Development of New Ecological Ceramic Tiles by Recycling of Waste Glass and Ceramic Materials

D. Fraga, A. Gyozova, S. Kozhukharov, S. Allepuz, C. Lázaro, V.Trilles, J. Carda

Abstract: *The following research work shows the results of the introduction of waste generated by the ceramic industry, such as the calcined clay from fired porcelain of stoneware and raw biscuit, sludge and cleaning water, as well as waste from other sectors like the recycling glass. In this way, it can be obtained a stoneware porcelain slab, engobe-glaze and satin glaze that contain high percentage of recyclable raw materials.*

Key words: *Ceramic tiles, Environmentally friendly technology, recycling*

INTRODUCTION

According to literature [1-4], during the last decade the use of ecologic products has become an important aspect in the ceramic industry, in order to optimize and reduce the consumption of natural resources. Recycled glass can be obtained from several sources such as flat glass, glass bottle, lamps, television screens, etc. Moreover, its amorphous nature and composition (mainly silicon oxide, calcium oxide and sodium oxide) make it an excellent candidate for application in the ceramic industry as a flux agent and/or frits for glazes and engobes. For that reason, the recycled glass has to possess compositional homogeneity and must be available in large quantities.

The aim of the present work is to study the application of recycled glass and ceramic waste as raw materials in the production of ceramic tiles.

EXPERIMENTAL

The methodology followed in this work consisted in formulate a stoneware porcelain composition using kaolinitic clay (40-50%wt.), feldspar (30-35%wt.), sand (5-10%wt.) and also waste materials (15-20%wt.). Given materials contain glass waste (sodium-calcium nature), calcined clay from fired porcelain of stoneware and raw biscuit.

Therefore, the composition of the glass waste was analyzed by X-Ray Fluorescence (XRF). Also, dimensional and viscosity variation of the sample during thermal cycle were analyzed by thermal microscopy. Finally, several samples were analyzed by Scanning Electron Microscopy (SEM) with microanalysis (EDX). in order to confirm their chemical homogeneity.

On the other hand, a porcelain stoneware composition has been studied by chemical analysis by X-Ray Fluorescence (XRF). Also, vitrification plot was used to observe the paste behavior by linear contraction variation (%) against water absorption (%). Moreover, the ceramic paste formulation was characterized by dilatometric curve.

Finally, engobe-glaze and a satin glaze were developed using glass waste and calcined clay, and glass waste only, respectively.

RESULTS AND DISCUSSION

a) *Recycled glass Characterization*

The compositional homogeneity of the recycled glass was verified by X-ray fluorescence (XRF). Results of the chemical analysis showed a typical sodium-calcium composition as can be observed in detail in Table 1.

Table 1. Chemical analysis of the recycled glass.

Compound	Weight %
SiO_2	73,2
Al_2O_3	0,85
Na_2O	12,0
MgO	3,75
P_2O_5	0,013
SO_3	0,20
K_2O	0,30
CaO	8,87
TiO_2	0,05
Fe_2O_3	0,099

The waste glass behaviour during the thermal treatment (200 ºC < T < 1300 ºC) was analyzed using a Heating Microscope. It is important to notice that the sample reached the sphere form at 936 ºC, followed by the total fusion of the sample at 1116 ºC, as shown in Figure 1. This is an adequate value for its use as raw material.

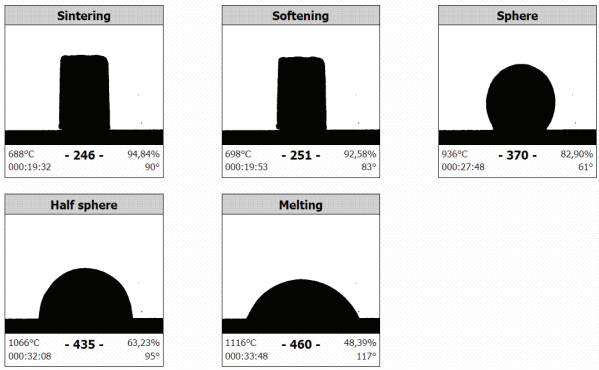


Fig. 1. Thermal behavior of the recycled glass.The sample reached total fusion at 1116ºC.

The morphological and microanalytical characterization of waste glass were performed by Scanning Electron Microscopy with microanalysis (SEM/EDX). The glass was previously grinded below 45μm (Figure 2). Several crystals were analyzed in order to confirm its chemical homogeneity. All observed areas exhibit uniform composition as presented in Table 2.

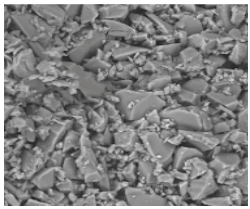


Figure 2. SEM image of grinded waste glass.

Table 2. Microanalysis of waste glass.

Element	Weight %	Atomic %	Compd %	Formula
Na	11.51	10.32	15.52	Na_2O
Mg	2.52	2.14	4.18	MgO
Al	0.55	0.42	1.04	Al_2O_3
Si	33.29	24.43	71.22	SiO_2
Ca	5.75	2.95	8.04	CaO
O	46.38	59.74		

.

b) *Formulation of ecologic ceramic paste*

Once the glass was characterized, and based on the obtained results, a ceramic paste was developed, using the waste along with another standard materials used in the ceramic industry in order to produce the tiles. Up to 20%wt. of waste materials (glass,

calcined clay, etc) was used in the formulation. The composition of given paste is represented in Table 3.

Table 3. Composition of ecologic ceramic paste.

Clays + Kaolin	40-45% weight
Feldspar	30-35% weight
Feldspathic sand	5-10% weight
Wastes (glass, chamotte y raw pot)	15-20% weight

c) Characterization of the ecologic ceramic paste

Chemical analysis of the obtained paste was determined by X-ray fluorescence (XRF). Results of the chemical analysis are observed in Table 4.

Table 4. Chemical analysis of ecologic ceramic paste.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	PPC	SUMA
Weight %	4.77	0.50	19.00	68.45	0.09	1.33	0.88	0.68	0.00	0.69	3.45	99.84

Dilatometric curve show a slight slope at 570ºC corresponding to a phase transition of quartz α→β SiO_2 (Figure 3). It was observed a lineal contraction of 7.56% and a water absortion of 0.28% at T= 1165ºC as is indicated on the vitrification plot (Figure 4).

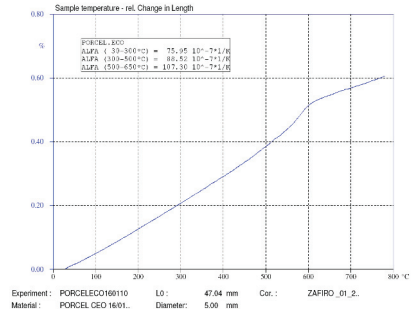


Figure 3. Dilatometric curve for ecologic ceramic paste

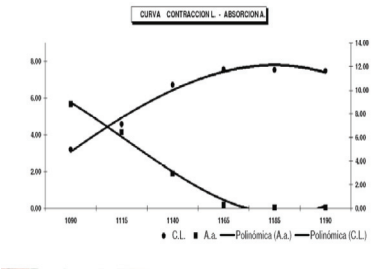


Figure 4. Vitrification plot for ecologic ceramic paste.

d) ***Formulation of engobe glaze and satin glaze***

Finally, two glaze formulations were developed using recycled materials, as shown in Table 5. The first one is an engobe-glaze for stoneware porcelain slabs. It uses 10%wt. of waste glass and 11% of calcined clay. Also, a satin glaze formulation was obtained using 10%wt. of sodium-calcium glass and 5% boronsilicate glass. Both formulations are currently being applied industrially at Cerámicas Plaza, S.A..

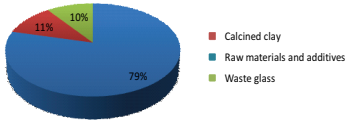
Table 5. Formulation of engobe and satin glaze.

ENGOBE-GLAZE (GCE-001-10-30)	
RAW MATERIAL	Weight %
Waste glass	10
Calcined clay	11
Clay HYPLAST-67	25
Kaolin	13
Zircosil five	7
Quartz	10
Calcium carbonate	10
Feldspar	14
Cmc	0.1
KD-8040 (zschimmer)	0.3

SATIN GLAZE(GCE-001-10-67)	
RAW MATERIAL	Weight %
Waste glass 1	10
Waste glass 2	5
Clay HYPLAST-67	15
Kaolin	10
Zircosil five	8
Quartz	16
Calcium carbonate	21
Feldspar	13
Zinc oxide	2
Cmc	0.2

CONCLUSIONS

- It was developed **NEW ECOLOGICAL TILES** that contains high percentage of recyclable raw materials, with technical characteristics similar to conventional porcelain.
- Engobe-glaze for stoneware porcelain slabs was prepared by the addition of 10% waste glass and 11% calcined clay (% in mass) (Figure 6).
- It was obtained satin glaze from recycled glass with different nature: sodium-calcium glass (Glass waste 1) and a borosilicate (Glass waste 2) (Figure 7).



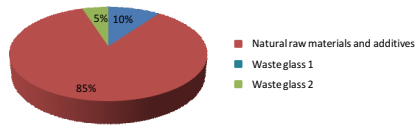


Fig. 6. Ecologic engobe-glaze composition

Fig. 7. Ecologic satin glaze composition

ACKNOWLEDGEMENTS

This work has been achieved through the collaboration of TIERRA ATOMIZADA S.A. and COLORES CERAMICOS S.A.

REFERENCES

[1] "ENCICLOPEDIA CERÁMICA", P.Escribano, J.B. Carda y E. Cordoncillo eds., Vol. I, II y III, Ed. Faenza Editrice Ibérica, Castellón, 2001.

[2] G. Monrós, M. Llusar, M.A. Tena, "La adaptación medioambiental de la industria cerámica" ,Técnica Cerámica, 283, 581-594, (2000).

[3] J. García-Ten, G. Mallol, E. Bou, G. Silva, J. Fernández, A. Molina, J. Romera, "Recycling marble working wastes in manufacturing ceramic products. II Ceramic wall tile manufacture. Ceramic Forum International, DKG 80(10), 30-32, (2003).

[4] J.M. Rebollo, P. Corma, "Modelo para la determinación de aspectos e impactos medioambientales en el sector cerámico", EDICERAM, 1, 19-37, (2000).

About the author:
D. Fraga Ph. D. E-mail: fraga@uji.es
University "Jaume I" Castellon de la Plana (Spain), www.uji.es

Докладът е рецензиран

РУСЕНСКИ УНИВЕРСИТЕТ „АНГЕЛ КЪНЧЕВ”
UNIVERSITY OF RUSE „ANGEL KANCHEV“

Д И П Л О М А

Програмният комитет на
Научната конференция РУ&СУ’11
награждава с КРИСТАЛЕН ПРИЗ
“THE BEST PAPER”
D. FRAGA, A.GYOZOVA, S.KOZHUKHAROV
S.ALLEPUZ, C.LAZARO, V.TRILLES, J.CARDA
автори на доклада
“ Development of New Ecological Ceramic Tiles by Recycling of Waste Glass and Ceramic Materials”

D I P L O M A

The Programme Committee of
the Scientific Conference RU&SU'11
awards the Crystal Prize "THE BEST PAPER"
to D. FRAGA, A.GYOZOVA, S.KOZHUKHAROV
S.ALLEPUZ, C.LAZARO, V.TRILLES, J.CARDA
authors of the paper
“ Development of New Ecological Ceramic Tiles by Recycling of Waste Glass and Ceramic Materials”

РЕКТОР *Проф. д.т.н. Христо Белоев*
RECTOR *Prof. DSc Hristo Beloev*

05.11.2011