SSV Stazione Sperimentale del Vetro
The Glass Research Centre

Passion and competence in glass since 1956

The Recyclage du Verre

Nancy

22/09/2021

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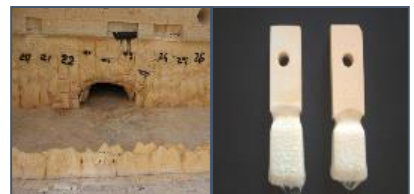
OPAL GLASS RECYCLABILITY

STAZIONE SPERIMENTALE DEL VETRO AT A GLANCE

- European Research Centre on Glass
- Founded in 1954 ; Team: 55 employees
- R&D Projects, consultancy, analyses and testing
- Accreditated according to ISO 17025

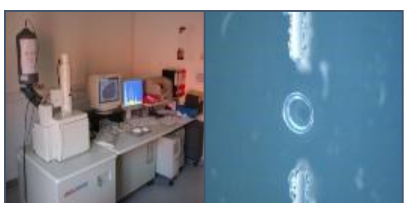
CHEMICAL ANALYSIS

ENERGY - ENVIRONMENT

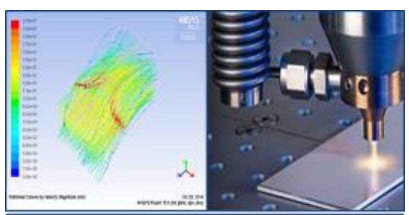


REFRACTORIES TESTING

TESTS ON FLAT GLASS



DEFECTS ANALYSIS



R&D PROJECTS

MECHANICAL TESTS

TRAINING

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GLASS RECYCLABILITY

- In recent years brands, retailers and consumers have developed an increasing consciousness regarding environment protection, climate change, natural resources preservation and circular economy, therefore there exists a growing pressure on the to enhance the recyclability of their packaging products, and to fully implement a "***Design for Recycling***" approach.
- Even with its consolidated status of permanent material, infinitely recyclable in a closed loop without loss of functional properties, glass is starting to be faced with more and more demands regarding the accurate evaluation of its effective industrial recyclability or its actual content of recycled material (especially PCR, i.e. Post-Consumer Recycled material).

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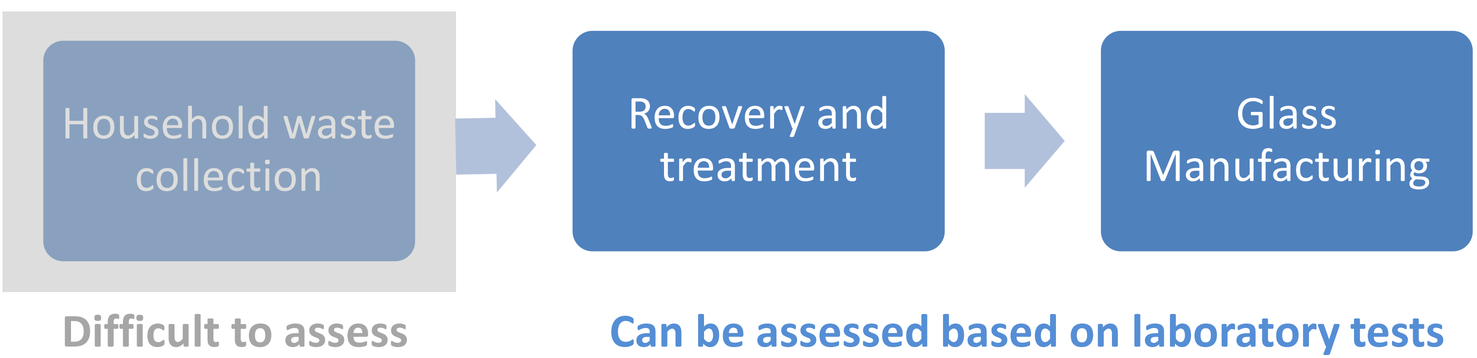
THE CONCEPT OF RECYCLABILITY

- The recyclability of a specific product or packaging is a complex concept, and is influenced by many factors, some of which related to the material’s chemistry, and some to the material’s *stewardship* (separate waste collection policies, recycling technologies, etc).

- Since most articles and packaging are composed of different materials, the recyclability of each single component should be assessed separately.

- In the case of glass recycling, we can consider the following “steps”:



AIM OF THE PROJECT

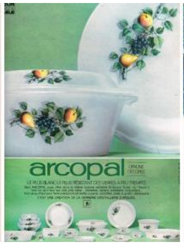
- The aim of the study was to verify the potential recyclability of opal glass in the production of soda-lime glass for containers.
- In particular, the study aimed to check if opal can be melted together with soda lime glass without adverse effects on production quality, and whether the obtained glass has properties that remain suitable for the production of containers, or if some issue occurs.
- Moreover, a first estimate of the environmental impact associated with the recycling of opal glass, with particular reference to its fluorine content, has been assessed. The verification has been performed by estimating the increase in fluorine emissions in flue gases compared to typical soda-lime glass production values.

STUDY SUPPORT

The study was supported by the 3 main producers of opal glass in Europe, i.e.

- Bormioli Rocco

- Arc International



Innovative glass for a better world

- Gerresheimer

PRELIMINARY CHARACTERIZATIONS

- A sample of opal has been submitted to XRF analysis.
- The results of the analysis are reported in the table
- Compare to standard soda-lime glass it is observed:
  - the presence of Fluoride
  - the presence of Boron
  - higher values of Alumina
  - lower values of Calcium

XRF % w/w	Opal glass
SiO_2	66 - 71
Al_2O_3	6,5 – 7,5
Na_2O	12 - 13
K_2O	0 – 1
CaO	2 - 3
MgO	0 - 1
BaO	1 - 2
Fe_2O_3	< 0,035
TiO_2	~0,05
ZrO_2	< 0,11
F	4 - 5
B_2O_3	0 - 3

LABORATORY SCALE MELTING TEST

To check the recyclability of opal glass, several laboratory melting trials in electric furnace have been performed in Platinum crucibles using different amounts of opal glass, ranging from 0% (base soda-lime glass) to 10%wt.

Raw materials (kg)	base glass	glass 5%	glass 10%
Felds. Sand	678,3	532,8	334,6
Sand	97,6	193,7	339,3
Soda ash	188,9	181,6	176,6
Calcium carbonate	175,2	173,4	168,5
Dolomite	77,8	77,3	79
opal glass*	0	49,6	99,9

LABORATORY SCALE MELTING TEST

- Experimenting up to such recycling percentages, much larger than the levels opal glass is ever expected to reach in cullet deriving from separate collection of municipal solid wastes, had the purpose of exploring the effects in worst case scenarios.
- Since opal glass has a chemical composition quite different from soda-lime glass, at recycling levels as high as 5 and 10% the batch formulation had to be adapted in order to match the final target composition, to conserve as much as possible the thermo-physical properties of the glass.

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LABORATORY SCALE MELTING TEST

- The platinum crucibles, filled with raw materials and opal cullet, have been introduced in an electric furnace at 1500 °C
- All the crucible have been left there in the oven the same duration, that is the melting time a reference soda-lime glass (at 0% opal recycling) needs to become free from seeds and undissolved silica.

LABORATORY SCALE MELTING TEST

- The obtained melts were cast in a square mould, annealed and then prepared for the chemical-physical tests.
- The produced glass no stones or cords that could be traced back to not-melted opal glass fragments have been detected.

n.1 base glass - n.2 glass at 5% opal - n.3 glass at 10% opal.

CHARACTERIZATION OF THE OBTAINED GLASSES

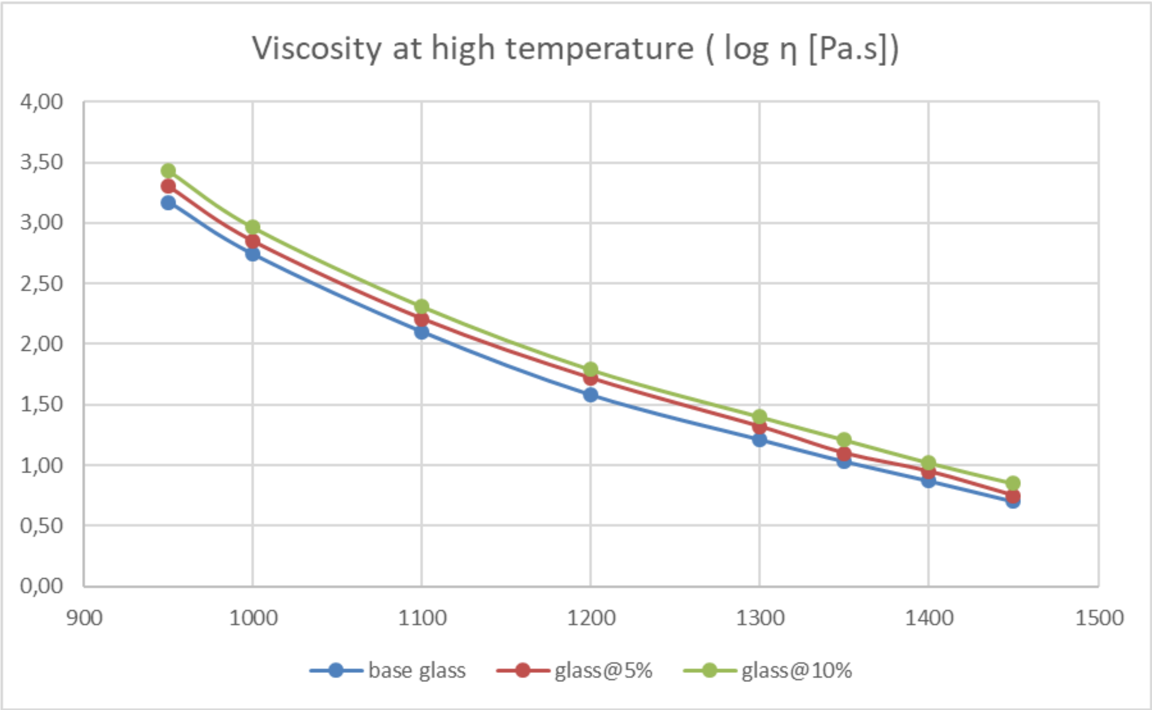
The chemical compositions of the obtained glass samples has been determined by XRF

It is observed an higher concentration of F and B2O3 due to the use of opal glass cullet on the glass obtained with 5 % and 10 % opal glass cullet

XRF % w/w	base glass	glass 5%	glass 10%
SiO_2	73,0	73,2	75,3
Al_2O_3	1,56	1,69	1,66
Na_2O	11	10,5	10,9
K_2O	0,91	0,95	0,96
CaO	11,43	11,31	9,31
MgO	1,88	2,09	1,56
BaO	0,01	0,01	0,01
Fe_2O_3	0.06	0.05	0.05
TiO_2	0.02	0.02	0.02
ZrO_2	-	0.01	0.01
F	-	0.24	0.44
B_2O_3	-	0.11	0.20

CHARACTERIZATION OF THE OBTAINED GLASSES

Measurements of the Viscosity at high temperature of each glass have been performed following ISO 7884-2 1987, from 900°C to 1450°C. The results are shown in the following figure



LABORATORY SCALE MELTING TEST CONCLUSIONS

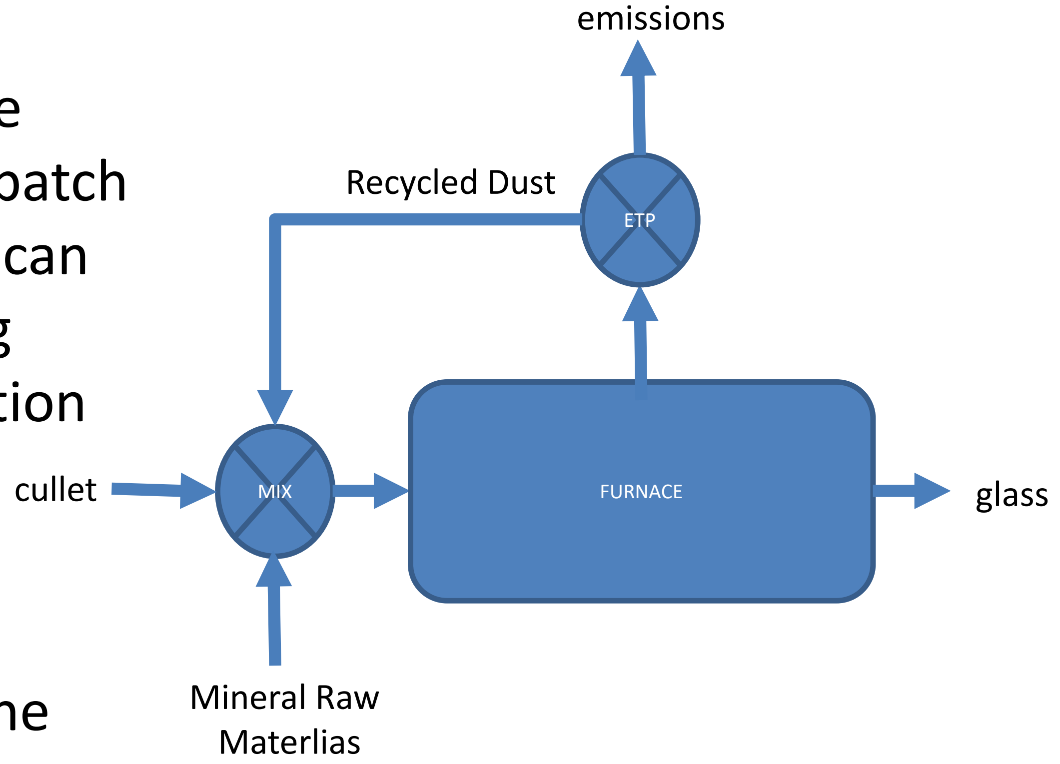
Based on the outcome of the lab scale melting trials and subsequent characterizations, from the point of view of the final soda lime glass properties it appears that no relevant drawback arises from the presence of opal glass fragments in the cullet, even at “unlikely” high recycling levels, provided that the batch formulation undergoes some minor adaptations to keep the viscosity curve variations negligible.

IMPACT OF FLUORINE ON EMISSIONS

- To check the potential impact of fluorine on furnace emissions the expected concentration of fluorine in the flue gases has been calculated based on the mass balance between the amount of fluorine brought by the opal glass into the batch and the amount of fluorine in the final soda-lime glass samples.
- It is worth noting that this calculation represents an approximated estimate, since inside an industrial furnace the fluorine evaporation rates could be different compared to the lab scale setup, , owing to different temperature regimes, flue gases speed and turbulence, furnace atmosphere composition, glass residence time, etc.

IMPACT OF FLUORINE ON EMISSIONS

- the total amount of fluorine added by opal glass to the batch to produce 100 kg of glass can be easily calculated starting from the weight concentration of fluorine in the opal glass and from the amount of opal recycled
- the amount of fluorine in the final glass sample is directly determined from the chemical analysis
- the amount of fluorine potentially emitted is calculated as the difference between the input and output contributions.



IMPACT OF FLUORINE ON EMISSIONS

Case 1

- Opal recycled in batch = 4,8 %
- Fluorine concentration in opal glass = 4,9 %
- Fluorine concentration in final glass = 0,24 %

- Fluorine input (for 100 kg of glass produced) = 4,8 * 4,9 /100 = 0,24 kg
- Fluorine output (for 100 kg of glass produced) = 0,24 kg
- Fluorine emitted ≈ 0 kg
-

Case 2

- Opal recycled in batch = 9,7 %
- Fluorine concentration in opal glass = 4,9 %
- Fluorine concentration in final glass = 0,48 %

- Fluorine input (for 100 kg of glass produced) = 4,8 * 4,9 /100 = 0,48 kg
- Fluorine output (for 100 kg of glass produced) = 0,44 kg
- Fluorine emitted ≈ 0,04 kg

IMPACT OF FLUORINE ON EMISSIONS CONCLUSIONS

- The results show that in laboratory test conditions the solubility of fluorine in glass is still very high, and the vast majority (but not all) of it is entrapped in the glass.
- Nevertheless, it is expected that a certain amount of fluorine could be emitted into the atmosphere during the melting process; this amount is proportional to the actual percentage of opal glass introduced into the batch and to the capability of the soda lime glass to retain fluorine.

- *In any case it should be note that in case opal glass was fed to the furnace as a furnace-ready cullet "contamination", at the very low concentration physiologically deriving from the collection of opal glass domestic waste **together** with soda-lime container glass expected values below some part per million, the final Fluorine emissions would be negligible.*

IMPACT OF FLUORINE ON EMISSIONS CONCLUSIONS

- In case a higher amount of opal glass (e.g. exceeding 0,5%wt of the overall batch) was purposely added as secondary raw material in a specific furnace, the level of fluorine emissions could be more significant, and therefore an in depth site-specific mass balance would need to be calculated to avoid to reach emission levels above the limit values; such an assessment would need to take into account not only the opal glass input, but also the furnace technology (fuel fired, cold top all electric), the temperatures of the melt, the flow rate, speed and turbulence of flue gases and in particular the flow gas treatment plant (acid gases scrubber system) which in the majority of cases can reach very high level of abatement (higher than 95 %), etc.
- Moreover, in this second scenario also the possible impact of Fluorine on the refractories of the furnace and on the heat recovery system (regenerator/recuperator, if any) should be carefully assessed, in order not to produce undesired adverse effects on furnace service life

GENERAL CONCLUSIONS

- This study demonstrated through melting trials that, provided the batch formulation is carefully adapted to achieve the appropriate target soda lime glass composition, recycling opal glass in percentages up to 10%wt does not produce any adverse effect on final glass quality (bubbles, cords, stones, etc), at least at the laboratory scale.

- Moreover, based on lab-scale meting tests data, mass balance calculations have shown that there is a potential for Fluorine emissions when opal glass is recycled to produce soda-lime glass; in particular, the higher the recycling percentages, the higher the expected Fluorine emissions. Nevertheless, considered the very low abundance levels (below the ppm) that opal glass is expected to reach inside furnace-ready cullet following the collection of opal glass domestic waste together with soda-lime containers, the Fluorine emissions increase in a typical soda-lime glass melting furnace is expected to be negligible.

THANK YOU FOR YOUR ATTENTION !

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