Recyclage du verre en mousses pour applications environnementales

Ronan Lebullenger

ISCR - UMR CNRS 6226
Eq. Verres et Céramiques

Université de Rennes 1

François MEAR

UCCS - UMR 8181

Université de Lille 1

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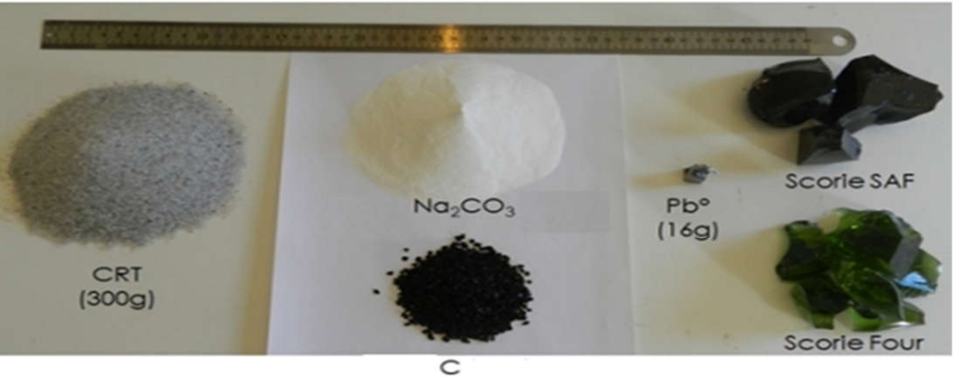
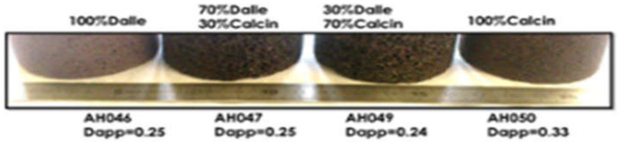
Le verre sous ses formes déchets - Recyver





eco-systèmes

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Recyver

TERbis

ARISTOT

ENVIRONNEMENT RECYCLING

Consortium industriel et académique soutenu par Eco-systèmes

22 Le Recyclage du verre
Atelier USTV
Nancy

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Le verre sous ses formes déchets - Recyver

- Lead extraction (> 98%) from CRT (cathode ray tubes).
- Valorisation of glass wastes (CRT, cullet , crystal glassware) in foam glasses (d_{app}<0,3 , λ_{therm}<100mW/m.K, $\sigma_{rupture}$ ~3MPa
- Production of expanded glass granules (civil engineering, …)
- Industrialisation of the laboratory developed process

- Foam glasses for supported catalysis treatment, chemical synthesis,..)

Sébastien Genty et Laure Cercueil

Institut des Sciences Chimiques de Rennes

Indoor air treatment by catalytic oxidation over an innovative support coming from recycled glass wastes

❖ Context of the study

❖ Air pollution is a major health concern

❖ Main focus on VOCs (Volatile Organic Compounds) removal
→ toxic for human health
→ disturb the chemical balance in the atmosphere

❖ More and more stringent laws about the decrease in VOCs' emissions
→ - 43% emissions for 2020
→ - 52% emissions for 2030

❖ 2 targeted fields
→ indoor air treatment
→ industrial air treatment

Indoor air treatment by catalytic oxidation over an innovative support coming from recycled glass wastes

❖ Context of the study

❖ Various processes are used to eliminate VOCs

→recovery processes (adsorption, condensation, physical scrubbing, etc.)

→destroying processes (biodegradation, chemical scrubbing, catalytic oxidation, etc.)

❖ Among these processes, catalytic oxidation has good performances for the treatment of complex mixtures and/or low concentrated pollutants

❖ Catalytic oxidation needs a catalyst for kinetic improvement

→ increase in production and decrease in reactor volume

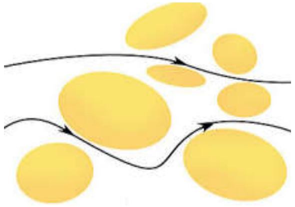
→ lower Temperature and Pressure

→ decrease in energy consumption and environmental impact

❖ Use of heterogeneous catalysts (easier to recover)

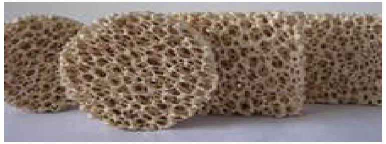
Indoor air treatment by catalytic oxidation over an innovative support coming from recycled glass wastes

- Various types of catalysts
  - acids
  - metal oxides
  - metals : Fe, Co, Ni, Pd, Ru, Rh, Pt…



- Sorption of metals on a porous support → open cell foams
  → increase in convection and radial stirring

- Different types of foams :
  - metal foam (very expensive, need of a Al_2O_3 washcoat layer)
  - ceramic foam (multi-step synthesis, energy consuming)



→ Goal : development of an original support (glass foam) for air treatment by catalytic oxidation using O_3 and O_2 as oxidants

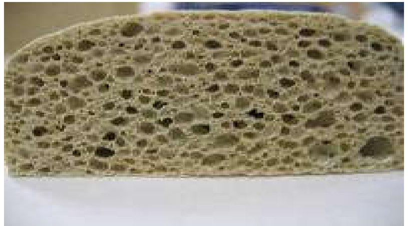
❖ Glass foam synthesis

- Use of crushed glass coming from recycling (circular economy)
  - glass bottles
  - screens
  - industrial glass wastes…

- Addition of foaming agents (AlN, MnO_2) and doping agents (TiO_2, Fe_2O_3)
- Heating at T=850°C – 950°C during 30 min – 1h

$$3\,TiO2 + 4\,AlN \xrightarrow{T\approx 900°C} 2\,Al_2O3 + 3\,TiN + 0.5\,N_2 \nearrow$$

Creation of gas bubbles which trigger the porous structure of the glass foam



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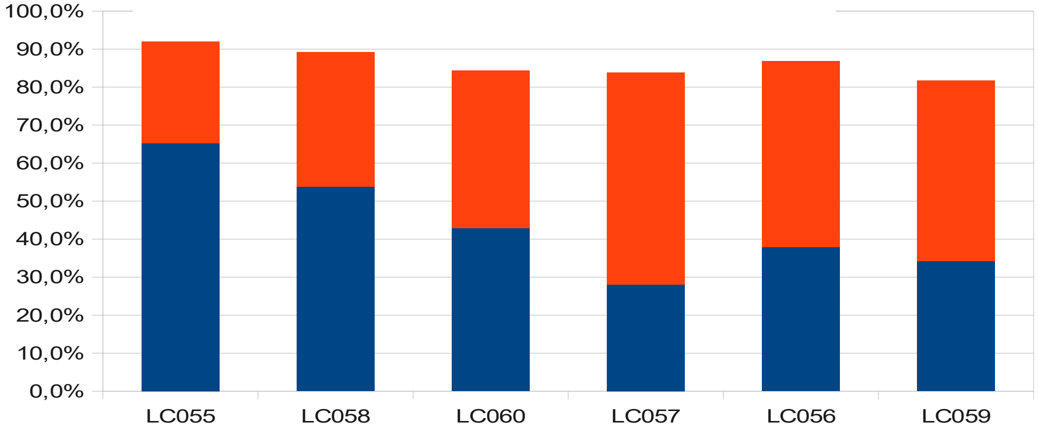
Tunning open / close porosity

Glass powder + x AlN + y TiO_2

Foaming @ 850°C



$$closed\ porosity\quad \frac{dapp}{dpyc}\quad \frac{dapp}{2,85}\quad 100$$

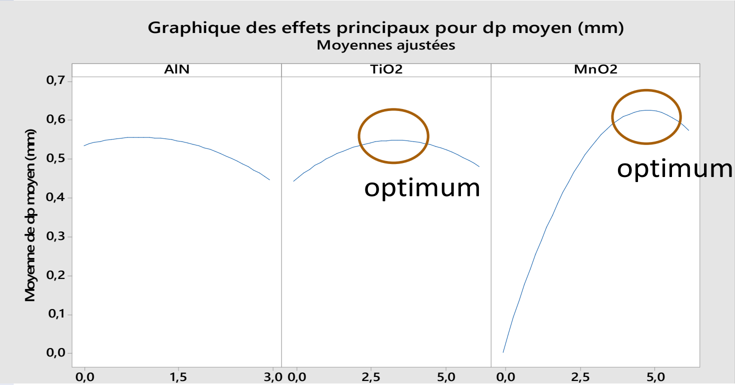
$$open\ porosity\quad 1\quad \frac{dapp}{dpyc}\quad 100$$

Open porosity ➪ Filtration, draining application

Closed porosity ➪ Insulation application

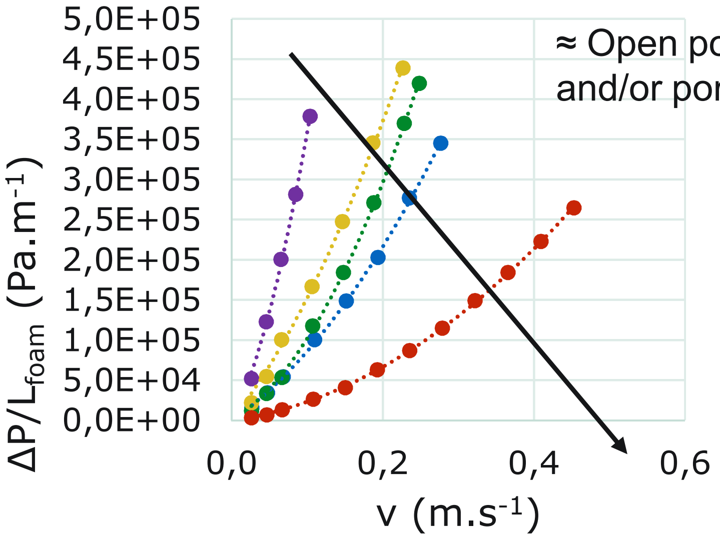
❖ Different properties depending on the quantity and type of foaming/doping agents

Glass foam	% AlN	% TiO_2	% MnO_2	Look of the glass foam	$d_{p\ average}$ (mm)	Open porosity (%)
1	1.48	0.00	3.00		0.199	90
2	0.05	3.00	3.00		0.331	90
3	1.48	3.00	0.00		0.186	73
4	0.60	1.16	1.16		0.109	77
5	0.60	4.84	4.84		0.427	92



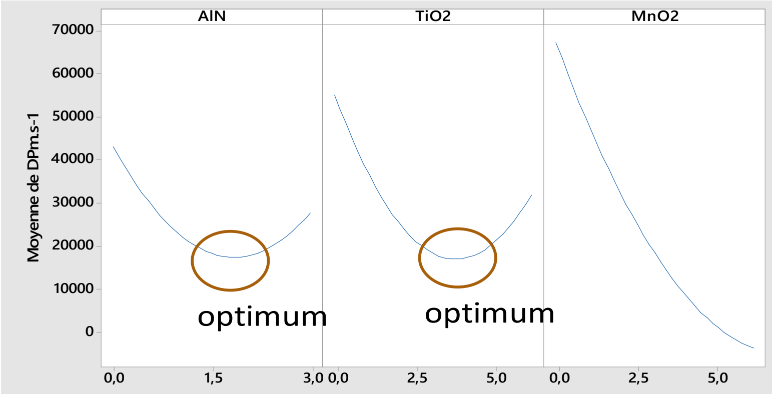
Synthesis conditions : T=880°C during 30 min (temperature increase of 10°C/min, granulometry of the glass : < 100 µm)

❖ Linear pressure drop in function of the speed of air circulation



Glass foam	% AlN	% TiO_2	% MnO_2
1	1.48	0.00	3.00
2	0.05	3.00	3.00
3	1.48	3.00	0.00
4	0.60	1.16	1.16
5	0.60	4.84	4.84

Type of foam	Synthesis	d_p average (mm)	Open porosity (%)	Linear pressure drop at 0.1 m.s^{-1}
Glassy foam	**Eco-friendly** (recycling of glass) and **cheap** (few steps and energy)	0.1 – 1.0	73 - 93	< 250-1500 Pa.m^{-1} for the « best foams »
Al_2O_3 ceramic foam from Vesuvius Inc.	**Multi-step synthesis** (complex) and **energy consuming** (1,500°C)	1.529*	75**	204*
		1.582*	85**	440*
Metal foam (stainless steel) from Glatt GmbH	**Expensive material**, need a **washcoat layer** (Al_2O_3)	0.802*	95**	231*



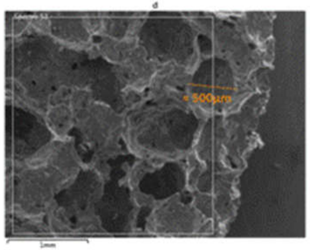
❖ Impregnation of metal catalysts on the glass foam

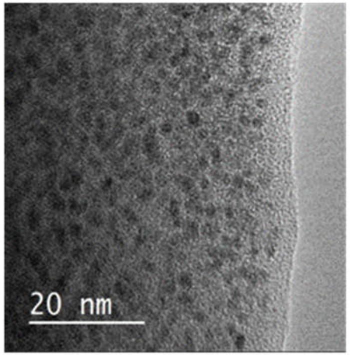
❖ Synthesis of metal Nanoparticles (NPs)

→ use of various metals (Rh, Ru, Pt, Au…)

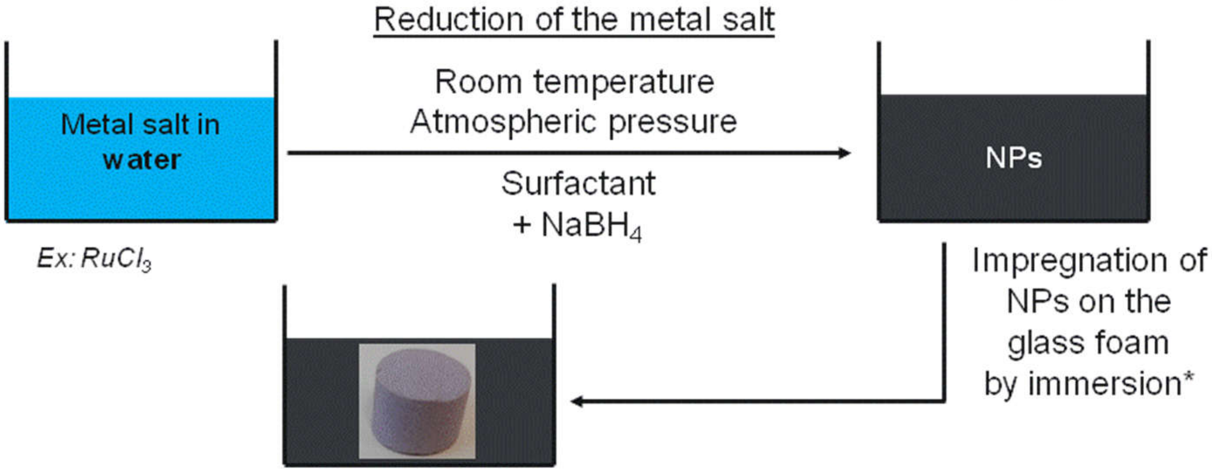
→ NPs of 2-5 nm

→ high specific area and lot of active sites





MET : NPs 2-3 nm



- METAL NANOPARTICLES SUPPORTED ON A GLASS-FOAM SUBSTRATE AND USES FOR THE CATALYSIS OF CHEMICAL REACTIONS,
- WIPO Patent Application WO/2017/064418

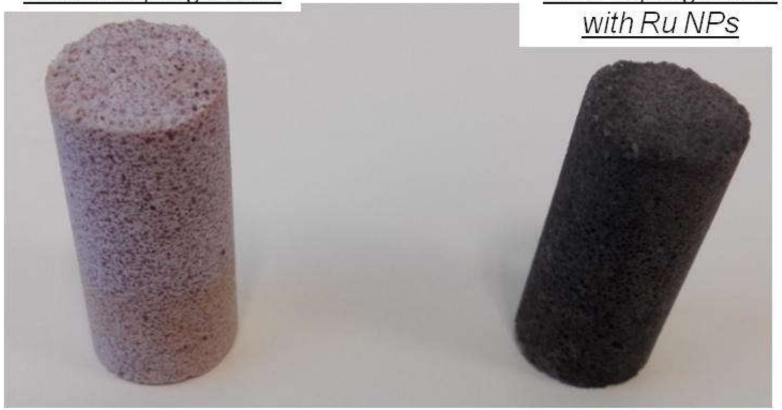
→ easy and reproducible impregnation method with a low amount of metal (≈0.1 %)

❖ Successfull deposits of Rh, Ru, Au, Pd

- drying in an oven
- without washcoat

Before impregnation

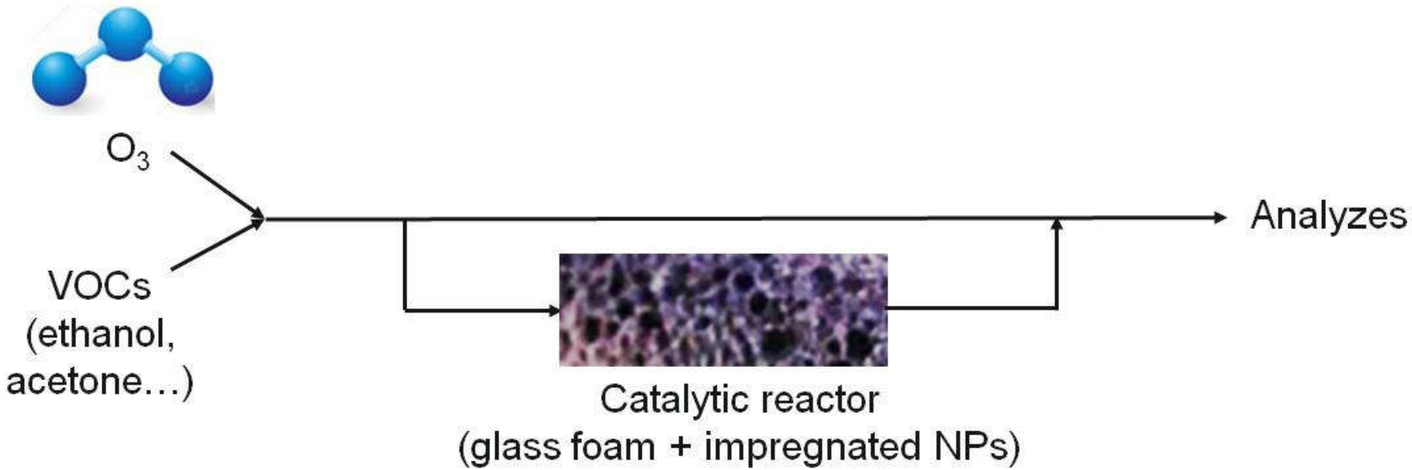
After impregnation with Ru NPs



Glass foam composition :
0.60%wt AlN, 1.16%wt TiO_2, 1.16%wt MnO_2

❖ Performances of the impregnated glass foams in catalytic ozonation

❖ Tests of VOCs removal at room temperature with a continuous reactor



Glass foam composition	Metal	Acetone removal	Ethanol removal
$AlN + TiO_2$	Ru	30 %	75%

Operating conditions :

- **Low gas superficial velocity of 1 $mm.s^{-1}$ → need to improve the mass transfer**
- 13.5 $g.Nm^{-3}$ of ozone at the input of the reactor
- Residence time : 30 secondes

❖ Conclusion and prospect

- ❖ Development of the synthesis of an innovative catalytic material from recycled glass wastes

  → glass foams with modular properties (porosity, pore size, hydrophilicity…) synthesised from recycling glass wastes

  → easy to do NPs solution, various metals can be used, low amount of metal (≈0.1%)

- ❖ Impregnated glass foams are active in catalytic ozonation to remove a lot of VOCs (acetone, ethanol…) for industrial air treatment
- ❖ Other tries in catalytic ozonation are in progress in order to optimize material properties
- ❖ Tests with O2 as oxidant (250°C ≤ T ≤ 350°C) are in progress for indoor air treatment

Mousses de verres et Arts & Design...

➢ Glass recycling: a link between Arts and Sciences

EESAB, École européenne supérieure d'art de Bretagne
Steven AKOUN (stevenakoun.com)

EESAB

Funding
CPER VERRES

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UNION EUROPÉENNE
Projet bénéficiaire
du Fonds européen
de développement régional

cnrs

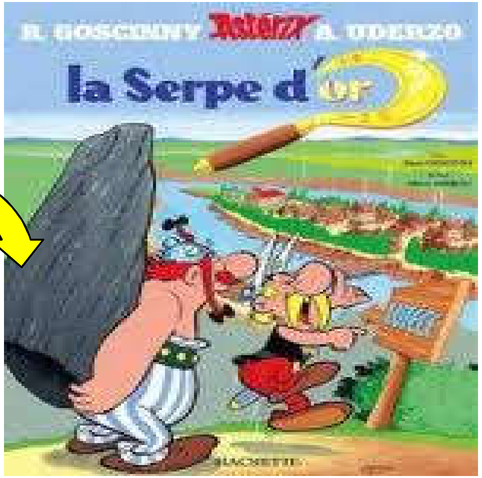
OUEST VALORISATION

Ecole Nationale Supérieure de Chimie de Rennes

Gracias
Obrigado
Thanks
谢谢
Merci
Trugarez

à toutes et à tous…

Natural granite
from Brittany
Or
Foam glass ?



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Mechanical properties

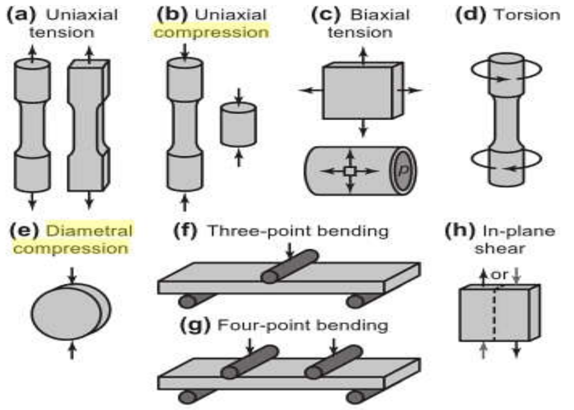


FIGURE 3.7 Common modes of loading materials for mechanical characterization include (a) uniaxial tension, (b) uniaxial compression, (c) biaxial tension, either by in-plane loading of a sheet or pressurizing (p) a vessel, (d) torsion, (e) diametral compression, (f) three-point bending, (g) four-point bending, and (h) in-plane shear.

Characterization of Biomaterials
publié par Amit Bandyopadhyay,Susmita Bose

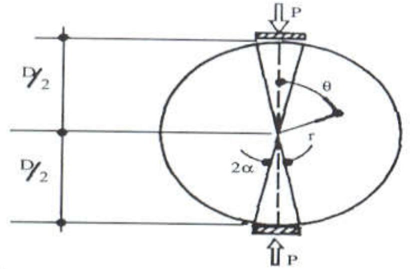
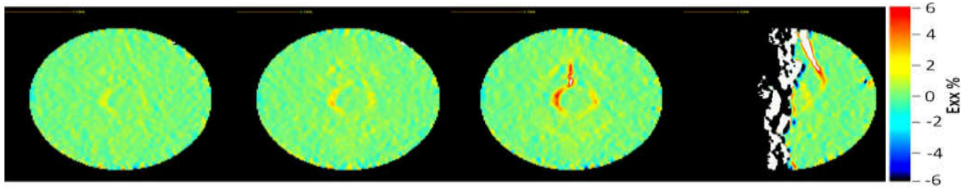


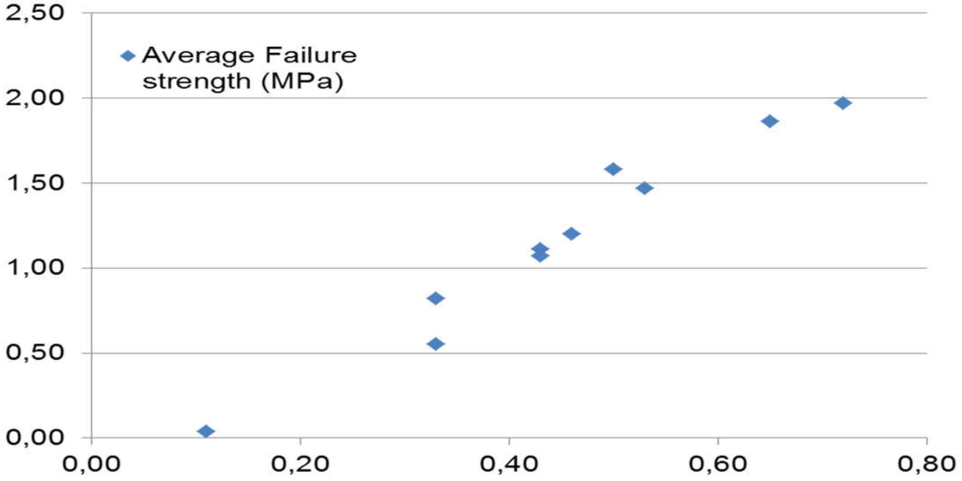
Figure 2. Schematic load position in the Brazilian test

Migliore et Zanotto , Glass technology, 1996



Acta Biomater. 2012 Apr;8(4):1597-602. doi: 10.1016/j.actbio.2011.12.036. Epub 2012 Jan 15.
A novel dentin bond strength measurement technique using a composite disk in diametral compression.
Huang SH[1], Lin LS, Rudney J, Jones R, Aparicio C, Lin CP, Fok A.

Foam sample	apparent density (g/cm^3)	pycnometric density (g/cm^3)	Open porosity (%)	Closed porosity (%)	total porosity (%)	Average Failure strength (MPa)	Weibull 1	Weibull 2
Foamglas™	0,11	0,21	46,79	48,81	95,60	(0,04)	-	-
SG 14	0,33	2,31	85,71	1,09	86,80	0,82	9,51	-
NF 39	0,33	2,24	85,27	1,53	86,80	0,55	6,97	-
LM 6	0,43	2,31	81,36	1,44	82,80	1,07	8,26	-
SG 15	0,46	2,34	80,38	1,22	81,60	1,2	8,68	-
FG 2008-2	0,5	1,73	71,06	8,94	80,00	1,58	5,32	67,24
AM 03	0,53	2,32	77,14	1,66	78,80	1,47	4,21	25,79
LM 10	0,65	2,36	72,50	1,50	74,00	1,86	10,40	-
NF 02	0,72	2,34	69,29	1,91	71,20	1,97	13,10	-



- Average Failure Strength ↗ when density ↗

Ashby cube
Granta Design database