# *Innovative methods of glass valorization*

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Kosice – 18.10.2012

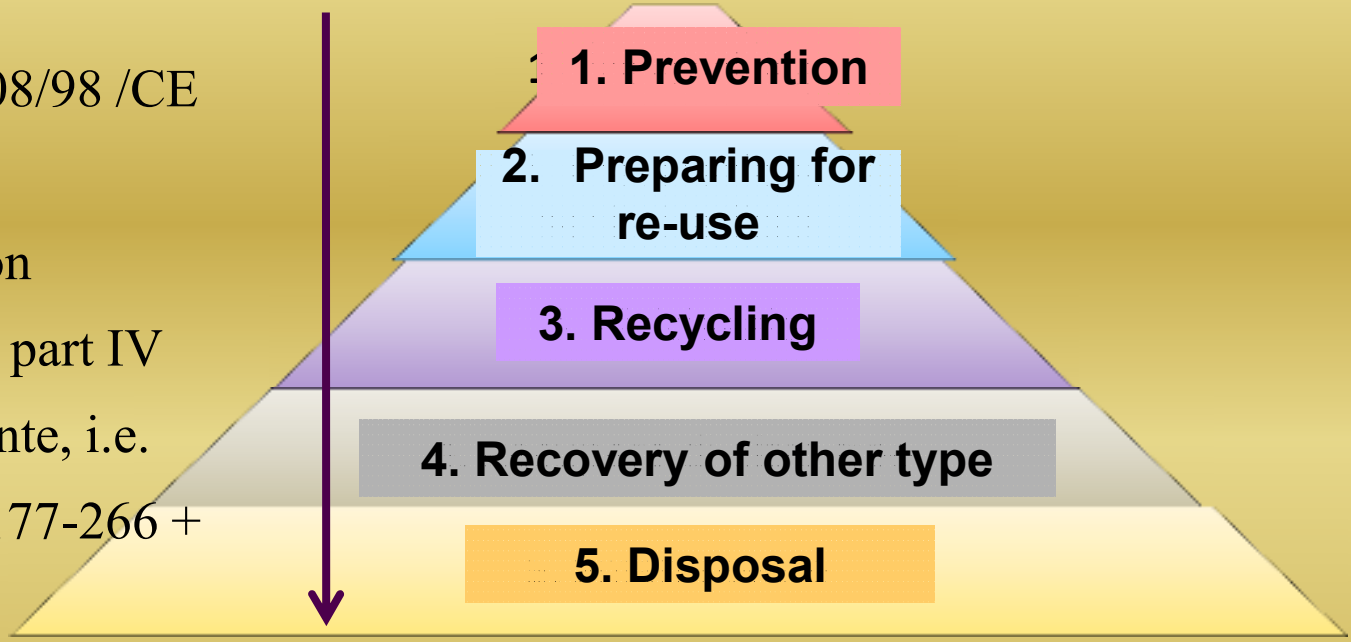
# *Waste vs. "end of waste (EOW)"*

European regulation 2008/98 /CE

→

Italian Regulation

D.Lgs.205/2010 - new part IV of Codice dell'Ambiente, i.e. D. Lgs. 152/2006 (artt. 177-266 + attachments)




**Waste is no longer a WASTE if…….**

subjected to recovery operation

a) is used for specific applications
b) a market or a demand exists
c) satisfies both the technical requirements for the specified targets and existing rules/standards applied to products
d) does not impact negatively on health and environment

# *History of glass recycling*

- 1800 years ago, a Roman shipwreck witnesses import of containers carring broken glass to be melt and reshaped in the Italic ground

- In 1832 in Neaples a new rule imposed the separation of glasses from other wastes

# *History of glass recycling*

PREFETTURA DI POLIZIA

*Regolamento per lo spazzamento ed inaffiamento delle strade*

IL PREFETTO DI POLIZIA

**ORDINA QUANTO SEGUE**

other wastes

# *Glass: End of Waste*

## Reasons for recycling

- Stable chemical composition (uncontamined)
- In a termovalorization plant soften clogging the grids
- Undegradable in environment

**1 ton of recycled glass**

SAVE

**1.2 tons of raw materials batch ($SiO_2$, $Na_2CO_3$, $CaCO_3$)**

**0.32 tons of $CO_2$**

**2.5% energy saving each 10% of recycled glass in the batch**

# *The numbers*

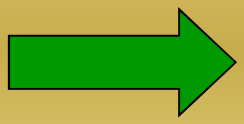
- 4.2 million tons which represents only 25% of total glass manufactured, is the amount of glass collected annually for recycling in the world

- about 1.5 millions ton/year from sorted waste collection of glass containers in Italy

- about 50 kilo ton/year from Waste Electrical and Electronic Equipment (WEEE) in Italy

# *Glass packaging cullet (data from CO.RE.VE.)*

Italian consortium for glass packaging recovery



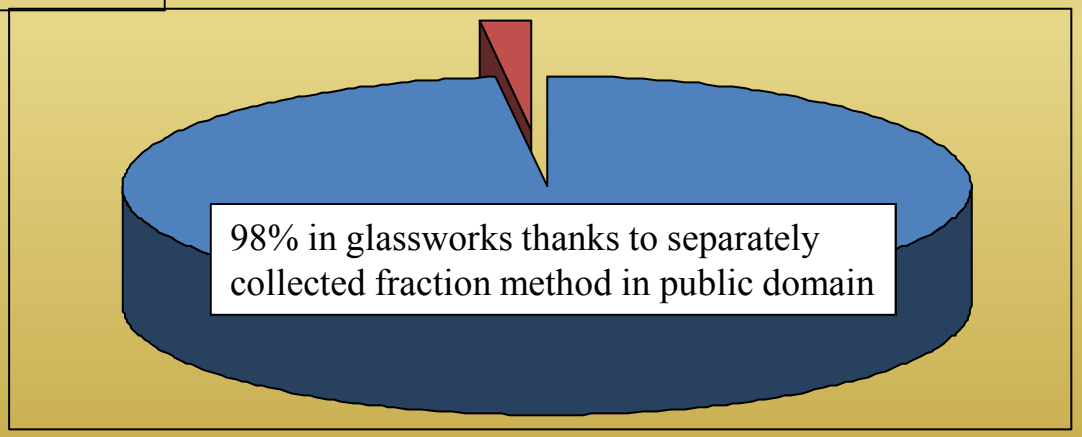
CoReVe

# *Glass packaging cullet (data from CO.RE.VE.)*

2% in building and ceramic industry. In particular about 20% of glass collected is not "serviceable", but became part of the manufacturing scrap and as such was delivered either for different and/or secondary recovery options (as glassy sand for glass furnace, ceramic sand for building and ceramic industry, etc) or for disposal in the landfill

Total: 1.500.000 ton

(glass recycled up to 80%)

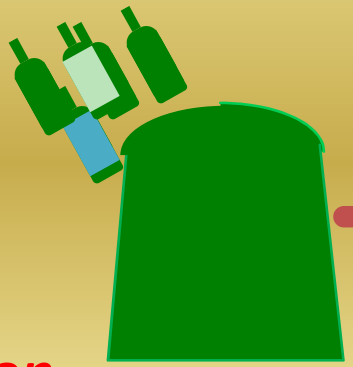



Italian national recycled glass: 2011

# Glass packaging cullet (re)cycle

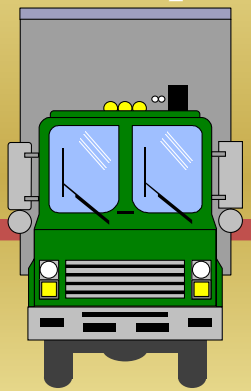
*Domestic separate collection in "bell-shaped" containers*

*Movimentation to treatment plant*



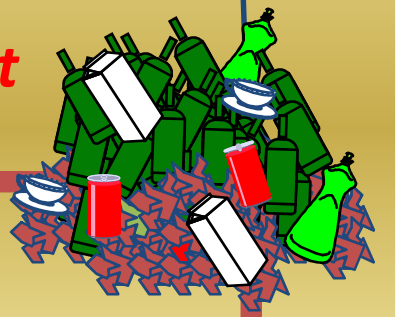
**collection**

*~80.000 bell-shaped containers distrrbuted in over 5.000 cities*

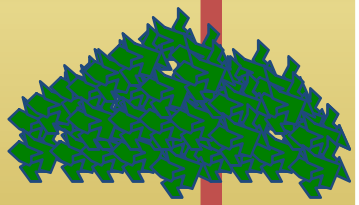


*glass packaging scraps*

**treatment**



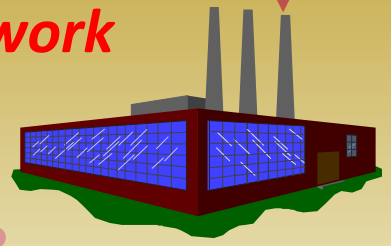
*starting cullet*



*"furnace ready" cullet with a maximum of impurities (inerts, metals, organic) of 0.068%*

| OXIDE (WT%) | GLASS PACKAGING |
|---|---|
| $SiO_2$ | 73.3 |
| $Al_2O_3$ | 1.5 |
| $Fe_2O3+TiO_2$ | 0.06 |
| CaO | 9.8 |
| MgO | 0.34 |
| PbO | - |
| $Na_2O$ | 14.2 |
| $K_2O$ | 0.6 |

**glasswork**



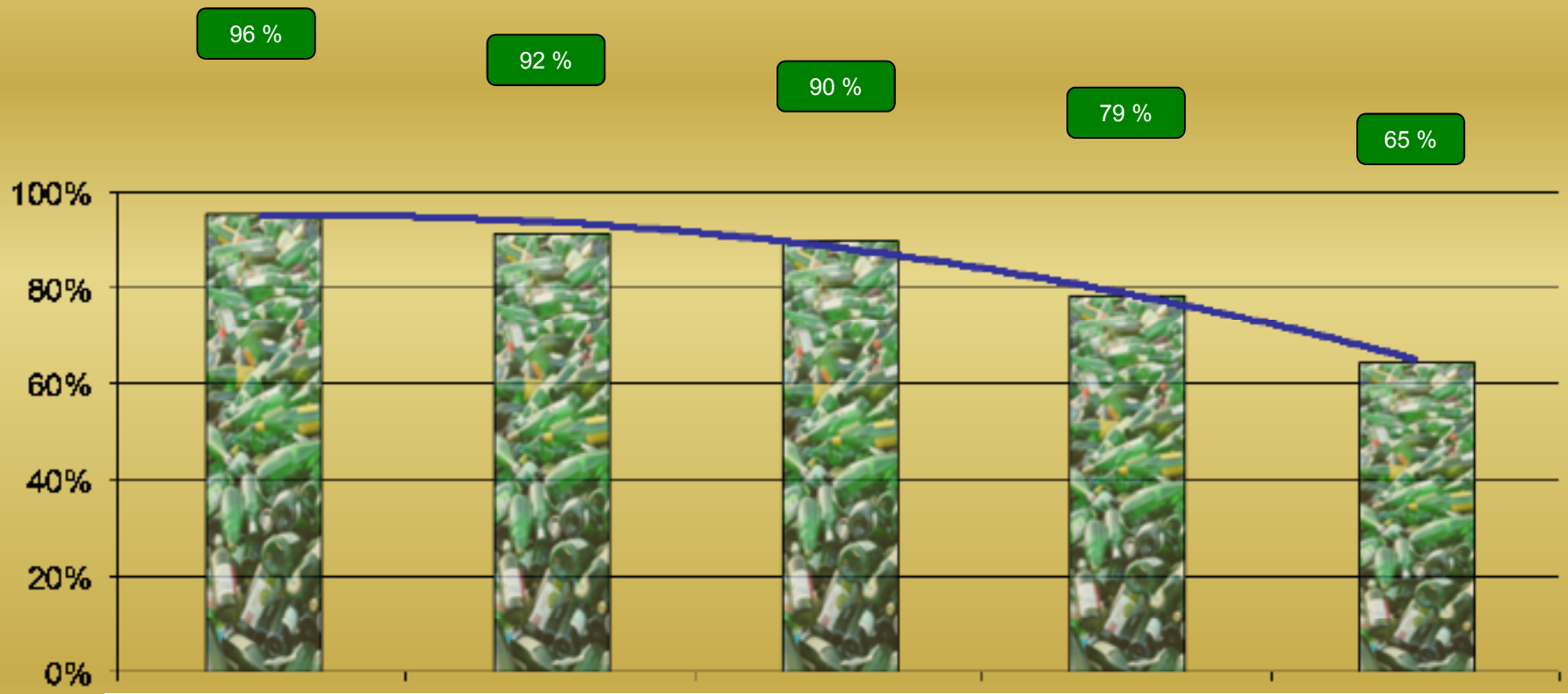
# *Average composition of scrap deriving from treating glass packing waste*

| | Quantity of glass in scrap |
|---|---|
| **Scrap derived from mechanically separating metals** | **from 30% to 50%** |
| **Scrap derived from separating waste** | **50%** |
| **Ceramic machined scrap** | **< 90%** |

**GLASS MAKES UP THE GREATEST PART OF SCRAP PRODUCED IN THE PLANTS**

CoReVe

# *Glass recyclable for each 100 kg of wastes collected by the different collecting systems*




CoReVe

# *WEEE glass*



NEW ECO-COMPATIBLE MATERIALS

Classification of CRT glass:

- **panel glass:** containing Ba and Sr up to 10%, but not lead oxide.
- **funnel glass**: containing up to 25% of lead oxide.
- **neck glass**: containing up to 40% of lead oxide.

The Cathode Ray Tube (CRT) glass can not be treated in the same way that cullet glass from packaging, as it is composed by different types of glasses having different composition. The mainly glasses are panel and funnel.

Light tubes are made by sodium calcium glass. The main environmental hazard is the presence of low mercury content. In Italy CRUSH and SIEVE technology is adopted and the crushed materials are separated into glass, metal and fluorescent powder.

END CUT Technology (in the world)

CRUH & SIEVE Technology (in Italy)

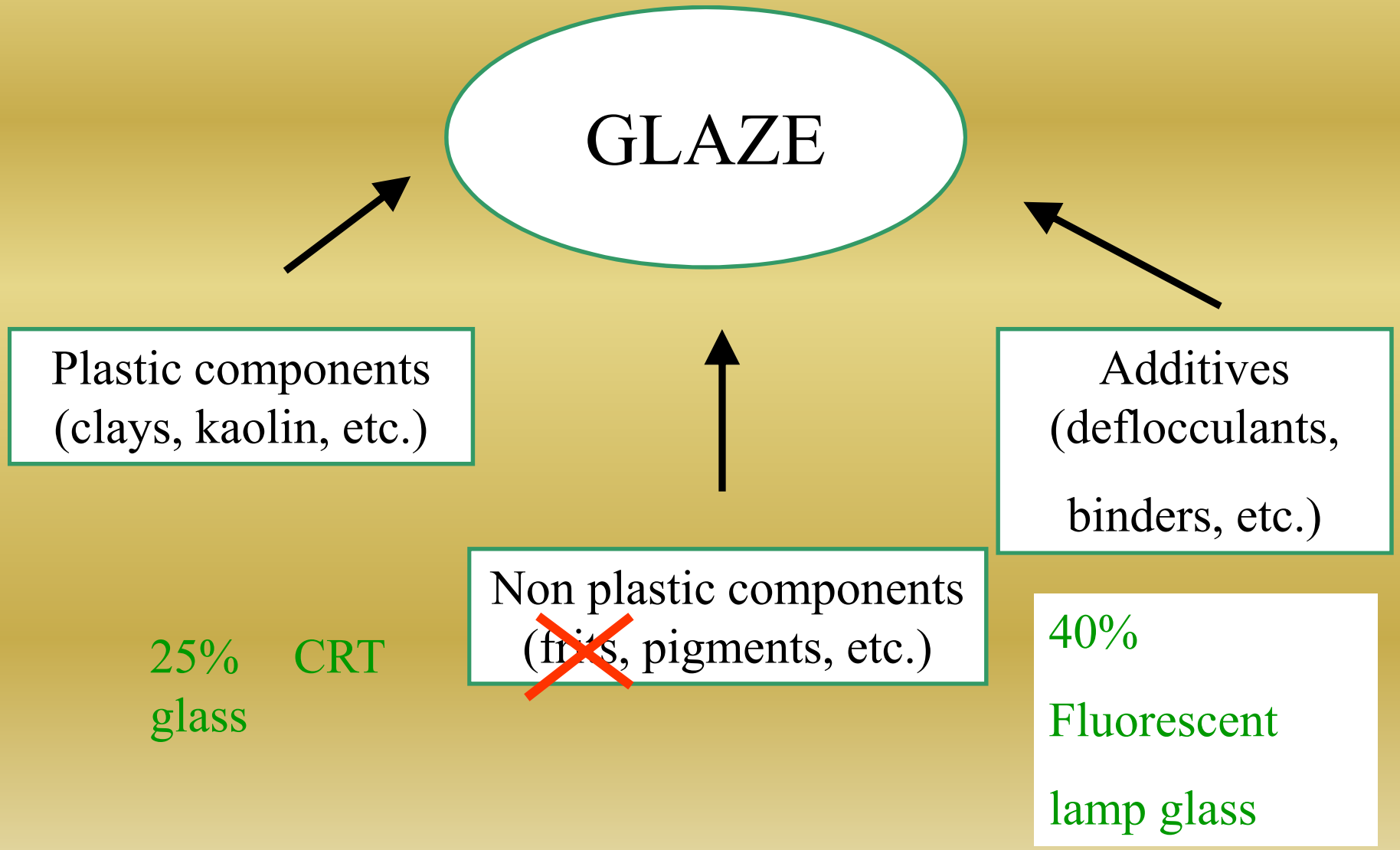
Sparation of fluorescent powder and glass

Distillation of fluorescent powder(~600°C) in order to separate the mercury


NEW ECO-COMPATIBLE MATERIALS

The EOL (End of Life) fluorescent lamps glass is a typical sodium (~16wt%)-calcium (~5wt%) silicate glass and shows a tendency to not crystallize with a low melting nature, confirmed by low softening and transition temperatures (respectively $T_s$: 567°C, $T_g$: ~500°C) and high thermal expansion coefficient ($\alpha$=9.7 $10^{-6}$ $_*$°$C^{-1}$).

# *WEEE glass as ceramic glaze component*



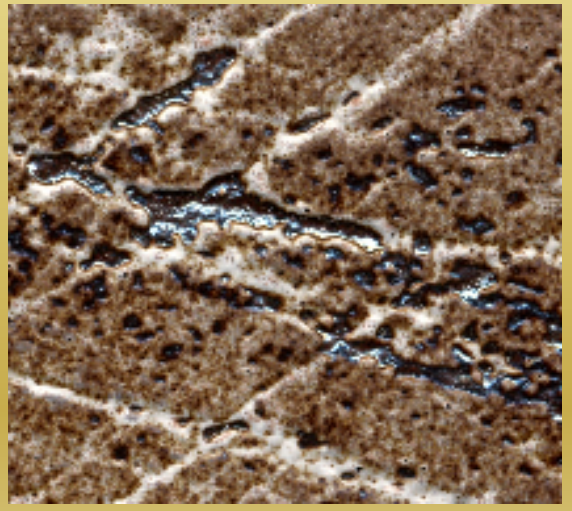
# *WEEE glass as ceramic glaze component*

CRT Glass

Two tile types:
Single firing (1150 – 1180°C)
Porcelanized stoneware (1200 – 1250°C)

Smooth surface

Rough surface

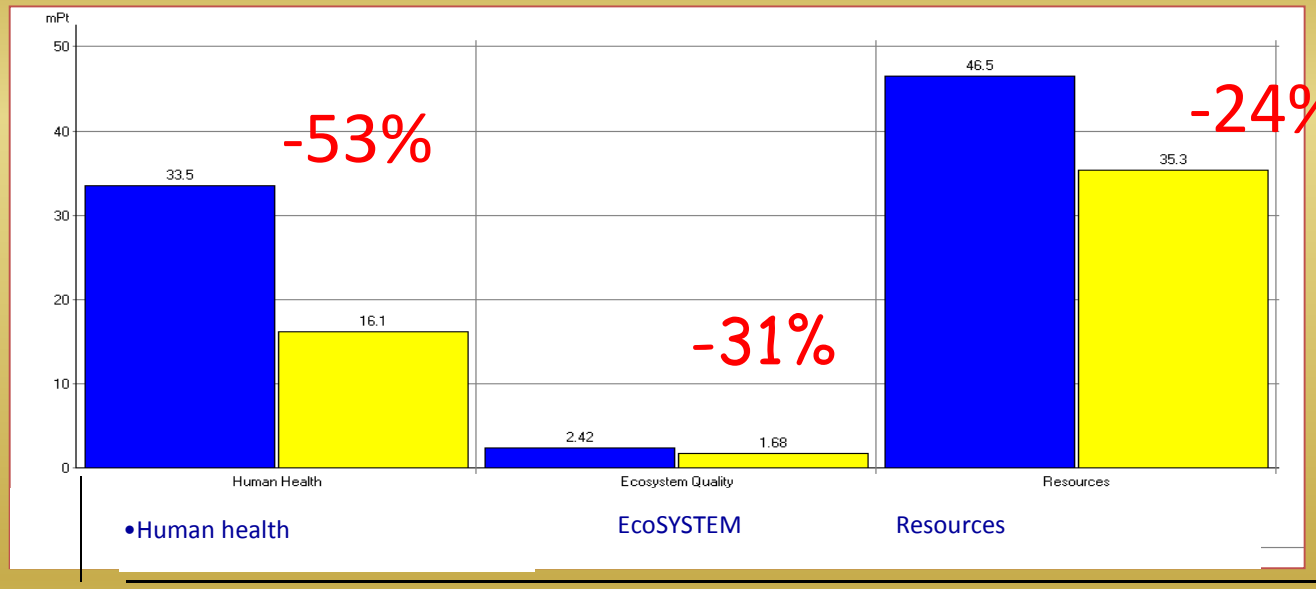


Luster

# *WEEE glass as ceramic glaze component*

Estimated SUSTAINABILITY PARAMETERS

Life Cycle Assessment (LCA)



# *WEEE glass as ceramic glaze component: scale-up*

EOL fluorescent lamps glass was used as substitute to industrial frits. The characteristics of this glass are similar to some industrial frits with high expansion coefficient, so the recovery of this e-waste glass into engobes formulations was tested. Zircon ($ZrSiO_4$) was added in different percentages in order to compensate the absence of this constituent into the glass. The substitution of EOL lamp glass does not affect the final engobe particle size distribution and not cause changes on the related parameters (already industrially optimized) such as: fluency during application, porosity, drying time, etc.


**Colorimetric parameters (L*, a*, b*) for the different engobe compositions**

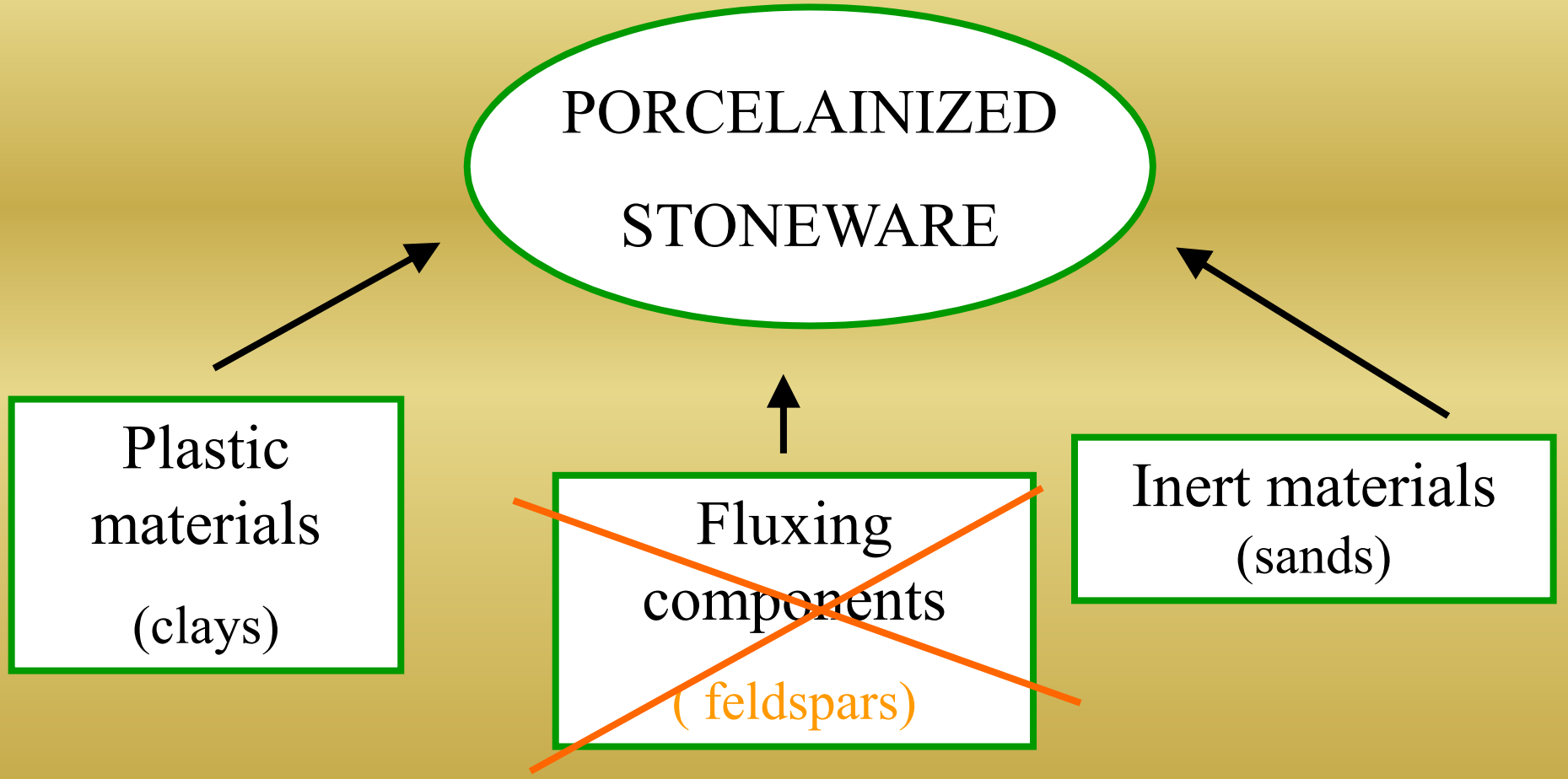
| SAMPLE | L* | a* | b* | ΔE* |
|---|---|---|---|---|
| STD | 92,37 | 0,05 | 2,45 | 0 |
| VL | 91,55 | - 0,04 | 2,15 | 0,87 |
| VL2 | 92,27 | - 0,28 | 1,78 | 0,75 |
| VR2 | 89,98 | 0,19 | 1,77 | 2,48 |

L* (brightness) absolute white L=100, black L=0; a* (red-green); b* (yellow-blue); ΔE*: f(a*, b*, L*)

The research has been extended to industrial scale. The developed technology, called Relux, consists in the production of innovative tiles with reduced environmental impact by implementing an environmentally ethical management system and allows to recycle one EOL fluorescent lamp for 1 $m^2$ of glazed tile. Since 2007, when began the production, up to the end of 2011, 655.000 $m^2$ of this commercial ecological product were produced.

*F. Andreola, L. Barbieri, I. Lancellotti, in "Handbook on Environmental Quality", Chap. 10: WEEE Problems and Perspectives: The Case of Glass Recovery in the Ceramic Industry, Eds. E. K. Drury, T. S. Pridgen, Nova Science Publishers, Inc., ISBN 978-1-60741-420-9, 2009*

# *WEEE glass as ceramic body component*




PARTIAL SUBSTITUTION:
Panel CRT glass (2.5 – 10 wt%)

*F. Andreola, L. Barbieri, E. Karamanova, I. Lancellotti, M. Pelino, Recycling of CRT panel glass as fluxing agent in the porcelain stoneware tile production, Ceram. Int., 2008, 34, 1289-1295*

# *WEEE glass as ceramic body component*

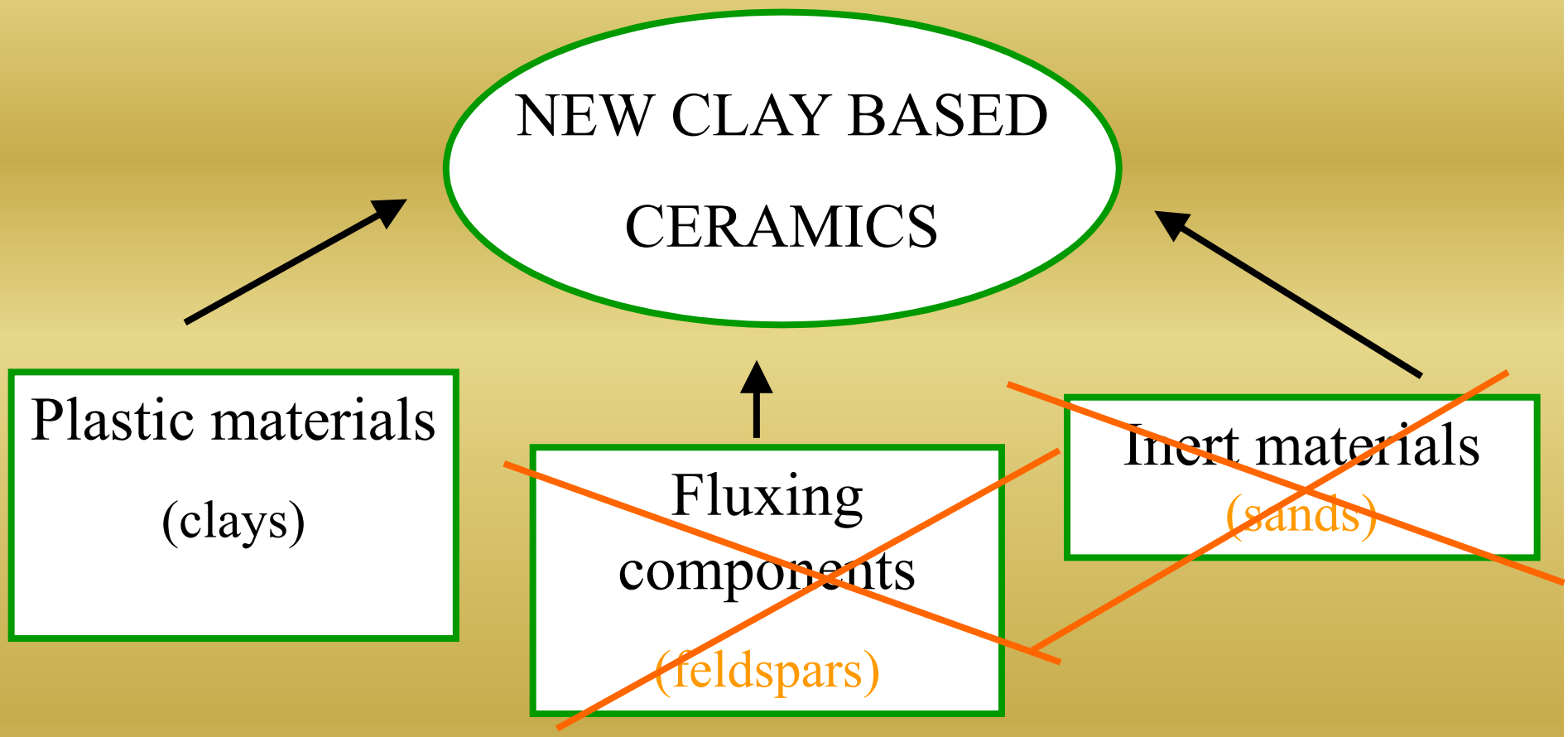
| Sample (wt%CRT glass) | CRT glass (0.0) | CRT glass (2.5) | CRT Glass (5.0) | CRT glass (10.0) |
|---|---|---|---|---|
| Linear Shrink. % | 7.67 | 7.85 | 7.60 | 7.34 |
| W.A.% | 0.017 | 0.002 | 0.003 | 0.006 |
| Dap ($g/cm^3$) | 2.38 | 2.40 | 2.40 | 2.39 |
| Young' mod.(GPa) | 70.64 | 72.60 | 71.78 | 68.65 |
| Shear modulus (GPa) | 29.5 | 30.22 | 29.7 | 28.45 |
| Poison ratio (μ ) | 0.19 | 0.20 | 0.20 | 0.21 |
| Total Porosity | 6.02 | 4.92 | 4.99 | 5.36 |
| Closed Porosity | 4.67 | 4.28 | 4.26 | 4.51 |
| Open Porosity | 1.35 | 0.64 | 0.73 | 0.85 |

industrial tolerance

L.S.% : ± 0.5%

W.A.% ≤ 0.05%

# *WEEE glass as ceramic body component*




Panel CRT glass (5 – 20 wt%)

*F. Andreola, L. Barbieri, F. Bondioli, I. Lancellotti, P. Miselli, A. M. Ferrari, Recycling of screen glass into new traditional ceramics materials, Int. J. of Appl. Ceram. Technol., 2010, 7[6], 909-917*

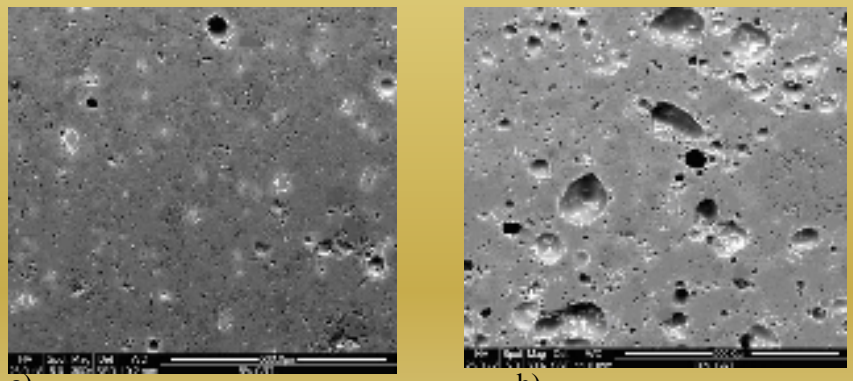
# *WEEE glass as ceramic body component*

The aim of the study was firstly to tailor new formulations using only ball clays and panel glass replacing completely both feldspatic and inert components of a traditional ceramic body. The laboratory samples were obtained by fast firing industrial cycle (1200°C, 40 min) and characterized following UNI EN rules requirements.

**Technology features of laboratory samples**

| Sample | 5 wt% glass | 10 wt% glass | 20 wt% glass | Porcelain stoneware tile |
|---|---|---|---|---|
| **Linear shrinkage (%)** | 10.45± 0.01 | 9.40± 0.01 | 4.20± 0.01 | 7.80± 0.01 |
| **Water absorption (%)** | 0.09 ± 0.01 | 0.05± 0.01 | 0.02± 0.01 | 0.04± 0.01 |
| **Apparent density (g/cm$^3$)** | 2.47 | 2.40 | 2.25 | 2.40 |
| **Bending strenght (MPa)** | 80.70 ± 4.07 | 60.71 ± 3.20 | 43.71 ± 5.49 | 53.59 ± 3.50 |
| **Open porosity(%)** | 1.604 | 3.090 | 4.834 | 2.802 |
| **Closed porosity (%)** | 4.034 | 6.224 | 14.399 | 5.037 |
| **Total porosity (%)** | 5.637 | 9.780 | 19.234 | 7.840 |

The presence of glassy phase in higher quantities causes swelling at the firing temperature (1200°C). It is possible to observe a low linear shrinkage at 20wt% of glass and an increase of porosity (~ 20%). Regarding mechanical properties, all the samples tested show values higher than >35 MPa as prescribed in the EN ISO 10545.4 rule for the ceramic materials belonging to BIa group and >50 MPa generally associated to commercial products. These satisfactory findings confirm the feasibility of the reuse into ceramic formulation of the panel glass.



a) b)

SEM images of sample section: a) 5 wt% CRT; b) 20 wt% CRT

***F. Andreola, L. Barbieri, F. Bondioli, I. Lancellotti, P. Miselli, A. M. Ferrari "Recycling of screen glass into new traditional ceramics materials", Int. J. of Appl. Ceram. Technol., 2010, 7[6], 909-917***

# *MSWI bottom ash and packaging glass cullet as ceramic body components*

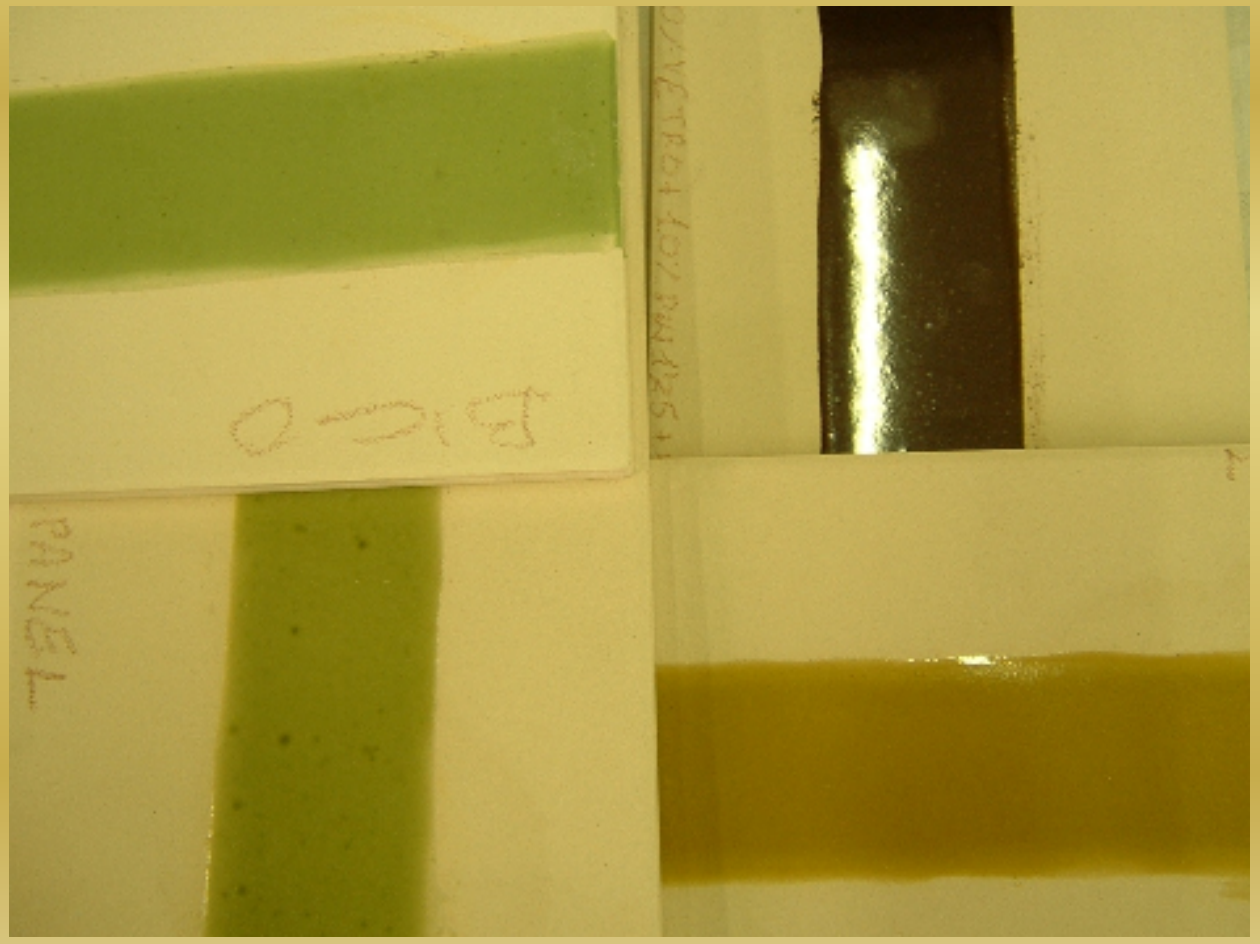
**Gres porcellanato smaltato** — **Caratteristiche Tecniche**
EN 14411 ANNEX G BI A

| Caratteristiche Tecniche | Norme | Valore prescritto dalle norme | RE-LIFE |
|---|---|---|---|
| Dimensioni | EN ISO 10545 - 2 | • Lunghezza e larghezza ± 0.8% max<br>• Spessore ± 0.5% max<br>• Rettilinearità spigoli ± 0.5% max<br>• Ortogonalità ± 0.6% max<br>• Planarità ± 0.6% max | Conforme |
| Assorbimento d'acqua | EN ISO 10545 - 3 | ≤ 0.5% | 0.12% |
| Densità apparente | EN ISO 10545 - 3 | | 2.28 g\cm$^3$ |
| Resistenza alla flessione | EN ISO 10545 - 4 | 35 N\mm$^2$ | 42 N\mm$^2$ |
| Resistenza allo sforzo di rottura | EN ISO 10545 - 4 | 1300 N | 2144 N |
| Resistenza all'abrasione | EN ISO 10545 - 7 | ❶ ❺ | ❹ ❺ |
| Dilatazione Termica (+20 °C a +100°C) | EN ISO 10545 - 8 | ≤ 9MK $^{-1}$ | Conforme |
| Resistenza agli sbalzi Termici | EN ISO 10545 - 9 | Nessun campione deve presentare difetti visibili | Resistenti |
| Resistenza al gelo | EN ISO 10545 - 12 | Nessun campione deve presentare alterazioni sulla superficie | Non gelivo |
| Resistenza all'attacco chimico | EN ISO 10545 - 13 | Nessun campione deve presentare alterazioni visibili | Resistente |
| Resistenza alle macchie | EN ISO 10545 - 14 | ❶ ❺ | ❺ |
| Cessione Cd e Pb | EN ISO 10545 - 15 | Cd 0.07 mg\dm$^2$<br>Pb 0.80 mg\dm$^2$ | <0.004 mg\dm$^2$<br><0.029 mg\dm$^2$ |
| Resistenza dei colori alla luce | EN ISO 10545 - 16 | Non devono presentare apprezzabili variazioni di colore | Campioni inalterati |

Ecological tile, containing materials pre and post consumer (MSWI bottom ash + packaging glass cullet + other) in percentage over 30%, manufacturable in different sizes and thicknesses, capable to combine high aesthetic levels and high performances

***F. Andreola, L. Barbieri, A. Corradi, I. Lancellotti, T. Manfredini "Utilization of municipal incinerator grate slag for porcelanized stoneware tiles manufacturing", J. Europ. Ceram. Soc., 2002, 22[9-10], 1457-1462***

# *MSWI bottom ash and packaging glass cullet as ceramic glaze*



Glaze

50% municipal solid waste incinerator bottom ash

+

50% recycled glass

+ pigment

# *Glass as new product (60-90 wt% glass)*

**Festival Green Economy 2011, 1st ed. - Ceramic district of Sassuolo (Mo), Fiorano (Mo) 6-9 October 2011**

**Design surface**

**Handle for yacht – 52nd International Boat Show, Genova 6-14 October 2012**

**16th International Food Exhibition – CIBUS 2012, Parma 7-10 May 2012**

***PATENT UNIMORE (L. Barbieri, C. Leonelli, F. Andreola, E. Reggiani) – M. Ingrami, Glassy material for the production of ceramics and method for its preparation, 2011, MI2011A000369***

**2012 National prize for the Municipality (Modena) with highest amount of recycled glass**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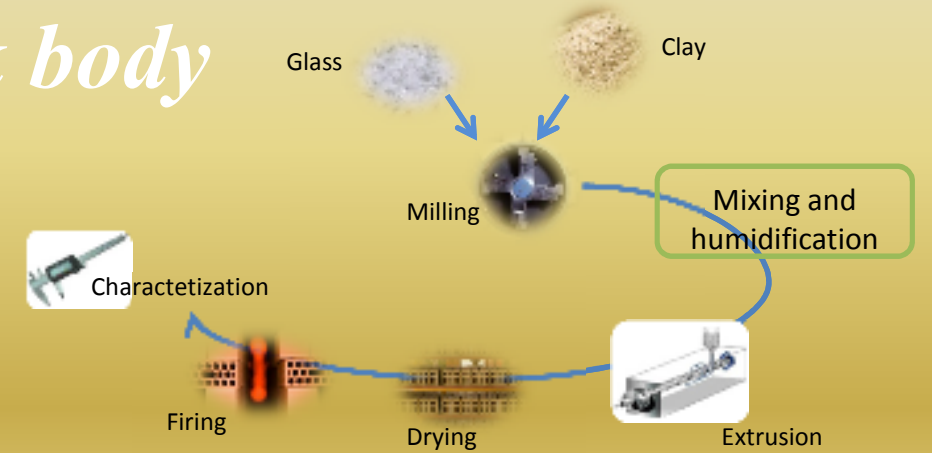
# *WEEE glass as brick body*

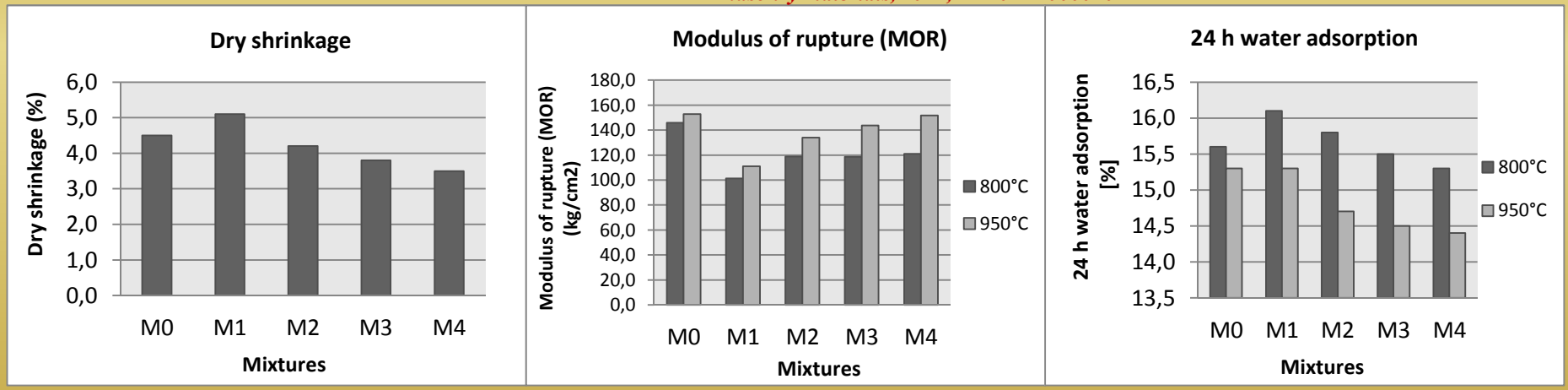



The purpose of this study was to improve the properties of products and reduce the use of virgin raw materials. The insertion of CRT glass in brick produces lower water absorption, lower drying shinkage and similar mechanical strength compared to the commercial bricks without glass. In this experience, the CRT glass used is a mix of panel and funnel glass from old TVs or PCs monitors.

*F. Andreola, L. Barbieri, D. Giuranna, I. Lancellotti "New eco-compatible materials obtained from WEEE glass", in Proceed. of ISWA 2012, Florence, 17-19 September 2012*

*PATENT L. Barbieri – D. Giuranna, A composition for a mixture for production of masonry materials, 2011, RE2011A000020*

## Results of laboratory study



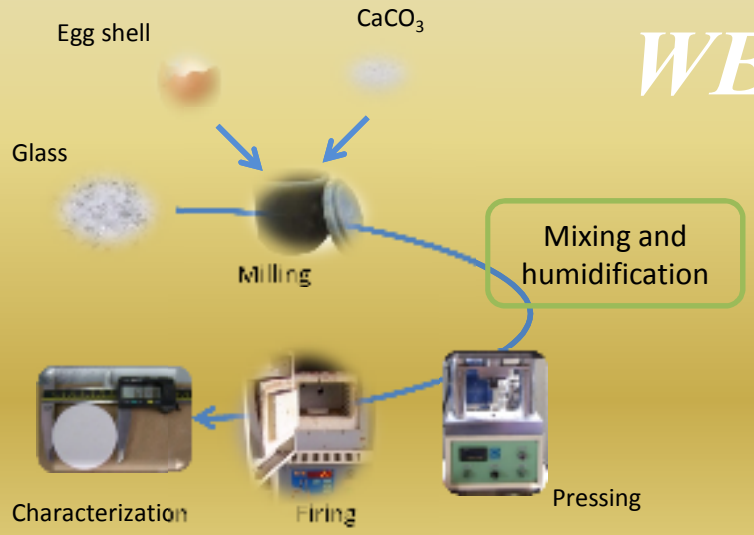

## Results of large scale trial firing

✓no apparent defects of surface;
✓same color of brick without glass;
✓similar compressive strength;
✓drying shrinkage 1% less than traditional brick values
✓ the concentration of lead and barium elements, present in CRT glass, as well as other dangerous elements, were always below limits of the rule (Decree No. 186, 05/04/2006, All.3).

## Results of leaching test

| Element | Brick without glass (mg/l) | Brick with glass (mg/l) | Limits (Decree No.186/2006) |
|---|---|---|---|
| Cu | 0 | 0 | 50 µg/l |
| Pb | 0 | 0 | 50 µg/l |
| Ba | 0.04 | 0.105 | 1 mg/l |
| Sulfates | 0 | 3 | 250 mg/l |
| Chlorides | 7 | 4 | 100 mg/l |

# *WEEE glass as glass foam*




Different compositions of foam glass were prepared using EOL fluorescent lamps as raw material and egg shell as foaming agent. It was found that the use of this kind of glass consents to decrease the firing temperature in order to achieve an important result in term of energy saving (T = 700-800°C, 45 min, saving 20% of gas).

**Results of laboratory study**

| SAMPLE | Apparent density ($g/cm^3$) | Absolute density ($g/cm^3$) | Porosity (%) | Compressive strength (MPa) |
|---|---|---|---|---|
| $V_{95}C_5$ | 0.37 | 2.47 | 85.0 | 2.69 ± 0.66 |
| $V_{95}C_{2.5}E_{2.5}$ | 0.31 | 2.44 | 87.3 | 2.69 ± 0.58 |

V = Glass; C = $CaCO_3$; E = Egg shells

$V_{95}C_5$

$V_{95}C_{2.5}E_{2.5}$

The properties of glass foams are comparable with those of typical commercial products and other results reported in litirature studies. The glass foams obatined by also egg shell is similar to the foam glass with only $CaCO_3$ as foaming agent and this is an important aspect of evironmental sustainability.

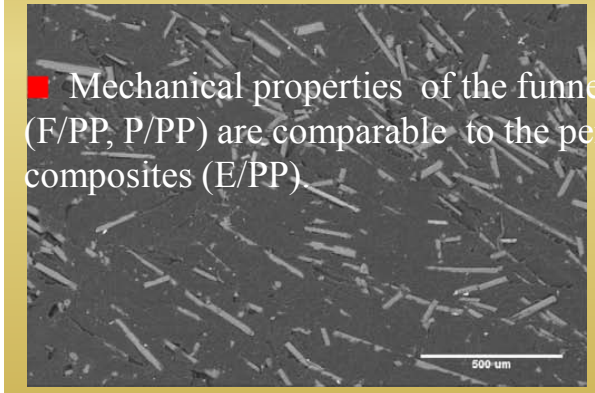
# *WEEE glass as glass fibers in plastic composites*

*P. Pozzi, R.Taurinio, T. Zanasi, F. Andreola, L. Barbieri, I. Lancellotti, Composites: Parta A, 41 (2010) 435-440*

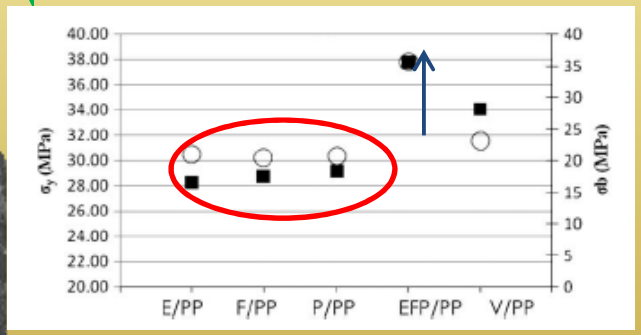
Fibers (10-15 µm of diameter) obtained by the recycling of CRT glass have been used as new filler for polypropylene material.

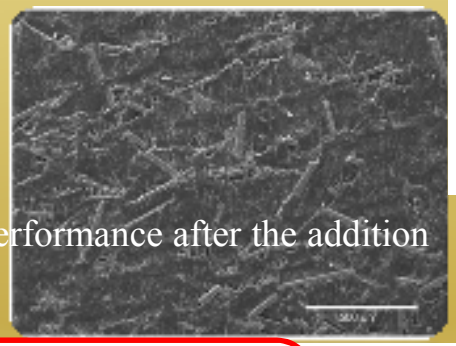
- Panel, funnel and E glass fibers were prepared by an external laboratory (Stazione Sperimentale del Vetro, Murano, Venice)
- Drawing temperature of 1130°C, lower than the common temperature used for the preparation of fibers starting from virgin raw material (1500°C to 1700°C)

| Fibers | E (GPa) | Φ (µm) |
|---|---|---|
| E glass | 70.0 | 10-15 |
| Vetrotex P968 | 73.0 | 10-15 |
| Panel | 73.6 | 10-15 |
| Funnel | 61.4 | 10-15 |




- Mechanical properties of the funnel and panel fibers/PP composites (F/PP, P/PP) are comparable to the performance of E glass fibers/PP composites (E/PP).



- Increase of the final mechanical performance after the addition of maleic-anhydride (MA-PP)

| Characterization | V/PP | E/PP | F/PP | P/PP | EFP/PP$_{ma}$ |
|---|---|---|---|---|---|
| Elongation at break (%) | 10.5 | 13.6 | 12.1 | 12.9 | 6.7 |
| Tensile modulus (MPa) | 3749 | 2934 | 3085 | 3261 | 3275 ↑ |
| Glass transition Tg (°C) | 35.6 | 20.1 | 20.5 | 23.4 | 20.5 |

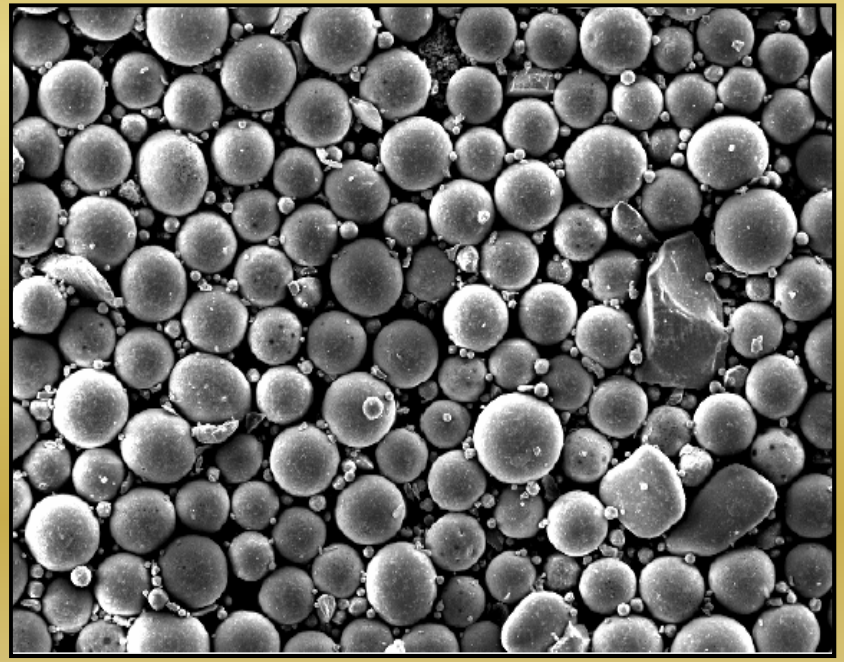
Glass transition temperature ($T_g$) is not afffected by the addition of different glass fibers

# *Composites*

**PATENT DIEM_UniBo/DIMA_UniMORE, Process and system for realizing composite materials, IT BO2006A000416 (patent n. 0001367627 of 16.11.2009) and PCT/IB2007001360**

**DIEM_UniBo: PLASMA SPHEROIDIZATION OF GLASS CULLET POWDERS**

SEM micrographs of starting glass powders injected into the plasma with irregular particle size of 35-75µm

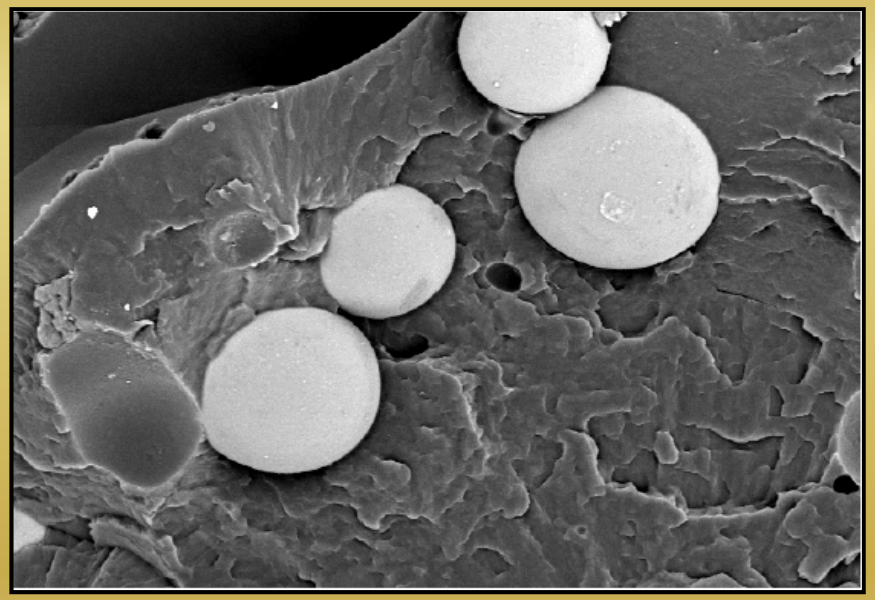


SEM micrographs of glass powders with high spheroidization degree after plasma treatment

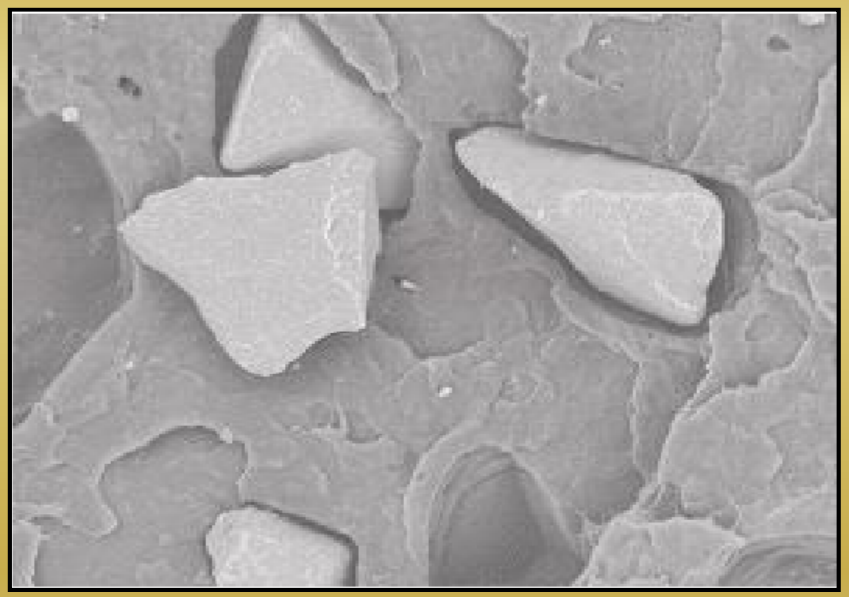
# *Composites*

**PATENT DIEM_UniBo/DIMA_UniMORE, Process and system for realizing composite materials, IT BO2006A000416 (patent n. 0001367627 of 16.11.2009) and PCT/IB2007001360**

## DIMA UniMORE: POLIMERIC MATRIX-BASED COMPOSITES OBTAINEMENT



SEM micrographs of glass powders plasma spheroidized used as filler in polypropylene



SEM micrographs of starting glass powders used as filler in polypropylene

# *Conclusions*

- technical properties comparable to those of a traditional ceramics
- environmental friendly products
- reduction of production costs
- recycled glass is an alternative raw material readily available on the market at low cost and of national origin
- production processes are less energy-intensive because they require lower temperatures
- same manufacture of conventional products
- multiple combinations of colour (bulk coloured or with shading) or may be glazed according to the applications
- cross-cutting interest in various sectors of market (with thin coatings for interior and / or outdoor furnishings, high quality art products)