

Green stoneware containing waste metals

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Abstract

Green stoneware tiles have been produced by the incorporation of galvanic waste to industrial compositions processed from kaolinitic clay, feldspar, quartz. Some compositions with recycled domestic glass are also prepared. The galvanic waste required a calcination step to eliminate the gas forming species prior its incorporation into industrial processes. The effective absorption of metal from the galvanic waste was attained through the formation of crystalline phases. The presence of chromite type particles in the porcelain matrix acts as “*in situ*” to form pigments. The crystallization process also produces a higher consume of metal cations in the surrounded area of the crystalline pigments. The followed procedure allowed to effectively immobilized up to 20 wt% metal waste in a porcelain stoneware that satisfy both the mechanical and the chemical standards required to massively commercialize such a product.

1. Introduction

The control of the hazardous wastes emissions to biosphere is an important issue to attain the sustainable development. The deposition of galvanic wastes is obviously a potential danger to public health due to the possibility of toxic metal (Cr, Ni, Cu, Zn and Pb) lixiviation¹⁻⁶.

Traditional ceramics, such as bricks, or roof and floor tiles, generally are tolerant for incorporating several kinds of wastes replacing natural raw materials^{6,8}. To attain this regard galvanic waste and domestic recycled glass can be consider as oxides source. Fernandes et al⁶, pointed out the final properties of chromium content porcelain tiles fired at the optimal sintering temperatures are superior (lower water absorption, higher bending strength) comparing to the similar chromium free compositions. However the chemical stability and possible environmental impact of Cr, Ni, Cu, Zn and Pb containing porcelain have not been investigated in detail.

The objective of the present investigation is to study the mechanisms and the chemical stability of the galvanic waste contents ceramics.

2. Experimental Procedure.

2.1 Starting Materials.

Galvanic waste (GW) from a metal electroplating plant with an average grain size $\approx 8 \pm 3 \mu\text{m}$ (São Paulo, Brazil) with composition average: **SiO₂**, 23.75 wt%; **Al₂O₃**, 0.91 wt%; **CaO**, 5.12 wt%; **K₂O**, 0.22 wt%; **Na₂O**, 1.30 wt%; **MgO**, 3.78 wt%; **Fe₂O₃** 1.19 wt%; **MnO**, 0.11 wt%; **Cr₂O₃**, 22.68 wt%; **CuO**, 7.45 wt%; **NiO**, 14.04%; **ZnO**, 5.08wt% and **PbO**, 1.46 wt% and recycled glass from domestic garbage (Santa Olalla e Hijos S.A. Burgos – Spain) with composition average: **SiO₂**, 71.40 wt%; **Al₂O₃**, 2.31 wt%; **CaO**, 10.90 wt%; **K₂O**, 0.96 wt%; **Na₂O**, 12.50 wt%; **MgO**, 1.46 wt% and **Fe₂O₃**, 0.25 wt% were used as raw materials. Industrial quartz, kaolinitic clay and feldspar (Spain) as auxiliary reactants were used.

2.2 Ceramics formulation.

Standard commercial porcelain stoneware tile composition labeled P00 (porcelain only) and G00 (recycled glass added porcelain). After that the batches were prepared using standard industrial quartz, kaolinitic clay, feldspar and recycled glass as raw materials with ratios 10/40/50/0

wt% for P00 chosen as a blank to determine their initial concentration before the experiments. Compositions with 10/40/40/10 wt% for G00 composition.

The porcelain stoneware prepared with 20 wt% of calcinated galvanic waste (GW) were respectively labeled as P20 and G20. The corresponding porcelain calculated chemical compositions are reported in Table I, below.

The different compositions were ball-milled for 20 min in a porcelain jar with alumina balls using water as media and 0.2 wt% of sodium tripolyphosphate as dispersant. Slips were oven dried at 60 °C for 24 h, crushed and sieving at $500\mu\text{m}$. The resulting powders were moistened up to $\approx 6\text{wt}\%$ water content, hand granulated and uniaxially pressed at 45MPa into 8mm \times 3mm tiles. Specimens were fired in a laboratory electrical furnace simulating an industrial fast firing process in an air atmosphere involving basically: an average heating rate of 25.6 °C/min, soaking temperature of 1220 °C hold 0.1 h, and a furnace cooling step. In order to avoid the Cr, Ni, Cu, Zn sublimation, the samples formulation was designed taking into account that the Ceramic sinterization temperature must be $\leq 1300^\circ\text{C}^{9-10}$.

Table I – Porcelain samples calculated chemical composition (%wt)

Composition	P00	P20	G00	G20
SiO ₂	72.13	63,94	71.92	64,27
Al ₂ O ₃	18.24	18,79	19.89	18,85
Fe ₂ O ₃	0.44	0,6	0.42	0,59
TiO ₂	0.45	0,47	0.46	0,49
Na ₂ O	5.64	4,85	5.44	4,69
K ₂ O	1.16	1,17	1.09	1,18
CaO	1.54	3,59	0.51	3,61
MgO	0.31	1,58	0.17	1,58
P ₂ O ₅	0.08	0,35	0.09	0,08
ZnO	-	0,56	-	0,59
MnO	-	0,03	-	0,02
Cr ₂ O ₃	-	1,48	-	1,50
CuO	-	0,71	-	0,71
NiO	-	1,43	-	1,43
PbO	-	0,16	-	0,16
Minor element sum	-	0,28	-	0,23

2.3 Ceramic testing.

Water absorption and bulk density were quantified according to ISO 10543-3. The modulus of rupture was measured with a three points flexural method ISO 10545-4 (Instron Manufactures, Norwood, MA, USA). The hardness was determinate using a Vickers indenter (Buehler Micromet 5103, Buehler Ltd., Lake Bluff, IL, USA). Differential thermal and thermo-gravimetric analyses, DTA–TG, of the samples was carried using a STANTON, STA 781, Stanton Instruments, London, UK, and the measures were performed at a heating rate of 10 °C/min (). The microstructure was investigated by using a field emission scanning electron microscope, FE-SEM, (Hitachi S-4700, Hitachi High Technologies UK, Berckshire, UK). The porosity was evaluated using image analysis. The final porcelains were studied by X-ray diffraction - XRD (Bruker AXS D8 - Advance diffractometer, Madison, WI, USA) and the chemical resistance of the obtained porcelains was evaluated by PCT-B method (ASTM 1285 –02)¹¹.

3. Results and Discussion

The presence of SiO₂ (α -quartz), CaCO₃ (Calcite), and with minor phases Cr₂O₃ (Chromite) and CrO-OH were identified by x-ray diffraction.

The thermal analyses of the galvanic waste (TDA-TGA) indicate a significant mass loss accompanied with a sharp exothermic peak at about 380°C, attributed to SO₃ burned. Mass losses

attributed to different dehydroxylation of the GW precipitates between 500-700°C and between 1000-1200°C caused by calcite (CaCO_3) decomposition was also observed (Figure 1). To improve the porcelain technical characteristics and avoid the porosity of the material, the GW based porcelain (P20 and G20) were prepared by using calcined galvanic waste (1150°C for 30 min) in accordance with the TDA-TG data.

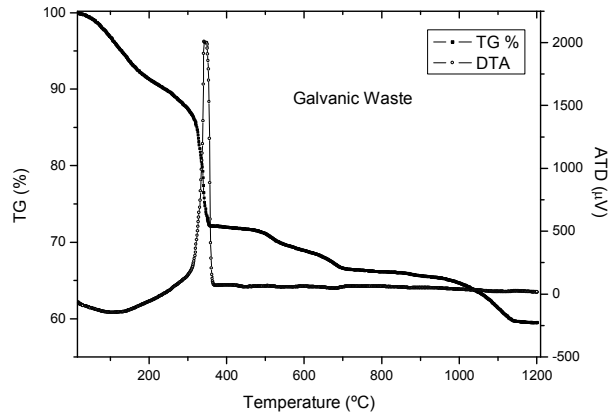


Figure 1 – DTA-TG of the as received Galvanic Waste.

After firing, the base compositions show low porosity and the water absorption values were 0.06 and 0.15 % for the P20 and G20, respectively. The porcelains presented an absence of bubbles and low porosity in comparison with established in the ISO 10543-3 for commercial porcelain.

The XRD patterns corresponding to samples P00, P20, G00 and G20 as can be seen in Figures 2-a and 2-b. It can be observed the presence of α -quartz (SiO_2) and sodium feldspar ($\text{NaAlSi}_3\text{O}_8$) in both compositions P00 and G00. In the GW containing samples it is interesting to point out that the content of sodium feldspar increases in a direct proportion with the GW contents.

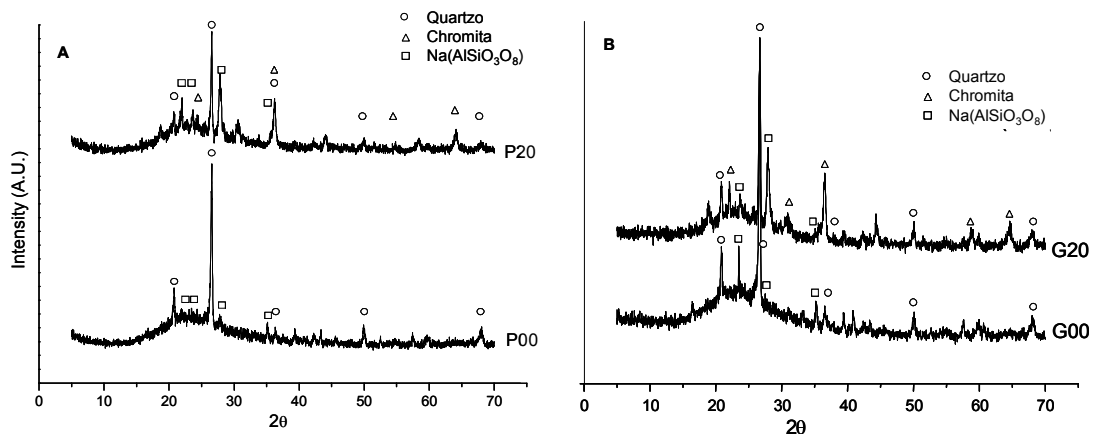


Figure 2 - XRD patterns corresponding to: a) P00, and P20; b) G00, and G20 compositions.

The XRD patterns clearly indicate that:

- 1) The fraction of α -quartz is almost independent on the fraction of galvanic waste.
- 2) During the sintering process at $T > 900^\circ\text{C}$ an increasing fraction of glassy phase was observed. This glassy phase may incorporate the more reactive fraction of the galvanic waste powder until its saturation and subsequent precipitation of chromite. In the figure 3 the micrographs of G20 and P20 porcelains are shown. Noticeable amount of pores was observed in the G20 sample.

As the incorporation of recycled glass increase the formation of the glassy phase occur because of the its low melting point comparing with the porcelain glass matrix.

3) The degree of carbonate displacement is controlled by how significant this difference in melting point is.

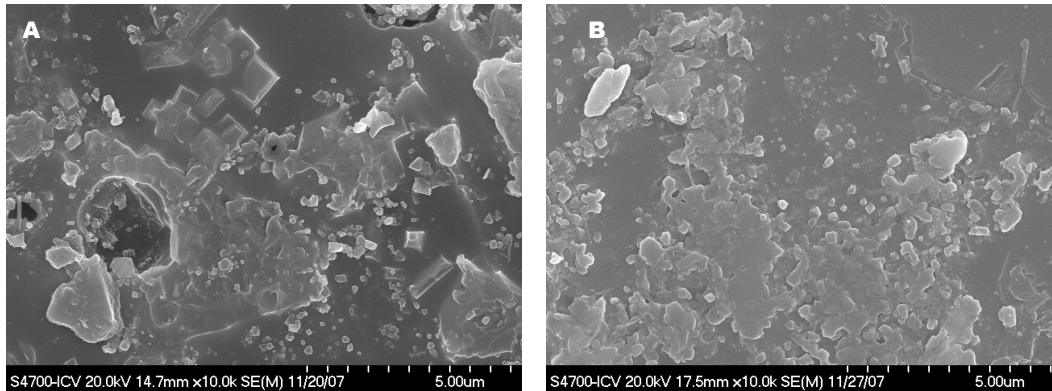


Figure 3 - FE-SEM micrographs of: a) G20 and b) P20 porcelain.

According to the Figures 3a and 3b, the large particles (5-10 μm) may correspond to quartz or feldspar coming from the raw materials. This fact is clearly evidenced from their morphology consisted in rounded partially attacked particles. In addition an important presence of small particles distributed throughout the entire sample was observed. These particles were presented only in porcelains with GW so its with the chromite crystalline phase related. (Figure 2-b).

The micrographs showed relevant differences in the morphology between the G20 and P20 porcelains. It was two kinds of particles for G20 porcelains consisted in well faceted crystals with sizes $\geq 1\mu\text{m}$ that trend to agglomerated and more isolated nanoparticles with sizes from 70 to 300 nm. In the P20 porcelain microstructure, the well faceted crystals were less evident and the agglomerated predominated over nanoparticles presence. However the designed stoneware porcelain showed an important feature, the selected fraction of alumina in the started composition exceeded the solubility of the glassy phase¹²⁻¹³. The alumina solubility in the glassy phase was defined as the ratio $Al_2O_3:(R_2O+RO)$, a ratio between alumina and flux components. R_2O where is Na_2O and K_2O , and RO is CaO and MgO . This ratio was established to be constant over the range of sintering temperatures and applicable to commercial porcelain stoneware compositions¹¹, and it is around 1.19 ± 0.1 . The excess of the alumina crystallizes from the glass as secondary mullite¹³ and the incorporation of glaze to the porcelain composition homogenized the system and inhibit the formation of the secondary mullite¹³. The $Al_2O_3:(R_2O+RO)$, that is a ratio in the G00 and P00 base compositions was 2.76 and 2.11 respectively decreasing 2.33 and 1.88 when 20 wt% of GW was incorporated. In both conditions the alumina solubility is exceeded and as expected the precipitated crystalline phase is observed. The porcelain glass matrix was formed starting from the kaolinitic clay and the feldspar that melted and partially dissolved quartz grains. Then the clay particles fraction is completely dissolved and consequently they were the main source for raw the total alumina content in the glass. So the glassy phase formed is saturated in alumina from the beginning of its formation. EDX analysis of the glassy phase shows no presence of Cr and high content of Al_2O_3 . Thus the GW is dissolved in a glassy matrix that is already saturated in alumina. This fact can limit the dissolution of new metals and contribute to increase the crystallization of the chromite base compositions. At higher temperatures the presence of recycled glass complete the melting of the other raw materials and the low viscosity of the resulting glass improved the homogeneity in the final porcelain¹³.

The chromite crystallization may affect the dissolution process of feldspar as it was noted by the high presence of crystalline feldspar in the XDR pattern of the samples with GW additions. Figure 4 exhibits the micrograph of sodium feldspar agglomerates remained uncompleted. Rest of feldspar typically could appear in stoneware if the started feldspar agglomerates are large enough

but in the present compositions the followed milling procedure ensured that the particle size remained in the same fraction. The correlation between the higher feldspar amounts and higher chromite suggests that the crescent amount of crystalline phase could be the key factor to reach an adequate viscosity of the glassy phase to complete the subsequent dissolution of feldspar

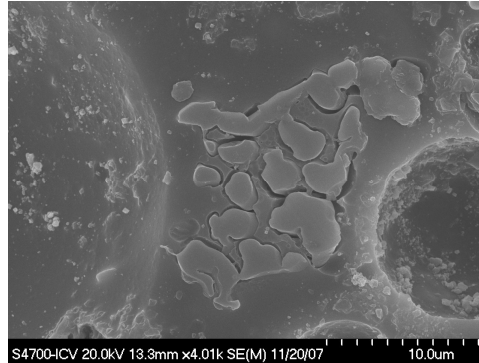


Figure 4 - FE-SEM micrographs P20 porcelain samples illustrating the remainder feldspar

The visual evaluation of the color of the sintered samples showed that the color varies from beige (formulations G00 and P00) to dark brown with increasing of darkness as the incorporated amount of galvanic waste at a given formulation (G20 and P20).

Table II gives the information that not significant hardness alteration with addition of the galvanic waste in the two original porcelain compositions took place. More significant differences were found in the modulus of rupture, in particular in those samples in which the GW was incorporated as received. The incorporation of galvanic waste decreased the modulus of rupture but the obtained values overpasses the 27.5 MPa industrial required standards so the porcelains can be used as tiles accordingly.

Table II – Mechanical properties of stoneware porcelains

Composition	σ_f (MPa)	Hv (GPa)
G00	55±7	6,21 ± 0,17
G20	48±3	5,61 ± 0,64
P00	49±5	4,94 ± 0,27
P20	37±2	5,79 ± 0,24

The chemical resistance and stability under environmental conditions were studied by 7 days PCT-B test (ASTM 1285 –02)¹¹. In Table III the ICP analyses of 7 days PCT-B test are presented. The results clearly indicates that the normalized elemental release of P00, P20, G00 and G20 porcelains are significantly lower compares with the corresponding PCT specifications for Handford LAW borosilicate glass for nuclear waste disposal¹⁴⁻¹⁵ (i.e. 2g/m² for Si, Na and 0.08g/m² for Cr). The Cr, Cu, Ni and Zn content presented values downward the detection limit of the ICP technique. The high resistance to chemical attack was related to the pigment transformation of the GW heavy metals into the glass matrix. This procedure thus allows to effectively immobilizing metal waste that was transformed to crystalline phases that contributed to color the matrix and shown high chemical resistance.

Table III – Normalized elemental release (g/m^2) from galvanic waste (GW) and P00, P20, G00 and G20 glasses after PCT-B test in ultra-pure water at 90°C for 7 days.

	R_{Si}	R_{Ca}	R_{Na}	R_{Cr}	R_{Ni}	R_{Cu}	R_{Zn}
GW	0.154	0.108	0.376	0.144	0.009	0.016	0.021
P00	0.083	0.177	0.388	-	-	-	-
P20	0.090	0.034	0.338	$<1.1 \times 10^{-5}$	$<2.0 \times 10^{-5}$	$<3.8 \times 10^{-5}$	$<5.5 \times 10^{-5}$
G00	0.053	0.153	0.231	-	-	-	-
G20	0.060	0.052	0.231	$<8,5 \times 10^{-5}$	$<1,4 \times 10^{-4}$	$<2.9 \times 10^{-4}$	$<4,4 \times 10^{-4}$

4. Conclusions

Porcelain stoneware industrial compositions have been processed in order to incorporate galvanic waste. The galvanic waste possesses an amount of volatile species that must be eliminated by calcination before its incorporation in the porcelain matrix. Because of the glass matrix of the porcelain was saturated in alumina cations, the incorporation of the galvanic waste produced a rapid crystallization of chromite and the galvanic waste acted as a pigment.

The produced tiles show similar porosity and mechanical properties compare with the commercial samples according with the required standards for these materials. In addition the incorporation of galvanic waste contributes for an aesthetic improvement that valorized the tiles. The higher chemical resistance of the tiles produced were attained on the base of the crystallization of the galvanic residues into the porcelain matrix.

The use of domestic recycled glass are not damaged to stoneware technical characteristics, but its use can to prevent the raw materials decomposition gas, implying in bulk porosity.

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