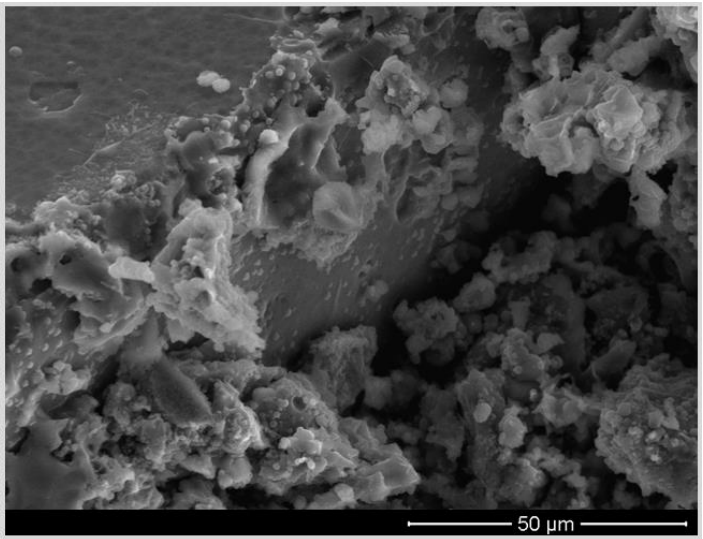
Other construction materials

Decorative ‘mosaic’ composites

Discarded glass fragments in glass-based cement matrix











General approach

Coarse granules may be flexible

- ***Glasses of different colour and composition***
- ***Glasses with PbO et al.***

Cement from activated BSG

Possible application also for SL

($NaAlO_2$ possibly replacing NaOH)

Other construction materials

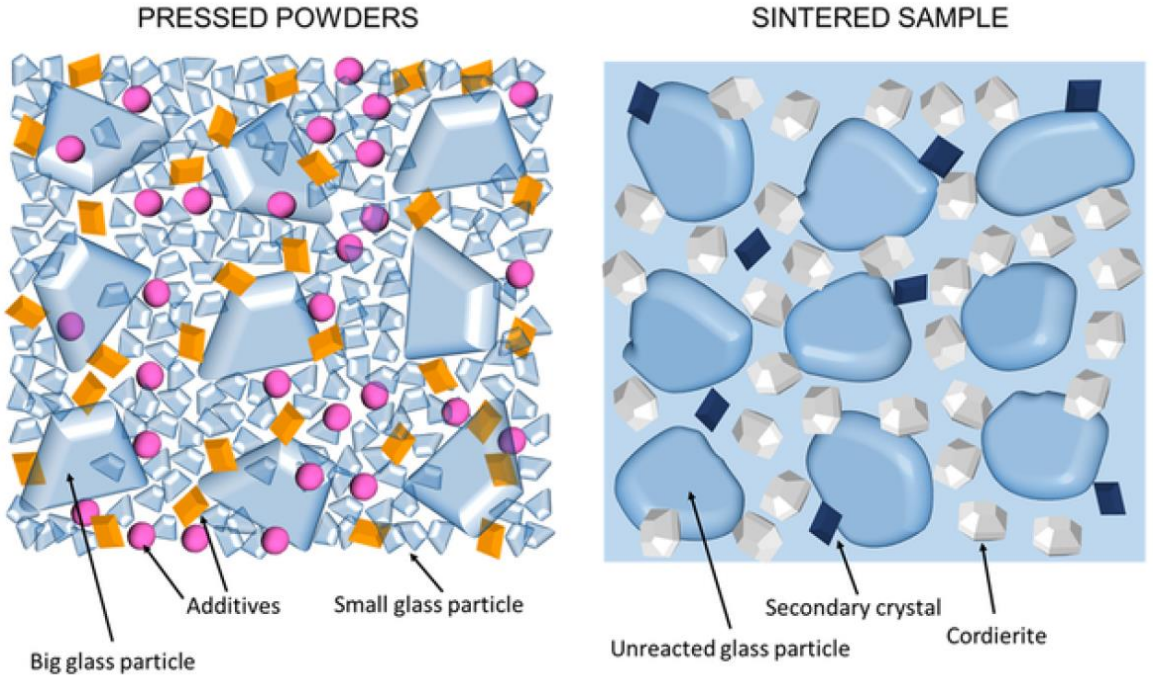
Reactive sintering

Focus on saving rare resources

GLASS FOR FUTURE
Nippon Electric Glass

LCD glass in fine and coarse powders

Limited recycling: optical quality needed

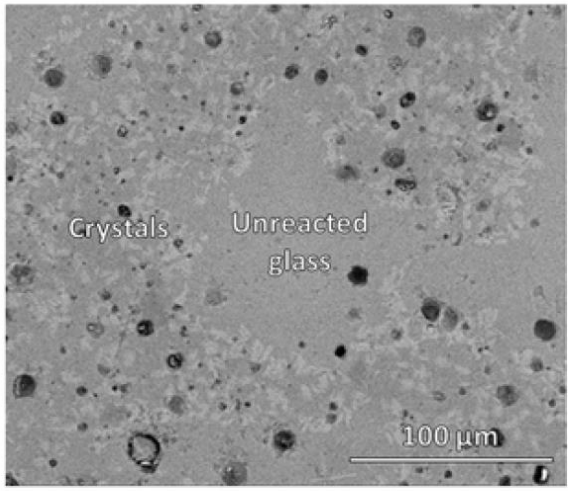


Added with MgO & Al_2O_3

Reactions involving powders <30 µm

Sintering at 1050 °C

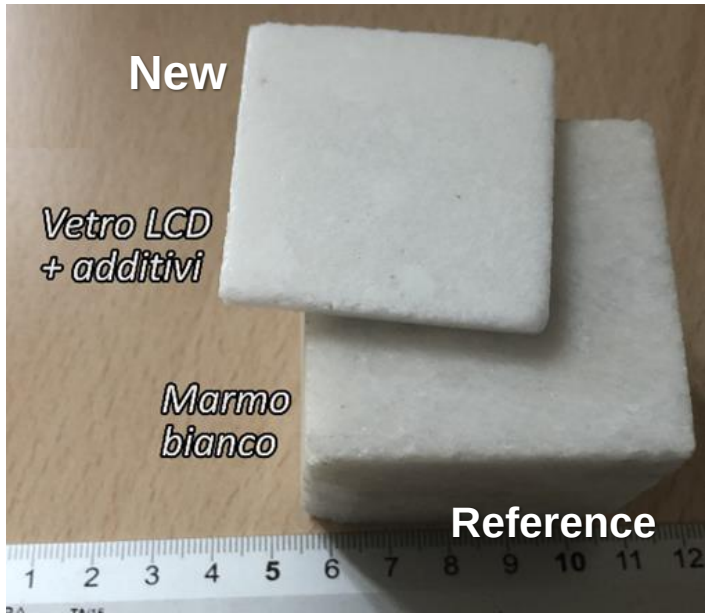
Island of transparent glass surrounded by opaque crystals



Sample after firing

Cordierite crystals, enhancing emissivity

Da: *Glass Reactive Sintering*
Acacio Rincon Romero, Hamada Elsayed, Jozef Kraxner, Enrico Bernardo,
Encyclopedia of Materials: Technical Ceramics and Glasses, 2021



Reference: Thassos Marble (rare white marble)

Bending strength: 34 MPa [marble, <20 MPa]
Durezza Vickers: 4.9 GPa [marble, <4.2 GPa]

Other construction materials

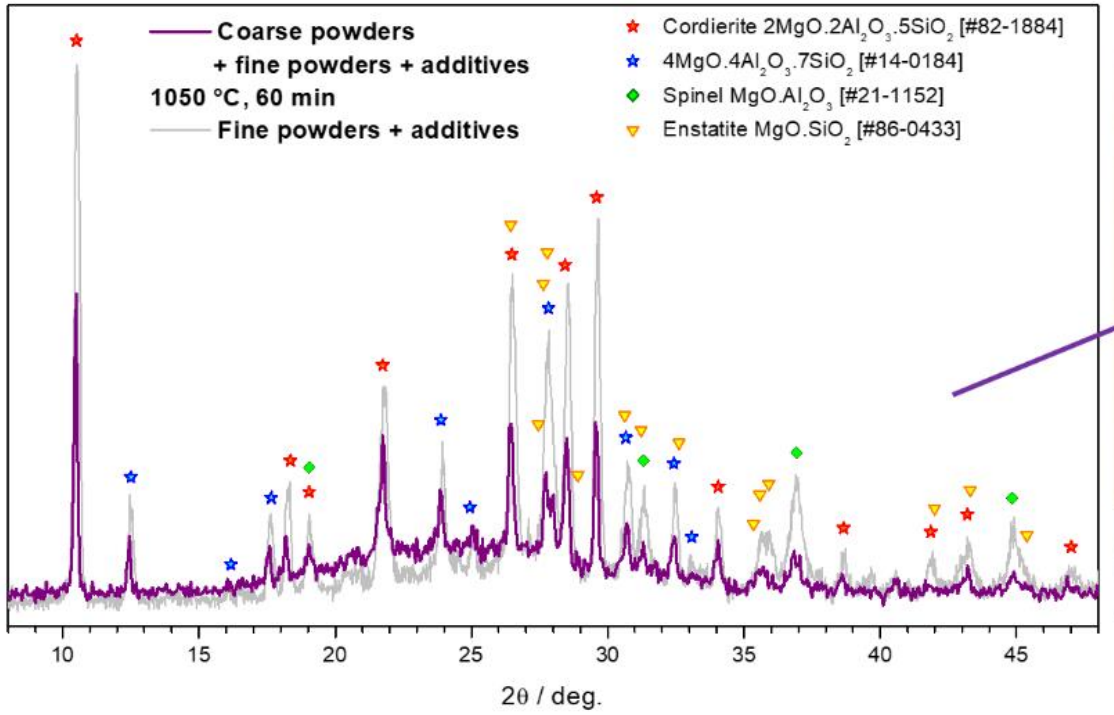
Reactive sintering
Engineered phases

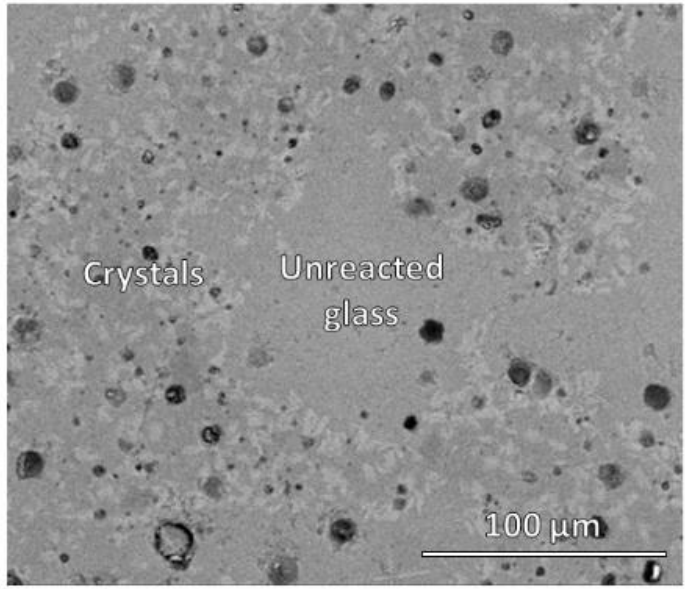
Alkali-free glass (NEG, Japan)
SiO_2: ≥55 wt%, Al_2O_3: 15%, B_2O_3: 10%, CaO: 10%, SrO: 5%; BaO: 1%

+ Additives: MgO & γ-Al_2O_3

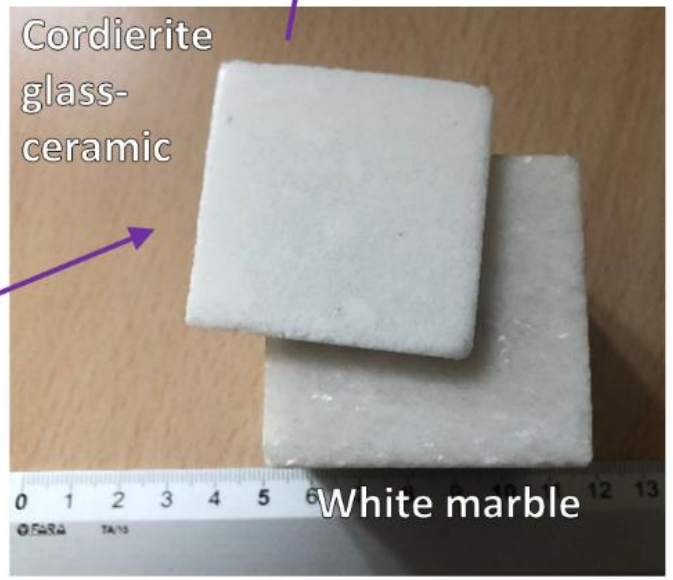
$(SiO_2, Al_2O_3)_{glass}$ + MgO + γ-Al_2O_3 → $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$

Cordierite: useful to give high emissivity





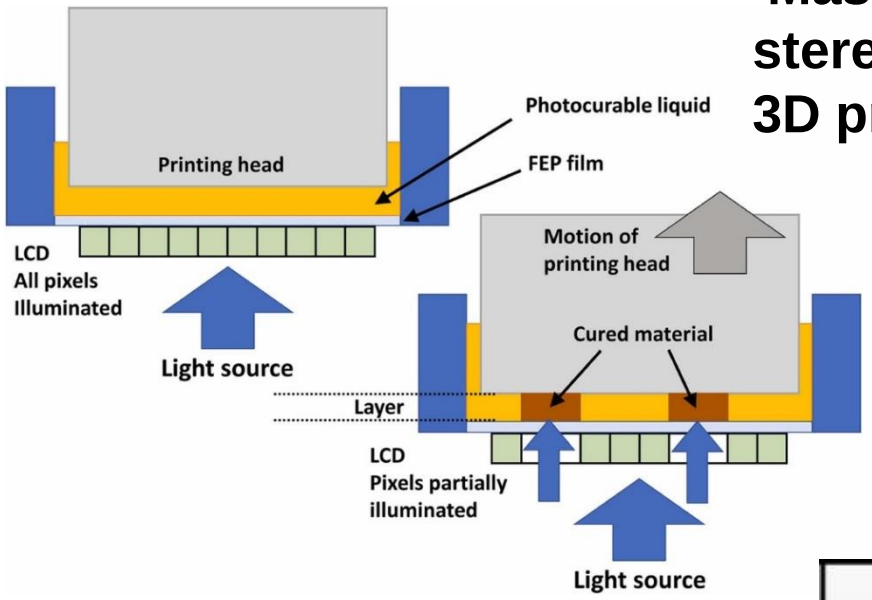
Sample after firing



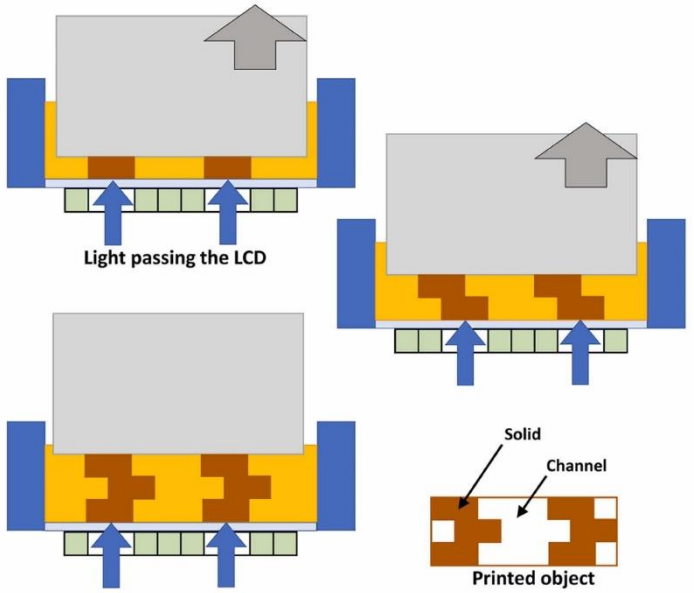
Beyond constructions, again

No remelting: sintering as key technology
New engineered components, with ordered porosity





'Masked stereolithography 3D printing'

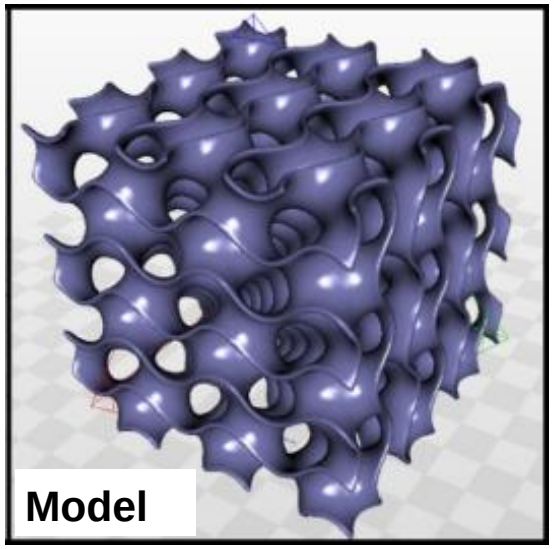


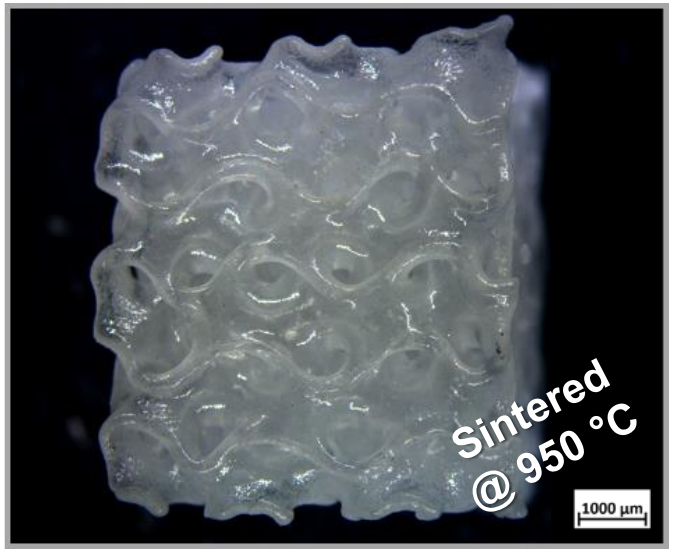
Ożóg et al. Journal of the European Ceramic Society 42 (2022) 6192-6198, https://doi.org/10.1016/j.jeurceramsoc.2022.06.057.

Glass embedded in photocurable liquid

Sintering after burn-out of binder

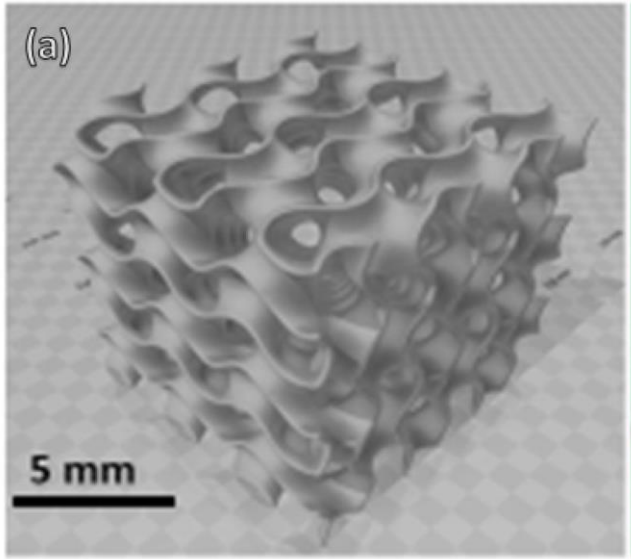
LCD glass usable as photocatalytic support



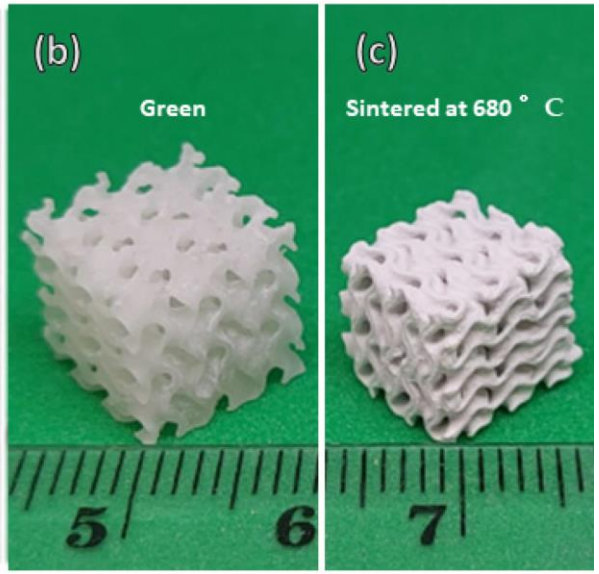


Beyond constructions, again

No remelting: sintering as key technology
New engineered components, with ordered porosity



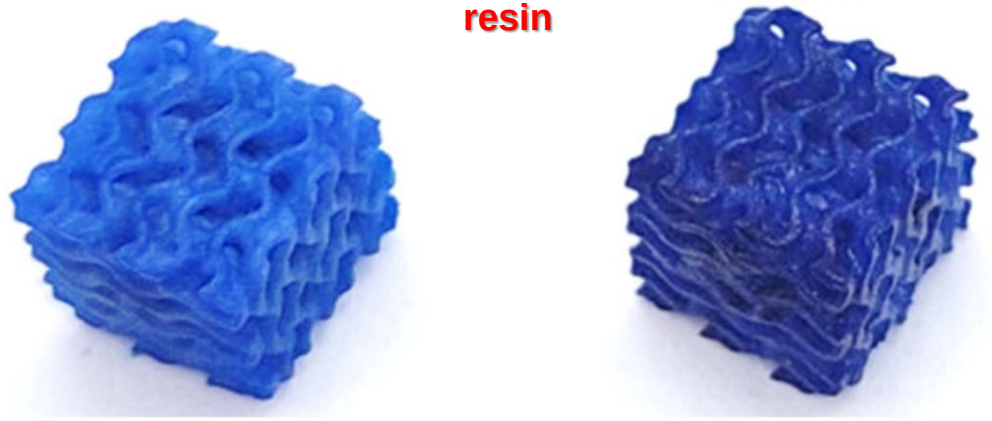
Gyroid model for SLA printing



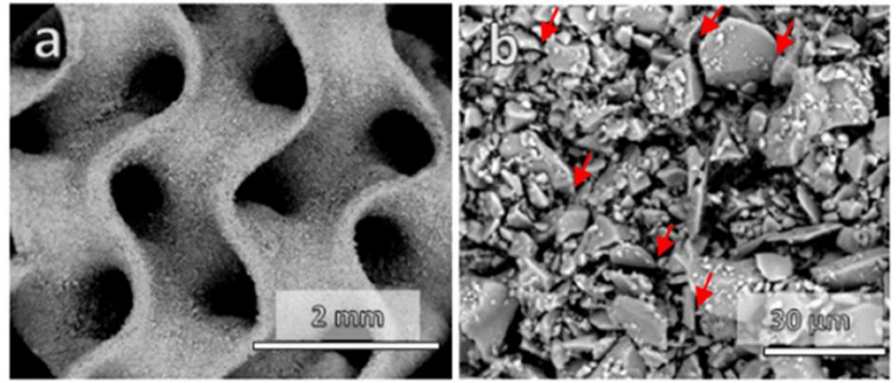
55wt% solid BSG in plant-based photocurable resin

Non-activated

Activated

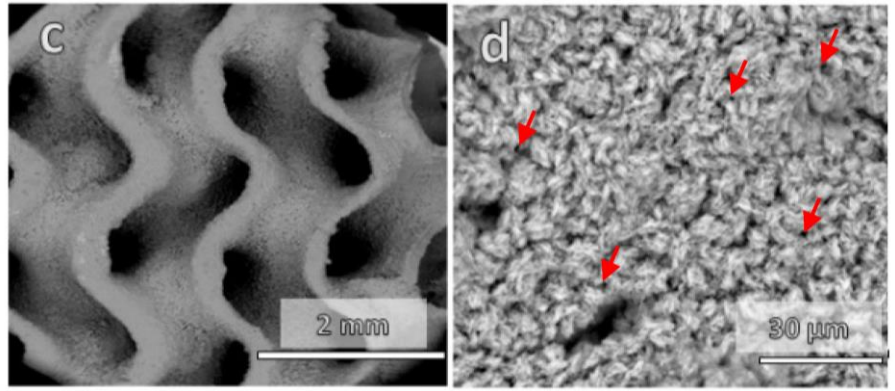


Sintered @ 680 °C



Partial sintering

Activated (1h in 2.5 NaOH solution)



Highly textured surfaces

Photocatalytic nanoparticles may be added to the activating solution: surface modification, only

Other AM in progress (e.g. FDM)

Concluding remarks
…and future perspectives

Waste glass expressing **great potential for the obtainment of multiform new products, according to alkali activation**

Take home messages

- ***'Cold consolidation' feasible even without additives***
- ***Inclusion of other inorganic waste***: **waste glass defines a stable matrix, series of sustainable construction materials feasible**
- **Potential for Additive Manufacturing: sustainable functional materials**

Further steps:

- **Disclosing the molecular mechanism of cold consolidation (work on 'pure' soda-lime glass still in progress)**
- **Development of unfired porous bodies**: still to be exploited in full
- **Application of functional scaffolds in various forms of water remediation (e.g. removal of other organic and inorganic contaminants)**

Acknowledgements

Funding and support

- **European Community's Horizon 2020 Programme through H2020-WIDESPREAD 2017-TeamingPhase2 project ('FunGLASS", g.a. no. 739566) - funglass.eu**

FunGlass

European Commission | Horizon 2020 European Union funding for Research & Innovation

- University of Padova (Department of Industrial Engineering) in the framework of the "**SusPIRe**" (Sustainable porous ceramics from inorganic residues, BIRD202134)
- ***National project MUR PON R&I 2014-2021***
- ***INSTM (Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali) - CaRiPLo project ['New recycling process for the foundry sands: innovation aimed to get materials with high added value']***



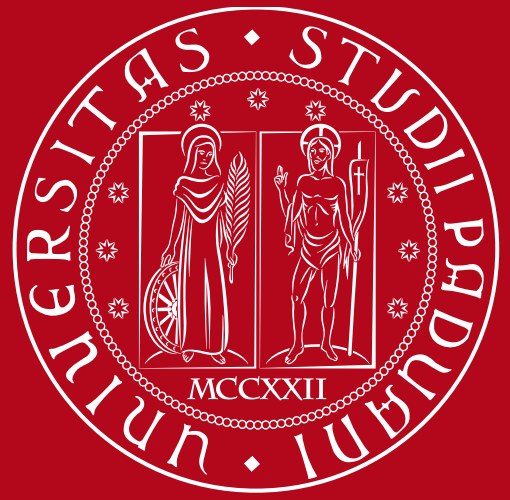
Grand Opening Ceremony of FunGlass Centre
Alexander Dubcek University of Trencin
May 24th, 2023

MANY THANKS FOR YOUR ATTENTION!

enrico.bernardo@unipd.it

1222 • 2022

800 ANNI



Università degli Studi di Padova