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UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA
Dipartimento di Ingegneria "Enzo Ferrari"

Recycling of waste in traditional ceramic manufacturing

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Overview

✓European legislation

✓Waste classification

✓Current status of recycling on tiles and bricks manufacturing

✓ **Case studies**:

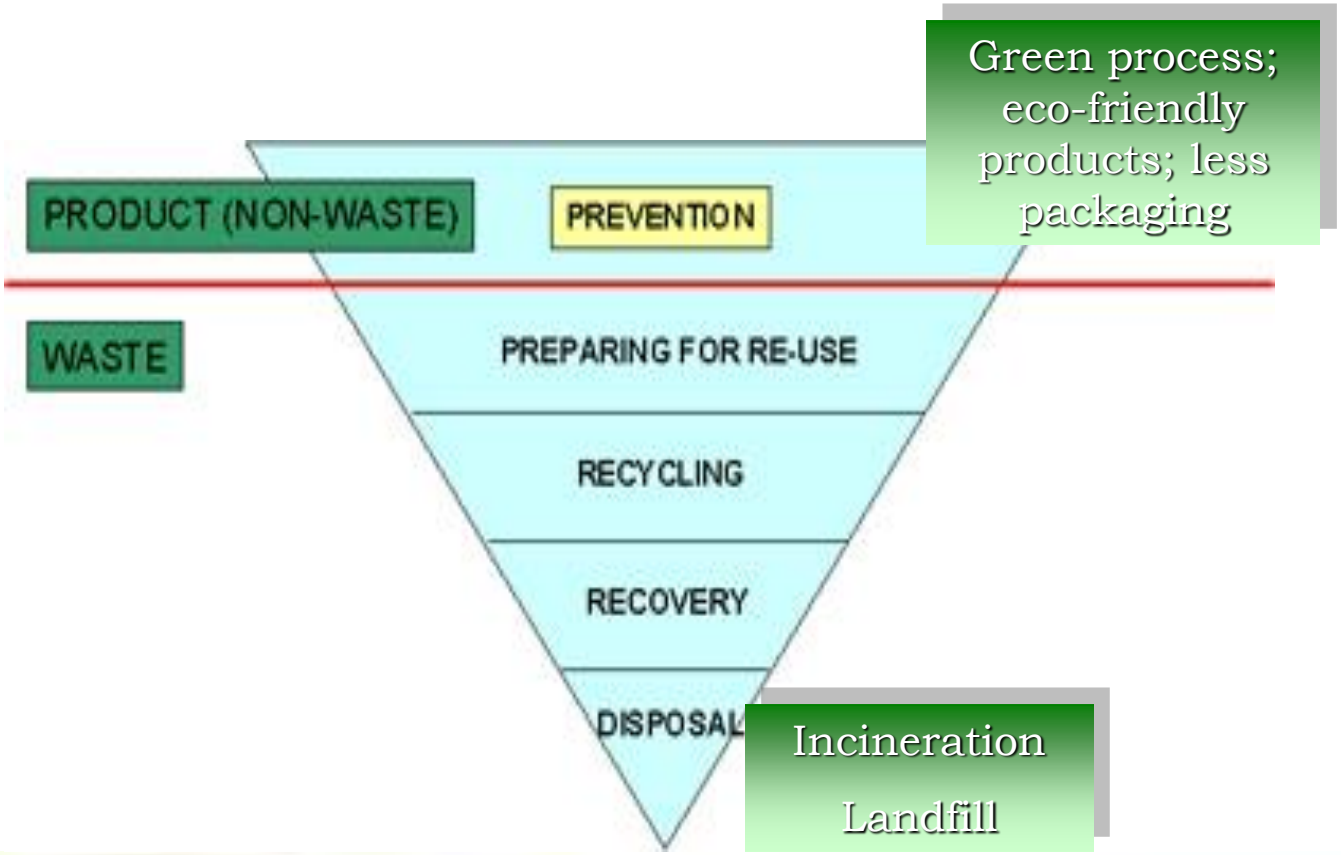
Use of waste glass

Use of urban waste

Use of agro-waste

European directives concerning waste

Directives 2008/98/CE and 2006/12/CE



Why use waste?

- The valorisation of industrial wastes and their up-grading to alternative raw materials can present several advantages when compared to the use of natural resources improving the performance in five key areas:

- **recycling high-quality materials**
- **reducing use of virgin raw materials**
- **reducing environmental impact (transport, extraction,…).**
- **reducing energy consumption**
- **reducing waste disposal**

Why use waste?

- Traditional building materials (bricks, roof tiles, floor/wall tiles,..) accommodate large variations in the chemical and mineralogical composition of their raw materials,…

- Scarcity of clayey and flux raw materials of high quality from foreign countries and the limited number of appropriate deposits.

- Ceramic manufacturing, involves great volumes of materials so is a potentially high consumer of wastes, even if the incorporation is done in small amounts

- Replacing natural raw materials by wastes is a key to a circular economy

- Energy represents a significant share of ceramic processing costs (heavily aggravated recently)

- Recycling has become a common practice, especially in those countries where raw materials are strategic, waste disposal is both rigorous and expensive and legislation for the environmental control is strict.

WASTE CLASSIFICATION

- FUEL WASTE
- FLUXING WASTE
- MODIFIER PLASTICITY WASTE

FUEL WASTE

- involves residues with high organic substances content
- permits energy saving during firing also obtain porous materials (pore forming)
- ligth weight bricks with insulating properties
- Coal ash, sawdust, textil, tanning and paper sludges, exhausted oils, agro and wood biomass, rice husk, urban residues.

FLUXING WASTE

- improves sintering process
- reduces porosity at the same T firing
- energy saving by reduction of Tmax
- are mainly composed of silica and alumina and alkaline and alkaline-earth oxides and heavy metals,…
- sludges from glazing ceramic lines, from plating plants of metallurgical and mechanical industry, waste glass (fine size).

MODIFIERS PLASTICITY WASTE

- **Reducer Plasticity**: attenuates the plasticity of clayed materials (good effects on workability and drying steps)
- usually are residues with high silica content (>50wt%) also the effect is related to the particle size (basalt mining and metallurgical dusts, C&D, waste glass, wastewater sludges), RHA and SCA.
- **Plastifying**: increases plasticity, used to valorise "thin" clays that would create problems in shaping step. Fired products have better Shrinkage
- generally they come from mineral process (bauxite, feldspar, quartz,..) and quarry residues.

Basic information for testing the potential waste as raw material

- Chemical and mineralogical composition
- Oxides and heavy metals
- Soluble salts
- Humidity
- Particle size distribution
- Odour /smell
- Firing colour, efflorescence
- Leaching test end products
- Emissions during firing

TILE MAKING PROCESS: RESIDUES DERIVED

The global quantity of residues 700,000 ton/year

UNFIRED UNGLAZED RESIDUES

DUST AND SLUDGES FROM DEPURATION

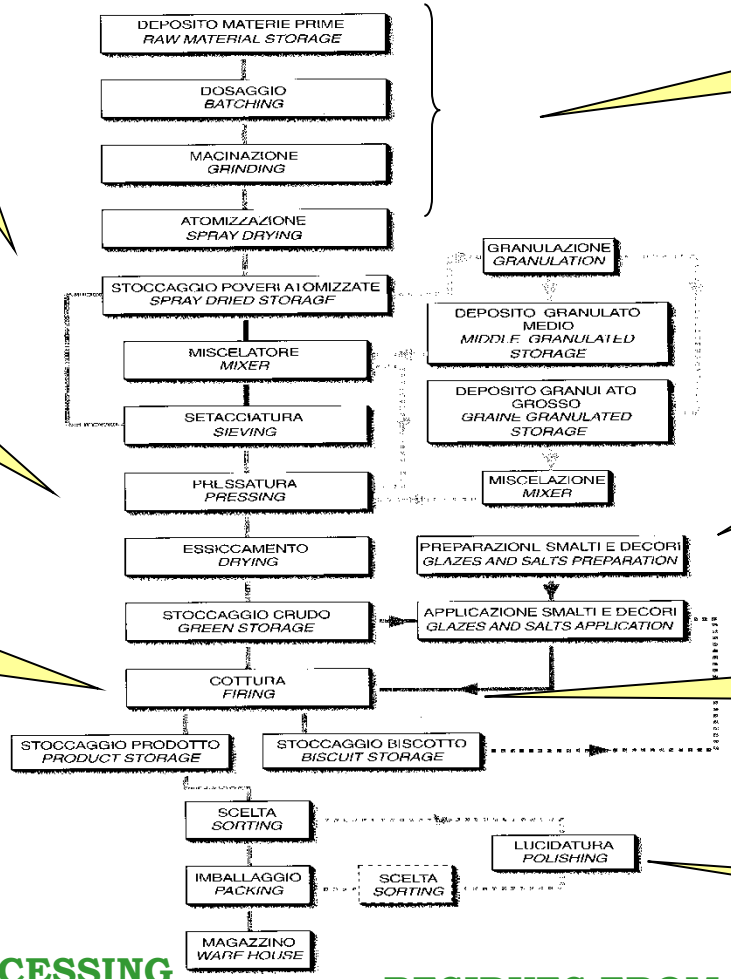
UNFIRED GLAZED RESIDUES

GLAZING SLUDGES

FIRED RESIDUES

EXHAUSTED LIME FROM GAS DEPURATION

POLISHING SLUDGES



RESIDUES FROM PROCESSING

RESIDUES FROM DEPURATION

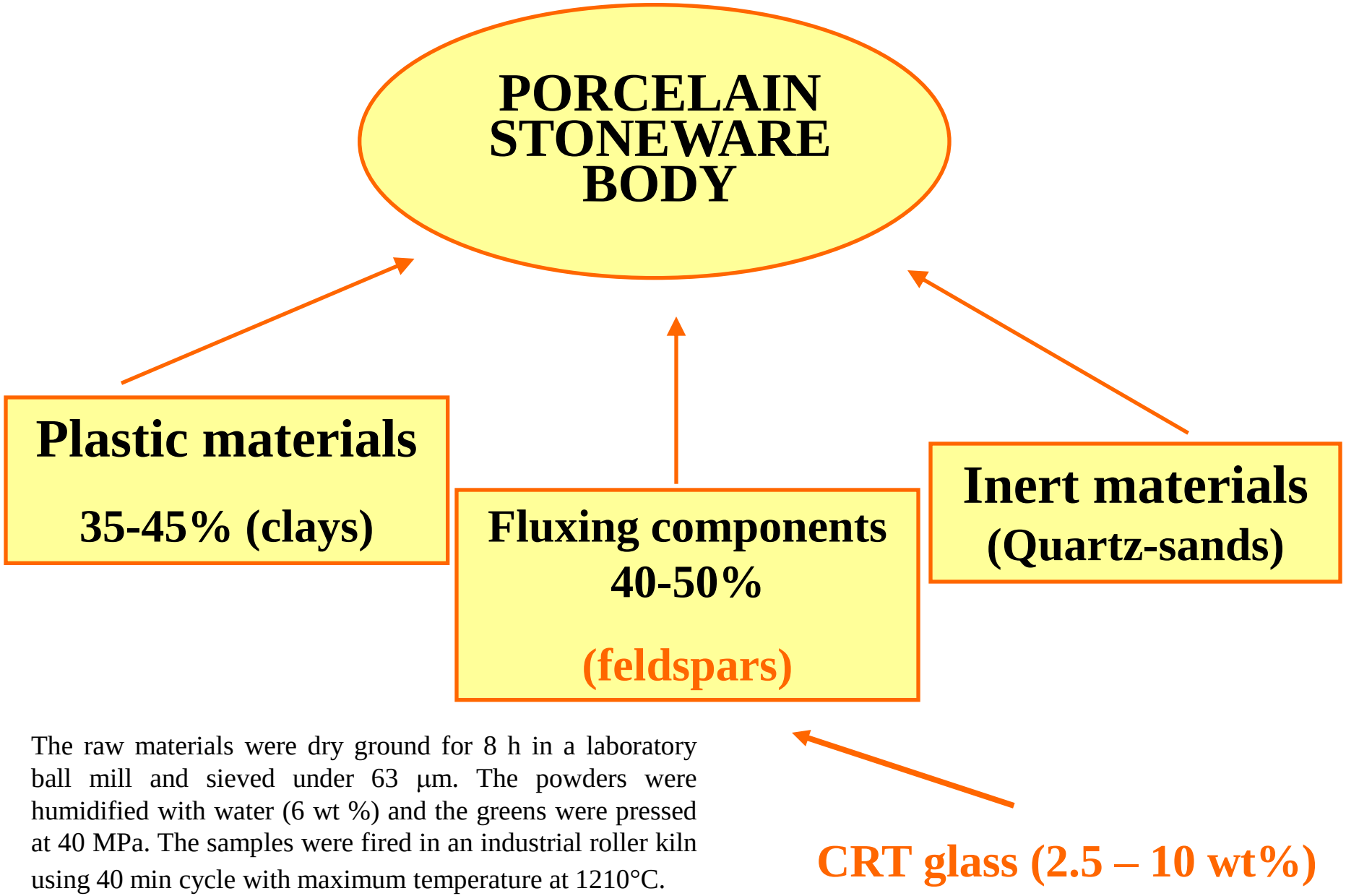
RESIDUES FROM CERAMIC TILE MANUFACTURING

Italian production: 395 .10^6 m^2/y (2015)

TIPOLOGY OF RESIDUE	HAZARDOUSNESS	SPECIF. PROD. (kg/m^2)	INNER RECYCLING (%)	EXTERNAL RECYCLING (%)	LANDFILL (%)
UNFIRED	non HAZARDOUS	1.3	58	42	0
FIRED	INERT	1.5	30	69	1
EXHAUSTED LIME	non * HAZARDOUS	0.01	6	15	79
WASTE WATER SLUDGES	non* HAZARDOUS	0.55	42	55	3
POLISHING SLUDGES	INERT	0.9	----	20	80

*It is codified as special waste and classified as hazardous or not hazardous as a function of heavy metals content.

Font: Report for ceramic tiles sector, Impact factor and environmental, Association of Italian Ceramic Tiles an Refractories Manufactures (CONFINDUSTRIACERAMICA), 2015



The raw materials were dry ground for 8 h in a laboratory ball mill and sieved under 63 μm. The powders were humidified with water (6 wt %) and the greens were pressed at 40 MPa. The samples were fired in an industrial roller kiln using 40 min cycle with maximum temperature at 1210°C.

Composition of colour CRT glass

OXIDE	PANEL	FUNNEL	NECK
SiO_2	61.23	56.72	50.00
Al_2O_3	2.56	3.42	1.00
Na_2O	8.27	6.99	2.00
K_2O	5.56	5.37	10.00
CaO	1.13	3.12	2.00
MgO	0.76	2.02	0.00
BaO	10.03	4.03	0.00
SrO	8.84	1.99	0.00
Fe_2O_3	0.10	0.11	0.00
Sb_2O_3	0.30	0.30	0.30
CoO	0.02	0.00	0.00
NiO	0.03	0.02	0.00
ZrO_2	0.91	0.24	0.00
ZnO	0.18	0.22	0.00
PbO	0.02	15.58	34.00
TiO_2	0.35	0.19	0.00
TOTAL	100.00	100.00	100.00

important differences were shown for panel and funnel

BaO, SrO, ZrO_2 and PbO: high X-ray absorption ability

Andreola, F., *Barbieri, L., Corradi, A.&, Lancellotti,I.,* ***Cathode Ray Tube glass recycling: an example of clean technology, Waste Manage Res. , 2005, 23, 1-8.***

CASE STUDY: GLASS

F.Andreola, L. Barbieri, A. Corradi, E. Karamanova, I. Lancelloti, M. Pelino, ***Recycling of CRT panel glass as fluxing agent in the porcelain stoneware tile production***, *Ceramics International, 34(5), 1289-1295 (2008).*

Batch compositions of samples prepared

Body	Clay 1	Clay 2	F-K	F-Na	S1	S2	G
C0	25	15	8	35	10	7	---
C1	25	15	7.5	33	10	7	2.5
C2	25	15	7	31	10	7	5
C3	25	15	6	27	10	7	10

Sintering parameters, mechanical properties , total (P_T), open (P_O) and closed (P_C) porosities

Sample (wt%CRT glass)	C0 (0.0)	C1 (2.5)	C2 (5.0)	C3 (10.0)
LS%	7.67	7.85	7.60	7.34
WA%	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
P_T	6.02	4.92	4.99	5.36
P_C	4.67	4.28	4.26	4.51
P_O	1.35	0.64	0.73	0.85

industrial values

L.S% : 7.5-8%

W.A% $\leq$ 0.05%

RIETVELD-RIR XRD RESULTS

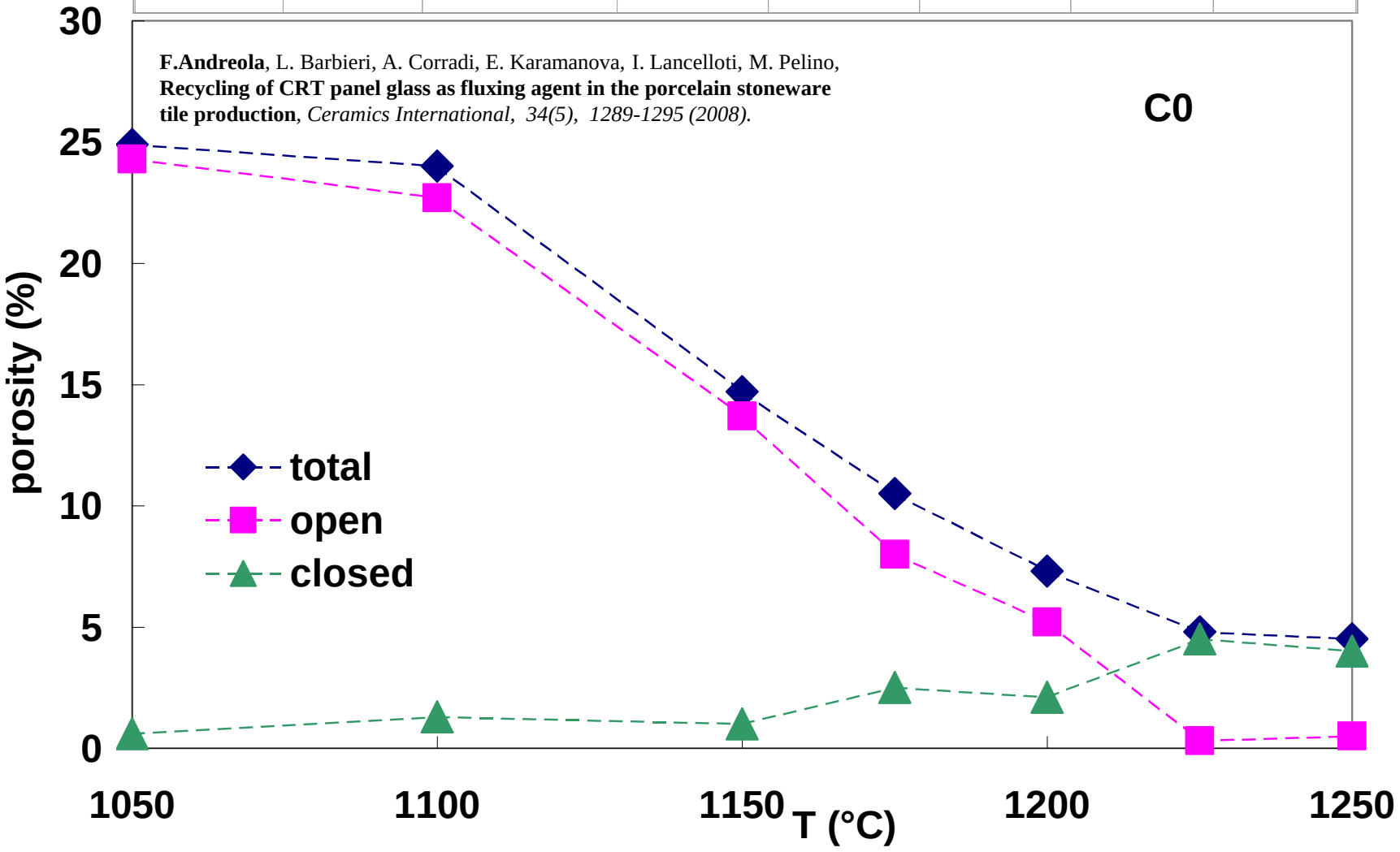
Phases	5	10	20	BIa product
Quartz	15.3(1)	10.1(1)	8.3(1)	22.7(1)
Mullite	15.7(1)	11.4(2)	5.9(2)	4.8(2)
Microcline ordered	1.0(1)	5.1(5)	/	/
Albite ord	/	/	/	3.6(2)
Ba-orthoclase	/	/	2.8(2)	/
Amorphous	68.0(3)	73.3(8)	83.0(5)	68.9(5)
Total	99.9	99.9	100.0	100.0
C^2	3.99	3.24	2.77	4.93
Rwp	0.076	0.068	0.065	0.058
Rp	0.056	0.050	0.049	0.043

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

CASE STUDY: GLASS

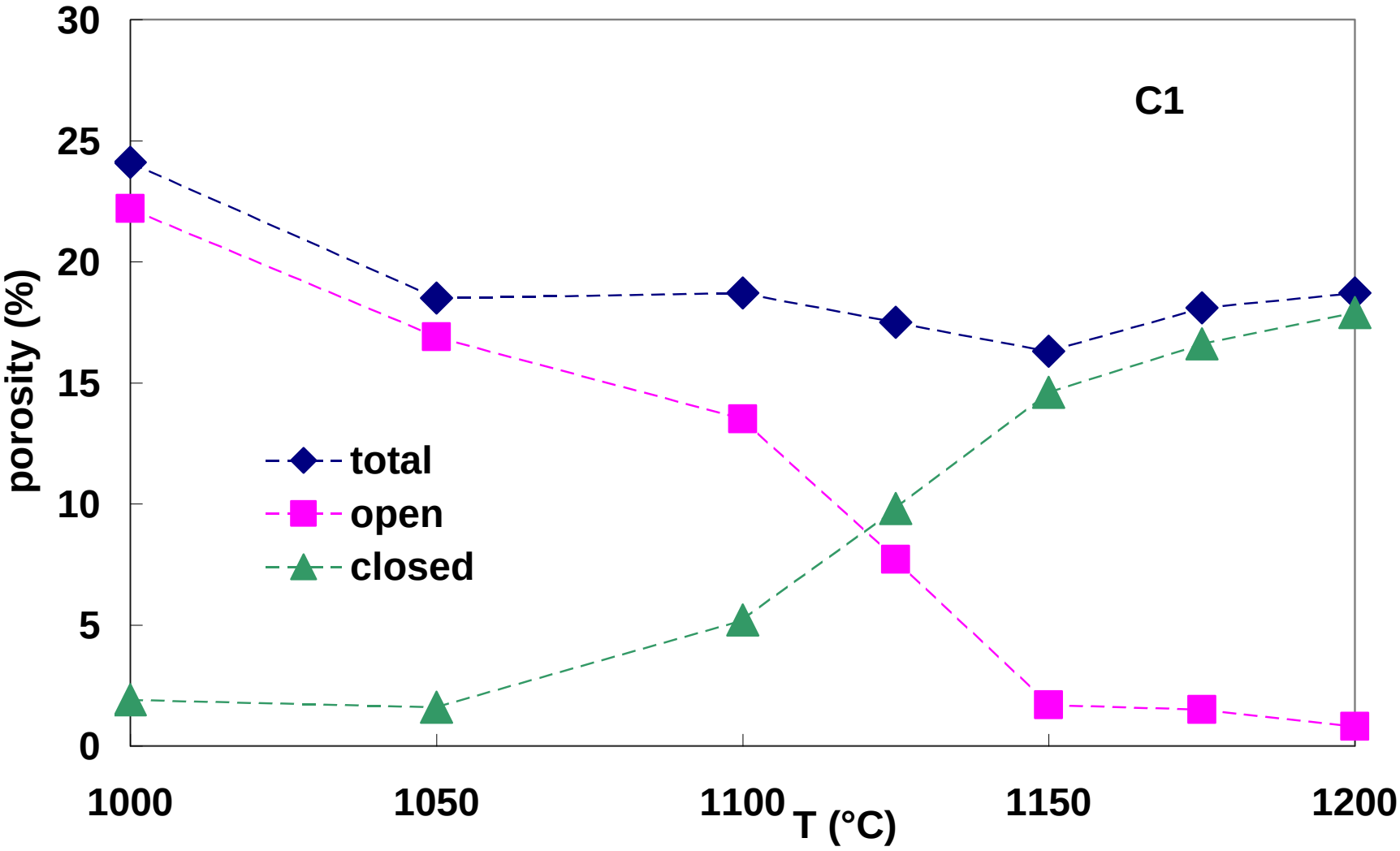
P_T, P_C, and P_O variations in C0

	G	F-Na	K1	K2	F-K	S1	S2
C0	0	35	25	15	8	10	7

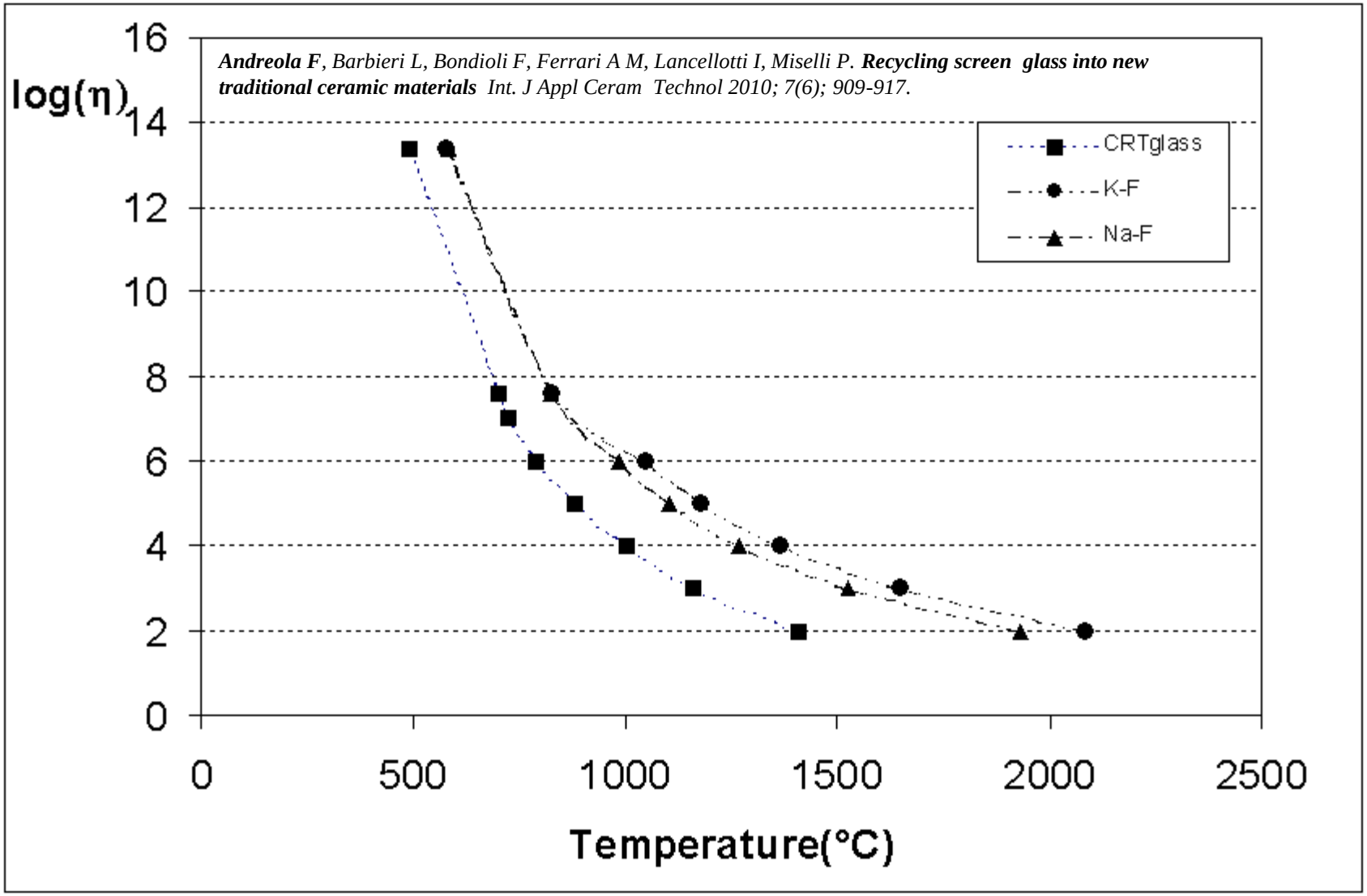


P_T, P_C, and P_O variations in C1

	G	F-Na	K1	K2	F-K	S1	S2
C0	0	35	25	15	8	10	7
C1	35	0	25	15	8	10	7

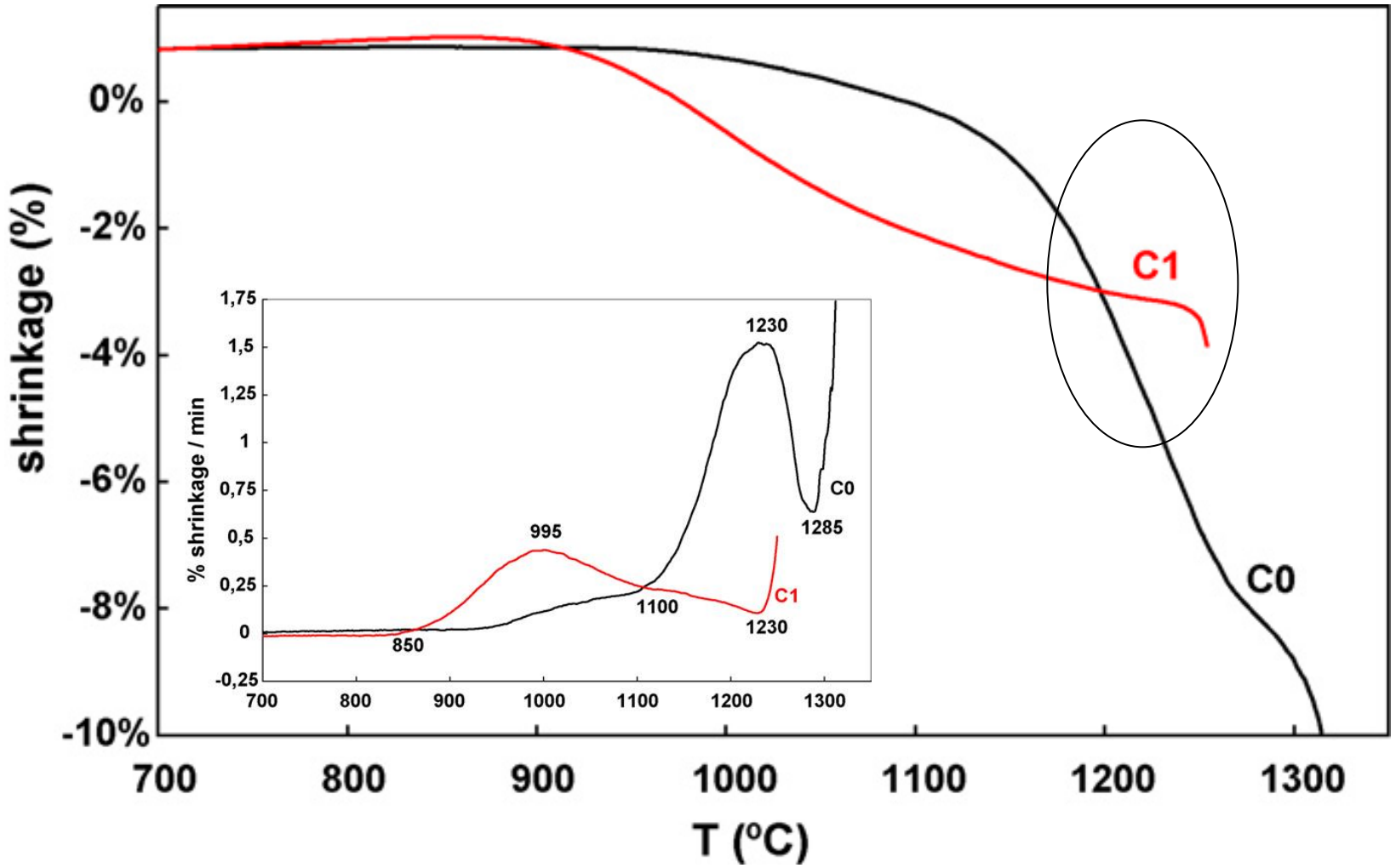


CASE STUDY: GLASS



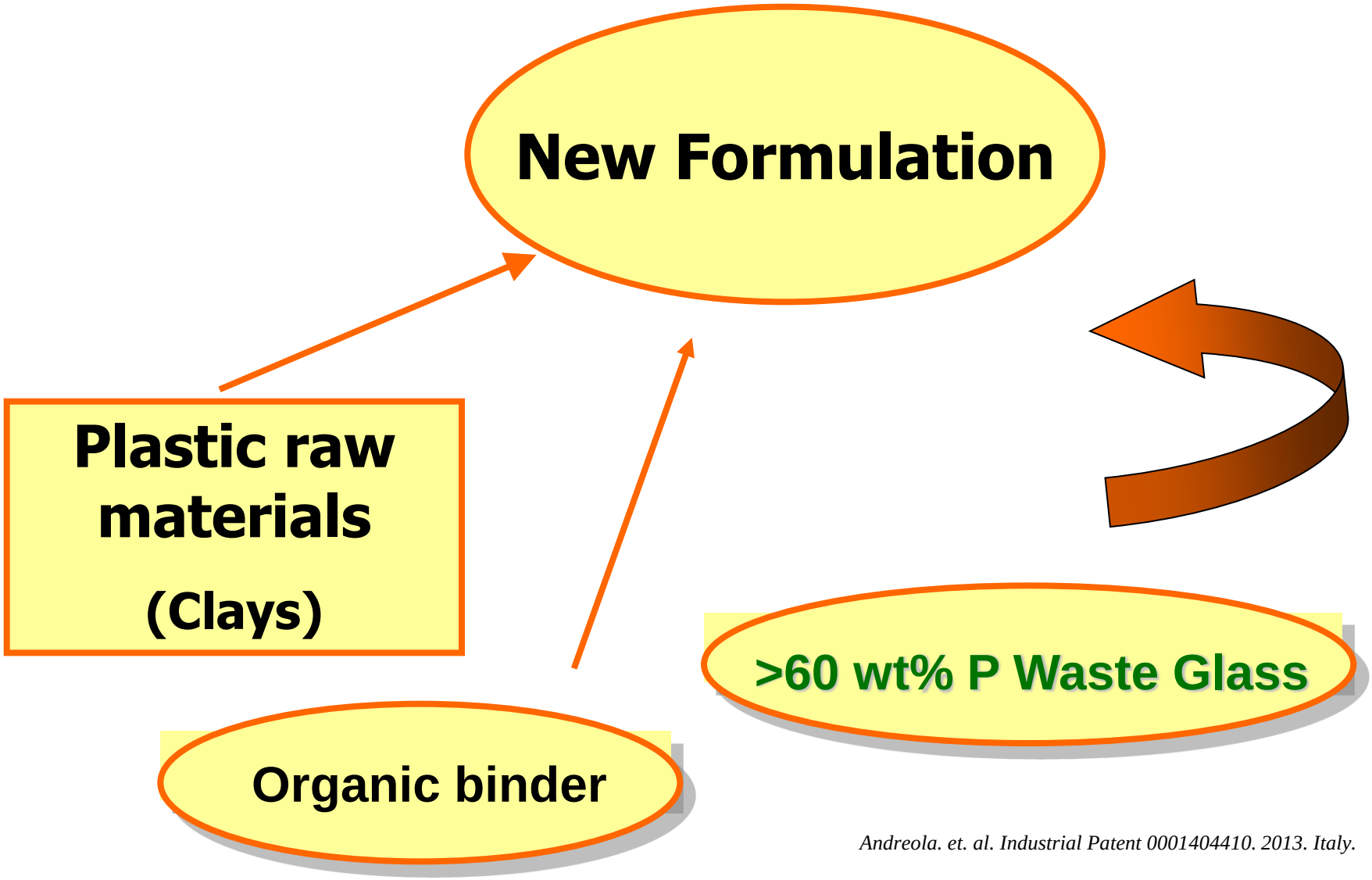
The curves underlines the lower viscosity of the panel glass with respect to both Na- feldspar and K- feldspar in all the temperature range analyzed (20-2000°C).

*Dilatometric sintering curves of **C0** and **C1***



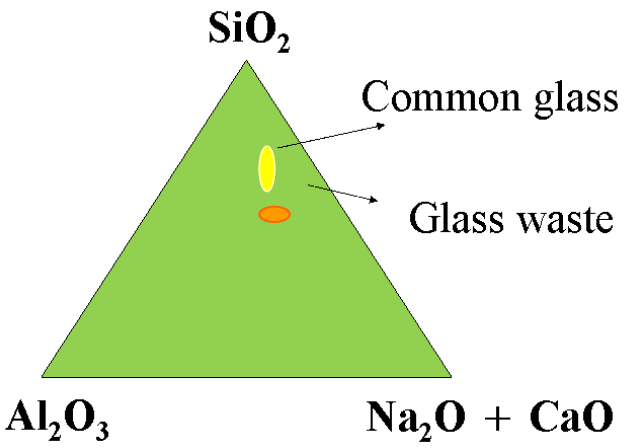
Andreola F**. Barbieri L. Karamanova E. Lancellotti I. Pelino M.* ***Recycling of CRT panel glass as fluxing agent in the porcelain stoneware tile production. *Ceramics International 34(5) (2008). 1289-1295.*

NEW CERAMICS



Andreola. et. al. Industrial Patent 0001404410. 2013. Italy.

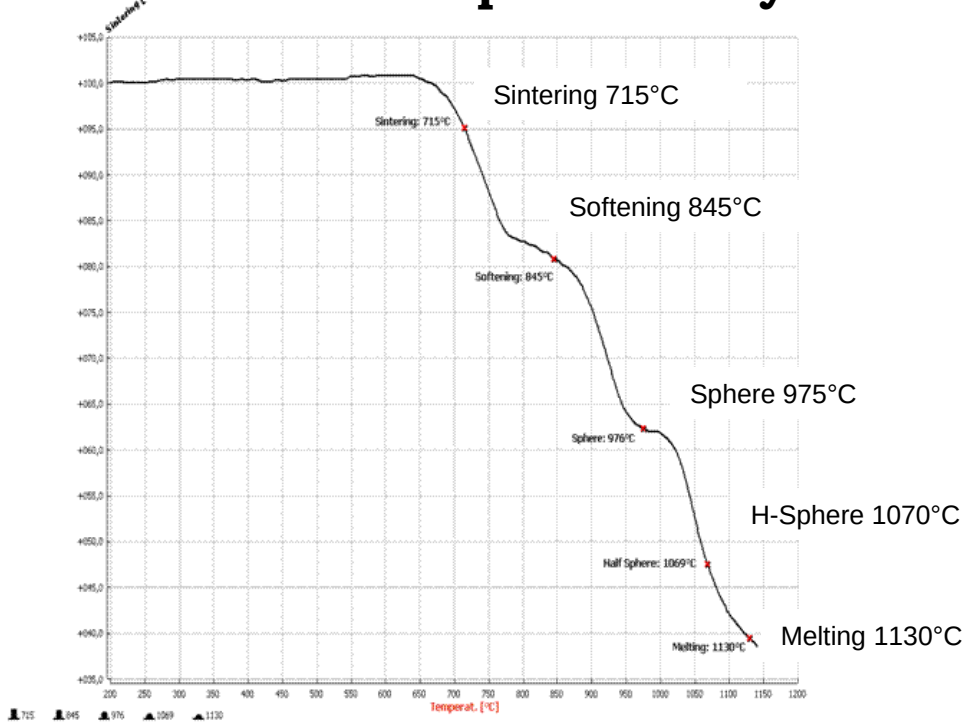
PACKAGING WASTE GLASS (PWG)



Chemical composition of PWG is similar to typical sodium-calcium silicate glasses. The difference is due to the presence of impurities (2%) inorganic such as ceramic and porcelain and organics as rubber, paper and plastics.

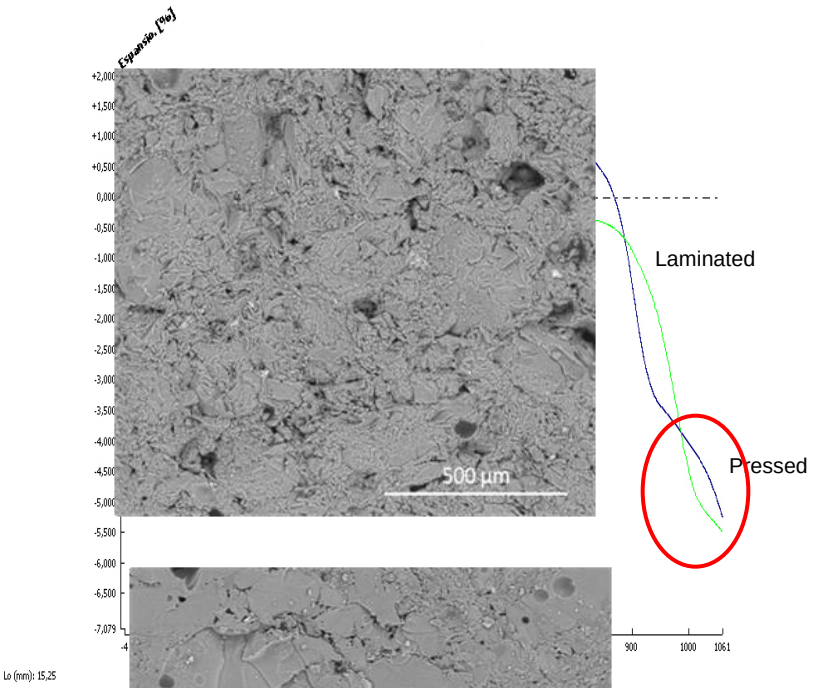
OXIDE (wt%)	PACKAGING GLASS WASTE
SiO_2	70.57
Al_2O_3	2.25
CaO	9.15
Na_2O	12.47
MgO	2.16
K_2O	0.87
Fe_2O_3	0.50
PbO	0.05
other	0.50
L.o.I (1000° C)	1.50
TOTAL	100

Characteristic Temperatures by OHM



F. Andreola, I. Lancellotti, R. Taurino, C. Leonelli, L. Barbieri, ***Production of Cement Blocks and New Ceramic Materials with High Content of Glass Waste*** *. Key Eng. Mat. (2016), Vol. 663 (2) 34-41.*

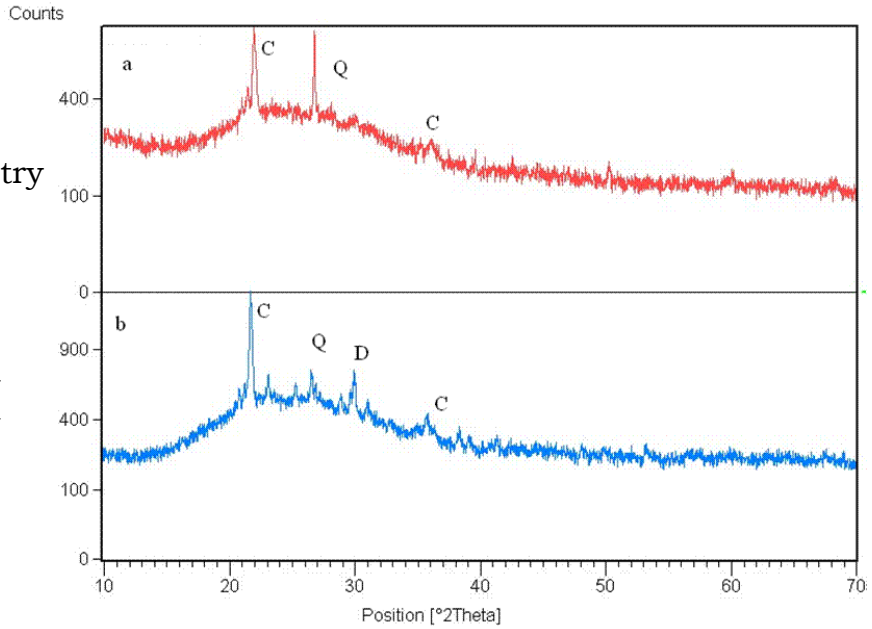
NEW CERAMICS



Sinte … by Optical Dilatometry

Samples	LS%	WA%	Apparent density (g/cm^3)	Bending Strength (MPa)
Pressed (<400 µm)	4.87	1.83	2.04	23
Pressed (<100µm)	5.46	0.29	2.10	31
Laminated (<400 µm)	2.2	11.15	1.84	25
Commercial tile BIb group	6	0.5-3	2.00	>27

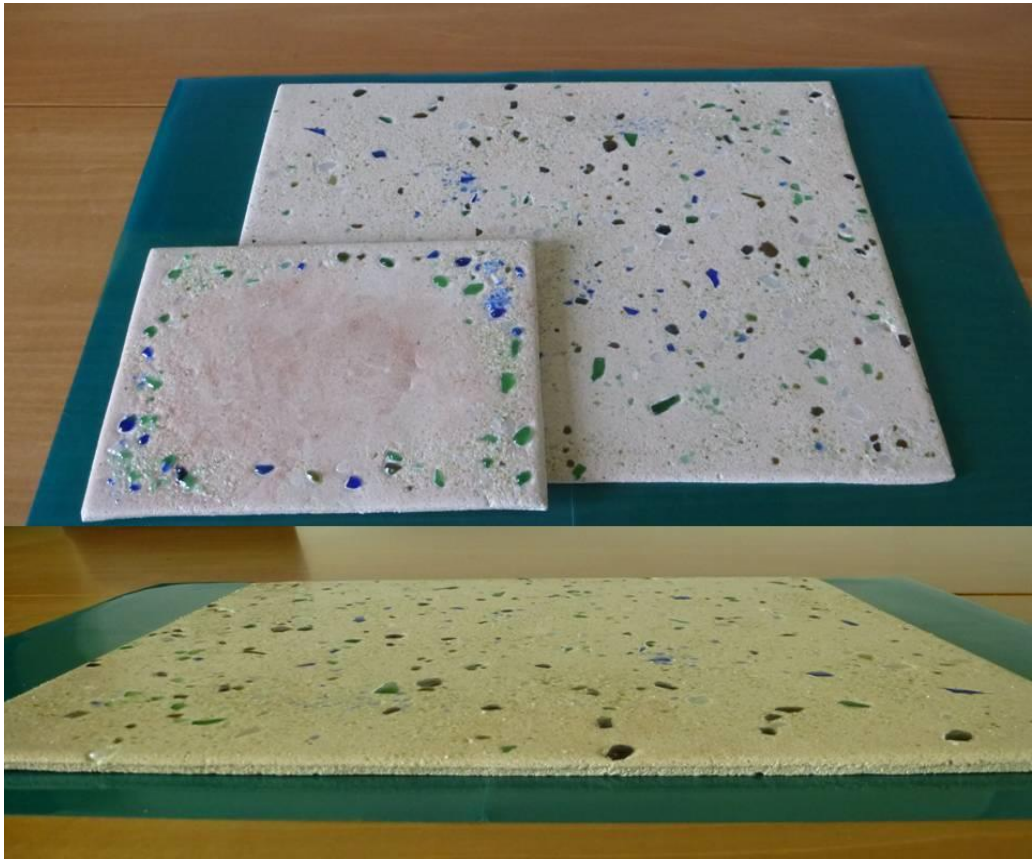
Final composition with 80 wt% of PWG



XRD … bodies (950°C) by the two techniques a) laminated; b) pressed. Q= low quartz (SiO_2); C= cristobalite (SiO_2); D=Diopside ($CaMgSi_2O_6$).

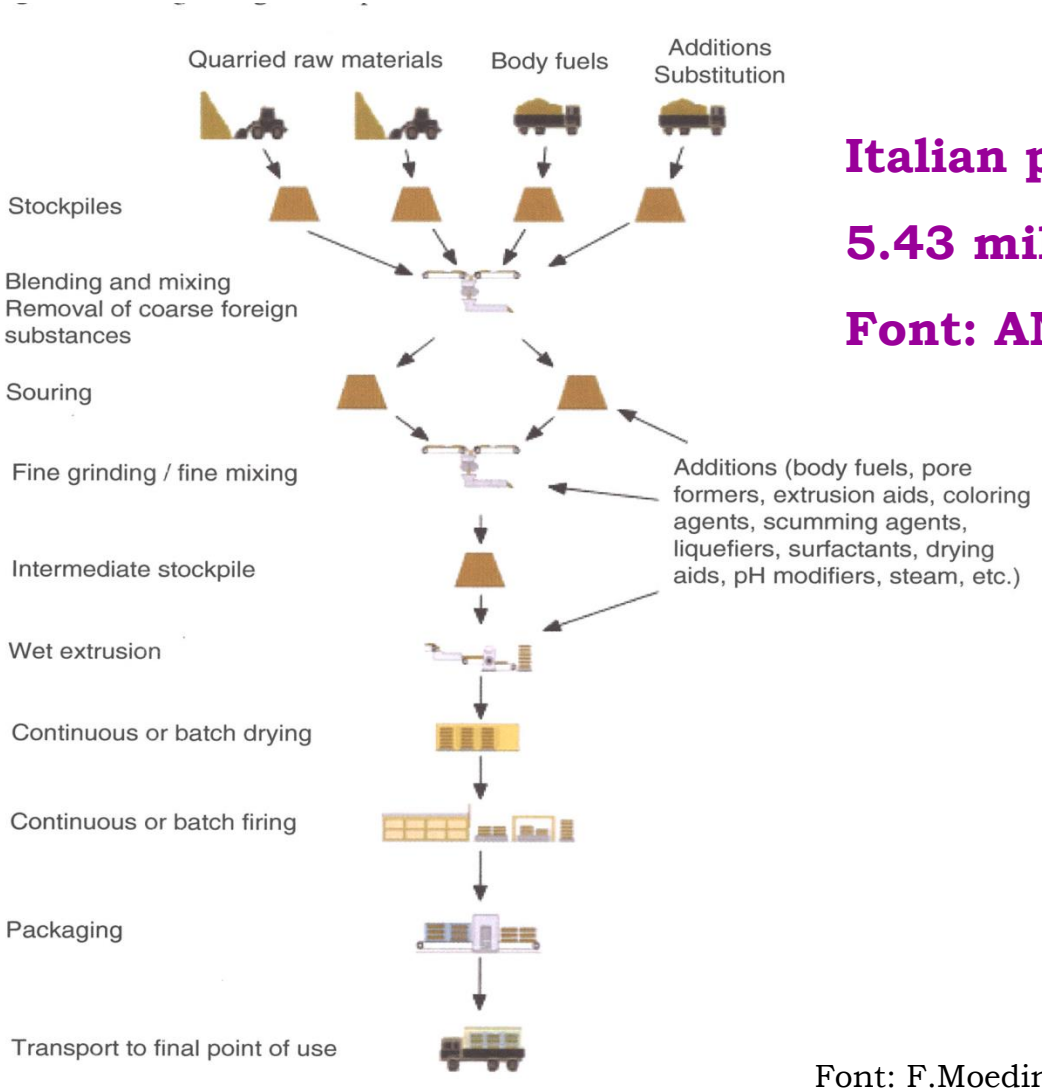
Andreola. et. al. Key Eng. Mat. (2016), Vol 663(2) 34-41.

NEW CERAMICS





BRICKMAKING PROCESS



Italian production:

5.43 million ton/y

Font: ANDIL (2014)

Font: F.Moedinger, 2011

AGRO/WOODY BIOMASS WASTE



Sawdust



Grapes seeds



Cherries seeds

High amount of organic matter (C≈50%)

USED AS PORE FORMING AGENT

Light weight and thermal insulating bricks

Elevated amount of crystalline silica ($SiO_2 \approx 61\%$)



Sugar cane ash

USED AS PLASTICITY REDUCER

Improvement of properties

CLAY USED

Chemical composition (wt%) by XRF

SiO_2	44,3%
Al_2O_3	21,5%
Fe_2O_3	12,9%
CaO	8,94%
K_2O	5,85%
TiO_2	2,66%
MgO	1,3%
Na_2O	0,934%
MnO	0,874%
SrO	0,132%
P_2O_5	0,096%
SO_3	0,095%
NiO	0,058%
Zr	0,056%
V_2O_5	0,045%
RbO_2	0,044%
ZnO	0,03%
Cr_2O_3	0,019%
Cl	0,009%
PF%	8,94%

Mineralogical Analysis by XRD

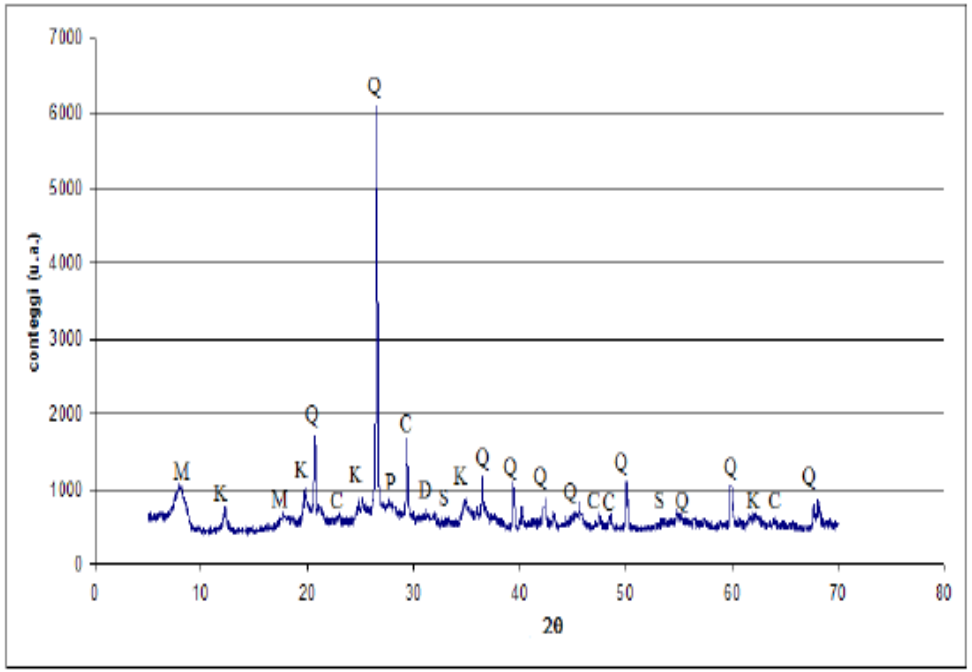
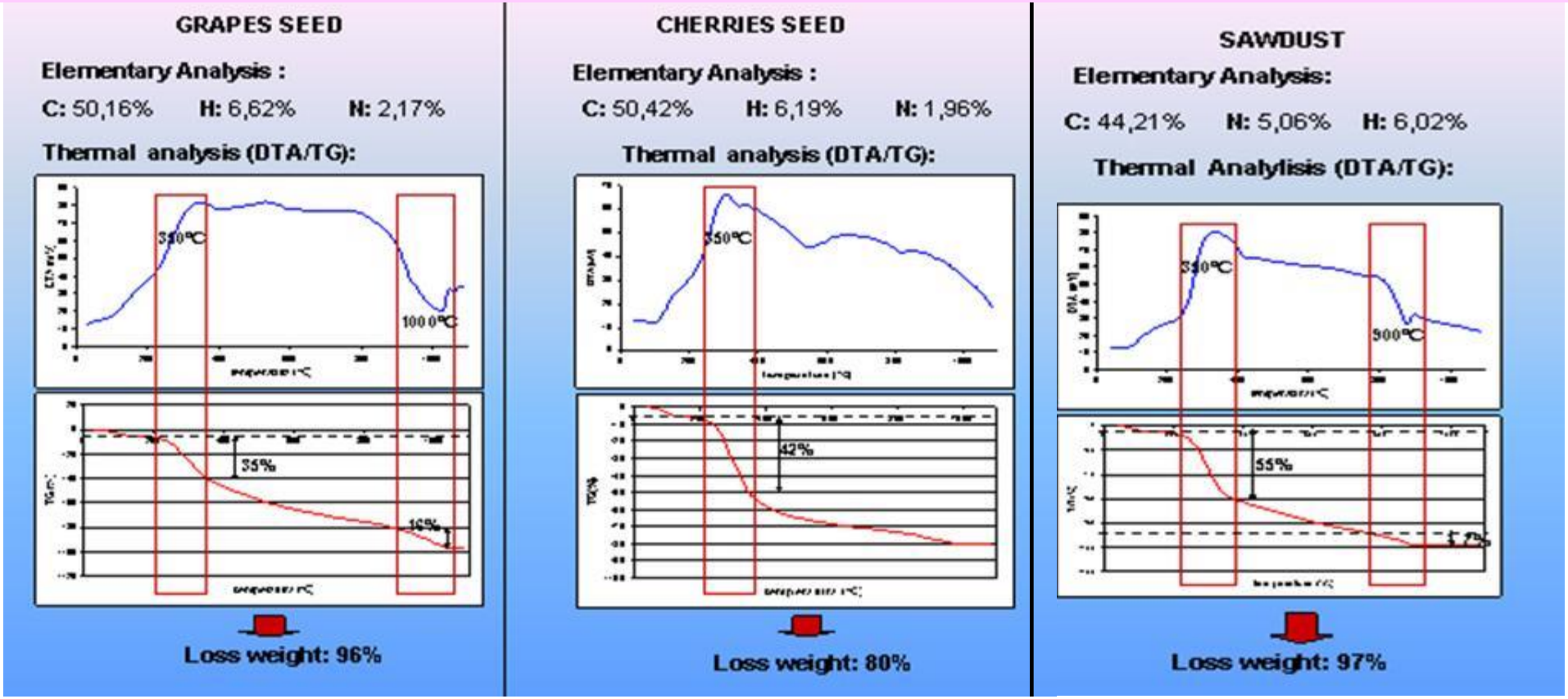


Figura 6.13: diffrattogramma a raggi X dell'argilla; Q: quarzo (SiO_2), M: muscovite ($KAl_2Si_3AlO_{10}(OH)_2$), K: caolinite–montmorillonite ($Na_{0,3}Al_4Si_6O_{15}(OH)_6 \cdot 4H_2O$), C: calcite ($CaCO_3$), D: dolomite ($MgCa(CO_3)_2$), P: plagioclasio ($(Na, Ca)(Si, Al_4)O_8$), S: siderite ($FeCO_3$)

AGRO AND WOODY BIOMASS WASTE USED

HHV (KJ/Kg): 19,928 18,075 17,773

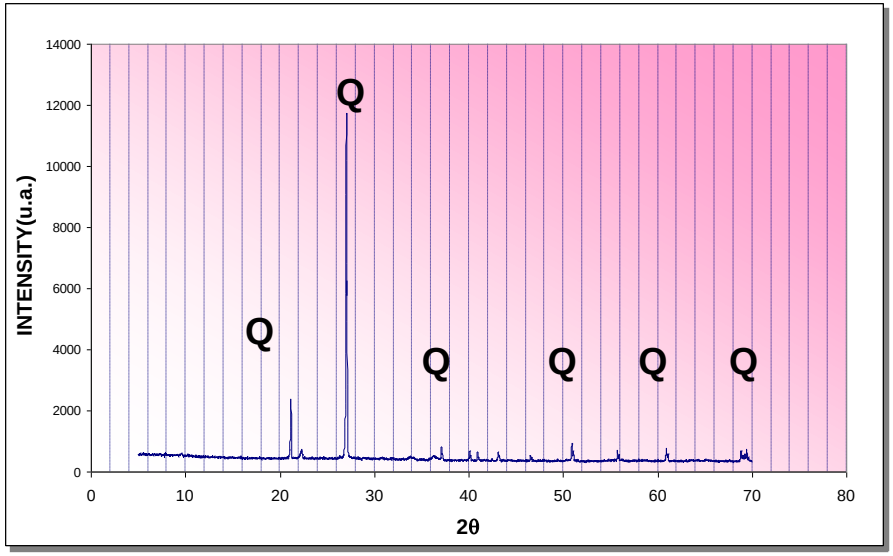


***F. Andreola** et al., **Management of agricultural biomass wastes: Preliminary study on characterization and valorisation in clay matrix bricks** Waste management 33(11) 2307-2315 (2013).*

SUGAR CANE ASH

Oxide	wt%
SiO_2	60.9%
Fe_2O_3	19.7%
K_2O	7.47%
CaO	3.71%
Al_2O_3	2.91%
MgO	1.36%
P_2O_5	0.91%
L.O.I	**1.24%**

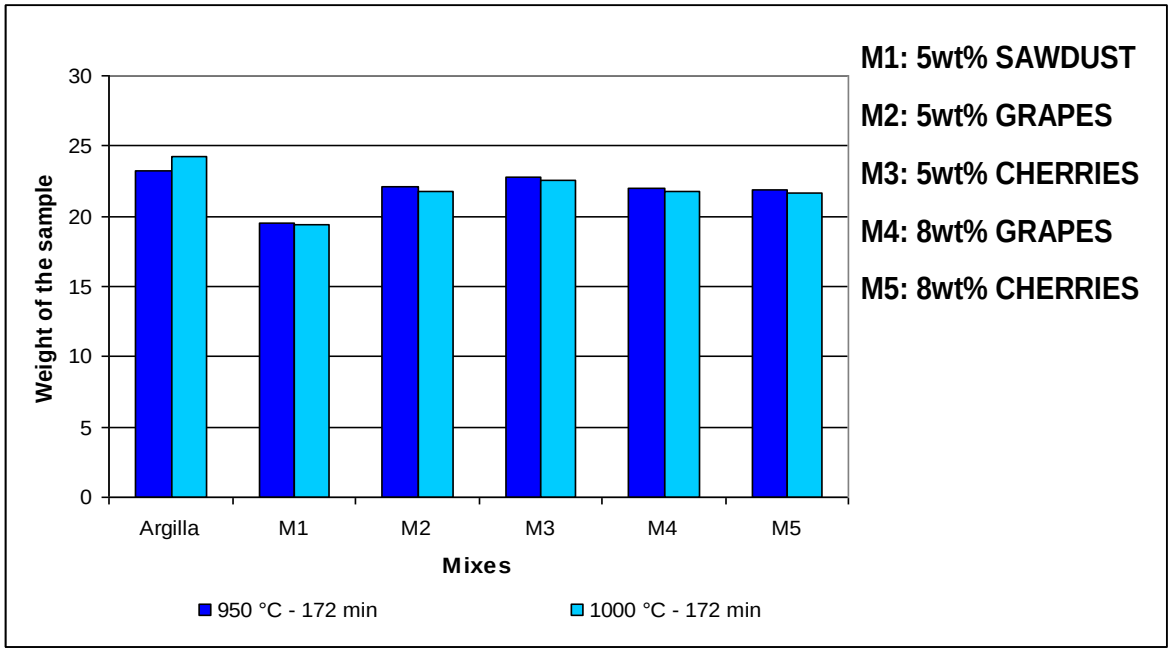
This agricultural by-product derived from the sugar cane combustion process. It shows a high crystalline silica content (61%) and low loss of ignition, indicating little amount of organic matter. The XRD spectrum confirms the presence of quartz as main crystalline phase. Due to these characteristics the ash was chosen to explain a filler and plasticity reducing effect on the brick bodies.



F. Andreola et al., Management of agricultural biomass wastes: Preliminary study on characterization and valorisation in clay matrix bricks Waste management 33(11) 2307-2315 (2013).

EFFECT OF AGRO/WOODY WASTE ON LOSS WEIGHT

Average weight of fired bricks (g) at two diffrent temperatures (950°C e 1000°C)

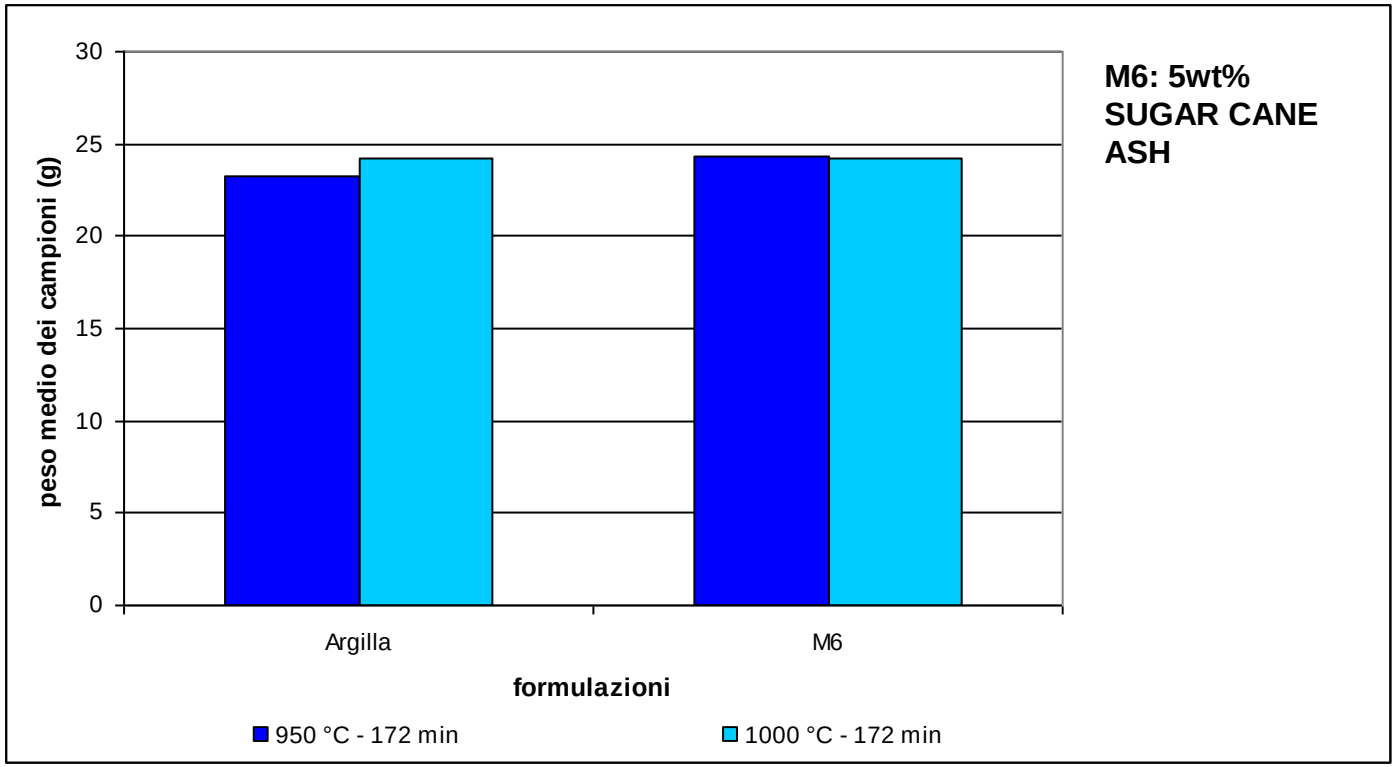


Loss weight of fired bricks

	STD	M1	M2	M3	M4	M5
950 °C - 172 min	Loss weight media	*16,18*	*4,82*	*2,88*	*5,51*	*5,9*
1000 °C - 172 min	Loss weight media	*20,03*	*10,14*	*6,97*	*10,22*	*10,92*

EFFECT OF SUGAR CANE ASH ON LOSS WEIGTH

Average weight of fired bricks (g) at two diffrent temperatures (950°C e 1000°C)



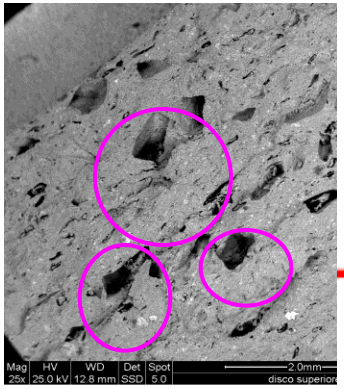
TECHNOLOGICAL PROPERTIES

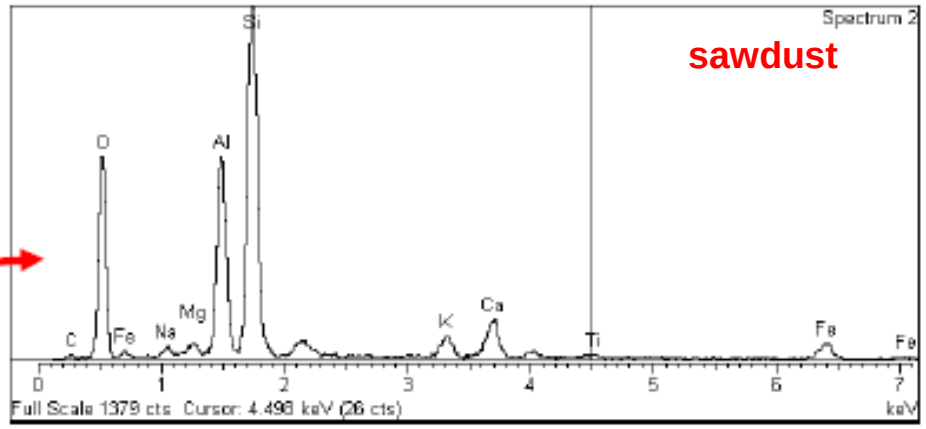
PROP.	M0	M1	M2	M3	M4	M5	M6
W.A%	8.90	18.20	12.70	10.40	14.40	12.70	10.40
W.L % after firing *	----	20	10.40	6.97	10.20	10.92	0.10
L.O.I%	11.20	11.30	11.90	12.10	14.80	15.30	7.40
M.O.R (MPa)	32.63	16.86	21.42	23.03	14.53	17.22	28.16

* WL%: calculated from the difference respect to the standard one (M0)

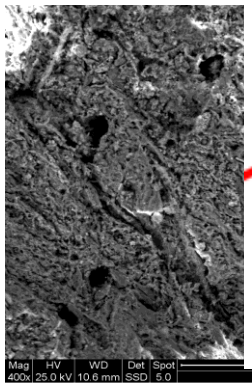
MICROSTRUCTURAL ANALYSIS

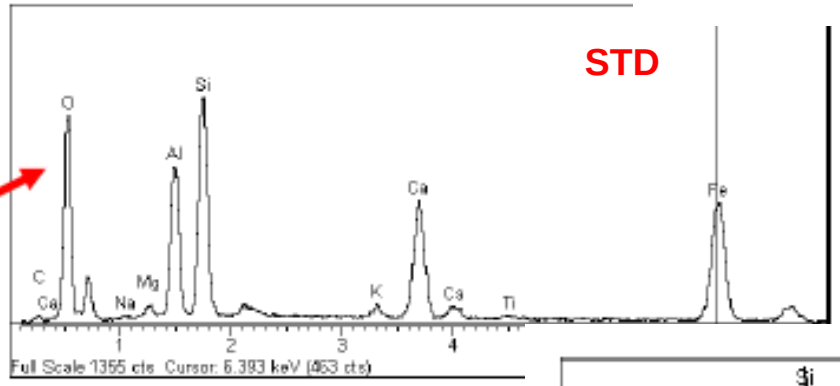
M1: 5wt% sawdust 1000°C

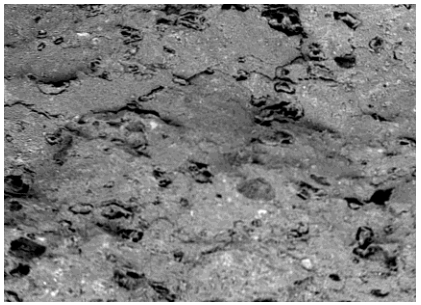




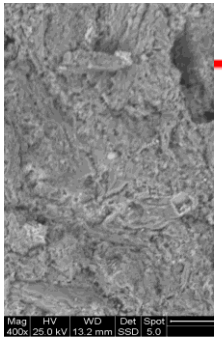
STD 100

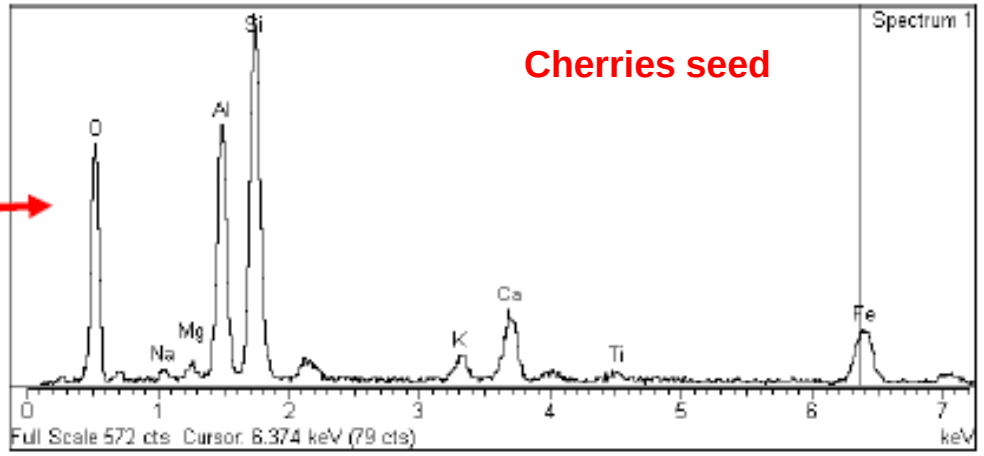




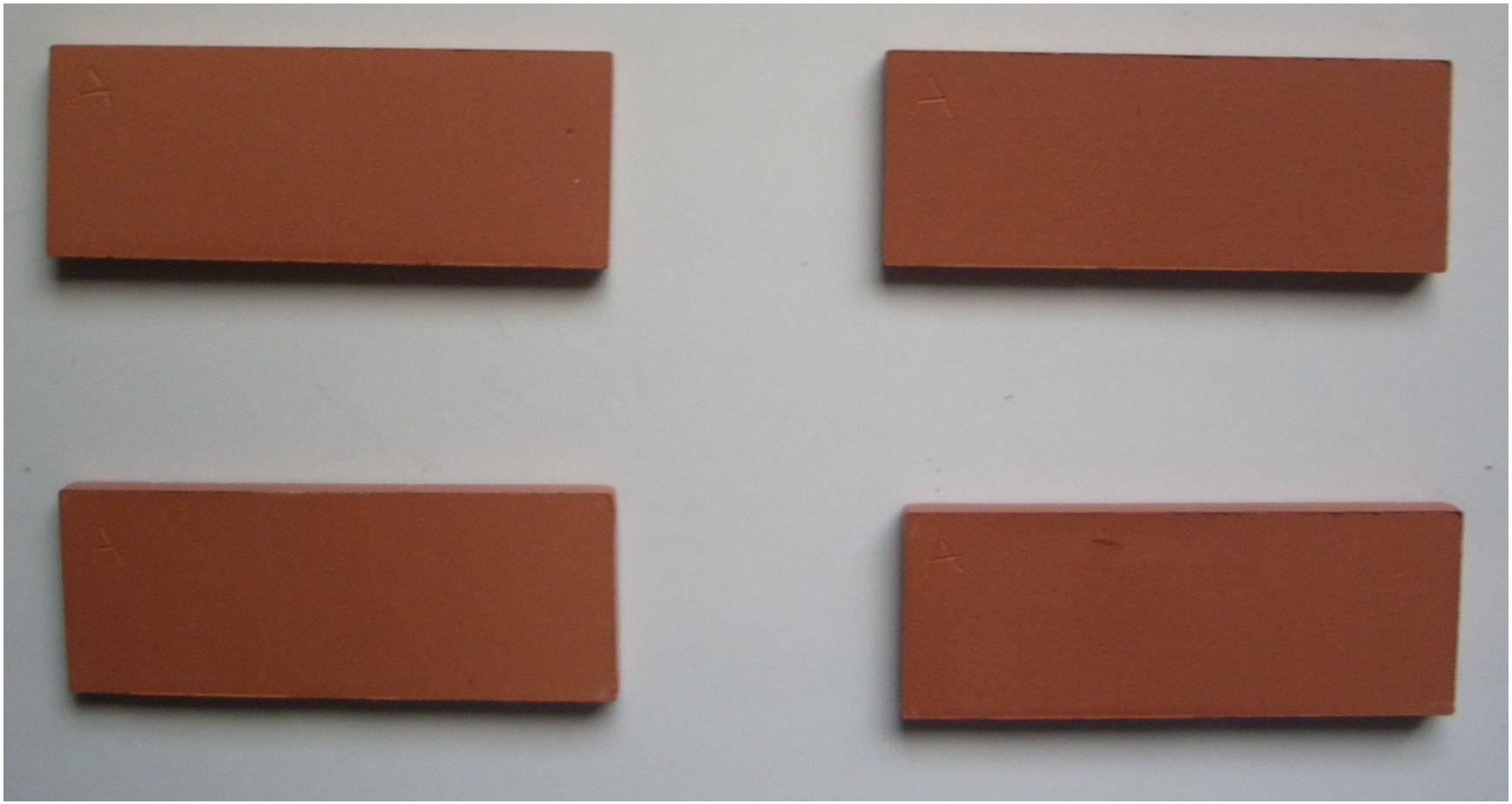


M3: 5wt%





FIRED SAMPLES



CONCLUSIONS

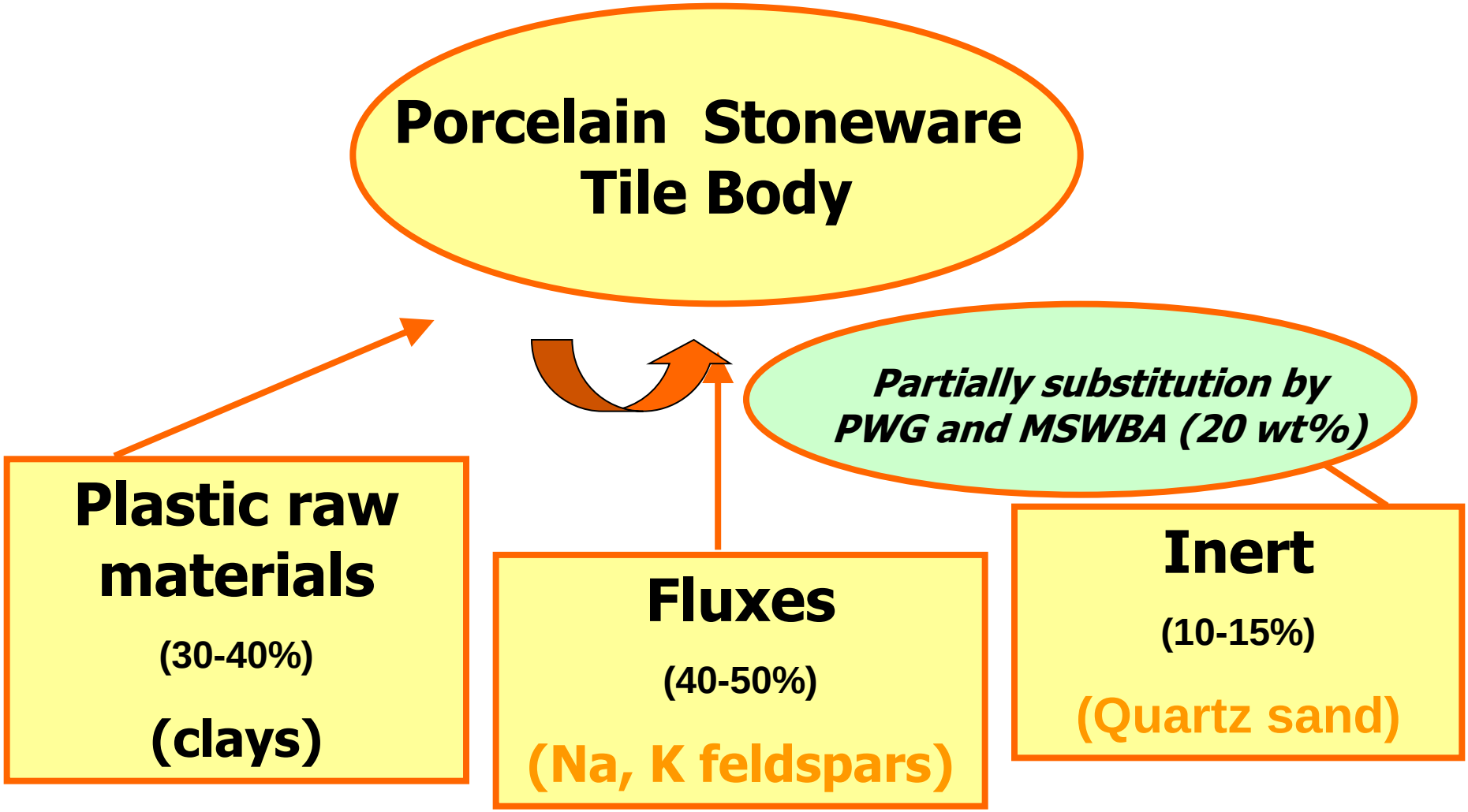
- The recycling of waste or EOW into ceramic manufacturing is theoretically useful because it is possible to absorb great amount of waste also hazardous that would otherwise will go to landfill
- Many researches published in the last 20 years relate to waste recycling but technological transfer to industrial production is not easy
- A suitable legislative framework, an open market and green consumers are therefore absolutely fundamental to increase the transformation of “waste as resource” in order to move to a circular economy
- The new challenge is to project ceramics made only by waste with high added value
- Vantages: contribute to earn LEED Certification (Leadership in Energy and Environmental Design) in buildings, ECOLABEL products
- Disadvantages: cost for pre-treatments, for environmental controls (leaching tests, gas emissions,….), transport, ….



THANK YOU FOR YOUR ATENTION!!!

Contact: andreola.fernanda@unimore.it

CASE STUDY: BOTTOM ASH



L. M. Schabbach, **F. Andreola**, L. Barbieri, I. Lancellotti, E. Karamanova, B. Ranguelov, A. Karamanov, ***Post- treated bottom incinerator bottom ash as alternative raw material for ceramic manufacturing,*** *J. Europ. Cer. Soc.* ***32*** *2843-2852 (2012)*

MSWI Bottom ash



Italian current situation

✓32.5 *10^6 tons/y MSW produced

✓ 45% landfilled only 11% incinerated, 44% separate collect and other disposal

Incineration process produces

	ORIGEN	CER CODE	ITALIAN PRODUCTION (TON/YEAR)
BOTTOM ASH (20-35% peso iniziale rifiuto in camera combustione)	griglia	19 01 12	1.250.000
FLY ASH (2,5-3 % peso iniziale rifiuto in camera combustione)	elettrofiltro e/o filtro a manica	19 01 13*	150.000

Font: National Waste Report ISPRA (2012)

End of Waste

Pre-treated MSW IBA incineration bottom ash

Technological Recovery Process

Sorting

Physical-Mechanical treatments
aging,
Fe and non Fe metals separation,
crushing, sieving, washing,…



Inert material silica based and rich in Ca, Al and Fe. Prepared in two fractions.

After treatment the inert material is delivered as EOW, it has not got a WEC code and the ceramic companies have not need the authorization for using it inside the process.

CASE STUDY: BOTTOM ASH

Chemical Analysis

Materials

	IBA F 0-2 mm	IBAL 2-8 mm lavato	PWG 100 - 200 microns
Oxide	**%**	**%**	**%**
SiO_2	30,31	47,40	71,00
Al_2O_3	13,33	9,95	2,30
Fe_2O_3	10,82	4,38	0,35
CaO	20,75	18,80	9,70
MgO	2,83	2,91	2,00
Na_2O	1,94	4,53	12,20
K_2O	0,94	0,98	1,00
TiO_2	1,07	0,75	0,07
B_2O_3	0,30	0,56	---
MnO	0,18	0,11	---
ZnO	0,83	0,34	---
PbO	0,36	0,31	0,02
Cr_2O_3	0,04	0,03	---
SO_3	1,74	1,01	---
P_2O_5	1,96	1,26	---
CuO	0,68	0,47	---
Cl^-	0,48	0,04	---
Others*	0,17	0,16	----
L.O.I (1000°C)	11,7	5,58	1,00
Tota	100,40	99,54	99,74

*Others
(BaO, NiO, As_2O_3, CdO, Sb_2O_3, V_2O_3)

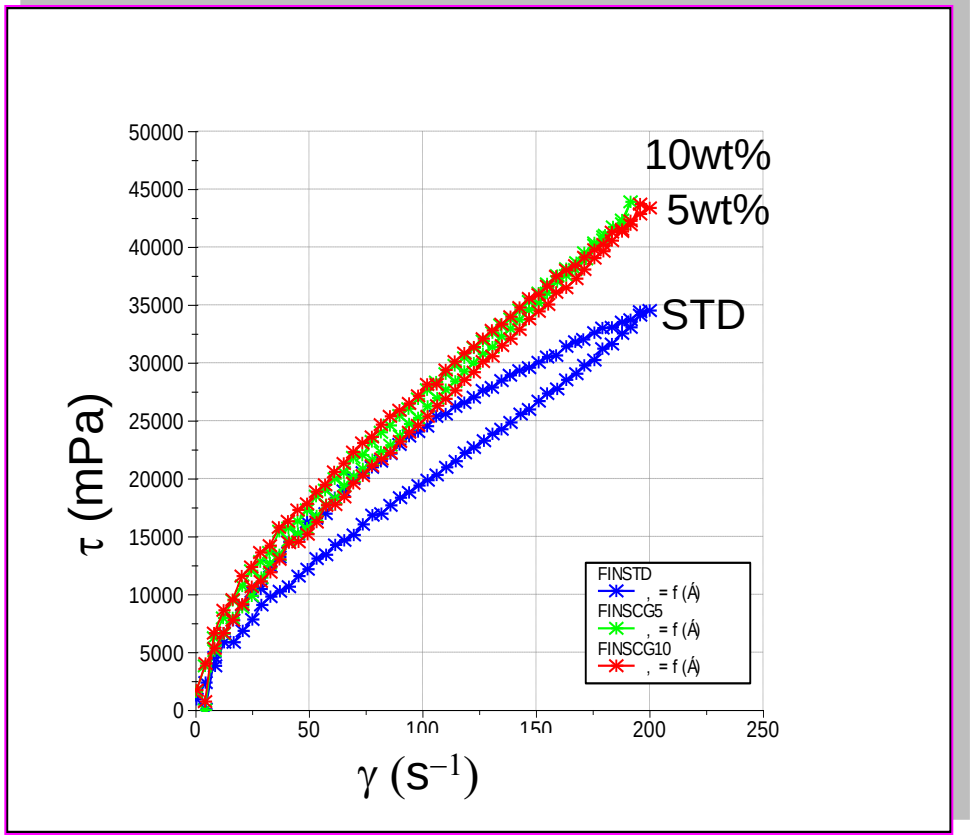
Σ[heavy metals]<3%

Solubility Test

(distilled water, 24 h, 20°C)

	F 0-2 mm	L 2-8 mm
SO_4^{2-} (mg/l)	570	145
Cl^- (mg/l)	340	70
Ca (mg/l)	123.80	40.43
Mg (mg/l)	1.43	0.92
Na (mg/l)	230.30	71.01
Specific.Cond. (mS/cm)	2.11	0.71

Effect on Rheology

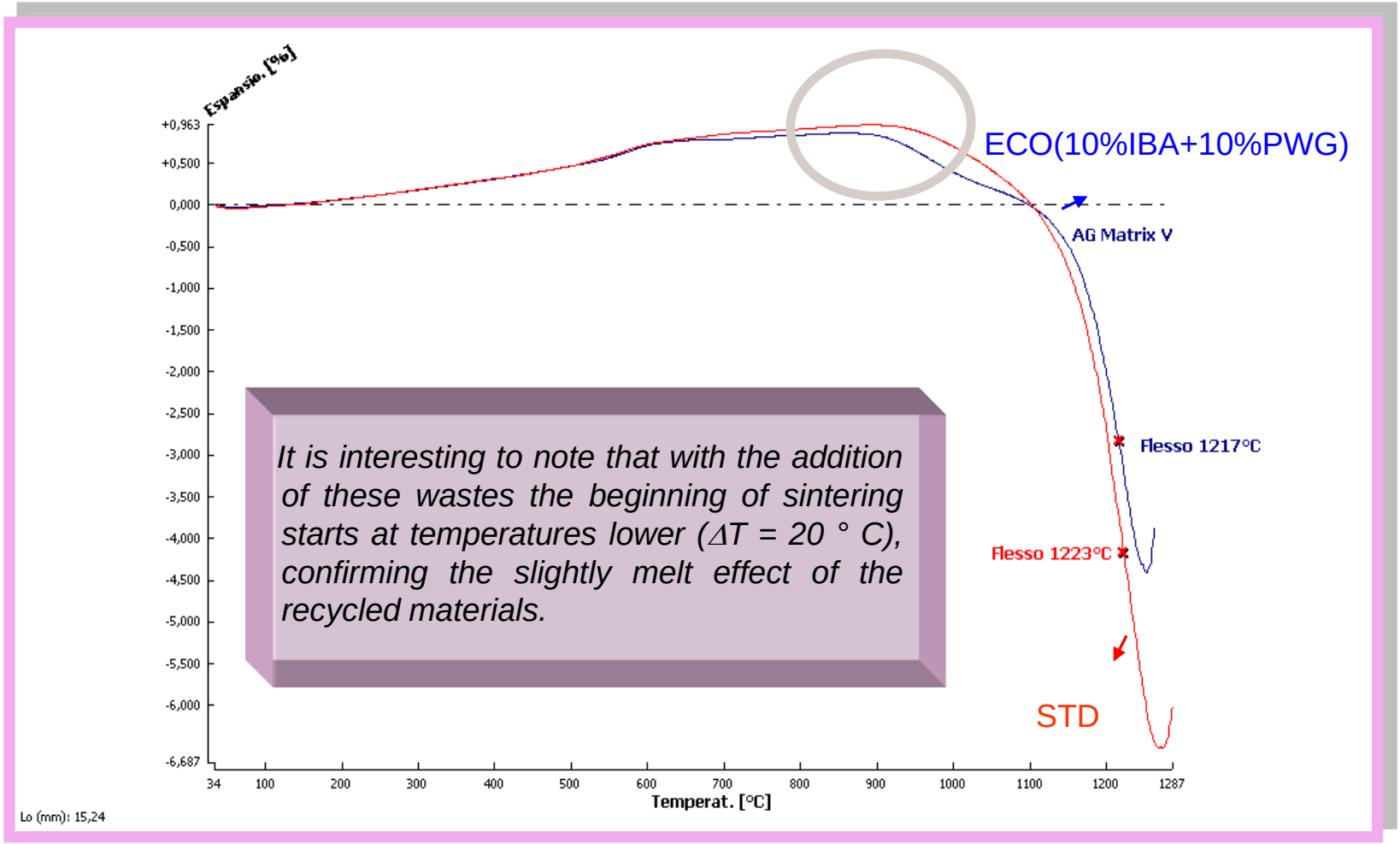


For wet –grinding process

MIXTURE	APP.VISCOSITY (mPa.s)
STD (0,6%def)	**171**
5% F (0,6%def+0,5%TPF)	**180**
10% F (0,6%def+0,5%TPF)	**333**
10% F (0,6%def+0,7%TPF)	**256**
5% GL (0,6%def+0,3%TPF)	**220**
10% GL (0,6%def+0,5%TPF)	**217**

The presence of IBA in the mixtures strongly influences the viscosity and the rheological behaviour of the suspensions. It was necessary added more deflocculating agent in order to fall within the industrial tolerance (250-300 mPa.s), so the maximum amount IBA permitted was 10 wt%.

Effect on Sintering



Optical Dilatometry of the ceramic bodies: STD e ECO

Commercial Product Sheet

BIa-Porcelain stoneware
EN 14411 ANNEX G BI A

Tecnical Parameters ***(10wt%IBAF+10wt%GLASS)***

Technical Features	Norm	Rule limits	Valori *ECO* System
Dimensions	EN ISO 10545 - 2	• Lunghezza e larghezza ± 0.6% max • Spessore ± 0.5% max • Rettilineità spigoli ± 0.5% max • Ortogonalità ± 0.6% max • Planarità ± 0.6% max	Conforme
Water Absorption	EN ISO 10545 - 3	< 0.5%	0.12%
Flexural Strength	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
Ice resistance	EN ISO 10545 - 12	Nessun campione deve presentare alterazioni sulla superficie	Non gelivo
Chemical resistance	EN ISO 10545 - 13	Nessun campione deve presentare alterazioni visibili	Resistente
Spot resistance	EN ISO 10545 - 14	❶ ❺	❺
Thermal Dilatation (+20 °C a +100°C)	EN ISO 10545 - 8	< 9MK^{-1}	Conforme
Shock Thermal resistance	EN ISO 10545 - 9	Nessun campione deve presentare difetti visibili	Resistenti
Colour resistance at UV-vis	EN ISO 10545 - 16	Non devono presentare apprezzabili variazioni di colore	Campioni inalterati
Abrasion resistance PEI	EN ISO 10545 - 7	❶ ❺	❹ ❺
Release Cd and Pb	EN ISO 10545 - 15	Cd: 0.07 mg\dm^2 Pb: 0.80 mg\dm^2	<0.004 mg\dm^2 < 0.029mg\dm^2

Good aesthetical, mechanical and quality features





Environmental Control

Leaching Test - Norm UNI 10802

Metal	STD (mg/l)	ECO (mg/l)	Italian Regulation Limits (mg/l)
Cr total	0.004	0.023	0.050
Cd	0.006*	0.001	0.005
Cu	0.018	0.015	0.05
Sr	0.013	0.036	-
Pb	0.03	0.00	0.05
Zn	0.03	0.01	3.0
Be	0.00	0.00	0.01
Fe	0.083	0.131	-
Ni	0.02*	0.02	0.01
Ba	0.01	0.01	1.00
As	0.03	0.04	0.05
Co	0	0	0.25
V	0.02	0.02	0.25

*instrumental limit :Cd 1.5ng/mL e Ni 6ng/mL

(deionized water, 24 h, with mixing, solid/liquid ratio=1/10)

Environmental Control

Emission analysis

TIPOLOGY	STD (mg/Nmc)	**ECO (mg/Nmc)**	REGULATION LIMITS (mg/Nmc)	METHOD
PARTICULATE MATTER	0.91	**0.54**	5	UNI-EN 13284-1
LEAD (Pb)	0.001	**0.002**	0.5	M.U. 723
FLUOR AND COMPOUNDS (AS HF)	2.73	**3.76**	4	D.M 25/08/00 All.2
NITROGEN DIOXIDE (NO_2)	7.92	**6.04**	200	D.M 25/08/00 All.1
SULFUR DIOXIDE (SO_2)	2.25	**1.06**	500	D.M 25/08/00 All.1

Partially substitution of fluxes by (CRT glass, cullet glass, granite volcanic ash)

•**F.Andreola, L. Barbieri, E. Karamanova, et. al, Recycling of CRT panel glass as fluxing agent in the porcelain stoneware tile production,** ***Ceramics International, 34(5), 1289-1295 (2008).***

•***S. Ergul, M. Akyildiz, A. Karamanov, Ceramic material from basaltic tuffs. Ind Ceram 37(2007) 75 80.***

•***R.D. Gennaro, P. Cappelletti, et. al, Influence of zeolites on the sintering and technological properties of porcelain stoneware tiles, J. Eur. Ceram. Soc. 23(13)(2003) 2237-2245.***

•***F. Matteucci, M. Dondi, G. Guarini, Effect of soda-lime glass on sintering and technological properties of porcelain stoneware tiles, Ceramics International 28(2002) 873–880.***

•***G. Carbonchi, M. Dondi N. Morandi, F. Tateo, Possible use of altered volcanic ash in ceramic tile production. Ind Ceram 1,9(1999) 67–74***

Pla… materials

(30-40%)

(clays)

(40-50%)

(Na, K feldspars)

…ert

(10-15%)

(Quartz sand)

BATCH COMPOSITIONS

MIXTURE	GLASS	CLAYS	SAND
1	5	95	/
2	10	90	/
3	15	85	/
4	20	80	/

MIXTURE	RUPTURE MODULUS (MPa)
1	80.70
2	60.71
3	55.45
4	43.71
INDUSTRIAL PRODUCT	53.59

SINTERING PARAMETERS

MIXTURE	LINEAR SHRINKAGE (LS%)	WATER ABSORPTION (WA%)	POROSITY (%) (Hg porosimetry)
1	9.11 ± 0.32	0.09 ± 0.01	5.98
2	9.11 ± 0.20	0.07± 0.01	3.79
3	7.81 ± 0.17	0.04± 0.01	3.32
4	5.52 ± 0.16	0.05± 0.01	4.01

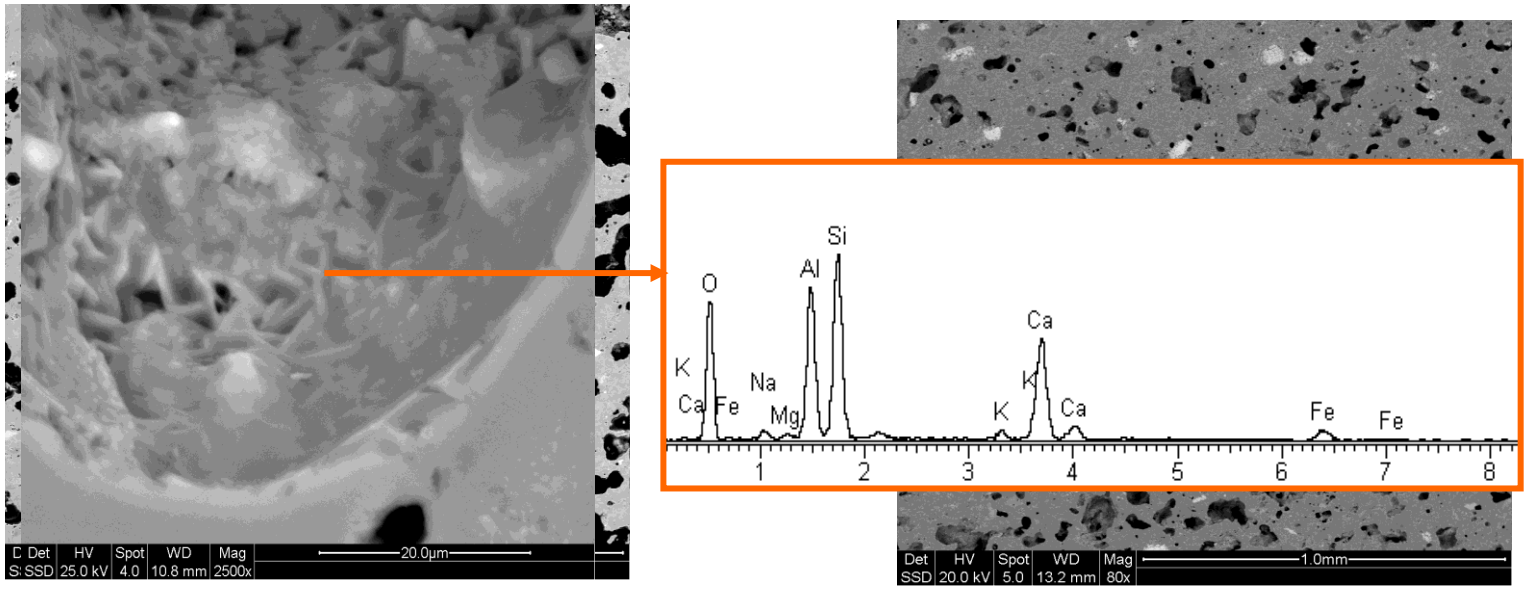
Industrial values
BIa products

LS% : 7.5-8.5
WA% ≤ 0.05
RM: > 50 MPa

MICROSTRUCTURAL ANALYSIS

CLK

CFK



1190°C, 60 min

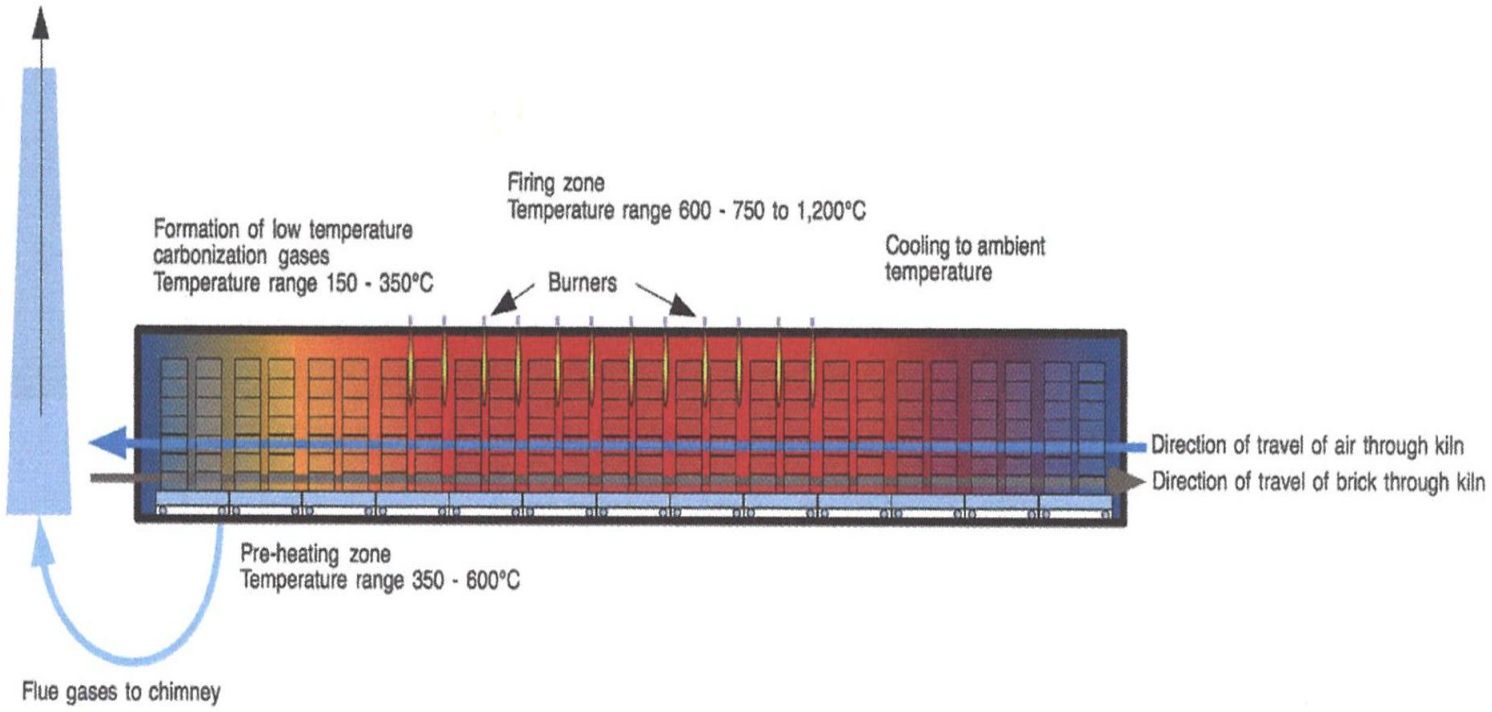
1210°C, 60 min

Fracture surface SEM images of fired samples

RIETVELD-RIR XRD RESULTS

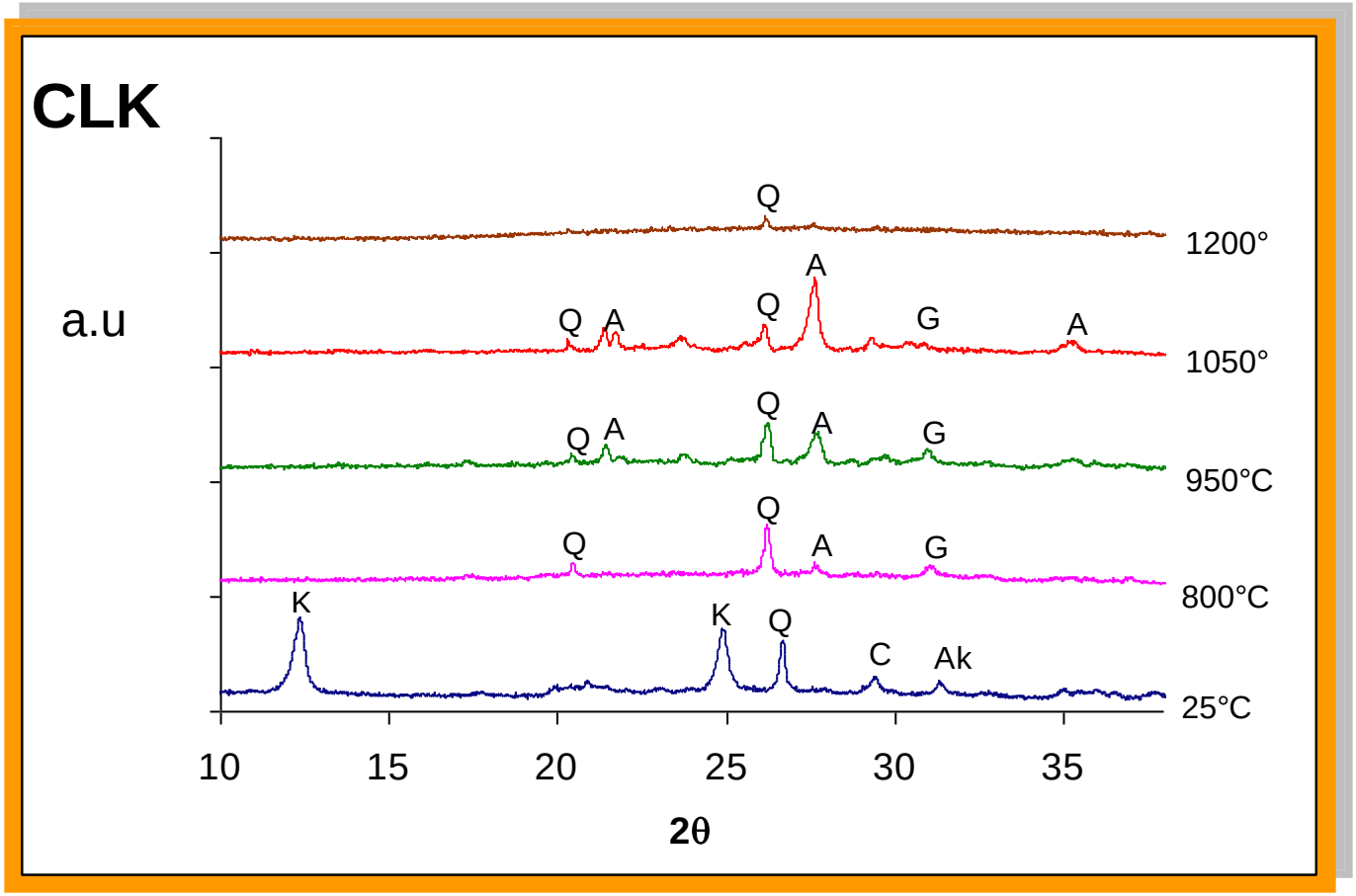
Phases	C0*	C1*	C0**	C2**	C3**	C4**
Quartz	17.6	10.7	22.7	21.0	19.8	18.5
Mullite	8.2	--	4.8	5.3	4.2	2.6
Albite	2.8	12.8	3.6	3.0	4.7	6.1
Ba-Orthoclase	--	16.3	--	--	--	--
Glassy	71.4	60.1	68.9	70.6	71.3	72.7

BRICKMAKING PROCESS



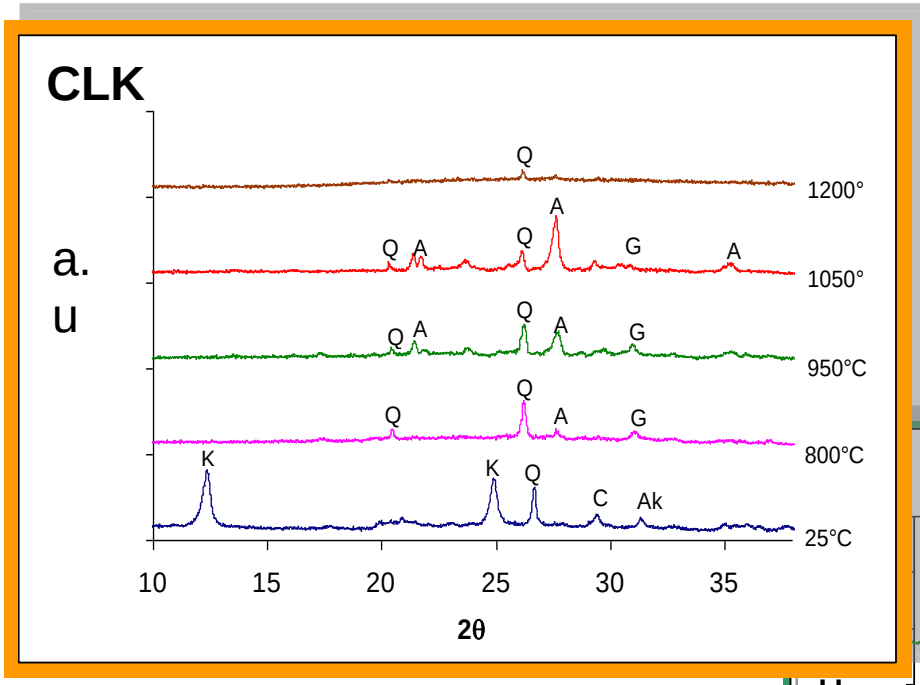
Font: F.Moedinger, 2011

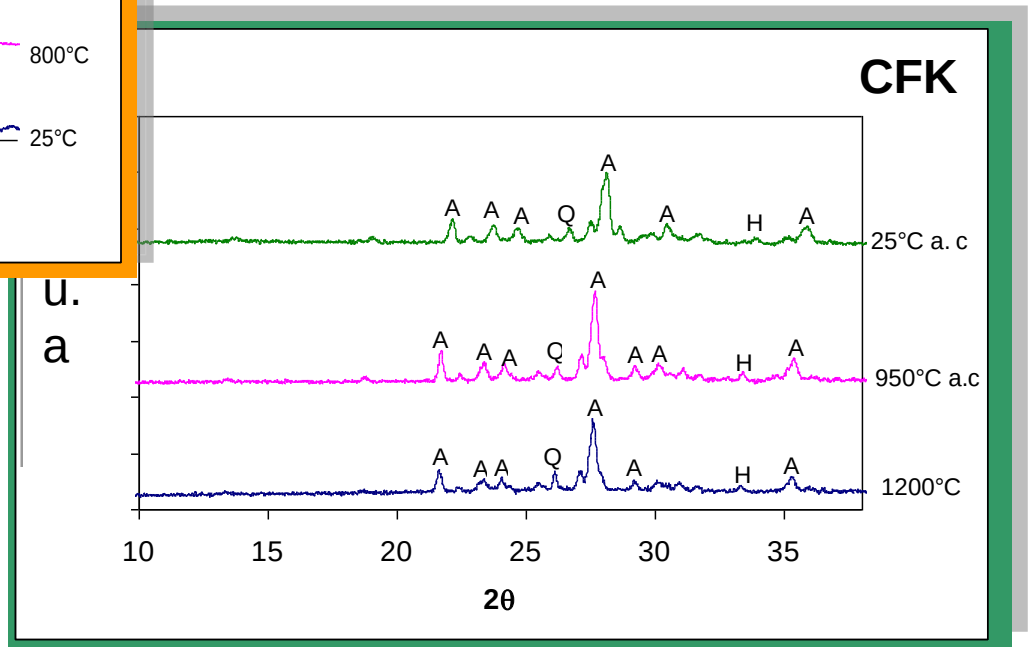
CRYSTALLIZATION STUDY BY HT-XRD ANALYSIS



K: kaolinite ($(Al_2 Si_2 O_5 (OH)_4$), C: calcite ($Ca CO_3$), Ak: akermanite ($Ca_{1.53}Na_{0.51}$) ($Mg_{0.39}Al_{0.41} Fe_{0.16}$)$Si_2O_7$, Q: quartz ($SiO_2$), A: anortite ($CaAl_2Si_2O_8$), G: gehlenite ($Ca_2Al(AlSi)O_7$), H:hematite (Fe_2O_3).

COOLING EFFECT ON CRYSTALLINITY

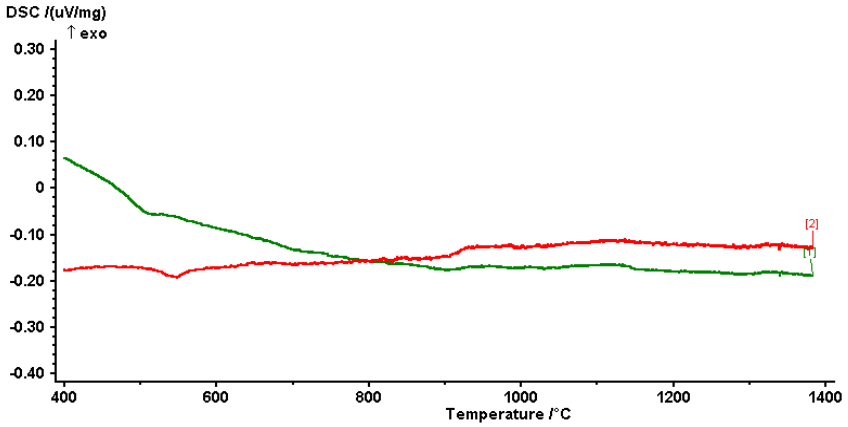




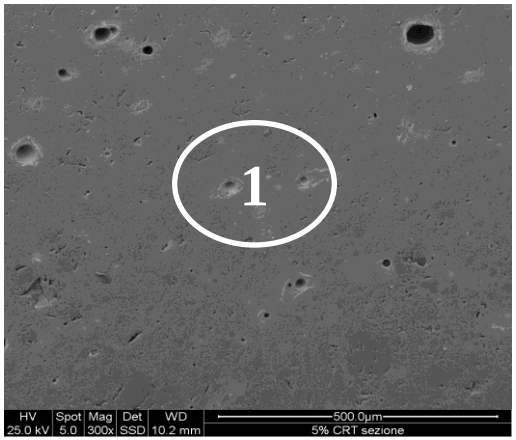
Thermal Characterization

DTA

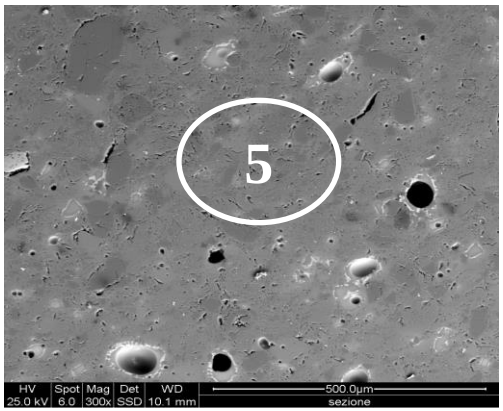
✓The CRT glasses do not cristallize, present a high thermal stability.



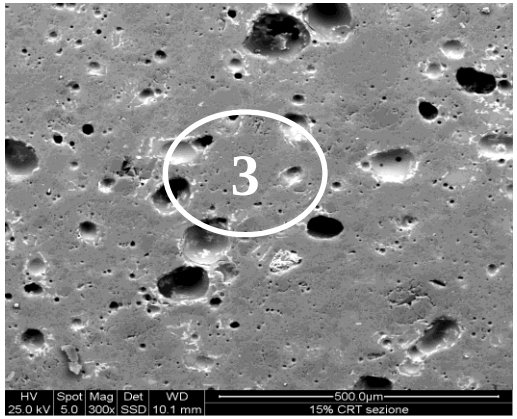
MICROSTRUCTURAL ANALYSIS



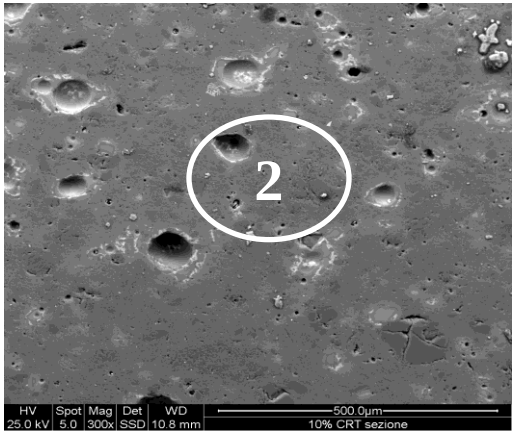
section 5 wt% glass



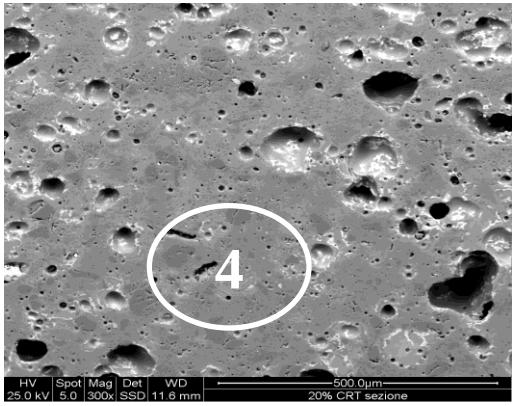
section 7 wt% glass+ 10wt% sand



section 15 wt% glass



section 10 wt% glass



section 20 wt% glass

Andreola F, Barbieri L, Bondioli F, Ferrari A M, Lancellotti I, Miselli P. Recycling screen glass into new traditional ceramic materials Int. J Appl Ceram Technol 2010; 7(6); 909-917.

Criteria to insert a Waste/EOW

- A complete characterization of waste (chemical, physical, thermal,….)
- Assessment of quantity introduced/effect on process
- Checking the quality and performance of the end products obtained

Conditioning factors

- Nature compatibility between the waste and the natural raw materials (host)
- Production cycle (wet or dry grinding, shaping, firing cycle, …)
- Characteristics of the finished product (sintered/porous)
- Availability and constant flow (variability)
- Origin, transport and pre-treatments costs
- Authorization to manage waste (not necessary for EOW)

Basic information for testing the potential waste as raw material

- Chemical and mineralogical composition
- Oxides and heavy metals
- Soluble salts
- Humidity
- Particle size distribution
- Odour /smell
- Firing colour, efflorescence
- Leaching test end products
- Emissions during firing

HIGH HEATING VALUES

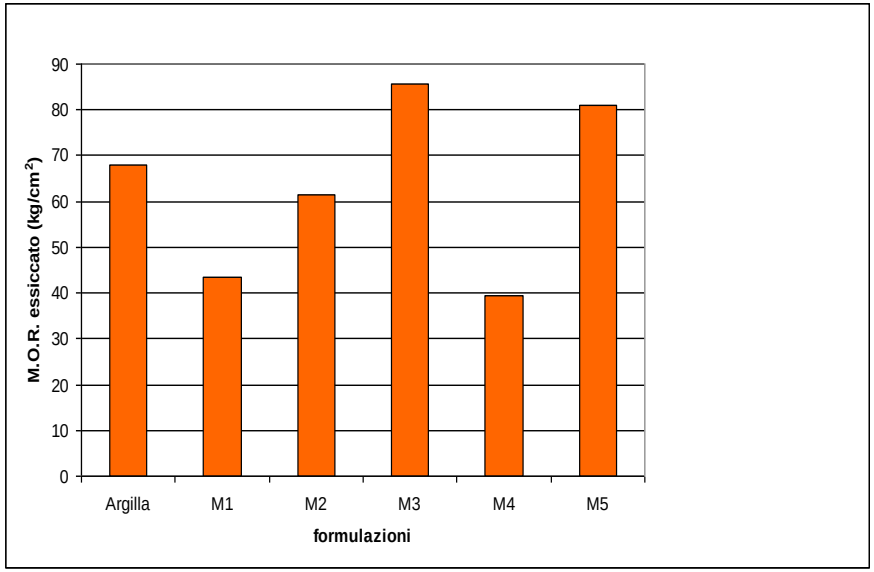
WOODDY BIOMASS	Calculated values (kJ/kg) *	Leterature values (kJ/kg)	Experimental ** values (kJ/kg)
SAWDUST	17,119	17,000-18,000	17,773
GRAPES SEED	15,561	18,000-18,800	19,928
CHERRIES SEED	17,148	17,500-18000	18,075

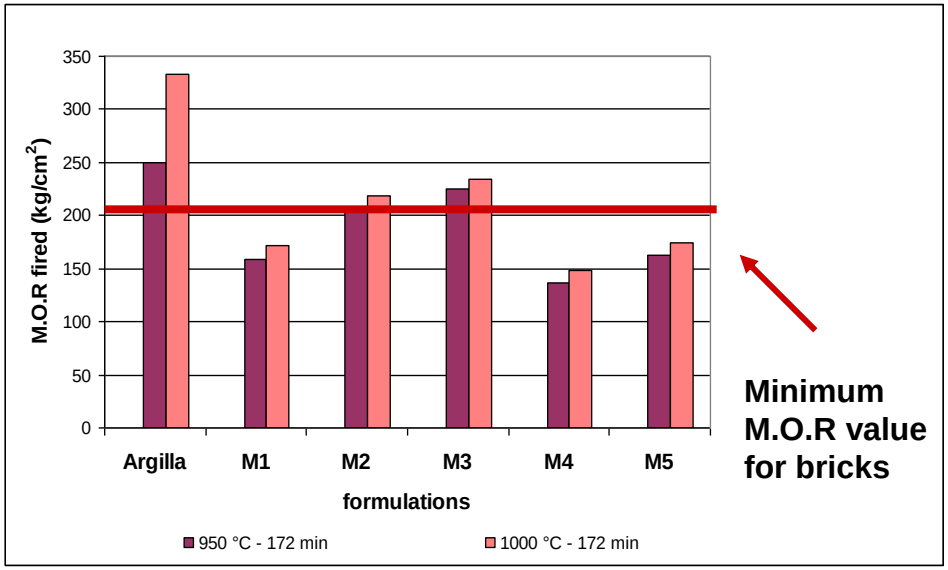
* Average values obtained by 3 stechiometric formules (Chang, Boie, e Dulong), using the C, H, N, S, O , P, percentages, Humidity and ash content from the Elementary analysis in collaboration with University of Urbino (Italy)

** Experimental values obtained by calorimetry in collaboration with researches of Environmental Engineering Dept., Lab. of Toxic and Hazardous Waste Management, Technical University of Crete (2011)

EFFECT OF AGRO/WOODY WASTE ON MECHANICAL PROP. (M.O.R.)

M.O.R. AFTER DRIYING (kg/cm^2) **M.O.R. AFTER FIRING (kg/cm^2)**

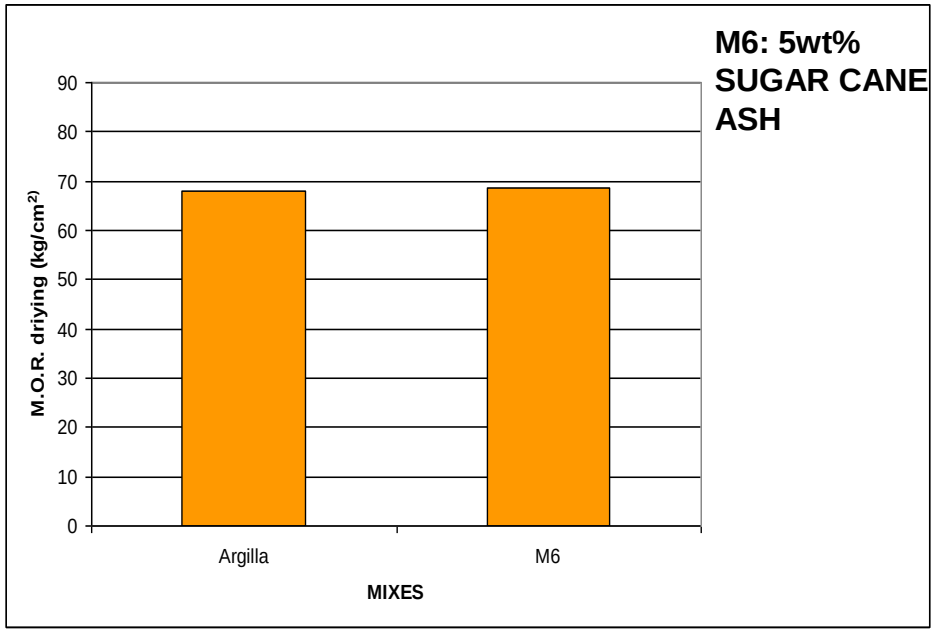




M1: 5wt% SAWDUST M2: 5wt% GRAPES M3: 5wt% CHERRIES M4: 8wt% GRAPES M5: 8wt% CHERRIES

EFFECT OF SUGAR CANE ASH ON MECHANICAL PROPERTIES (M.O.R.)

M.O.R. AFTER DRIYING (kg/cm^2)



M.O.R. AFTER FIRING (kg/cm^2)

