sumglass
September 25-29th 2023

Centre for Functional and Surface Functionalized Glass

FunGlass

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

Vitrification Technologies and glass waste form
Glass waste form and issues

25th September, 2022

Engineering of Inorganic Waste Mixtures for New Usable Glasses: from Glass-Ceramics to Alkali-Activated Materials

800 ANNI 1222·2022
Università degli Studi di Padova
DII Dipartimento di Ingegneria Industriale
CERAM GLASS research group
FunGlass

Enrico Bernardo, Giulia Tameni, Hamada Elsayed
Department of Industrial Engineering, University of Padova, Italy

Mokhtar Mahmoud, Abel Ourgessa, Jozef Kraxner
FunGlass, Alexander Dubcek University of Trencin, Slovakia

Background: waste-derived glasses

Glass may stabilize many pollutants from many types inorganic residues
Energy-intensive melting step to be 'repaid' with new products

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

Ashes, mining tailings, metallurgical residues, etc.

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

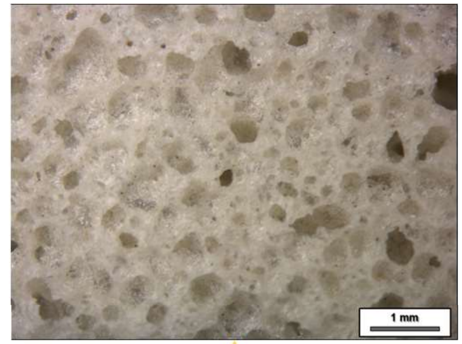
P. Colombo [a,b,*], G. Brusatin [c], E. Bernardo [c], G. Scarinci [c]

[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.



Glass foams, for thermal and acoustic insulation (firing at 700-1000°C)

Marble-like glass-ceramics
Glass powders experiencing sintering and crystallization
(firing at 900-1000 °C)

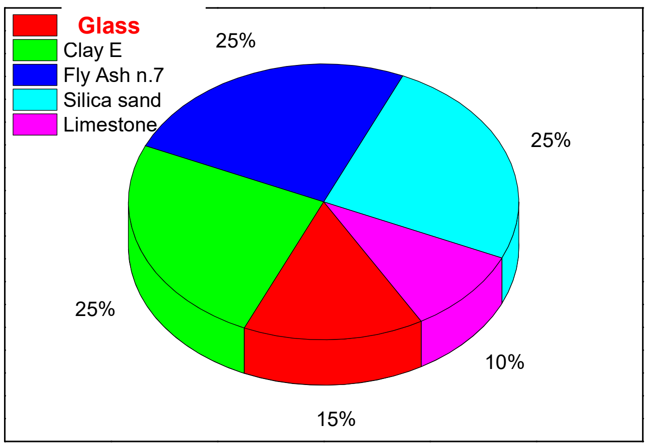
Waste glasses also as waste-derived glasses

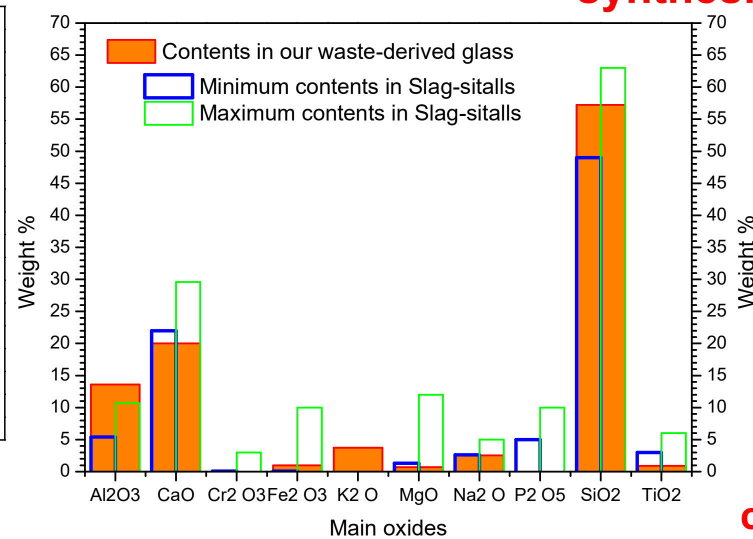
Glass may stabilize many pollutants from inorganic residues
Energy-intensive melting step to be 'repaid' with new products

Key idea of compositional design (glass from mixtures of waste):
- **To compensate variations in one type of waste**
- **To get a glass with quite established chemistry (favouring chemical durability, adjusting sintering/crystallization, tuning the colour etc…)**

Waste-derived glass: already stabilized material, easily transported → GC plant may be indipendent from vitrification plant

Discarded glasses typically used as fluxes for the synthesis of 'waste-derived' glass





Typical reference: ***CaO-Al_2O_3-SiO_2 glass-ceramics from metallurgical slags ('Slag-sitalls')***

Marble-like glass-ceramics
Glass powders experiencing sintering and crystallization
(firing at 900-1000 °C)

Case study: glass foams

Fundamental examples of sintering of glass (no remelting)
Very interesting complex of properties

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

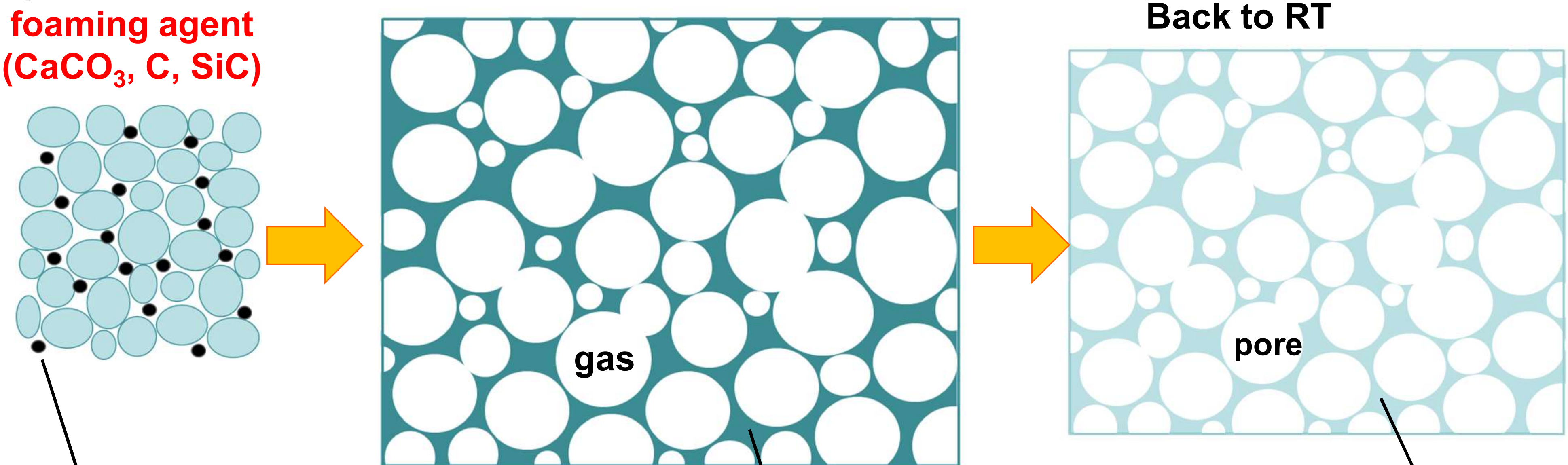
Fundamental examples of sintering of glass (no remelting)

Exploiting glass softening

Mix of fine glass particles and foaming agent ($CaCO_3$, C, SiC)

Sintering @ 850-950 °C

Back to RT



Additive releasing gas according to decomposition or oxidation reactions

Mass of softened glass (High viscosity liquid)

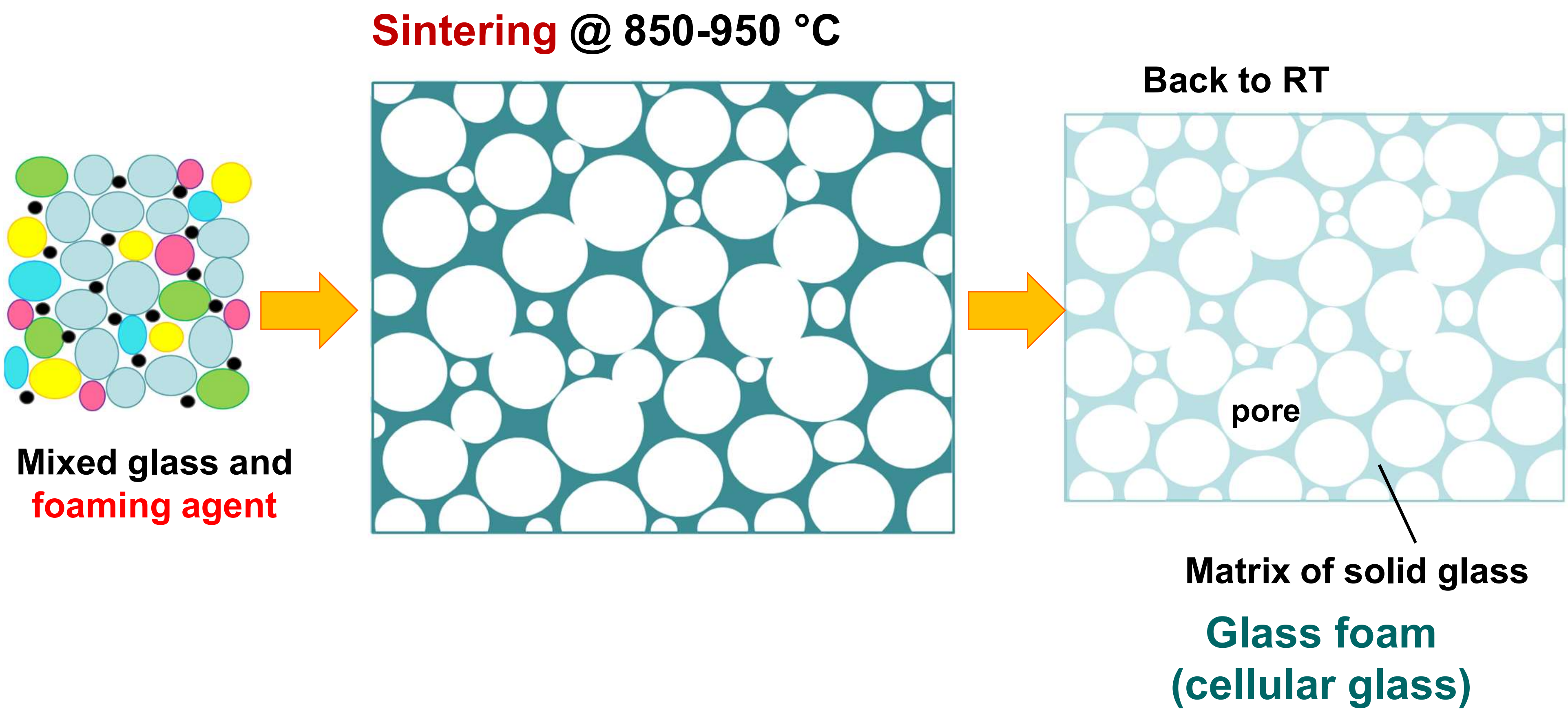
Matrix of solid glass

Glass foam (cellular glass)

Case study: glass foams

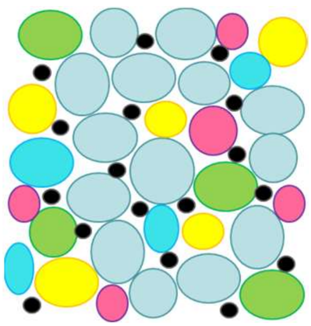
Fundamental examples of sintering of glass (no remelting)

Trying with glass mixtures…the ideal situation



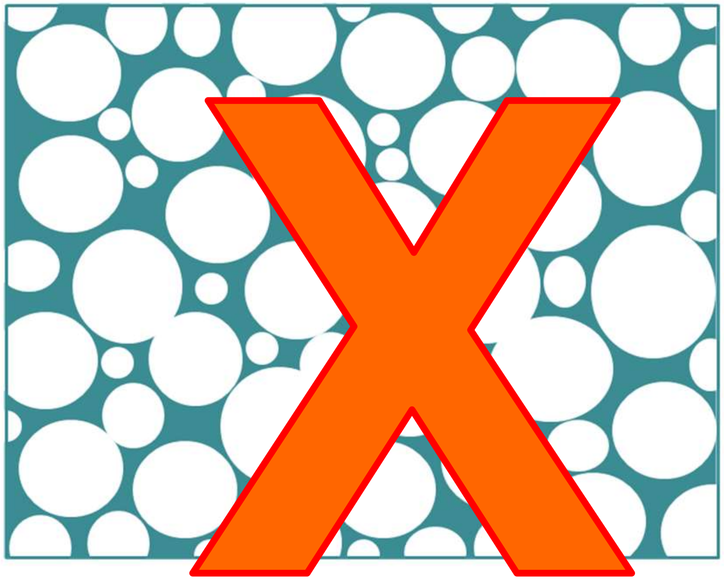
Case study: glass foams

Fundamental examples of sintering of glass (no remelting)
Trying with glass mixtures… the typical result



Mixed glass and **foaming agent**

Sintering @ 850-950 °C



Problem of homogeneity: compositional gradients implying viscosity gradients

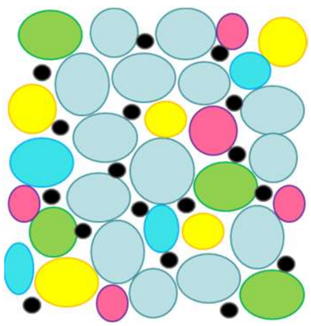
Cooperation with Sasil, Biella, Italy (2018-19)

Case study: glass foams

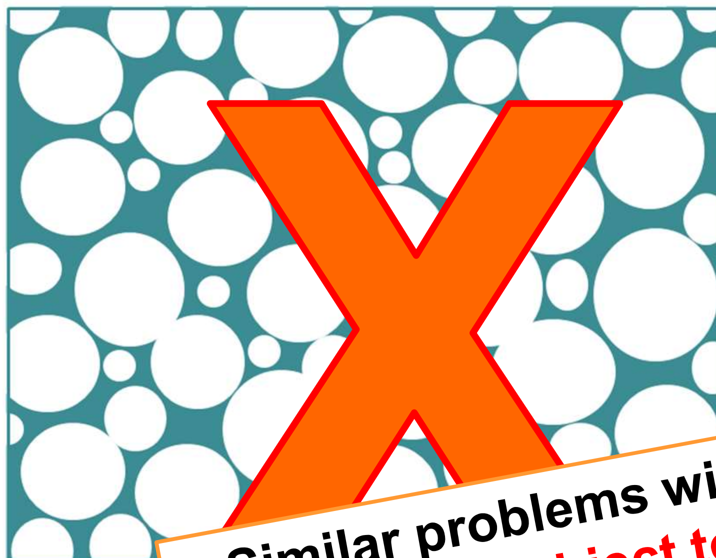
Fundamental examples of sintering of glass (no remelting)

Trying with glass mixtures… the typical result

Sintering @ 850-950 °C



Mixed glass and foaming agent



Probl… composit… …plying vis…ity gradients

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

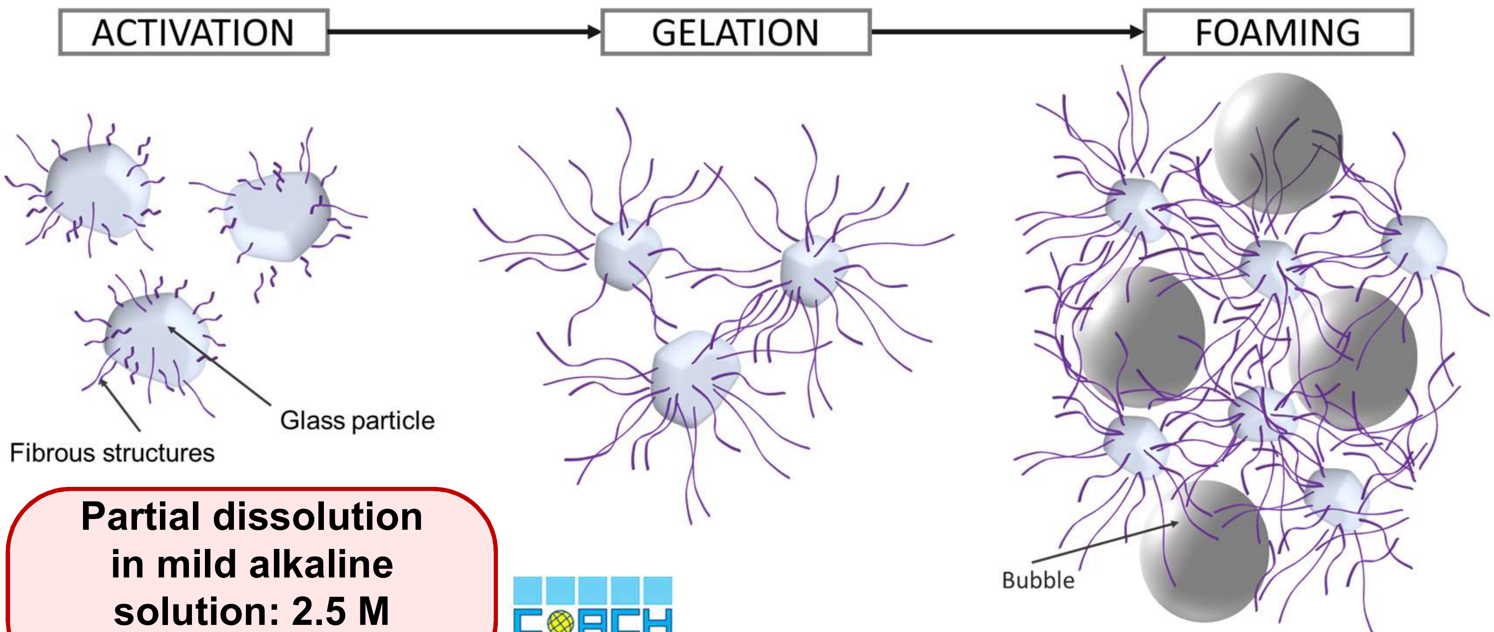
Cooperation with Sasil, Biella, Italy (2018-19)

Solution: 'mild' activation of waste glass and RT foaming

Glass foams obtained by low T firing of 'green' foams

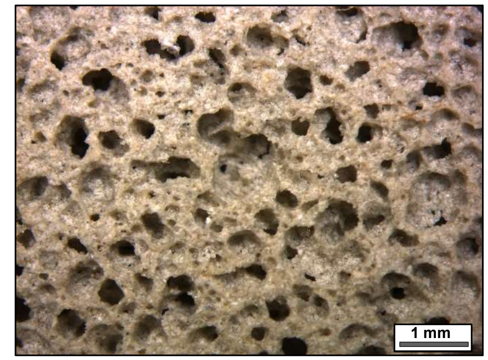
Green foams from mechanical foaming of alkali-activated glass suspensions

800 ANNI 1222·2022
Università degli Studi di Padova

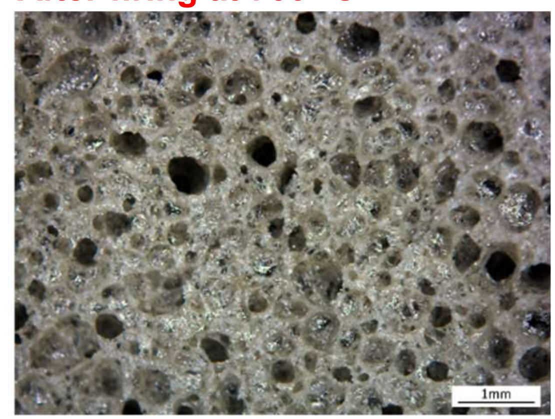


Partial dissolution in mild alkaline solution: 2.5 M NaOH/KOH

'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

800 1222·2022 ANNI

Università degli Studi di Padova

Immediate application to waste-derived glasses

Crystallization no longer an ‘enemy’, but an opportunity
Definition of foams with excellent strength-to-density ratios

Construction and Building Materials 192 (2018) 133–140

Contents lists available at ScienceDirect

Construction and Building Materials

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

ELSEVIER

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

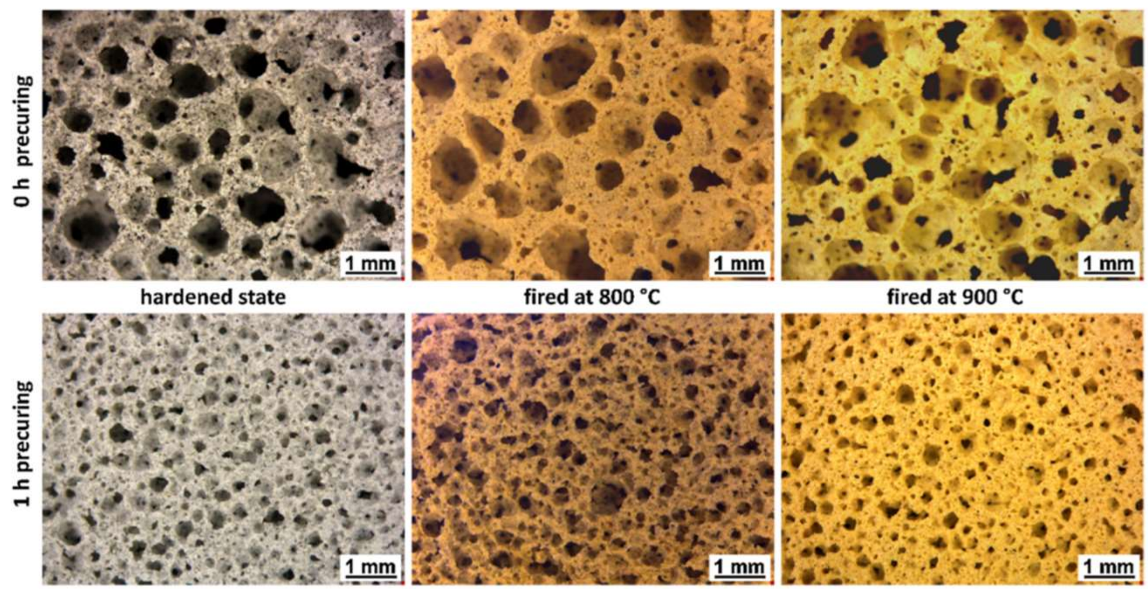
Glass from MSWI: $CaO-Al_2O_3-SiO_2$ of ‘Slag-sitall’ composition

Easily crystallized, yielding wollastonite ($CaSiO_3$) and other silicates

Crystallization during sintering, but AFTER foaming

~80 % porosity, Compressive strength >6 MPa

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



Università degli Studi di Padova

800 anni 1222·2022

Question

How to improve the sustainability?

2 firing treatments for waste-derived glasses (1=vitrification; 2=sintering): how to avoid one?

Introduction to unfired material

Main goal: exploration of glass for IPs

New generation of binders, alternative to conventional cements

- **Binders for the building industry (e.g. Portland cement) generally having a significant environmental impact**

  Gelation feasible at room temperature, but high temperature processing needed for the synthesis

- **Interesting replacement offered by inorganic polymers (IPs), i.e. gels typically achieved by low temperature dissolution of alumino-silicate raw materials, in alkaline environment, followed by condensation reactions**

  Demanding synthesis step still applied, for raw material preparation and/or definition of activating solution (e.g. alkali silicates)

Next slides aimed at:

- **Confirming the potential of 'IP-oriented glass', from waste vitrification, for direct activation just with NaOH solution**
- **Extending the application of waste glass-derived IPs to water purification**

No sintering: IP-yielding glass

New reference: Na_2O-CaO-Al_2O_3-SiO_2 glass for cold consolidation
Glass to be used as raw material for one-part IP

Red mud from Bayer process (Bauxite refinement to extract Al hydroxide)

Fly ash from coal combustion

'Un-recyclable' glass

Oxide	RM (wt%)	FA (wt%)	BS pharma (wt%)	Glass (wt%)	Ref
SiO_2	5.2	49.4	72.0	45.2	50.8
Al_2O_3	15.0	22.7	7.0	19.5	23.4
Fe_2O_3	52.9	7.4		15.3	4.3
Na_2O	2.4	0.9	6.0	8.5	8.3
K_2O	0.6	1.4	2.0	2.3	5.1
CaO	11.7	8.9	1.0	4.0	6.4
MgO	0.6	2.0		1.4	0.5
Other	5.1	6.1	12.0 (B_2O_3)	5.3	0.6
Balance (wt%)	18	58	13		
Additive:	11% Na_2CO_3				

Waste mixture

Contents lists available at ScienceDirect
Ceramics International
journal homepage: www.elsevier.com/locate/ceramint
Review article
Alternative prime materials for developing new cements: Alkaline activation of alkali aluminosilicate glasses
C. Ruiz-Santaquiteria*, A. Fernández-Jiménez, A. Palomo
Eduardo Torroja Institute (CSIC), c/ Serrano Galvache 4, 28033 Madrid, Spain

Inspiration: activation in NaOH solutions

New glass with Al_2O_3/SiO_2 and alkali/SiO_2 molar ratios close to reference

Fe_2O_3 in large excess: Expected phase separation during cooling

Objective:* *formation of a stable inorganic polymer, by dissolution in NaOH solution and subsequent gelation

Università degli Studi di Padova — 800 anni 1222·2022

No sintering: IP-yielding glass

New reference: Na_2O-CaO-Al_2O_3-SiO_2 glass for cold consolidation

Glass to be used as raw material for one-part IP

Contents lists available at ScienceDirect

Ceramics International

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

ELSEVIER

Review article

Alternative prime materials for developing new cements: Alkaline activation of alkali aluminosilicate glasses

C. Ruiz-Santaquiteria*, A. Fernández-Jiménez, A. Palomo

Eduardo Torroja Institute (CSIC), c/ Serrano Galvache 4, 28033 Madrid, Spain

Inspiration: activation in NaOH solutions

Red mud from Bayer process (Bauxite refinement to extract Al hydroxide)

Fly ash from coal combustion

'Un-recyclable' glass

Oxide	RM (wt%)	FA (wt%)	BS pharma (wt%)	Glass (wt%)	Ref
SiO_2	5.2	49.4	72.0	45.2	50.8
Al_2O_3	15.0	22.7	7.0	19.5	23.4
Fe_2O_3	52.9	7.4		15.3	4.3
Na_2O	2.4	0.9	6.0	8.5	8.3
K_2O	0.6	1.4	2.0	2.3	5.1
CaO	11.7	8.9	1.0	4.0	6.4
MgO	0.6	2.0		1.4	0.5
Other	5.1	6.1	12.0 (B_2O_3)	5.3	0.6
Balance (wt%)	18	58	13		
Additive:	11% Na_2CO_3				

Waste mixture

High Al_2O_3 content + some B_2O_3 contribution from BS (>1.5 wt%):

- **Synergistic effect on glass durability**
- **Synergistic effect on gel structure of IPs**

according to the formation of $[AlO_4]$ and $[BO_4]$ units, in turn stabilized by alkali ions

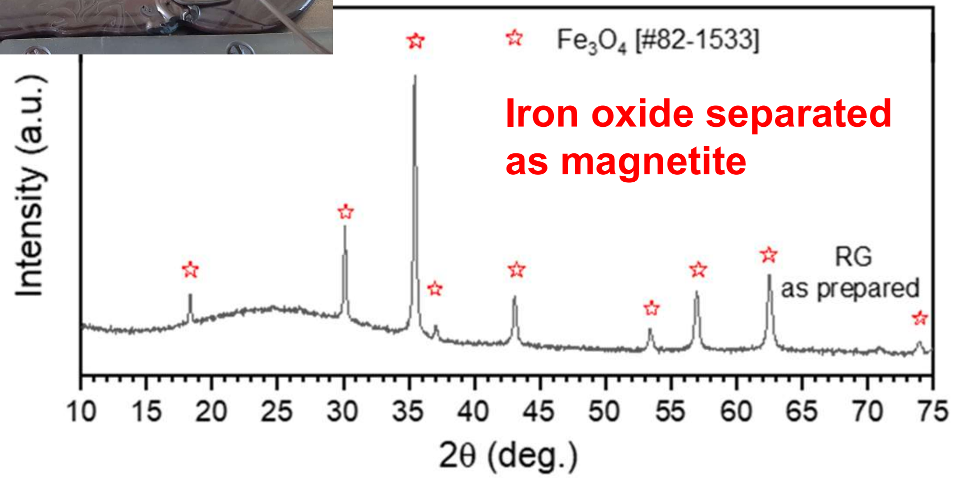
Engineering of formulation: vitrification ideally re-paid by the avoided disposal costs of several waste

First goal: waste stabilization

Homogeneous glass not achieved but…
…successful stabilization of pollutants

Element	Leachates [ppm]		
	Limits for not hazardous	Limits for inert	RG
As	2	0.5	<0.018
Ba	100	20	<0.140
Cd	1	0.04	<0.013
Cr	10	0.5	0.0290
Cu	50	2	<0.012
Mo	10	0.5	<0.013
Ni	10	0.4	<0.012
Pb	10	0.5	0.014
Sb	0.7	0.06	<0.013
Se	0.5	0.1	<0.012
Zn	50	4	<0.014

Dry mixing of raw materials
Melting at 1500°C for 2 hours



Not a homogeous glass, but still chemically stable

Leaching for samples fired in air: all elements well below the thresholds [EN-12457]
Confirmed expected stabilization from B_2O_3&Al_2O_3

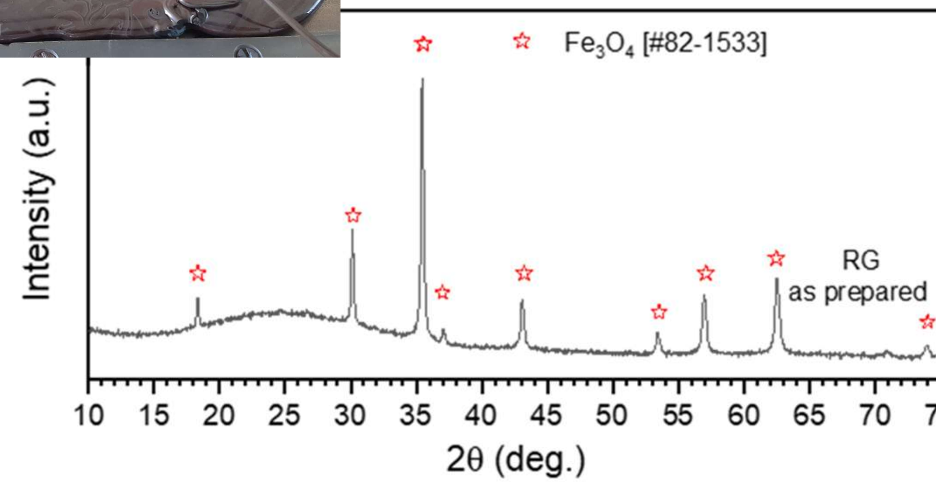
Università degli Studi di Padova
1222·2022 800 anni

First goal: waste stabilization

Homogeneous glass not achived but…
…successful stabilization of pollutants

	Leachates [ppm]		
Element	Limits for not hazardous	Limits for inert	RG

Dry mixing of raw materials
Melting at 1500°C for 2 hours



Attention to the (photo-)catalytic potential of magnetite, specifically for organic dyes

Materials Chemistry and Physics 179 (2016) 310–315
Contents lists available at ScienceDirect
Materials Chemistry and Physics
journal homepage: www.elsevier.com/locate/matchemphys
ELSEVIER

Phytosynthesis and photocatalytic activity of magnetite (Fe_3O_4) nanoparticles using the Andean blackberry leaf

CrossMark

Brajesh Kumar [a, b, *], Kumari Smita [a], Luis Cumbal [a], Alexis Debut [a], Salome Galeas [c], Victor H. Guerrero [c]
[a] Centro de Nanociencia y Nanotecnologia, Universidad de las Fuerzas Armadas ESPE, Av. Gral. Rumiñahui s/n, Sangolquí, P.O. BOX 171-5-231B, Ecuador
[b] Department of Chemistry, TATA College, Kolhan University, Chaibasa, 833202, Jharkhand, India
[c] Laboratorio de Nuevos Materiales, Departamento de Materiales, Escuela Politécnica Nacional, Quito, Ecuador

homogeous glass, but still chemically stable

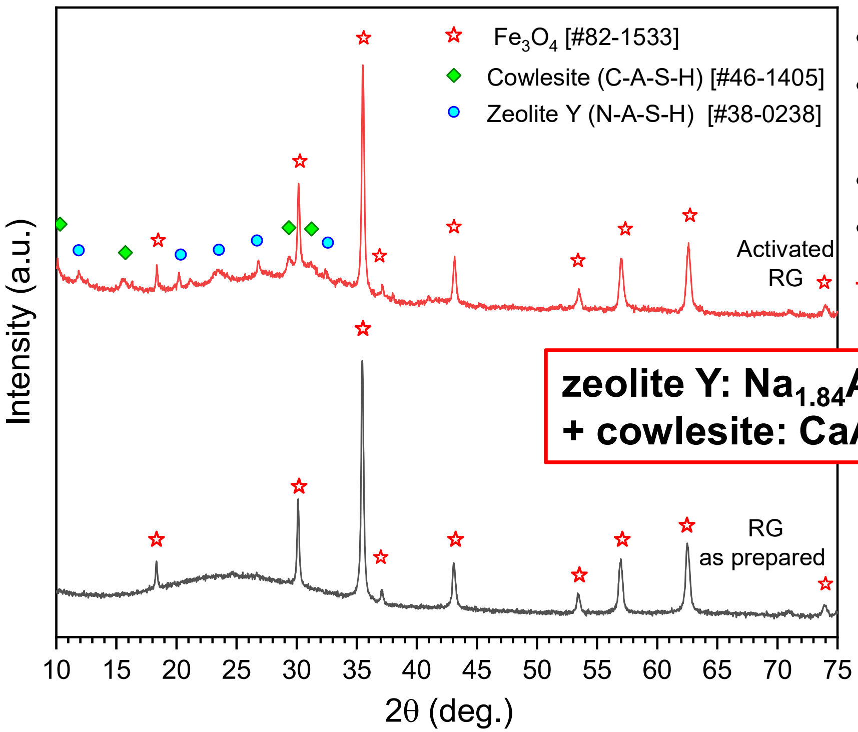
ing for samples fired in air: all elements well the thresholds [EN-12457]

med expected stabilization from B_2O_3&Al_2O_3

Second goal: activation

Fine glass powders in NaOH solution (8M)

Dissolution and gelation

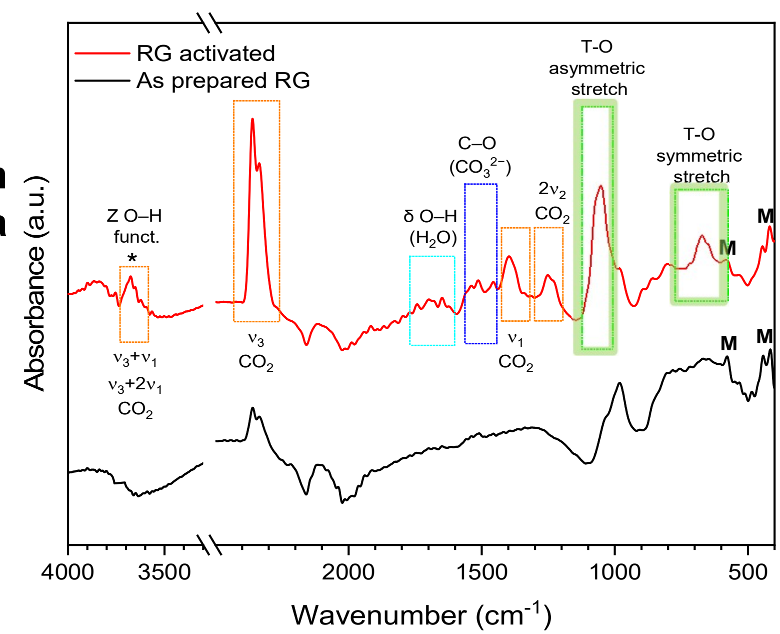


- **Coarse fragments manually crushed and dry ball milled**
- **Powders later, sieved <75 µm, cast in alkaline solution (8M NaOH), in PS containers, at 70-30 solid-liquid ratio**
- **Mechanically stirring (300 rpm) for 10 minutes**
- **Containers were covered by a lid and kept for 7 days at 40°C.**

→ Solid samples surviving boiling test

zeolite Y: $Na_{1.84}Al_2Si_4O_{11.92}\cdot 7H_2O$ + cowlesite: $CaAl_2Si_3O_{10}\cdot 6H_2O$

Confirmation from IR spectra



Amorphous matrix (shift of 'amorphous bump' to higher 2θ as usually seen in alkali-activated glass)

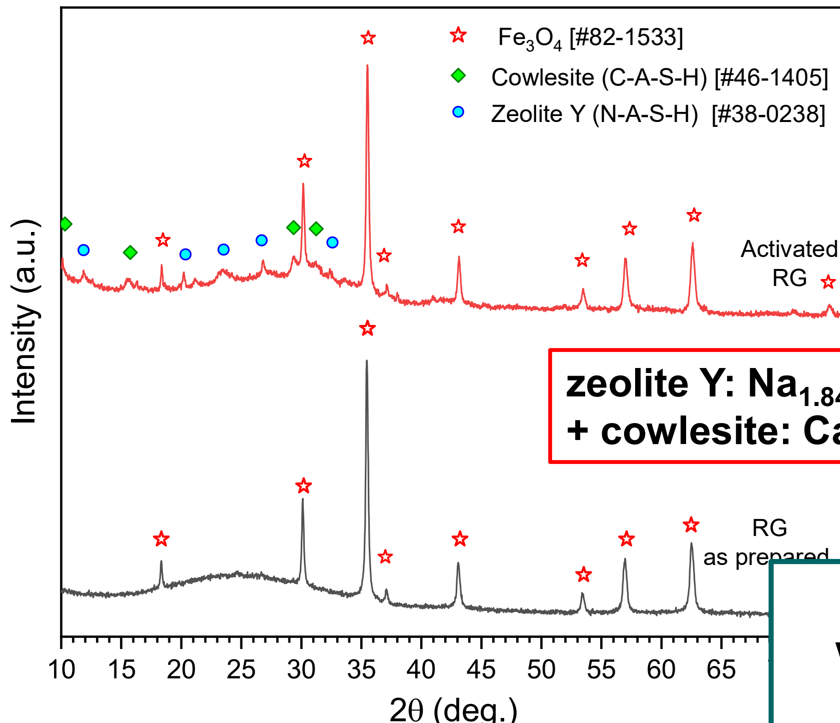
Ref: N-A-S-H/C-A-S-H mixed gel + zeolites

New samples: gel + zeolites

Università degli Studi di Padova — 800 anni 1222·2022

Second goal: activation

Fine glass powders in NaOH solution (8M)
Dissolution and gelation

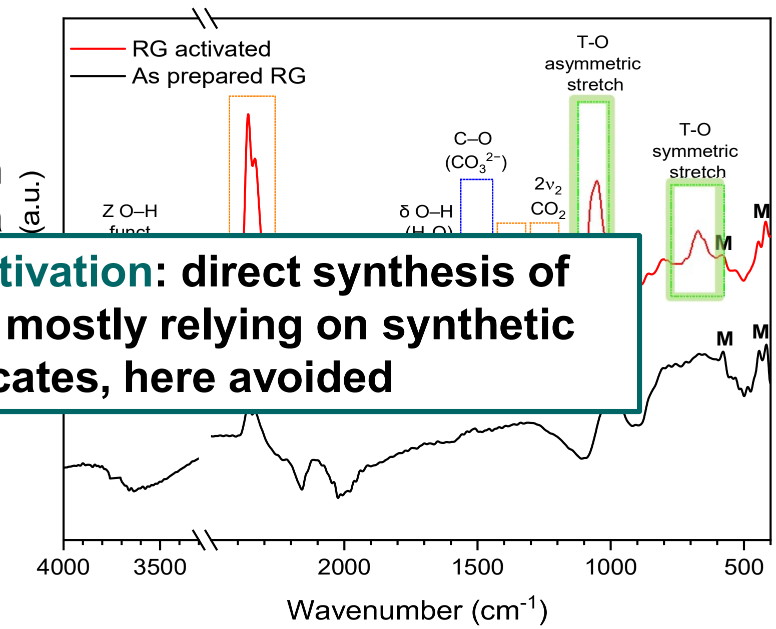


- **Coarse fragments manually crushed and dry ball milled**
- **Powders later, sieved <75 μm, cast in alkaline solution (8M NaOH), in PS containers, at 70-30 solid-liquid ratio**
- **Mechanically stirring (300 rpm) for 10 minutes**
- **Containers were covered by a lid and kept for 7 days at 40°C.**

→ Solid samples surviving boiling test

zeolite Y: $Na_{1.84}Al_2Si_4O_{11.92}\cdot 7H_2O$ + cowlesite: $CaAl_2Si_3O_{10}\cdot 6H_2O$

Confirmation from IR spectra



Engineering of activation: direct synthesis of waste-derived IPs mostly relying on synthetic alkali silicates, here avoided

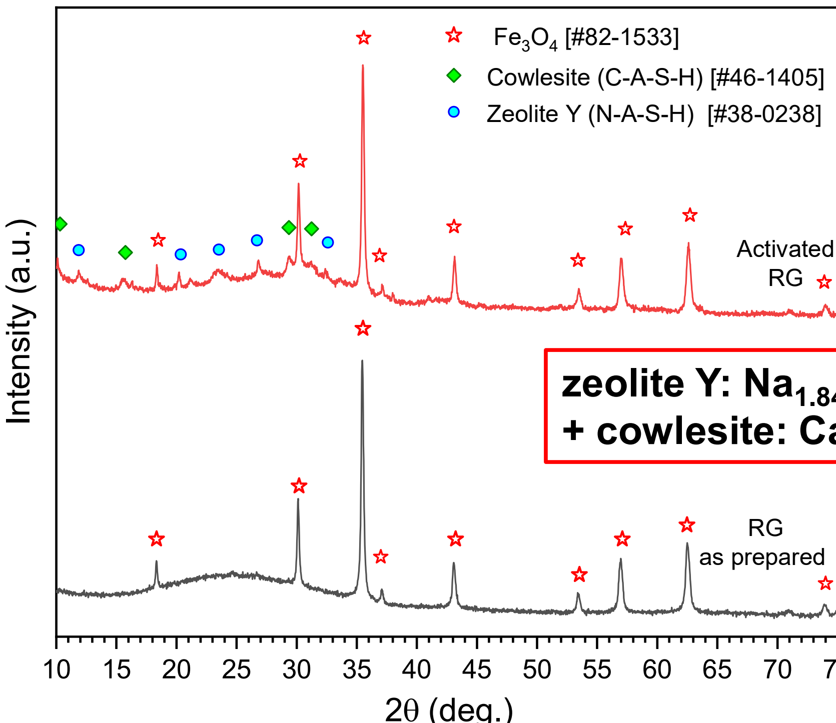
Amorphous matrix (shift of 'amorphous bump' to higher 2θ as usually seen in alkali-activated glass)

Ref: N-A-S-H/C-A-S-H mixed gel + zeolites

New samples: gel + zeolites

Second goal: activation

Fine glass powders in NaOH solution (8M)
Dissolution and gelation

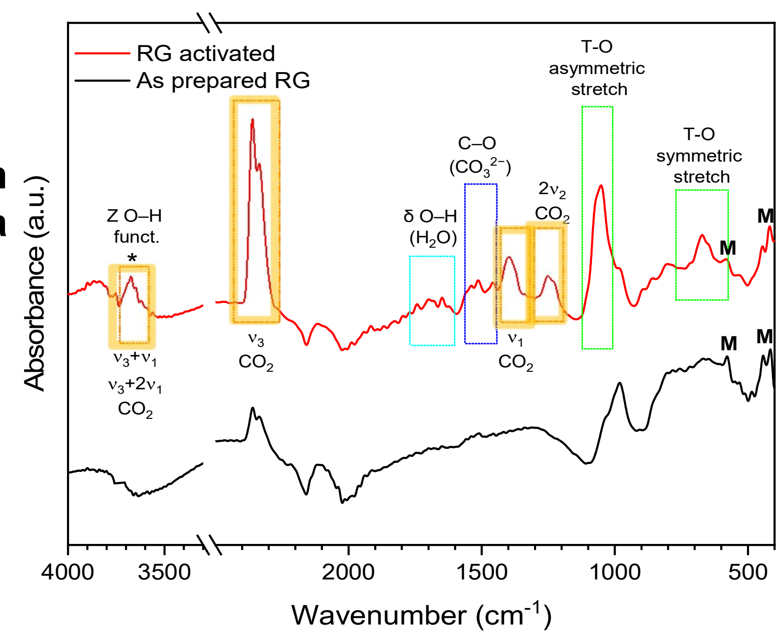


- **Coarse fragments manually crushed and dry ball milled**
- **Powders later, sieved <75 µm, cast in alkaline solution (8M NaOH), in PS containers, at 70-30 solid-liquid ratio**
- **Mechanically stirring(300 rpm) for 10 minutes**
- **Containers were covered by a lid and kept for 7 days at 40°C.**

→ Solid samples surviving boiling test

zeolite Y: $Na_{1.84}Al_2Si_4O_{11.92}\cdot 7H_2O$
+ cowlesite: $CaAl_2Si_3O_{10}\cdot 6H_2O$

Confirmation from IR spectra



Interesting: well distinguishable peaks correspond to CO_2 absorbed from the atmosphere (as occurring with Na-zeolites)

CO_2 absorption + magnetite phase (catalyst?) to be exploited for functional applications

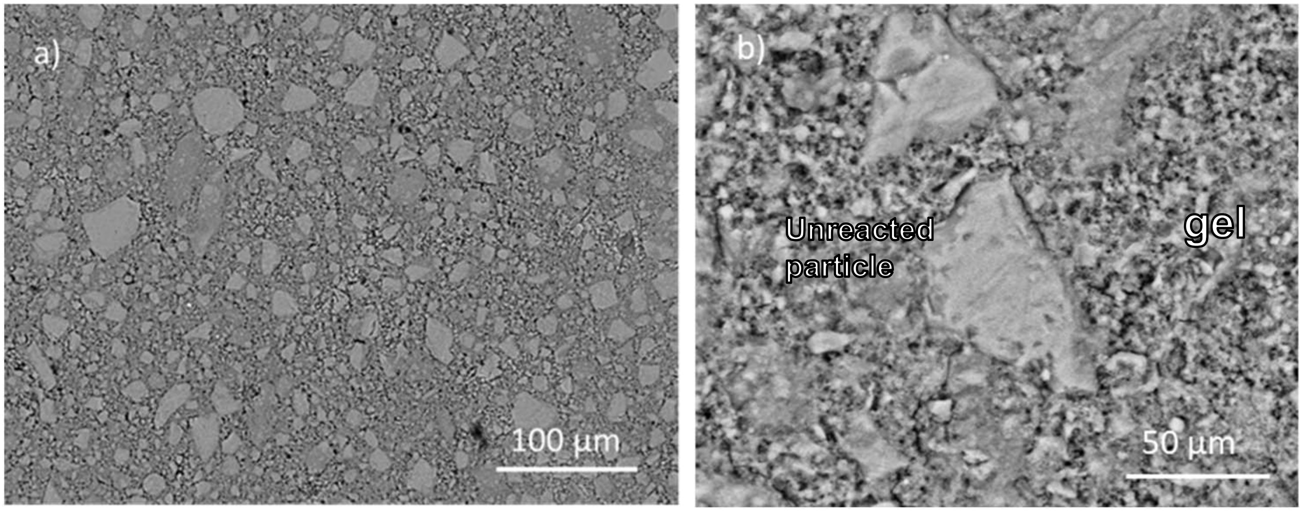
Second goal: activation

Properties of the gel

Good chemical stability, but still to be improved

	RG *Activated*	*Lightweight concrete*
Density ρ (g/cm^3)	1.75 ± 0.11	1.4 - 2
Closed porosity (vol%)	8.5	
Open porosity (vol%)	14.3	
Total porosity (vol%)	21.8	
Elastic modulus E (GPa)	7.9 ± 0.4	11 - 21
Bending strength σ_b (MPa)	8.1 ± 0.7	3 – 17
Crushing strength σ_c (MPa)	11.6 ± 1.6	11 - 28

(data extracted from the Cambridge Engineering Selector database



With the exception of E, quite good comparison with lightweight concrete
'Binder-only system': expected improvements by addition of aggregates

Second goal: activation

Properties of the gel

Good chemical stability, but still to be improved

	RG *Activated*	***Lightweight concrete***
Density ρ (g/cm^3)	1.75 ± 0.11	1.4 - 2
Closed porosity (vol%)	8.5	
Open porosity (vol%)	14.3	
Total porosity (vol%)	21.8	
Elastic modulus E (GPa)	7.9 ± 0.4	11 - 21
Bending strength σ_b (MPa)	8.1 ± 0.7	3 – 17
Crushing strength σ_c (MPa)	11.6 ± 1.6	11 - 28

With the exception of E, quite good comparison with lightweight concrete
'Binder-only system': expected improvements by addition of aggregates

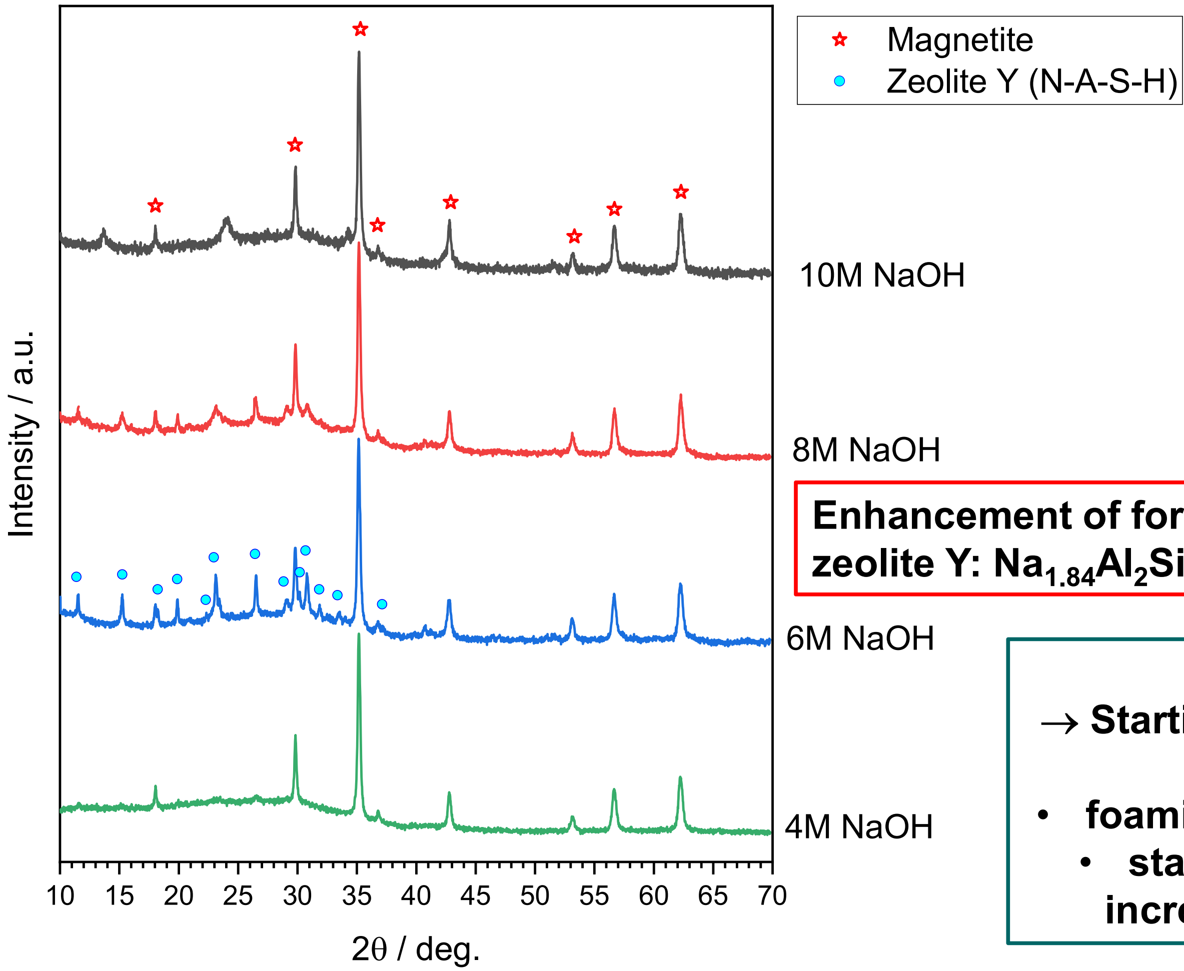
Leaching still below thresholds for not hazardous materials
Selected elements (As, Mo) slightly above limits for inertia

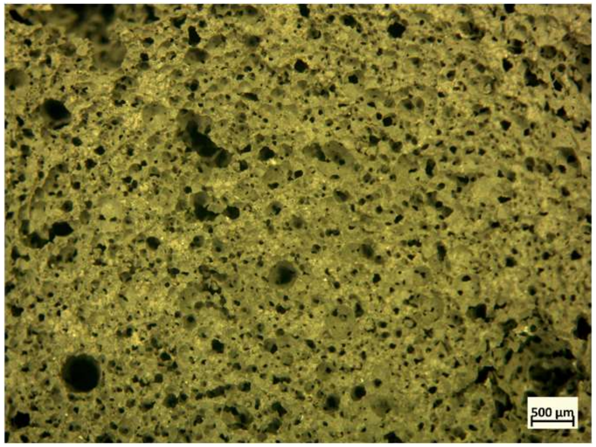
Element	Leachates [ppm] Limits for not hazardous	Limits for inert	RG	RG activated
As	**2**	**0.5**	<0.018	**0.638**
Ba	**100**	**20**	<0.140	<0.140
Cd	**1**	**0.04**	<0.013	<0.013
Cr	**10**	**0.5**	0.0290	<0.013
Cu	**50**	**2**	<0.012	<0.012
Mo	**10**	**0.5**	<0.013	**0.634**
Ni	**10**	**0.4**	<0.012	<0.012
Pb	**10**	**0.5**	0.014	0.068
Sb	**0.7**	**0.06**	<0.013	<0.013
Se	**0.5**	**0.1**	<0.012	0.0500
Zn	**50**	**4**	<0.014	<0.014

Extension: activation conditions revisited

Variation of molarity

Semi-crystalline IP obtained even at 6M





Enhancement of formation of zeolite Y: $Na_{1.84}Al_2Si_4O_{11.92}·7H_2O$

Synergy phase evolution/processing

Slightly less viscous slurry

→ Starting point for the development of foams by 'gel casting' approach

- **foaming of slurries at early stage of gelation**
- **stabilization of bubbles by the viscosity increase induced by progressive reaction)**

Application#1: direct foaming

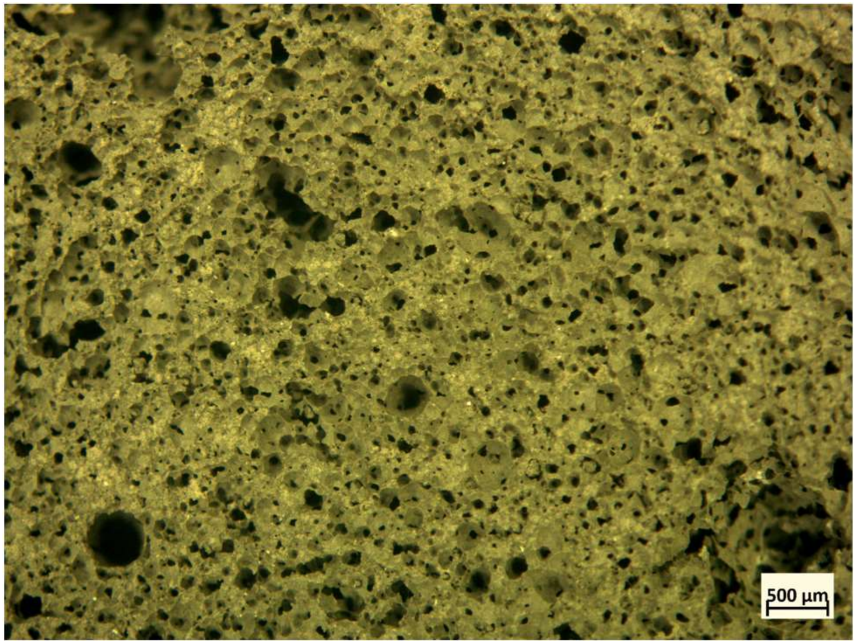
Exploitation of gelation for different materials
New functionalities according to enhanced porosity

Processing details…similar than in case of solid block

- **Coarse fragments manually crushed and dry ball milled**
- **[UPDATED] Powders later, sieved <75 µm, cast in alkaline solution (6M NaOH), in PS containers, at 70-30 solid-liquid ratio**
- **[UPDATED] Addition of Sodium dodecyl sulfate (SDS, $CH_3(CH_2)_{11}SO_4Na$, 1 wt% on glass content) + Sodium perborate (SPB, $NaBO_3{\cdot}4H_2O$, 1 wt% on glass content)**

→ Perborate decomposing in borate and H_2O_2, in turn leading to O_2 release

- **Mechanically stirring (300 rpm) for 10 minutes**
- **Containers were covered by a lid and kept for 7 days at 40°C.**



Total porosity of 82.1 vol%
(open porosity = 81.5 vol%)
SSA (BET) = 83 m^2/g

Compressive strength: 0.34±0.04 MPa

UNIVERSITÀ DEGLI STUDI DI PADOVA

Extension#1: direct foaming

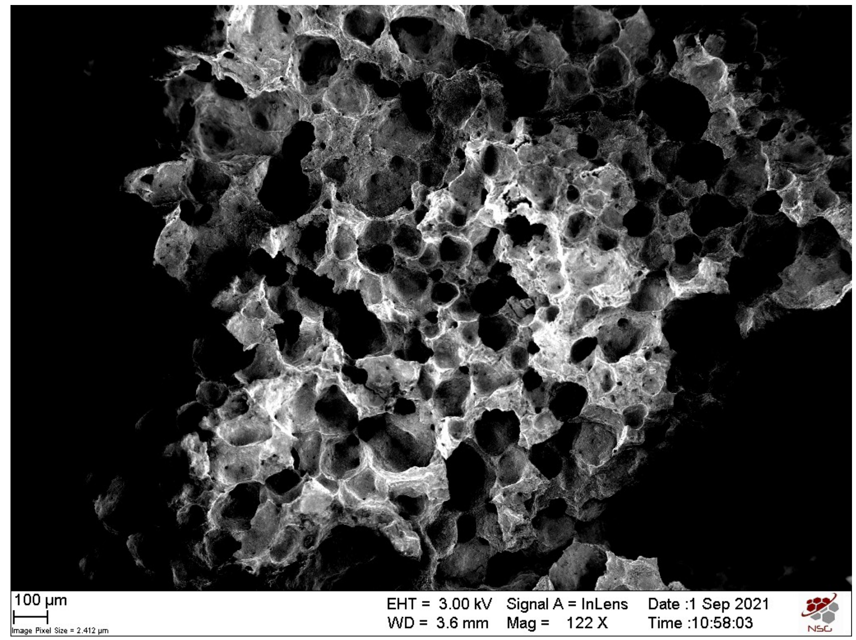
Exploitation of gelation for different materials
New functionalities according to enhanced porosity

Processing details…similar than in case of solid block

- **Coarse fragments manually crushed and dry ball milled**
- **[UPDATED] Powders later, sieved <75 µm, cast in alkaline solution (6M NaOH), in PS containers, at 70-30 solid-liquid ratio**
- **[UPDATED] Addition of Sodium dodecyl sulfate (SDS, $CH_3(CH_2)_{11}SO_4Na$, 1 wt% on glass content) + Sodium perborate (SPB, $NaBO_3 \cdot 4H_2O$, 1 wt% on glass content)**

→ Perborate decomposing in borate and H_2O_2, in turn leading to O_2 release

- **Mechanically stirring (300 rpm) for 10 minutes**
- **Containers were covered by a lid and kept for 7 days at 40°C.**



Total porosity of 82.1 vol%
(open porosity = 81.5 vol%)
SSA (BET) = 83 m^2/g

Compressive strength: 0.34±0.04 MPa

Application#1: direct foaming

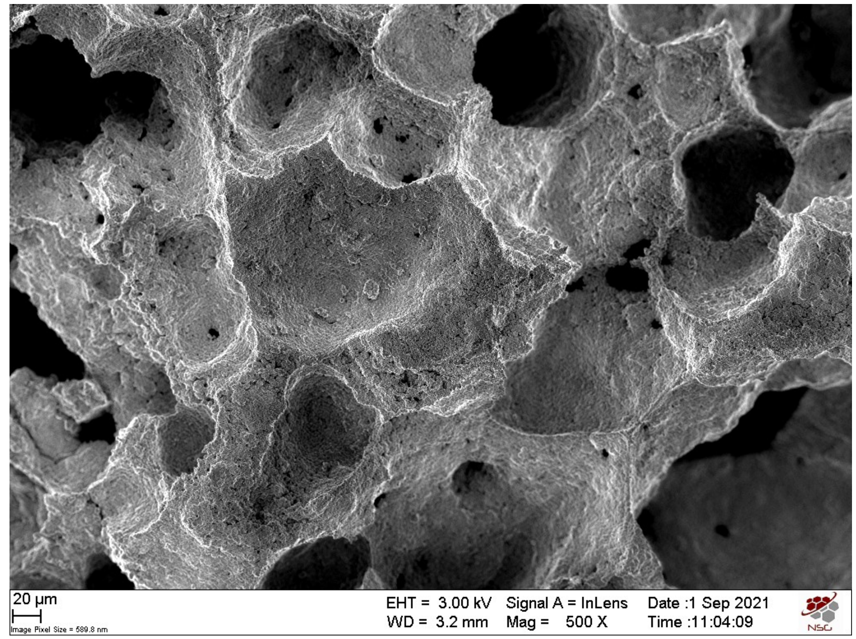
Exploitation of gelation for different materials
New functionalities according to enhanced porosity

Processing details…similar than in case of solid block

- **Coarse fragments manually crushed and dry ball milled**
- **[UPDATED] Powders later, sieved <75 µm, cast in alkaline solution (6M NaOH), in PS containers, at 70-30 solid-liquid ratio**
- **[UPDATED] Addition of Sodium dodecyl sulfate (SDS, $CH_3(CH_2)_{11}SO_4Na$, 1 wt% on glass content) + Sodium perborate (SPB, $NaBO_3 \cdot 4H_2O$, 1 wt% on glass content)**

→ Perborate decomposing in borate and H_2O_2, in turn leading to O_2 release

- **Mechanically stirring (300 rpm) for 10 minutes**
- **Containers were covered by a lid and kept for 7 days at 40°C.**



Total porosity of 82.1 vol%
(open porosity = 81.5 vol%)
SSA (BET) = 83 m^2/g

Compressive strength: 0.34±0.04 MPa

Application#1: direct foaming

Exploitation of gelation for different materials
New functionalities according to enhanced porosity

Processing details…similar than in case of solid block

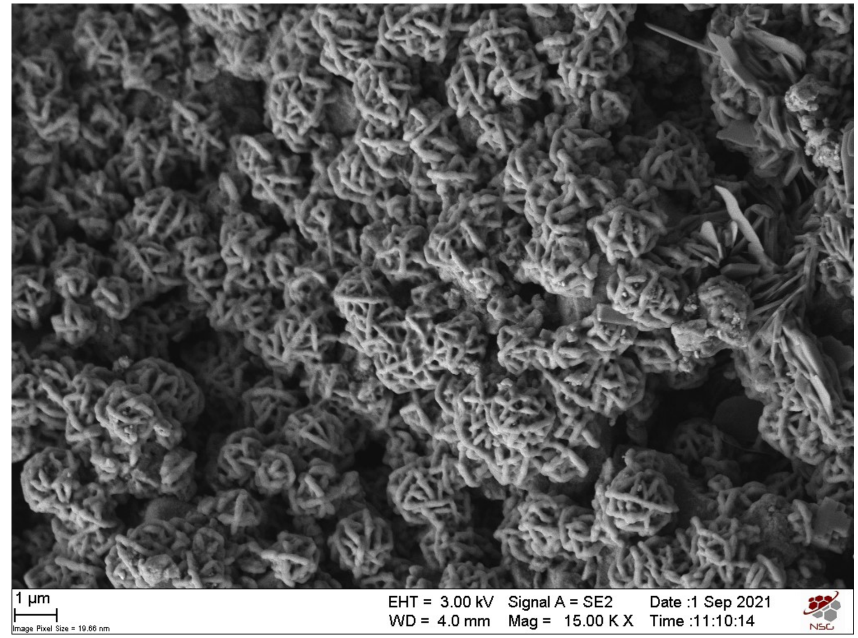
- **Coarse fragments manually crushed and dry ball milled**
- **[UPDATED] Powders later, sieved <75 µm, cast in alkaline solution (6M NaOH), in PS containers, at 70-30 solid-liquid ratio**
- **[UPDATED] Addition of Sodium dodecyl sulfate (SDS, $CH_3(CH_2)_{11}SO_4Na$, 1 wt% on glass content) + Sodium perborate (SPB, $NaBO_3 \cdot 4H_2O$, 1 wt% on glass content)**

→ Perborate decompo[…]rn leading to O_2 release

- **Mechanically stirrin[…]**
- **Containers were co[…]lays at 40°C.**

High magnification details

Clear evidence of zeolite formation at cell walls



Total porosity of 82.1 vol%
(open porosity = 81.5 vol%)
SSA (BET) = 83 m^2/g

Compressive strength: 0.34±0.04 MPa

Application#1: direct foaming

Exploitation of gelation for different materials
New functionalities according to enhanced porosity

Processing details…similar than in case of solid block

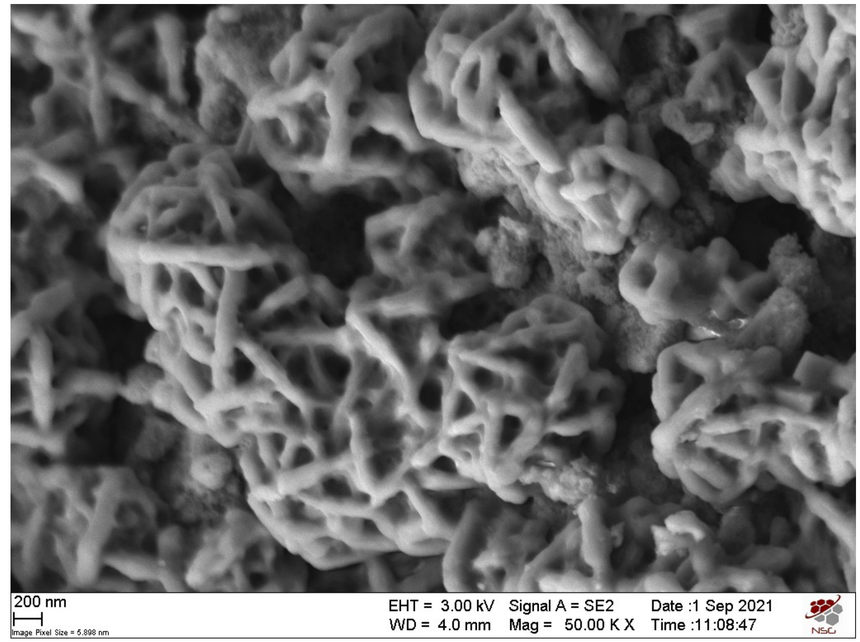
- **Coarse fragments manually crushed and dry ball milled**
- **[UPDATED] Powders later, sieved <75 µm, cast in alkaline solution (6M NaOH), in PS containers, at 70-30 solid-liquid ratio**
- **[UPDATED] Addition of Sodium dodecyl sulfate (SDS, $CH_3(CH_2)_{11}SO_4Na$, 1 wt% on glass content) + Sodium perborate (SPB, $NaBO_3 \cdot 4H_2O$, 1 wt% on glass content)**

→ Perborate decompo… urn leading to O_2 release

- **Mechanically stirrin…**
- **Containers were co… lays at 40°C.**

High magnification details

Clear evidence of zeolite formation at cell walls



Total porosity of 82.1 vol%
(open porosity = 81.5 vol%)
SSA (BET) = 83 m^2/g

Compressive strength: 0.34±0.04 MPa

Application#2: powders

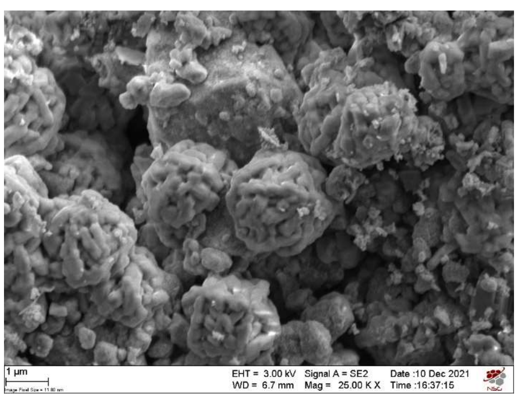
Reuse of fragments from crushed foams
Evidence of photocatalytic activity

Application in Dye Removal from Water: analogy with AAMs [surface hydroxyl groups can attract and hold cationic organic species]

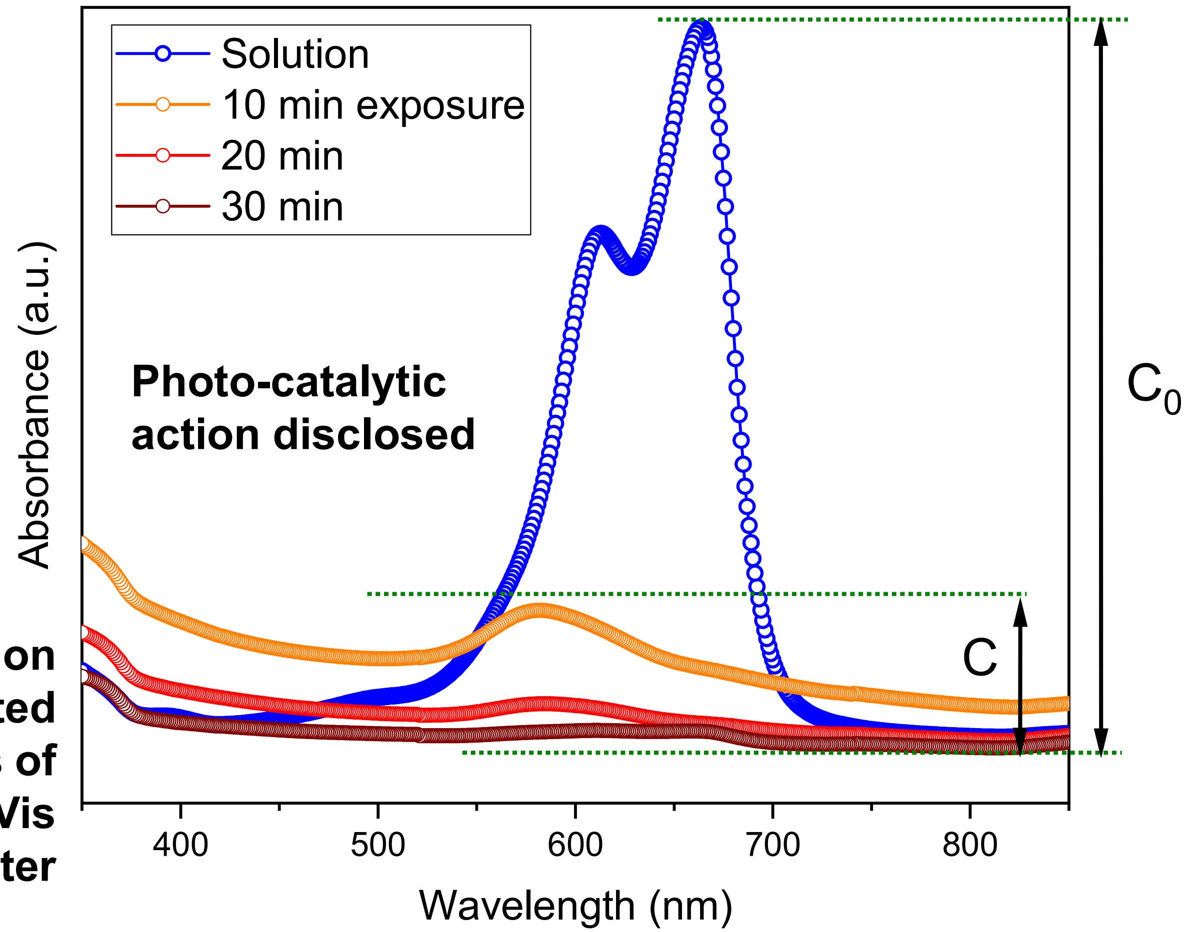
→ Test with model Dye: Methylene Blue, 10mg/mL

- **Powders cast in solution (50 mg/20 mL)**
- **UV irradiation (Hg lamp, λ=366 nm, P=125 W)**

Fragments milled&sieved <75 µm
Still zeolite-coated



Concentration changes detected by means of UV/Vis spectrometer



Università degli Studi di Padova — 800 anni 1222·2022

Application#2: powders

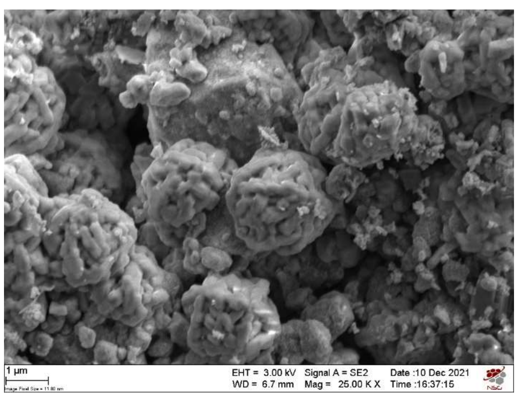
Reuse of fragments from crushed foams
Evidence of photocatalytic activity

Application in Dye Removal from Water: analogy with AAMs [surface hydroxyl groups can attract and hold cationic organic species]

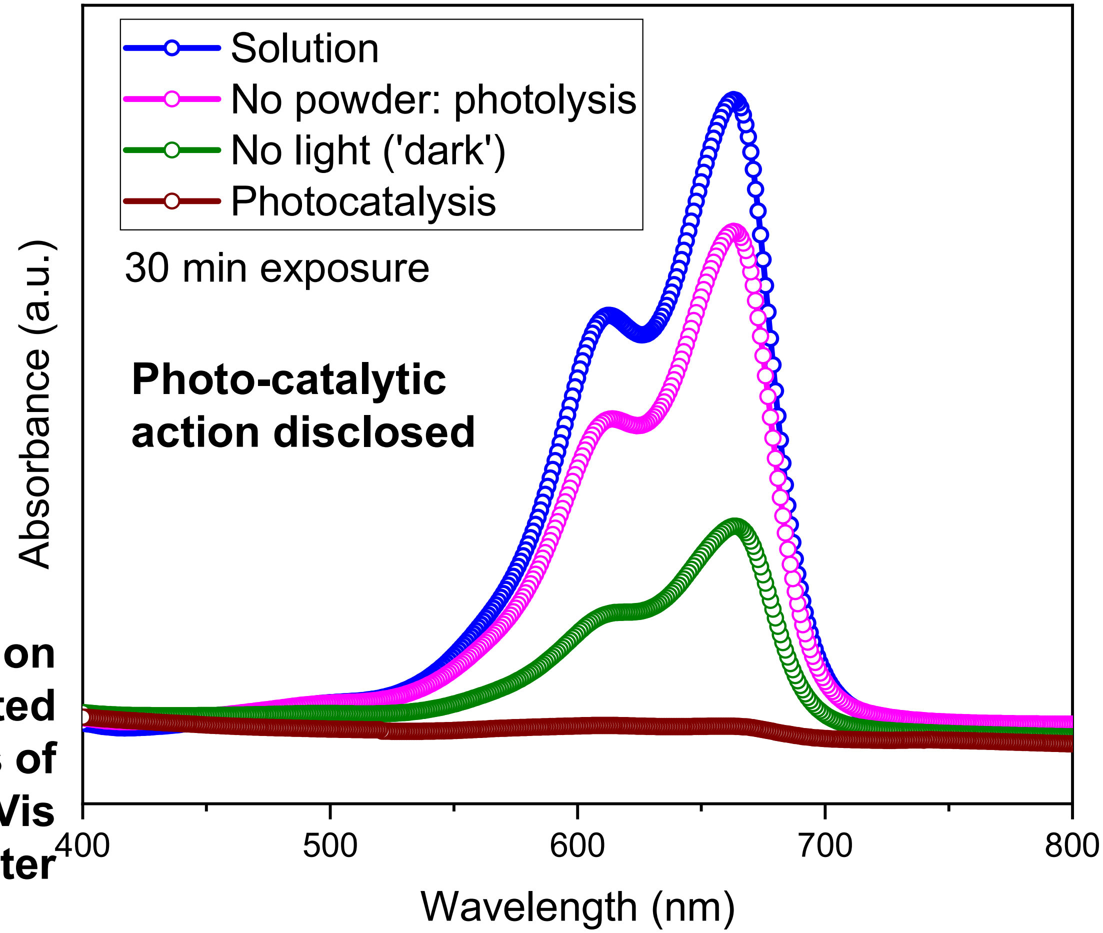
→ **Test with model Dye: Methylene Blue, 10mg/mL**

- **Powders cast in solution (50 mg/20 mL)**
- **UV irradiation (Hg lamp, λ=366 nm, P=125 W)**

Fragments milled&sieved <75 µm
Still zeolite-coated



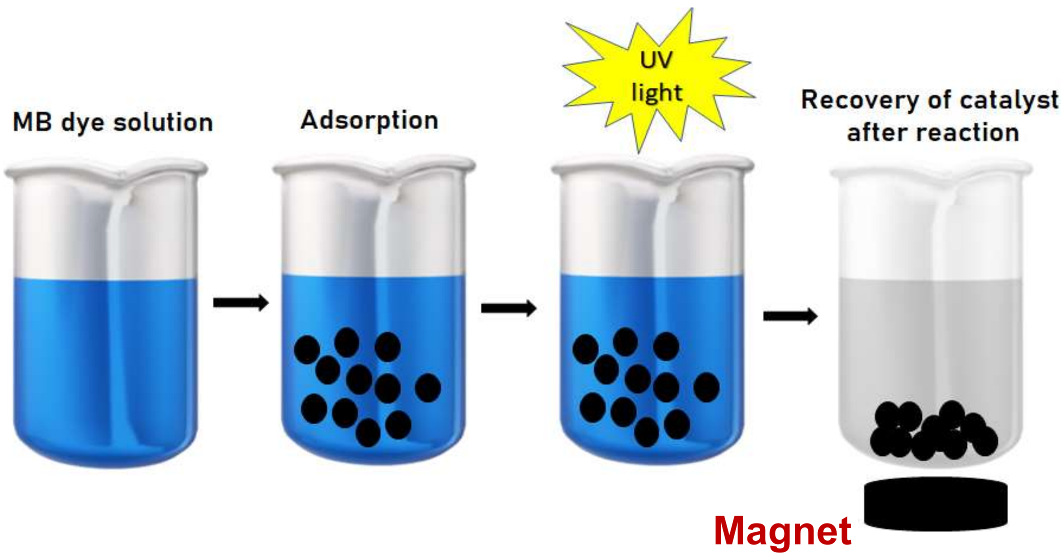
Concentration changes detected by means of UV/Vis spectrometer

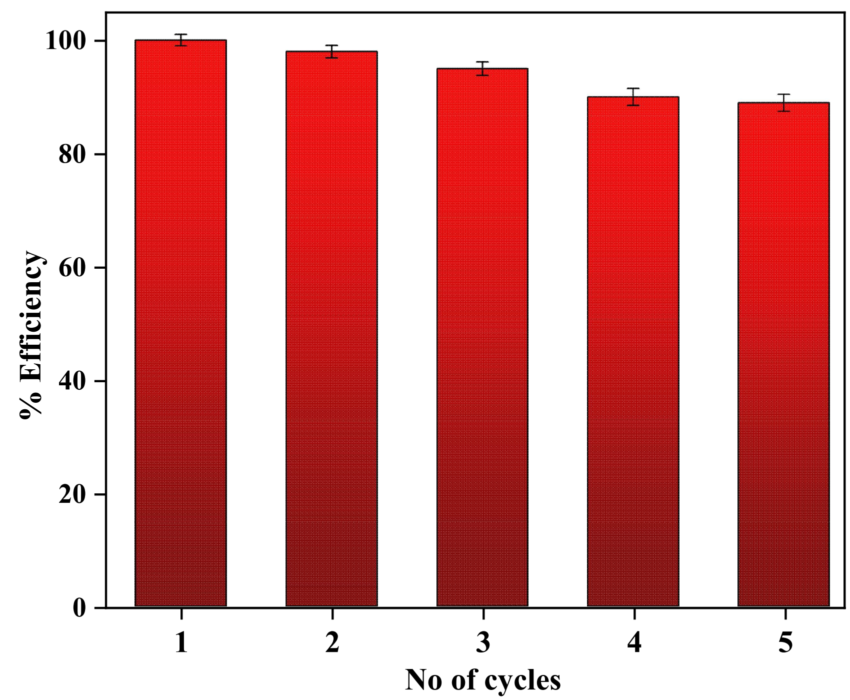


Application#2: powders

Foams as doubly sustainable product

Powders from the crushing of foams useful as sorbents!





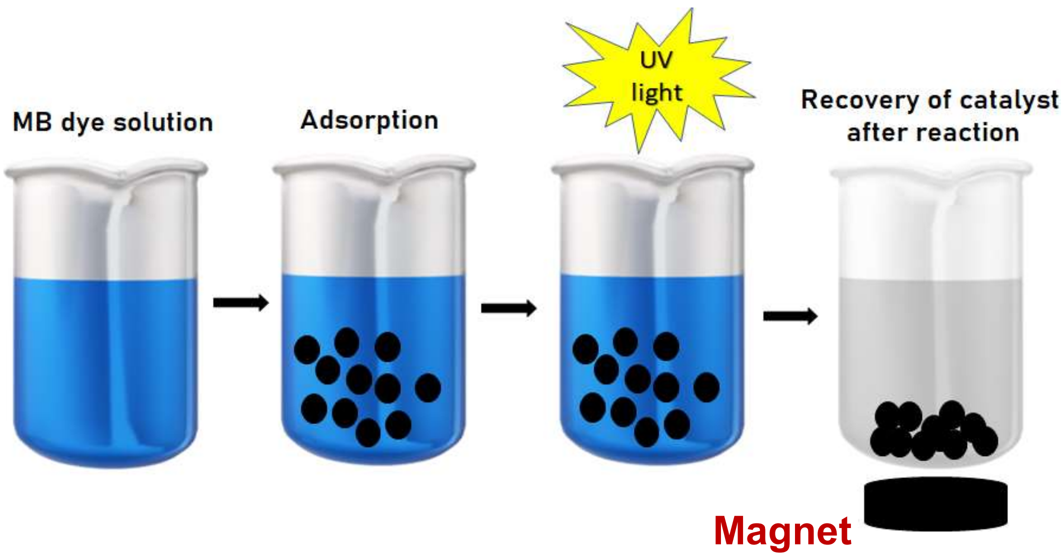
Excellent reusability:

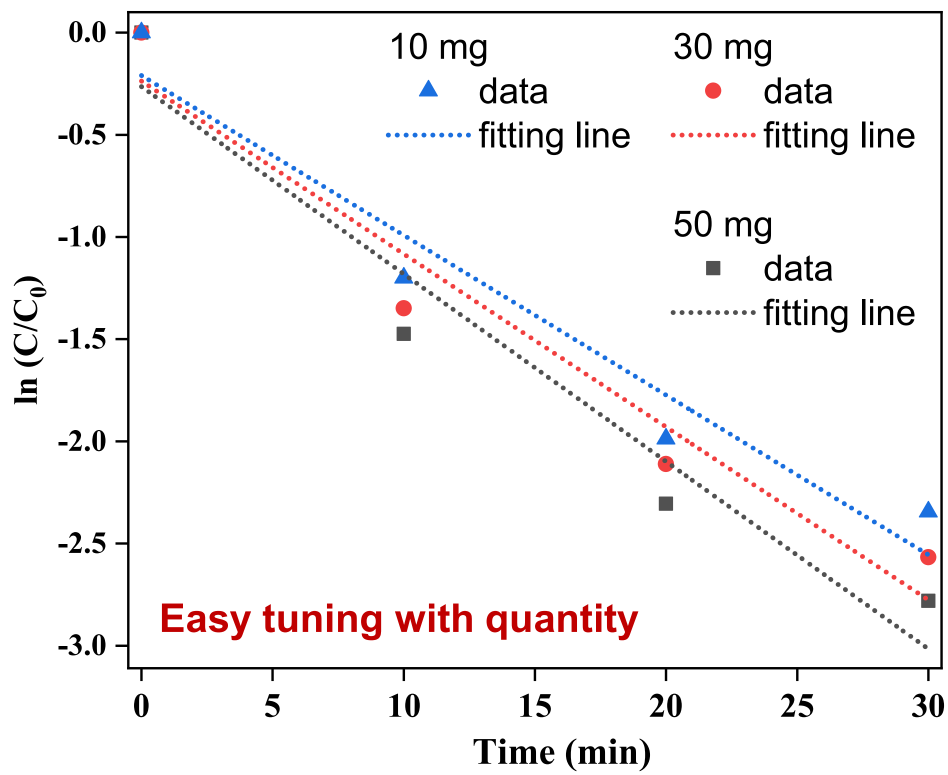
- **Easy separation with a permanent magnet**
- **Efficiency confirmed cycle after cycle**

$$\text{Efficiency}=\frac{(C_{cycle\ N,@30\ min}-C_0)}{(C_{cycle\ 1,@30min}-C_0)}\cdot 100\%$$

Application#2: powders

Reuse of fragments from crushed foams
Evidence of photocatalytic activity





Excellent reusability:

- **Easy separation with a permanent magnet**
- **Efficiency confirmed cycle after cycle**

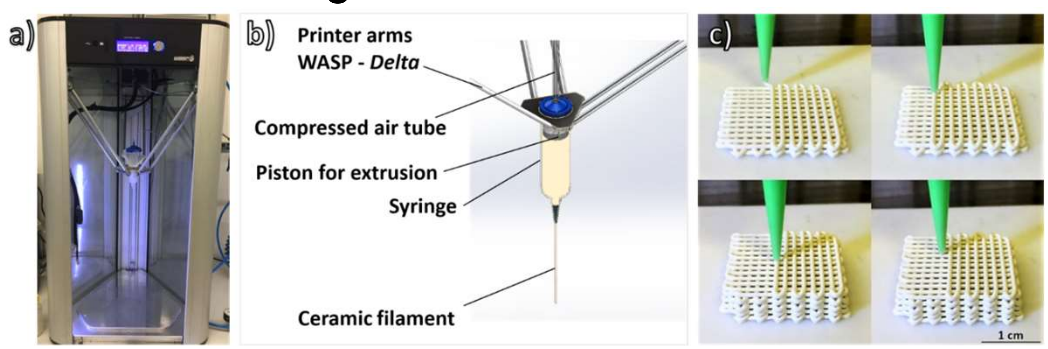
$$\text{Efficiency}=\frac{(C_{cycle\ N,@30\ min}-C_0)}{(C_{cycle\ 1,@30min}-C_0)}\cdot 100\%$$

Preliminary conclusions

…and further developments

Waste-derived glasses expressing **great potential for the obtainment of stable inorganic gels**

- **Development of porous bodies**: very easy foaming by pore generation at the early stage of gelation (gas release from decomposition of H_2O_2, Na-perborate, etc.) → setting conditions to be further explored to maximize strength; thermal conductivity to be assessed on much bigger samples (current: discs 50 mm diameter, 15 mm height, cut into cubic blocks for characterization)
- **Very interesting photocatalytic activity: exploitation of waste-derived material 'in full' (reactive glass matrix properly yielding semi-crystalline IP, magnetite inclusion acting as catalyst)** → reference for new waste-derived glass formulations
- Catalytic activity to be tested on **whole porous components**
- Partially gelified suspensions to be tested as **inks for additive manufacturing**

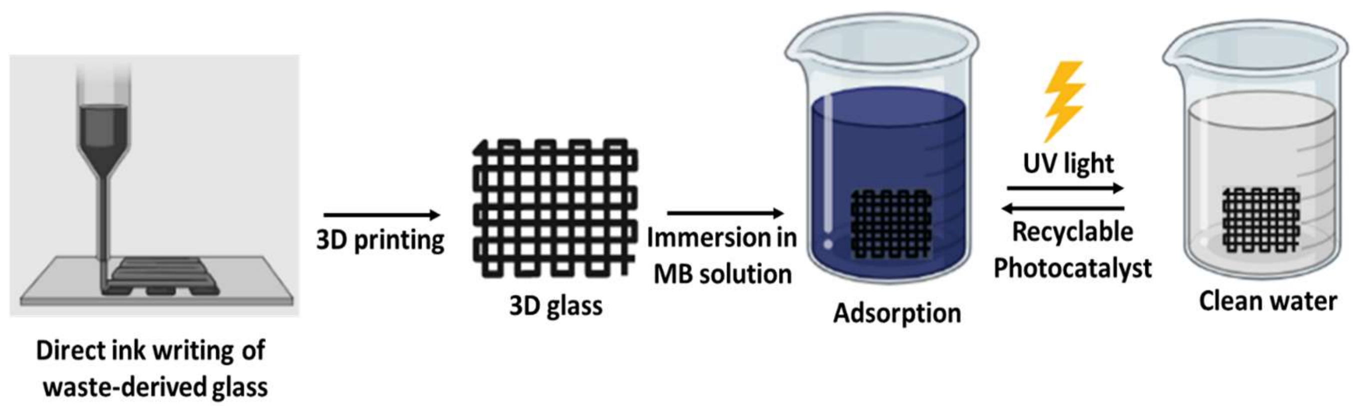


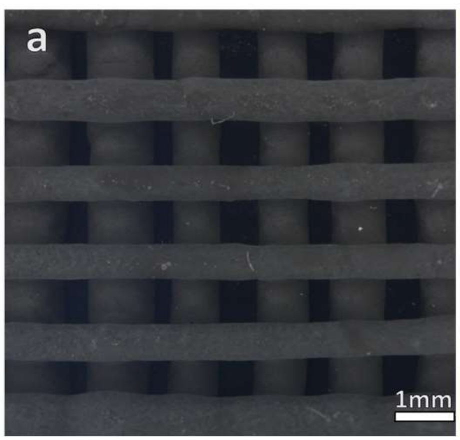
Current studies

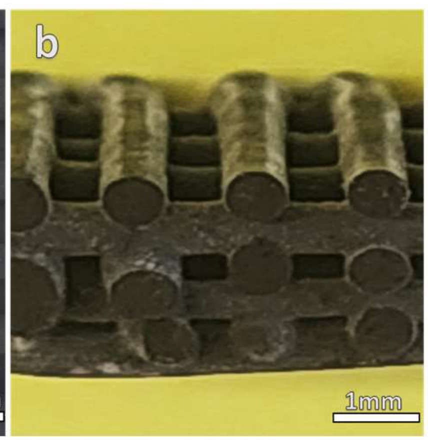
Inorganic direct ink writing
Porous photocatalytic bodies feasible

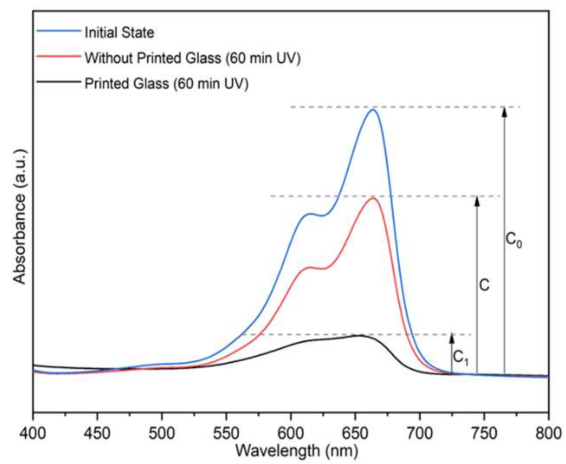
Cooperation with
Dr. Mokhtar Mahmoud (FunGlass)

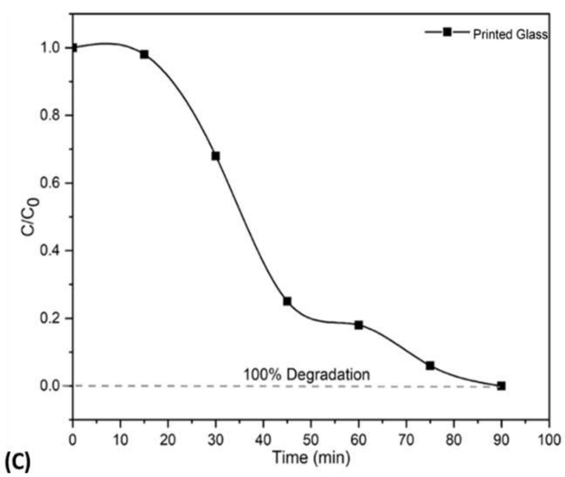
Extrusion of 5M NaOH slurry (65 wt% solid loading)
Drying 24 h at RT











Università degli Studi di Padova

Switch

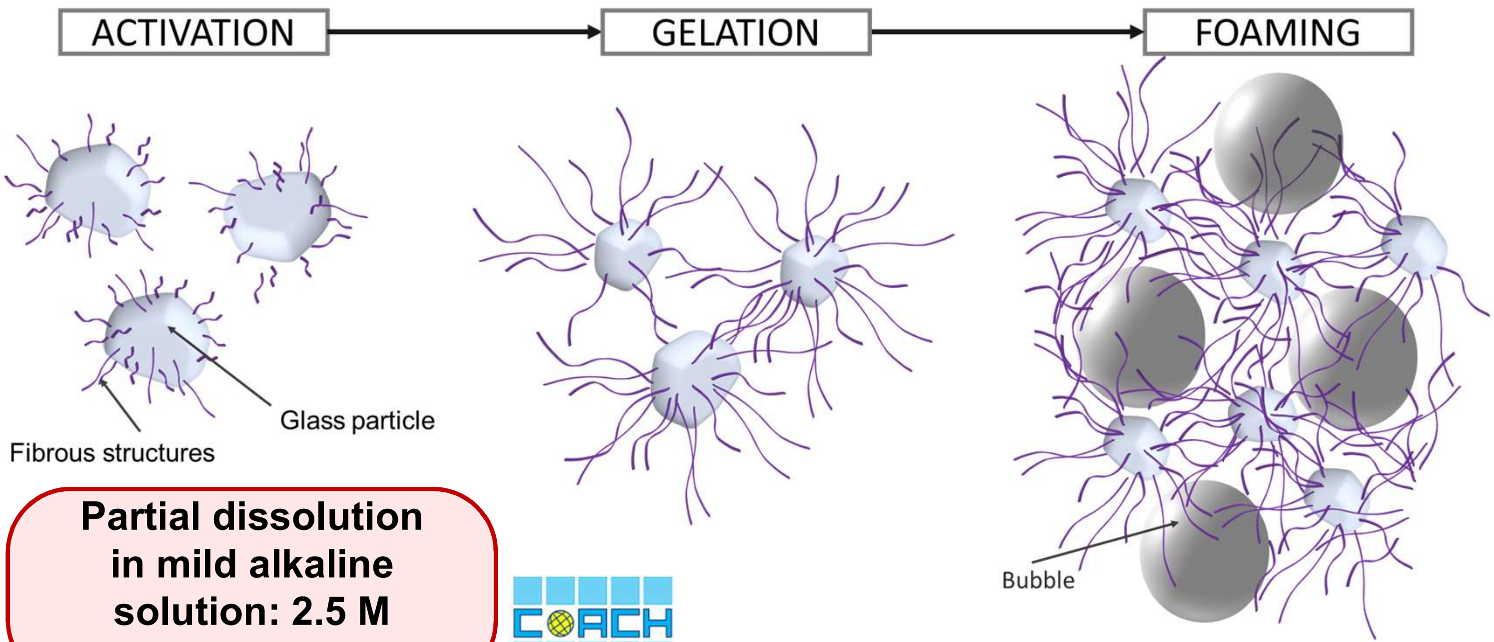
Alkali activation of waste glasses, instead of 'waste-derived glasses'

Sustainable reuse of discarded fractions of commercial glasses

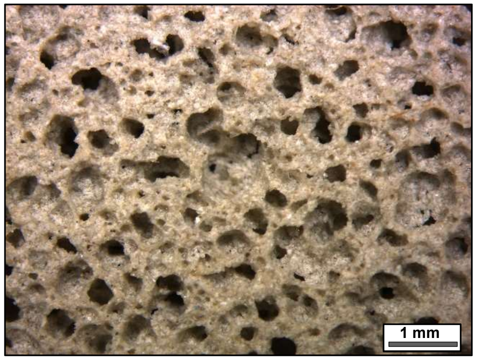
Solution: 'mild' activation of waste glass and RT foaming

Glass foams obtained by low T firing of 'green' foams

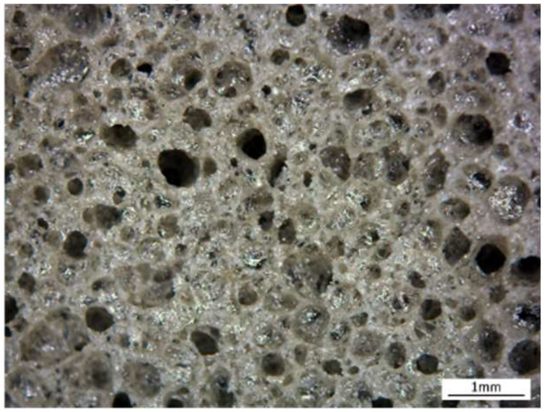
Green foams from mechanical foaming of alkali-activated glass suspensions



'Green foam' (room T)



After firing at 700 °C



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

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

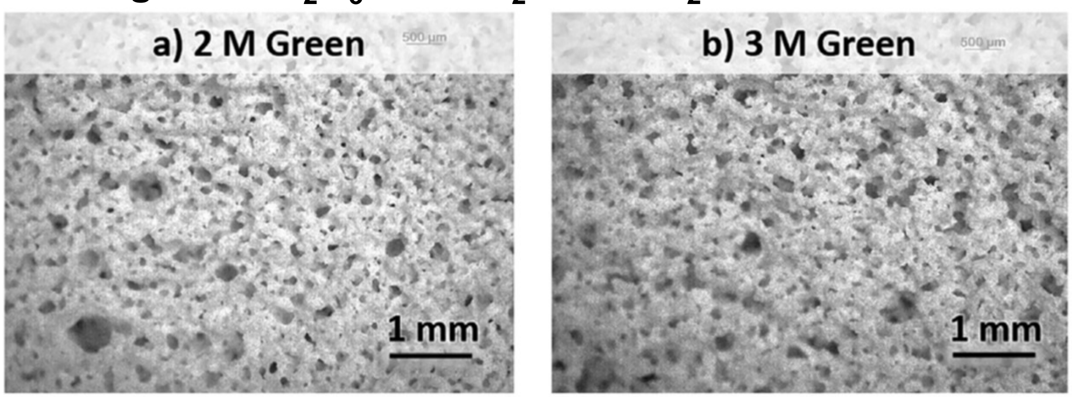
Beyond soda-lime glass

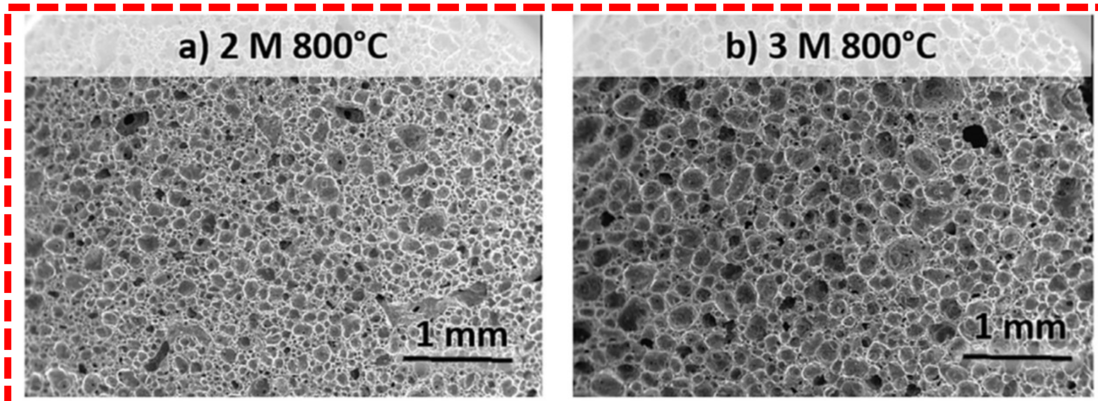
Glass for fibres: subject to crystallization

New process exploiting crystallization just as reinforcement option

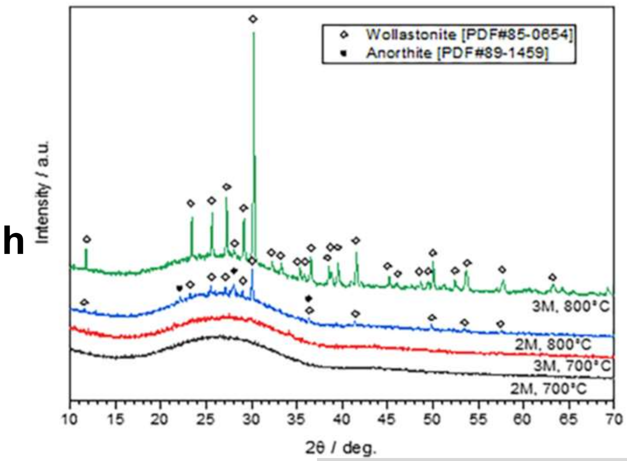
UNIVERSITÀ DEGLI STUDI DI PADOVA — 800 ANNI 1222·2022

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

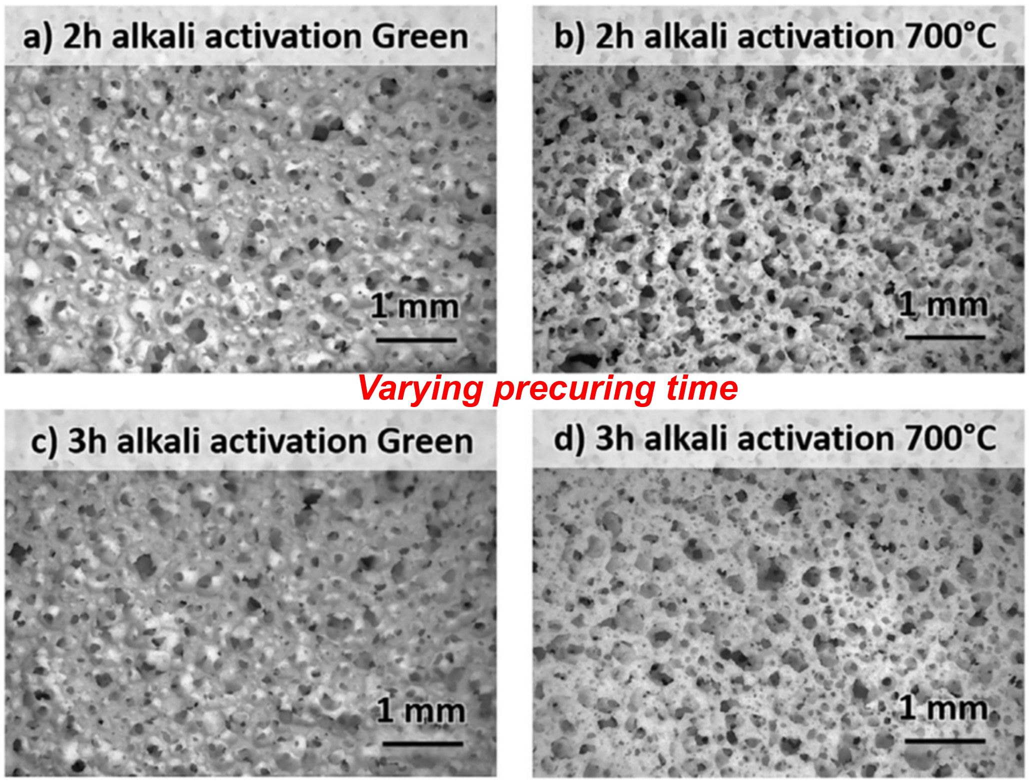
Main collaborators: Dr D. Ramteke, Dr. M. Hujova

Beyond soda-lime glass

Opal glass: subject to fluorine evolution

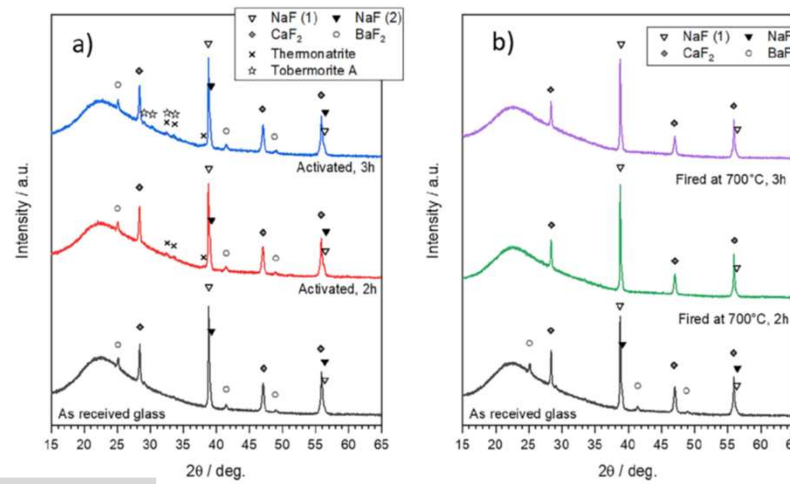
New process keeping fluorine content unchanged

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



Varying precuring time

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

UNIVERSITÀ DEGLI STUDI DI PADOVA — 800 ANNI 1222·2022

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.		

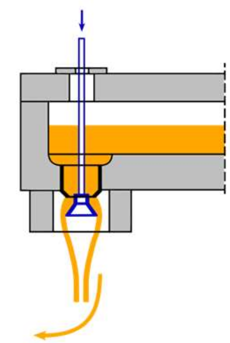
SL: Partially unrecyclable (highly contaminated fractions)

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

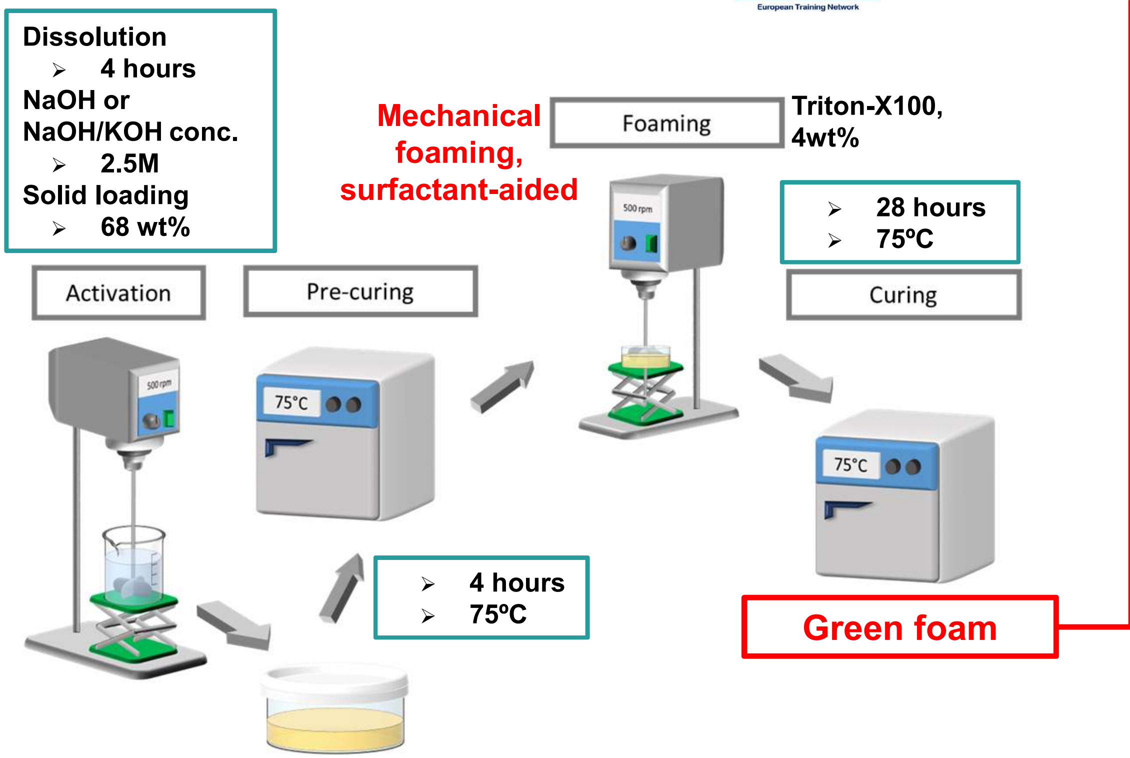
Mechanical foaming of alkali activated suspensions
Structural modifications with activation compounds

materials MDPI

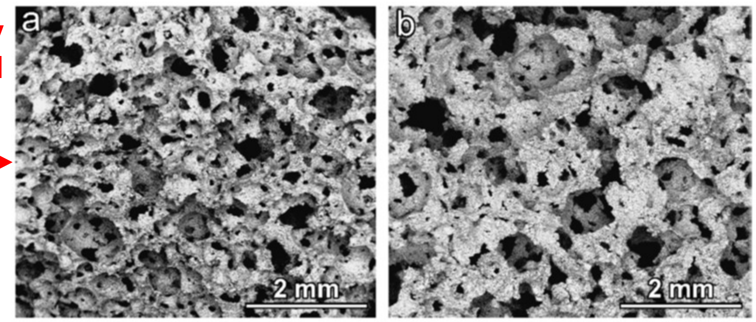
Article

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

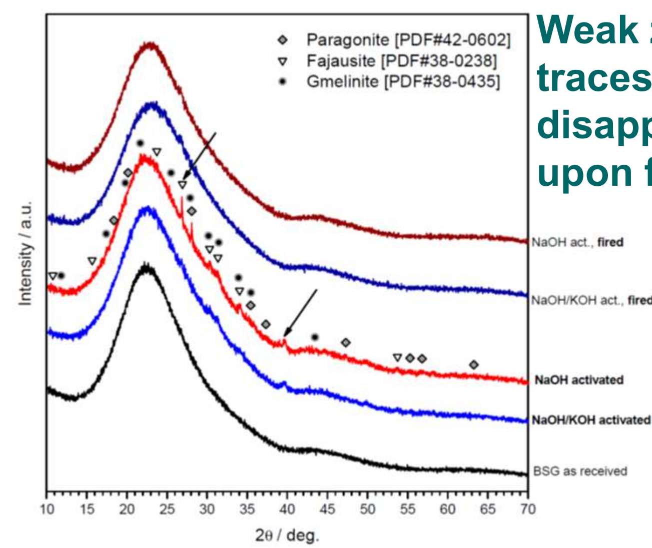
COACH European Training Network



Particles bound by surface gel



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



Weak zeolite traces, disappearing upon firing

UNIVERSITÀ DEGLI STUDI DI PADOVA
800 ANNI 1222·2022

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

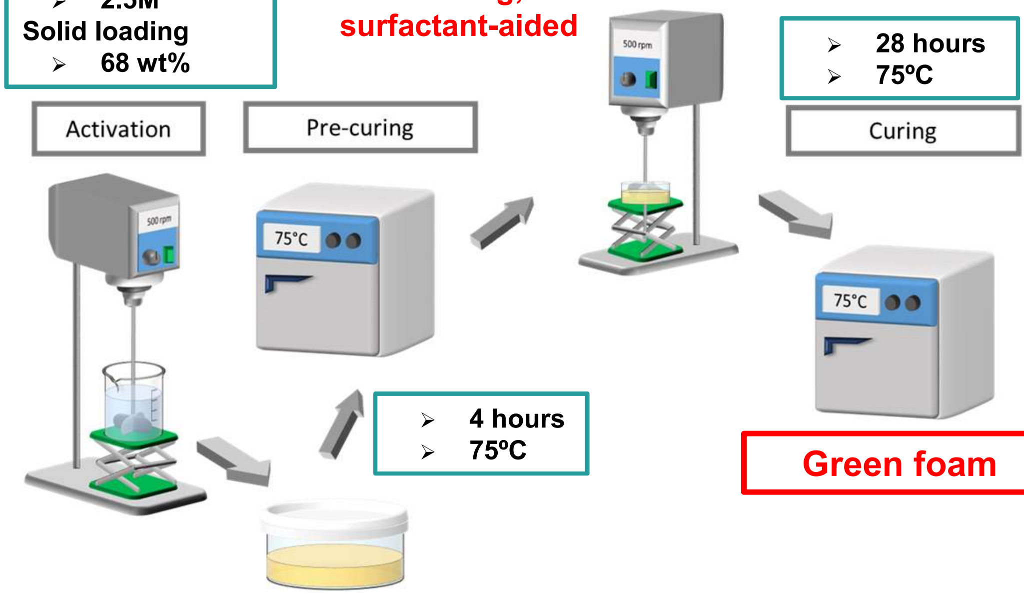
Dissolution
- ➢ 4 hours

NaOH or NaOH/KOH conc.
- ➢ 2.5M

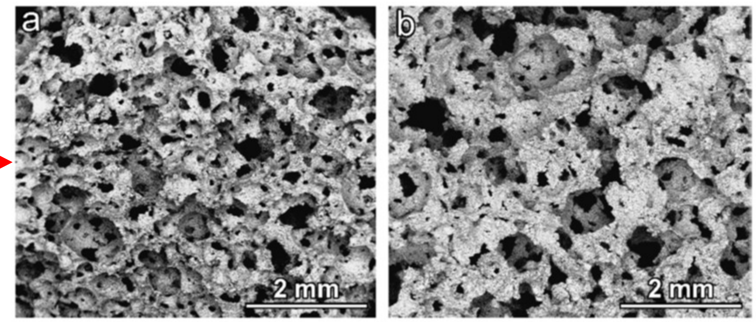
Solid loading
- ➢ 68 wt%

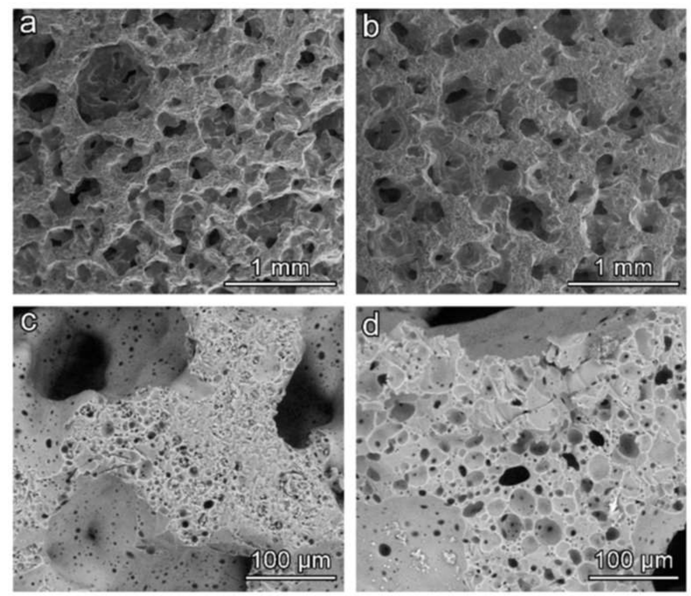
Mechanical foaming, surfactant-aided

Triton-X100, 4wt%



Green foam





Fired at 700°C
T_g +150°C

800 ANNI 1222·2022

UNIVERSITÀ DEGLI STUDI DI PADOVA

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, Dr. Mokhtar Mahmoud)

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

No foaming: highlighting low T binding

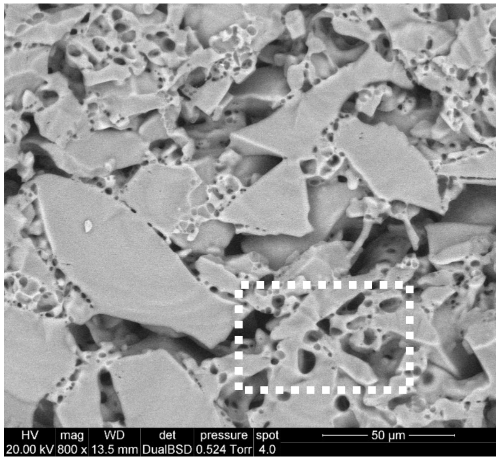
Enhanced strength with no firing

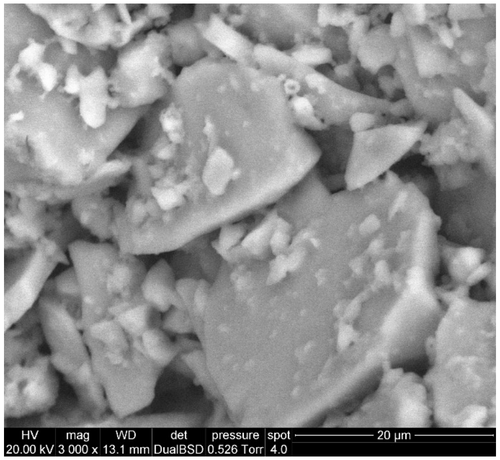
Attention to binding phase: active also without thermal treatment

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'

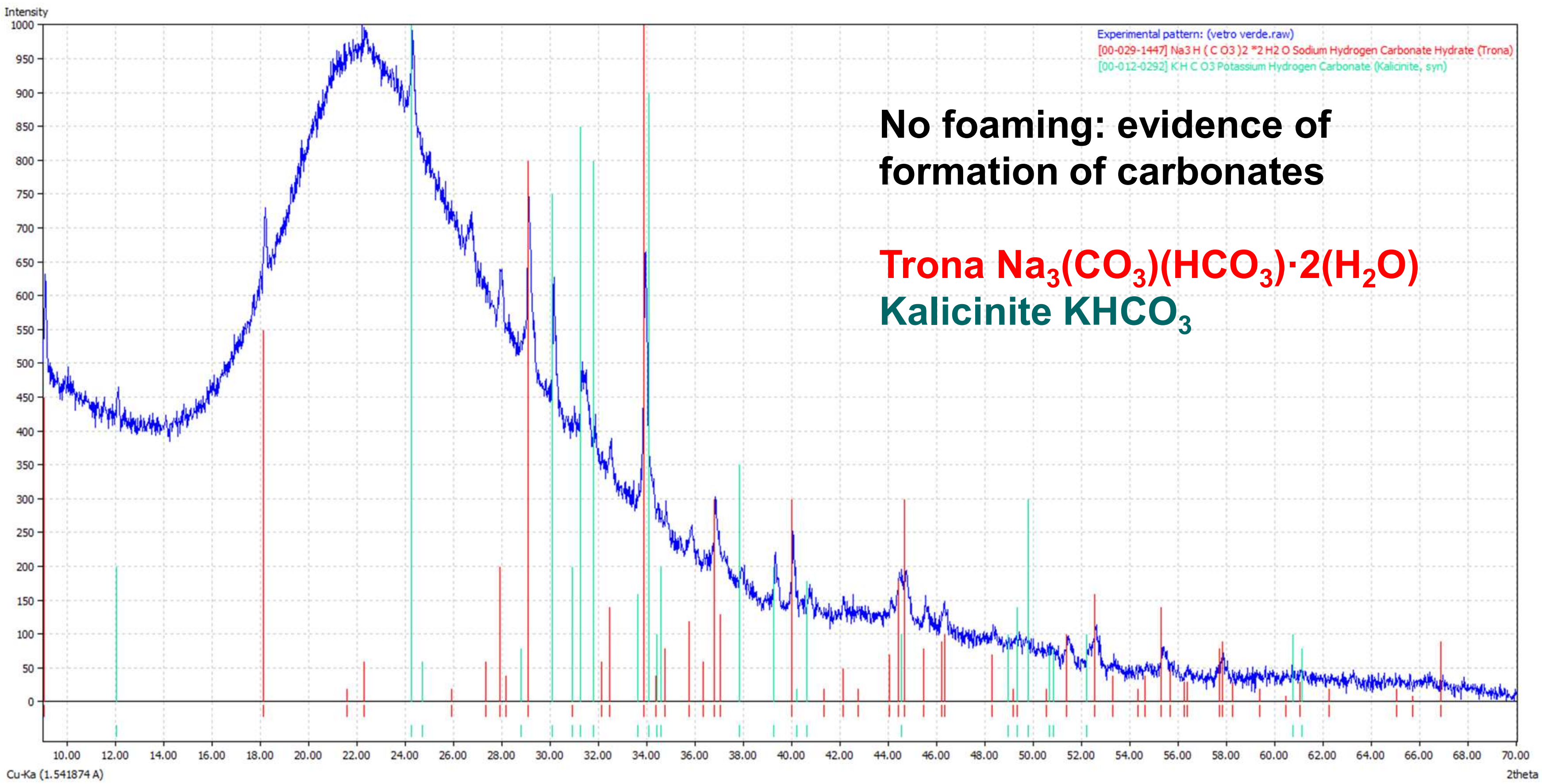
Unfired dried suspension: mineralogy

Attention to new phases

Are they responsible for gelation?

800 ANNI 1222·2022

Università degli Studi di Padova



No foaming: evidence of formation of carbonates

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

Kalicinite $KHCO_3$

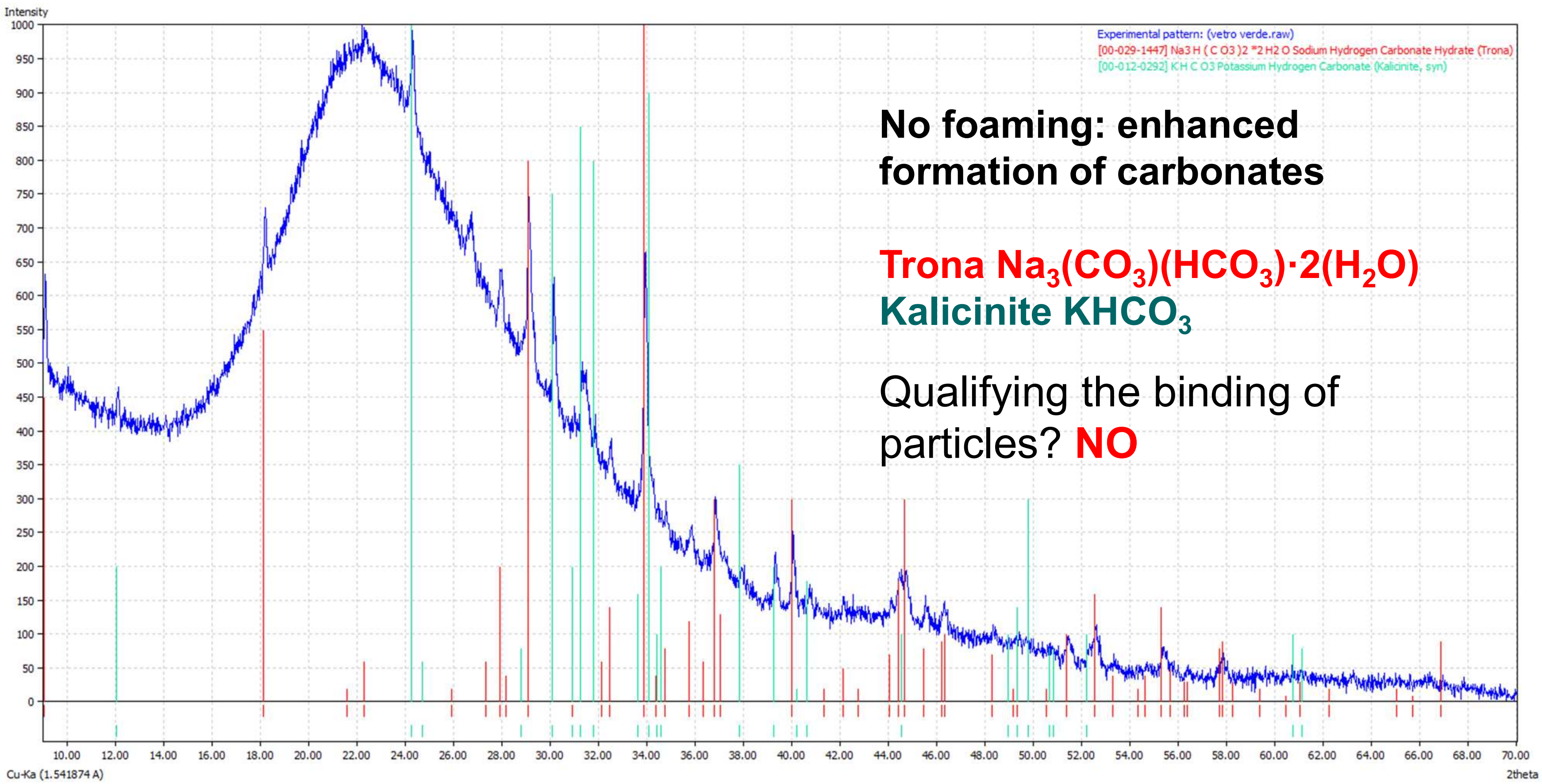
UNIVERSITÀ DEGLI STUDI DI PADOVA

800 ANNI 1222·2022

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**

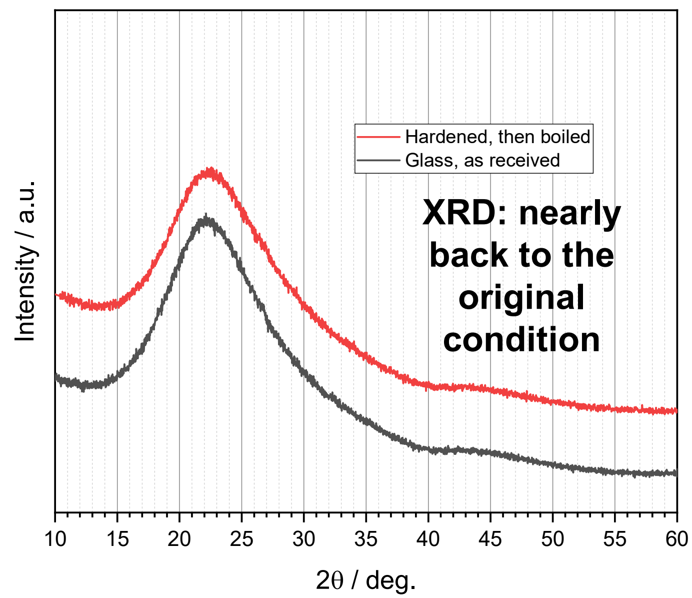
Unfired dried suspension: boiling

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?

1222·2022 800 ANNI

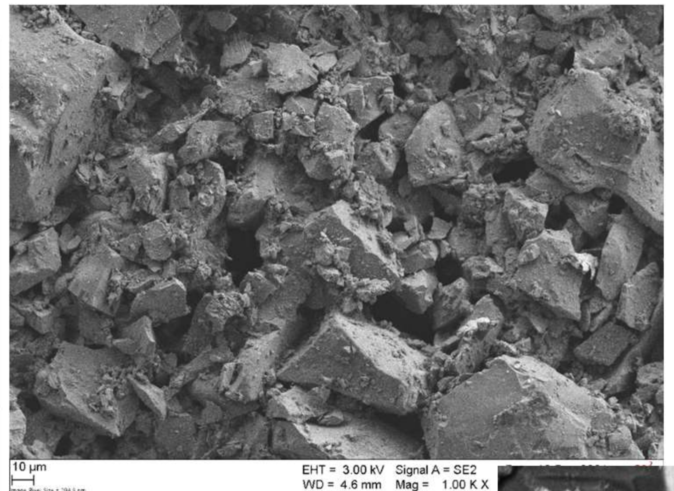
UNIVERSITÀ DEGLI STUDI DI PADOVA

Unfired dried suspension: boiling

Alkali-rich phase removed, no dismantling of binding phase

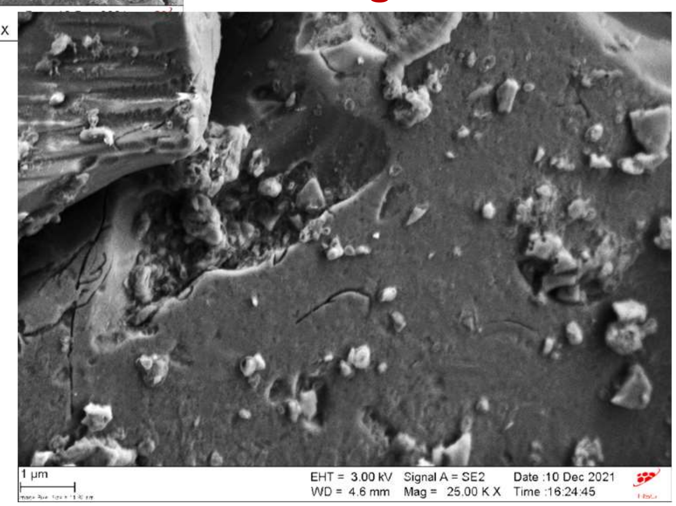
Confirmation by SEM: binding of particles by means of thin surface layers

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



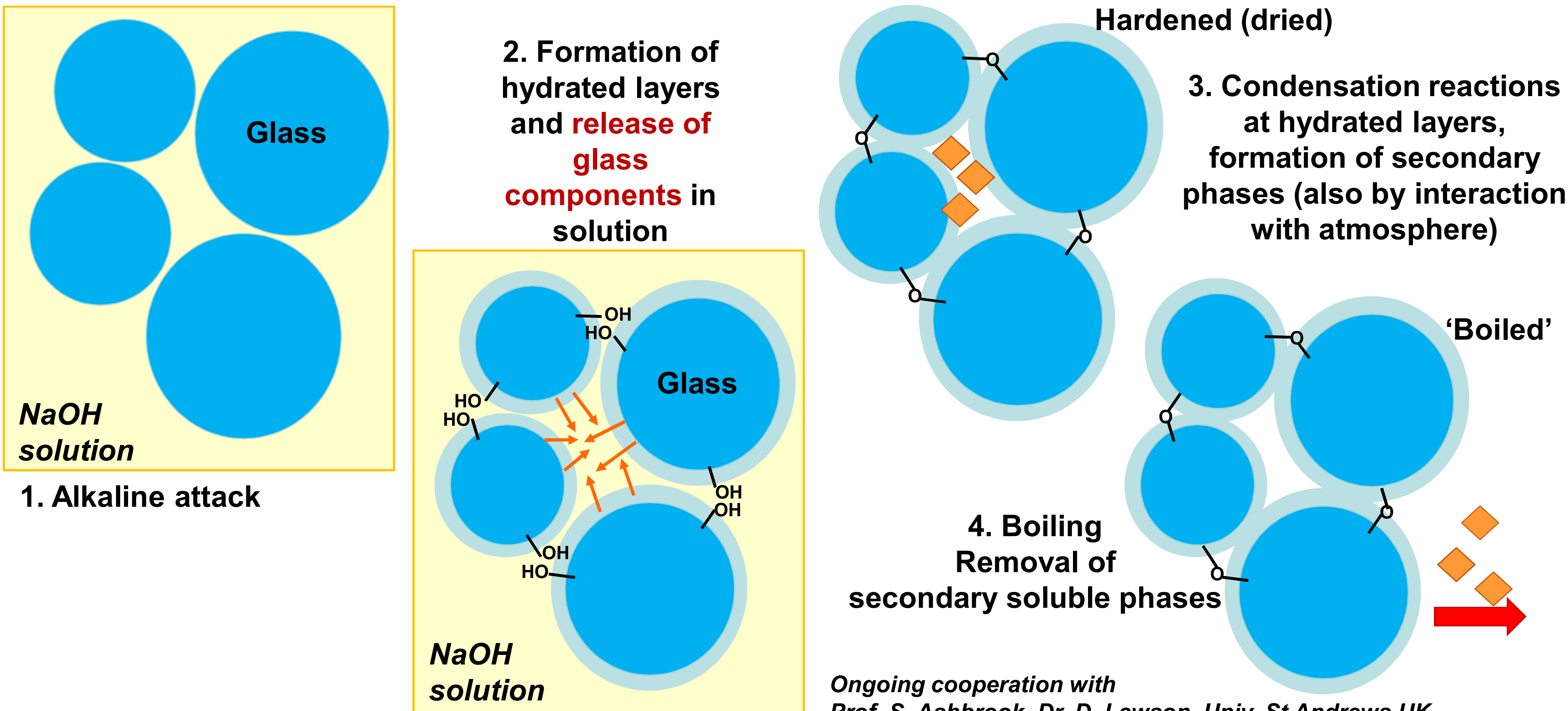
Hint for a new generation of unfired glass-based materials for *structural* and… *functional applications*

Università degli Studi di Padova — 800 anni 1222·2022

Possible mechanism

Cold consolidation by 'mild' alkali attack

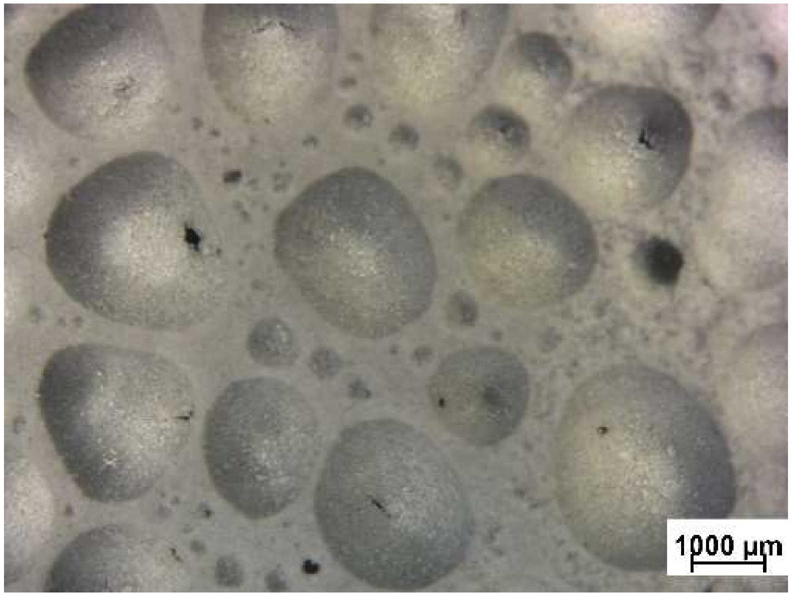
Ongoing studies (e.g. NMR) to confirm [key difficulty: thin reaction layer]



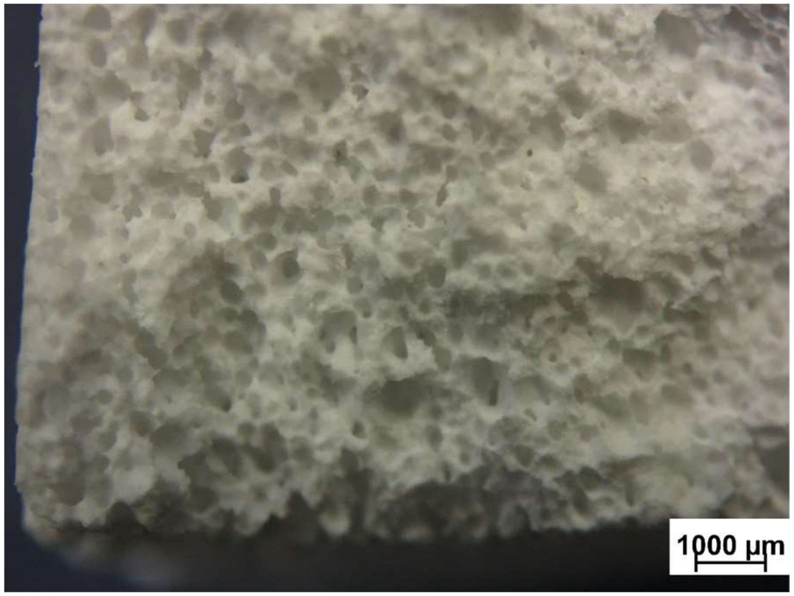
Ongoing cooperation with
Prof. S. Ashbrook, Dr. D. Lawson, Univ. St Andrews UK

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)**



FOAM obtained starting from BSG
Only perborate



FOAM obtained starting from BSG
+ SDS : enhanced homogeneity

Much less surfactant: unfired foams surviving boiling test!

Total porosity of 60.1 vol% (open porosity = 58.1 vol%)

Compressive strength: 3.2 ± 0.3 MPa

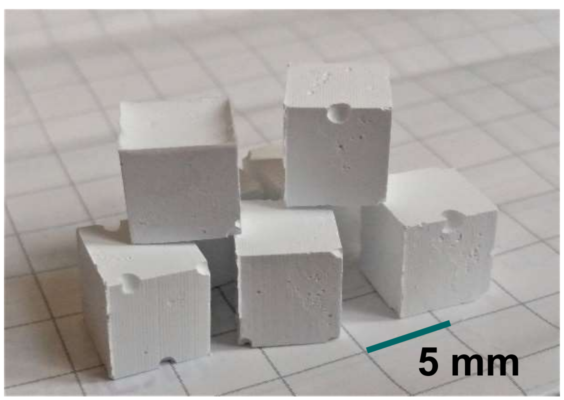
Confirming the strong bonding

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**

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

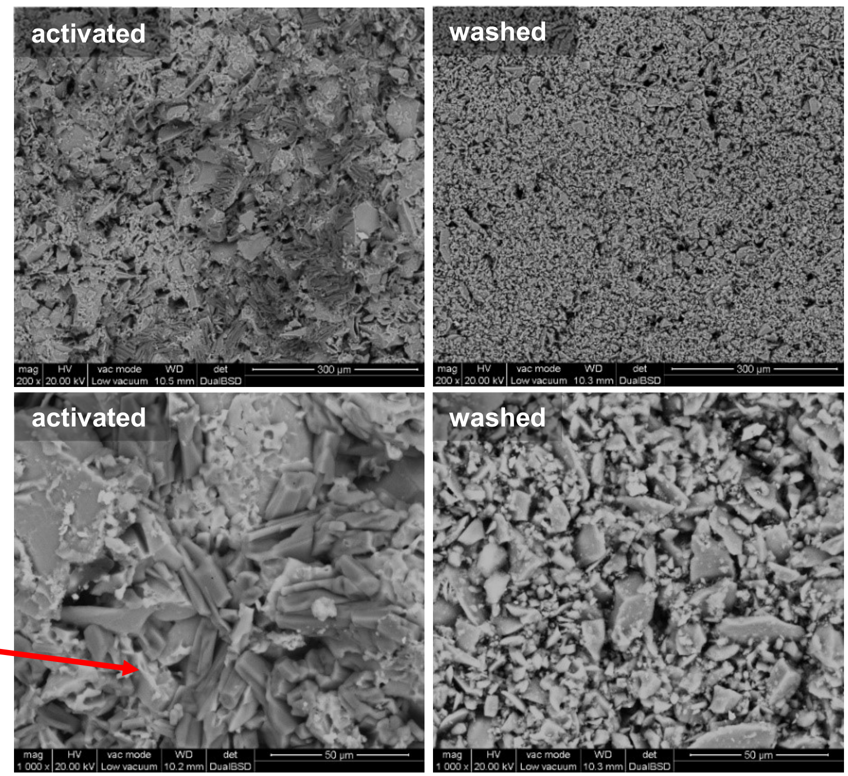


Washing: application of boiling test

Alkali carbonates leaving

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



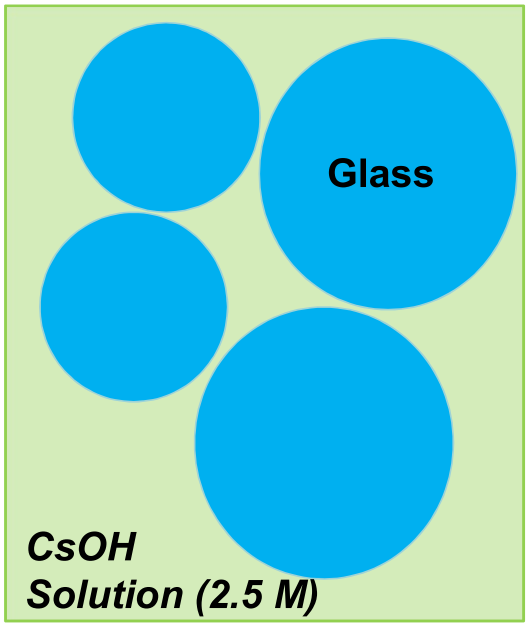
Main collaborator: Dr Diana Carolina Lago

800 ANNI 1222·2022

UNIVERSITÀ DEGLI STUDI DI PADOVA

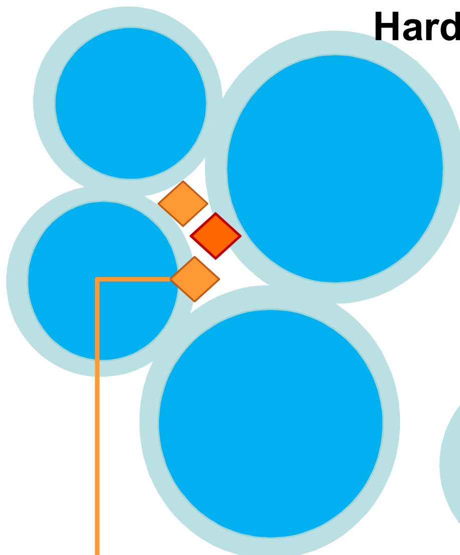
Beyond NaOH: CsOH (latest tests)

Prototype of nuclear waste of difficult stabilization
Confirming the overall mechanism



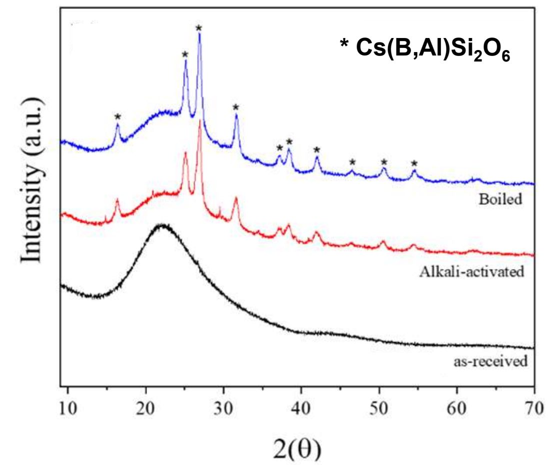
1. Alkaline attack

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

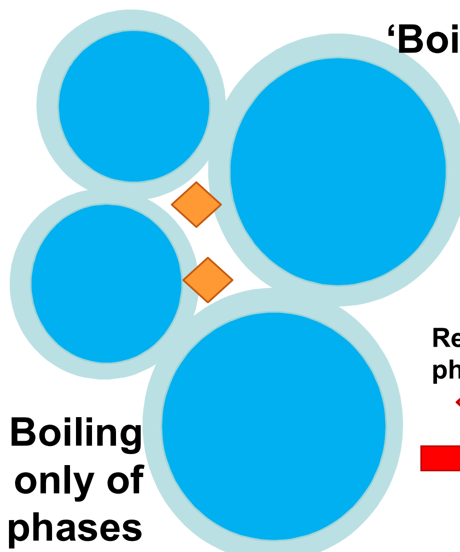


Hardened (dried)

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

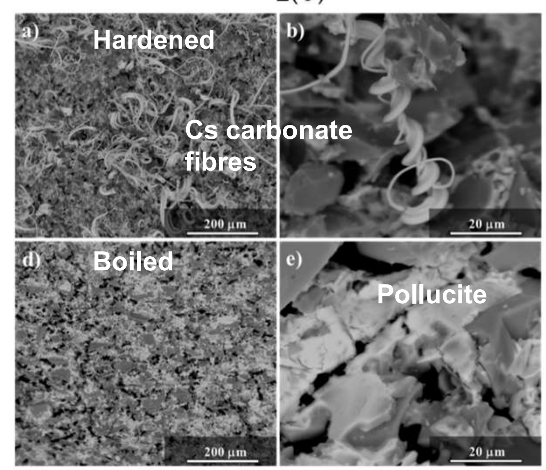


'Boiled'



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

Removed phase



Final stabilization by sintering

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**
- Beyond waste: possible alkali-free, basic activation

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)**

UNIVERSITÀ DEGLI STUDI DI PADOVA

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

UNIVERSITAS STUDII PADUANI
MCCXXII

Università
degli Studi
di Padova