High chemical stability of stoneware tiles containing waste metals

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Abstract

Stoneware tiles were produced by the incorporation of galvanic waste to industrial compositions that were processed from kaolinitic clay, feldspar, quartz and recycled domestic glass. The galvanic waste required a calcination step to eliminate the gas forming species prior to its incorporation into industrial processes and crystalline phases were formed. After that, the effective incorporation of metals from the galvanic waste was attained through the formation and the refinement of crystalline phases that acted as pigments. During the fast firing the calcined galvanic waste only got partially dissolved in the liquid phase that developed in spinel phase nanocrystals. The followed procedure allowed to effective immobilization of up to 10 wt% of waste with heavy metals in a porcelain stoneware that satisfy both the mechanical and the chemical standards required to massively commercialize such a product.

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1. Introduction

The sustainable development concept concerns a wide range of actions, but without doubt, one of the most important is the control of the hazardous wastes emissions to biosphere. Many of these wastes contain heavy metals, whose presence in the biosphere is considered undesirable because of their deleterious impact on human health.[1–4]

The deposition of huge quantity of galvanic wastes is obviously a potential danger to public health due to the possibility of oxidation of the comprised chromium(III) into toxic chromium(VI). This type of chromium has serious toxic and carcinogenic effects even in very small concentration. Some forms of Cr(VI) are taken into human body through the respiratory system and are known to cause different illnesses as nasal polyps, septum deviation or rhino pharyngitis. The Cr(VI) also can be if ingested with water or food (due to irrigation with polluted water) the cause of acute gastroenteritis and bladder cancer.[5,6]

An industrial process like electroplating deposition, is highly water consuming and, in the end, a huge flow of wastewater has to be treated, leading to the formation of high amounts of sludge, usually named galvanic waste.[7] The production of toxic galvanic waste (Cr, Ni, Zn, Cu, Pb) in developed and underdeveloped countries is higher than 10^6 ton/year.[4,8]

The waste recycling to its original raw material (primary recycling) is only possible in a limited number of cases. The obtaining of a new product from industrial wastes, i.e., secondary recycling is in many cases the best way. Recycling of wastes, generated by the industries, as alternative raw materials has been done successfully in many countries. The reasons that motivate these countries generally are: the exhaustion of the natural resources; the conservation of not renewable resources; improvement of the population health and security; preoccupation with environmental matters; reduction in wastes disposal costs. Recycling of wastes has unambiguously beneficial environmental and economical impact. The building industry is the most indicated technological activity sector to absorb solid wastes, due to the large quantity of raw materials used by the sector as well as by the large volume of final products required. The use of wastes as alternative raw materials in the ceramic industry, which embodies part of the building construction industry, can contribute to diversify the offer of

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raw materials in the production of glass, ceramic bricks and tiles.[1,8–14]

Traditional ceramics, such as bricks, or roof and floor tiles, generally feature high heterogeneity due to the wide range of the composition of natural clays used as raw materials in their fabrication.[10] For these reasons there is tolerance for incorporating several kinds of wastes replacing natural raw materials, even in considerable percentages. This fact attracts further importance since ceramic industry is classified as heavy industry and consumes huge amounts of diminishing mineral resources.[6,15]

In general, the composition of a specific waste product reflects its source, showing various levels of contamination according to the processing/conditioning methods. In terms of chemical composition, the dominant oxide in the great majority of waste materials is silica (SiO_2), closely followed by lime (CaO), and finally by fluxing oxides (alkalines and iron). If a prediction is needed, of the effect and/or the role of the waste material within a given process or product, it can be looked for in the system SiO_2–Al_2O_3–CaO–(Na_2O, K_2O, iron oxide).[7] Fernandes et al.[6] show that the final properties of porcelain tiles with chromium content fired at the optimal sintering temperatures are superior (lower water absorption, higher bending strength) in comparison to the similar chromium free compositions. However the chemical stability and possible environmental impact of Cr, Ni, Cu, Zn and Pb into porcelain have not been investigated in detail yet.

A large amount of work has been carried out to validate the inertization of galvanic waste in a clay based matrix[16–19] or to develop a pigment based material by using chromium waste as precursor.[20–22] However an effective mechanism has not been developed up to now that allows combining the inertization aspects and a commercial product with aesthetical differences keeping the standard industrial process.

The main objective of the present investigation is to study the inertization of toxic transition metals (Cr, Ni, Cu, Zn and Pb) which are always present in the galvanic wastes when they are incorporated into an appropriate ceramic stable matrix. For such reason stoneware tile was chosen as adequate matrix due to their properties. The study focused on the derived technical properties of tiles in order to enable their future commercialization.

2. Experimental procedure

2.1. Starting materials

Galvanic waste from a metal electroplating plant from São Paulo (Brazil) with an average grain size $\approx 8\,\mu m$ previously analyzed[23] was heat treated at $1125\,°C$ for 1 h in order to eliminate the CO_2, H_2O and SO_2 with a mass loss of 44.3 wt%, as recommended in the literature,[17] thus producing the galvanic waste raw material (GW) to be incorporated into the stoneware composition. In order to change the behaviour of the porcelain matrix and to modify the influence of the stoneware glass matrix, a recycled glass from domestic garbage (Santa Olalla e Hijos S.A. Burgos – Spain) was also used as raw materials. The recycled glass fragments were milled and a homogenized white powder was obtained with an average grain size of 12 μm.

Table 1
Starting materials chemical analyses (wt%) (ICP-AES).

Elements	Galvanic waste (calcined 1125 °C)	Recycled glass
SiO_2	23.75	71.40
Al_2O_3	0.91	2.31
CaO	15.12	10.90
K_2O	0.22	0.96
Na_2O	1.30	12.50
MgO	3.78	1.46
Fe_2O_3	1.19	0.25
MnO	0.11	0.01
Cr_2O_3	22.68	0.06
CuO	7.45	–
NiO	14.04	–
ZnO	5.08	0.02
PbO	1.46	–
P_2O_5	–	0.03
TiO_2	–	0.06
Minor elements sum	2.85	0.04

The chemical compositions of the recycled raw materials are shown in Table 1, and were determined by X-ray fluorescence – XRF (Philips MagiX spectrometer). The total amounts of waste metals in the calcined galvanic waste exceed 50 wt%.

2.2. Ceramics formulation

A typical commercial stoneware tile composition labelled P00, and a modified G00 composition with a higher glass former cations content, were prepared using standard industrial quartz, kaolinitic clay, feldspar and recycled glass as raw materials, with ratios 10/40/50/0 wt% for P00 and 10/40/40/10 wt% for G00.

Different stoneware compositions with increasing amount of treated galvanic waste were prepared. 1 wt%, 3 wt%, 5 wt% and 10 wt% of the calcined GW were introduced in P00 composition being labelled as P01, P03, P05, P10, respectively. For G00 composition 10 wt% of the calcined GW were also added, labelled as G10. The chemical compositions of the corresponding porcelains are reported in Table 2.

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 passed through a $500\,\mu m$ sieve. The resulting powders were moistened up to ≈ 6 wt% water content, hand granulated and uniaxially pressed at 45 MPa into $80\,mm \times 30\,mm \times 50\,mm$ tiles. A total of five tiles for each composition were prepared to follow the measurement standards. 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.

2.3. Ceramic testing

Water absorption and bulk density were quantified measuring the dry weight, the water-saturated samples weight and the

Table 2
Chemical composition (wt%) of porcelain samples as formulated and as determined by XRF in fired samples.

Composition	P00 formulated	P10 formulated	P10 by XRF	G00 formulated	G10 formulated	G10 by XRF
SiO_2	72.13	63.94	64.21	71.92	64.27	63.00
Al_2O_3	18.24	18.79	18.52	19.89	18.85	19.00
CaO	1.54	3.59	3.77	0.51	3.61	3.75
K_2O	1.16	1.17	1.23	1.09	1.18	1.20
Na_2O	5.64	4.85	4.78	5.44	4.69	4.53
MgO	0.31	1.58	1.74	0.17	1.58	1.67
Fe_2O_3	0.44	0.6	0.64	0.42	0.59	0.62
MnO	–	0.03	0.05	–	0.02	0.05
Cr_2O_3	–	1.48	1.57	–	1.50	1.48
CuO	–	0.71	0.64	–	0.71	0.63
NiO	–	1.43	1.26	–	1.43	1.20
ZnO	–	0.56	0.38	–	0.59	0.35
PbO	–	0.16	0.14	–	0.16	0.12
P_2O_5	0.08	0.35	0.39	0.09	0.08	0.38
TiO_2	0.45	0.47	0.61	0.46	0.49	0.65
Minor element sum	–	0.28	–	–	0.23	–

weight of the samples suspended in water, according to ISO 10543-3. The modulus of rupture was measured with a three points flexural method (ISO 10545-4) using an Universal Instron machine from Instron Manufactures, Norwood, MA, USA. A hardness Tester using a Vickers indenter (Buehler Micromet 5103, Buehler Ltd., Lake Bluff, IL, USA) was used to determine the micro hardness. The microstructure of the polished, chemical etched (25 vol% HF + 75 vol% water) and gold-coated surfaces was also investigated by using a field emission scanning electron microscope, FE-SEM (Hitachi S-4700, Hitachi High Technologies UK, Berckshire, UK). The final porcelains were studied by X-ray diffraction – XRD (Bruker AXS D8 – Advance diffractometer, Madison, WI, USA). The chemical resistance of the obtained porcelains was evaluated by PCT-B method (ASTM 1285-02).[24] The PCT-B was performed with crushed samples (d_{50} ∼28 μm) immerse in ultra-pure water during 7 days at 90 °C, and the lixiviate composition was determined by Inductively Coupled Plasma (ICP) spectrometry (Varian Inc. Liberty 2000, Palo Alto, CA, USA). The colour of the samples was measured by a Konica Minolta CM-2600d/2500d Spectrophotometer using the specular component included.

3. Results and discussion

The XRD patterns of the as received GW powders (Fig. 1a) shows the presence of crystalline phases such as quartz (SiO_2), calcite ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$). After the heat treatment a dark green powder was obtained, and a phase related to spinel structure appeared ($NiCr_2O_4$) in addition to diopside ($CaMgSi_2O_6$) particles, Fig. 1b. Fig. 2 shows the appearance of the galvanic waste before and after the calcination process. The initial GW presented agglomerates of submicronic rounded particles (Fig. 2a). After the calcination process well faceted particles having 1–2 μm size highly agglomerated appeared (Fig. 2b). In addition, submicron particles also were observed in the calcined GW. The well faceted particles corresponded to the spinel phase that was identified by XRD as $NiCr_2O_4$, which

incorporated chromium as trivalent cation and nickel as divalent cation, the main metals of the GW.

The sintered GW added stoneware tiles presented no bubbles and low porosity just like commercial stoneware. The water absorption was lower than 0.5 wt% in all samples fulfilling the standard requirements,[25] and density slightly increased from 2.4 g/cm^3 for P00 to 2.5 g/cm^3 for P10 due to the incorporation of metals from GW. Chemical compositions of fired samples with incorporated GW were in good agreement with the formulated compositions (Table 2). Small differences were attributed to the fact that raw materials were minerals. These results demonstrated that no volatilization of the heavy metals took place during the firing process.

In Fig. 3a the XRD patterns corresponding to sintered samples P00, P01, P03, P05 and P10 are shown. The presence of a characteristic vitreous phase peak that corresponds to the glass matrix, can be observed at 17–32° 2θ. The vitreous phase probably increased by comparison with the standard formulation when galvanic sludge or glass were added to the compositions due to the high quantity of fluxing agents present in both, glass and GW. The main crystalline phases that appeared in the samples without GW were α-quartz (SiO_2), sodium feldspar ($NaAlSi_3O_8$) and mullite ($3Al_2O_3 \; 2SiO_2$). The galvanic waste incorporation
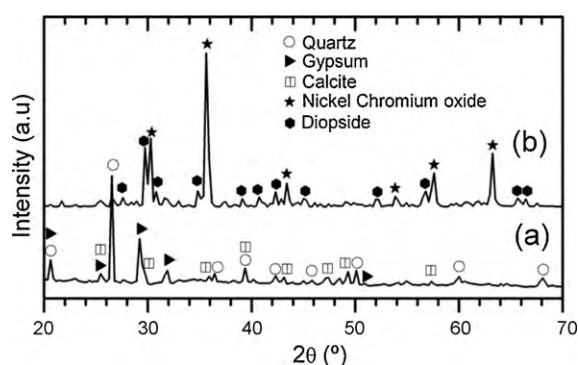

Fig. 1. XRD patterns corresponding to galvanic waste (a) as received and (b) thermally treated.

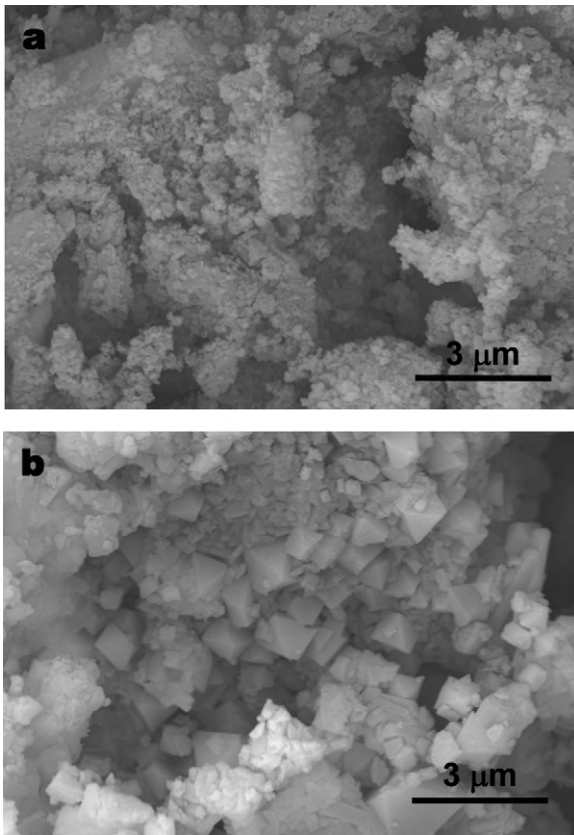Fig. 2. FE-SEM micrographs corresponding to galvanic waste (a) as received and (b) thermally treated.

Fig. 4. XRD patterns corresponding to sintered G00 and G10 composition.

produced a change in the crystallization kinetics of the stoneware based compositions. Increasing addition of GW to the samples is directly translates into a rise of the spinel phase content ($NiCr_2O_4$) (Fig. 3b). Fig. 4 shows the XRD patterns of G00 and G10 samples. The crystalline phases are similar to the phases that appeared in the P samples series. The main difference is the decrease of the quantity of crystalline quartz and albite due to the high quantity of fluxing agents of the added glass.

Fig. 5 shows the FE-SEM micrographs of P10 and G10 samples. The presence of a large amount of pores was more relevant in the P10 sample when it is compared with G10, Fig. 5a and b, respectively. This behav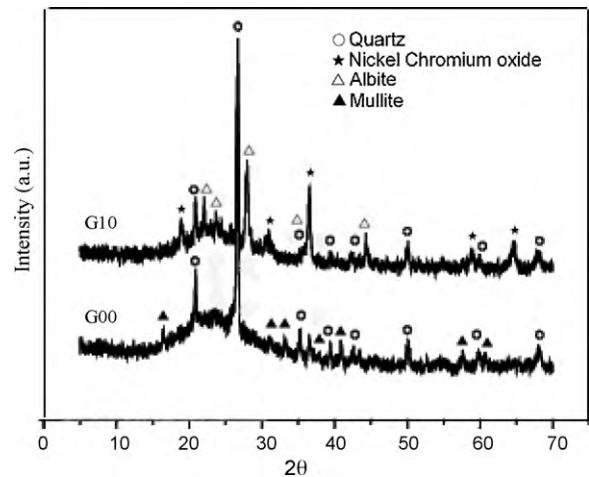iour is related to the incorporation of recycled glass which favoured the formation of the glassy phase because of its low melting point in comparison with the porcelain glass matrix. Typically the recycled glass powder started (not shown) to shrink at ∼680 °C while the porcelain requires temperatures >900 °C. The microstructures of P10 and G10 samples showed the presence of a general glassy matrix in which different crystalline phases were present. Both samples presented large particles of 5–10 μm corresponding to quartz or feldspar that were coming from the raw materials, as it was clearly evidenced from their rounded morphology. In addition, smaller particles distributed in the entire sample can be observed. They were correlated with the spinel crystalline phase due to their well faceted form and because they were present only in stoneware tiles with added GW, as it was confirmed by XRD.

The higher magnification micrographs (Fig. 5c and d) showed relevant differences in the morphology of the spinel phase particles. P10 samples show two kinds of particles characterized by: (i) well faceted crystals with sizes ≥1 μm that appeared both isolated and agglomerated (point A, Fig. 5c), and by (ii) well faceted nanoparticles that also tend to from agglomerates (point B, Fig. 5c and d). The G10 microstructure was similar to P10 but the well faceted crystals were less evident and the agglomerates of nanoparticles corresponding to B-type regions predominated. The agglomerated particles came from the thermally treated GW
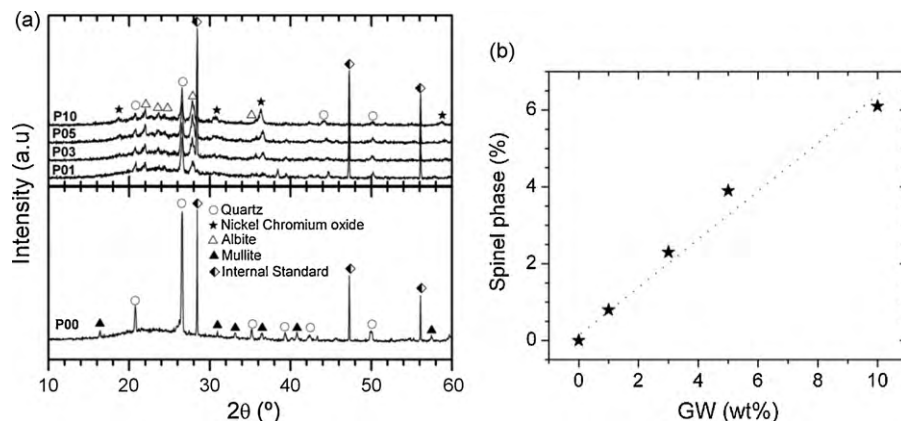

Fig. 3. XRD patterns corresponding to sintered P00, P01, P03, P05 and P10 compositions.
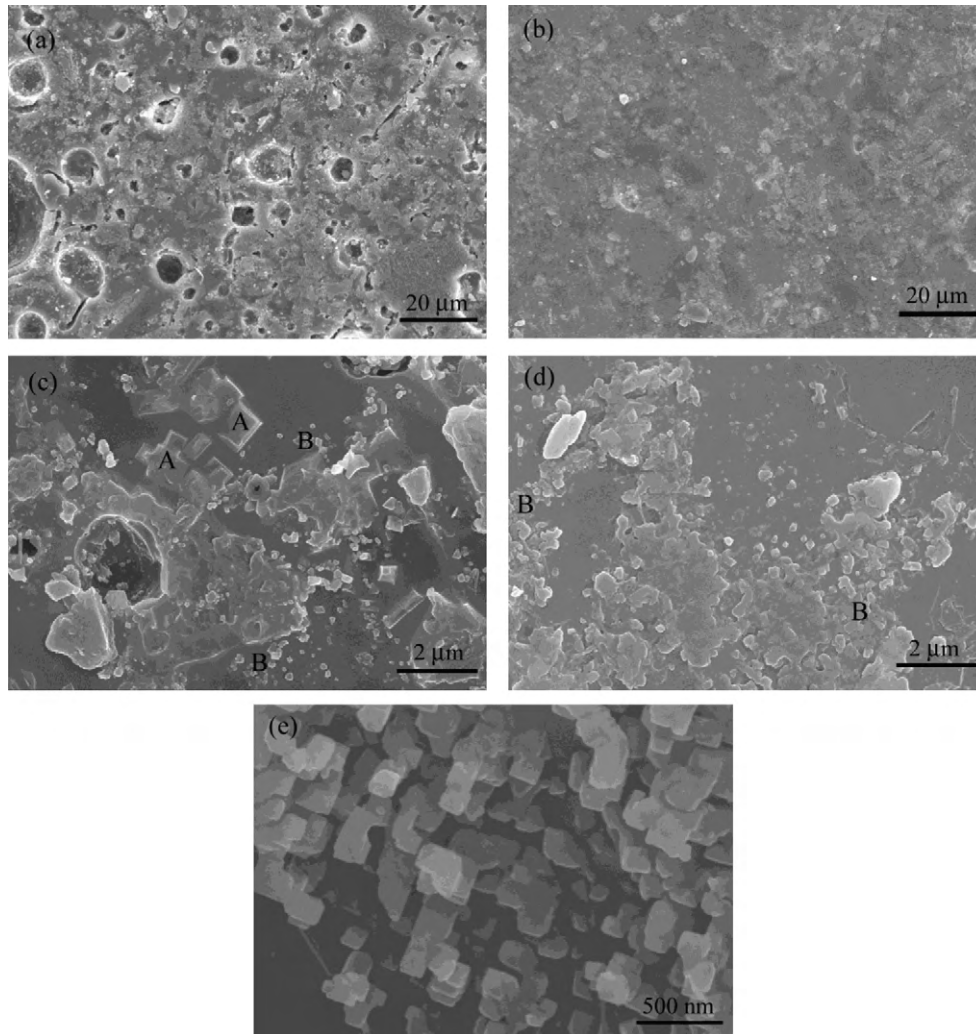
Fig. 5. Microstructure of polished and chemically etched surfaces of the P and G sintered porcelains (a) P10 and (b) G10. Detail of the different crystalline phases of the samples (c) P10 and (d) G10; the A and B regions show two kinds of particles of the spinel phase. (e) Magnification of the well faceted crystals with sizes $\geq 1\,\mu$m in P10 samples.

powders that remained in the microstructure as Fig. 5c shows (point A). Hence, the rearrangements of the agglomerates were partially incomplete. The size of the particles in B-type regions was ranged from 50 to 180 nm, and it was estimated from isolated nanoparticles, Fig. 5e. Their presence could be associated to the secondary spinel type particles which re-crystallized during the liquid phase sintering.

It should be expected that the glass matrix incorporated a limited amount of cations, up to the glass saturation level. However the stoneware compositions were designed to possess an important feature, the selected fraction of aluminium in the initial composition exceeded the solubility of the glassy phase.[26,27] The aluminium solubility in the glassy phase was defined as the ratio between alumina and flux components $Al_2O_3/(R_2O + RO)$. R_2O were identified as Na_2O and K_2O, and RO as CaO and MgO. This ratio was established as 1.19 ± 0.1 and it was constant over the range of sintering temperatures and applicable to commercial stoneware compositions.[26] The aluminium exceeding this solubility value crystallized from the glassy phase as secondary mullite[25] and the incorporation of recycling glass to

the porcelain composition reduced the formation of secondary mullite because reduces the mentioned ratio. In this study, NiO was added to the ratio Al_2O_3:$(R_2O + RO)$ that was 2.76 and 2.11 respectively in the G00 and P00 base compositions. It decreased to 1.44 and 1.36 when 10 wt% of GW was incorporated into P10 and G10. In both cases the ratio slightly exceeded the aluminium solubility and it was expected that mullite precipitated. Kaolinite undergoes various reactions and finally mullite results from kaolinite liberating excess silica,[28] which adds to melt formation in the presence of the feldspar. Consequently, clay and feldspar constituted the main source for the total alumina content in the glass matrix.

The not complete dissolution of feldspar was noted by the high presence of crystalline feldspar in the XDR pattern of the samples with GW additions. Fig. 6 shows a micrograph of how the dissolution of sodium feldspar agglomerates remained uncompleted due to the rearrangement of the particles during liquid phase sintering. Rests of feldspar usually appeared in stoneware when the initial feldspar agglomerates were large enough. In the present compositions the milling procedure
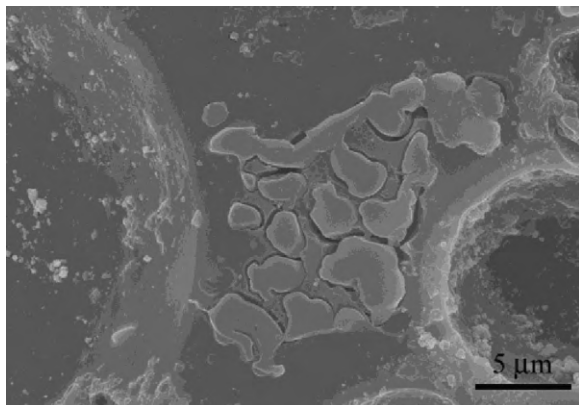
Fig. 6. FE-SEM micrograph of sintered P05 porcelain showing the presence of feldspar agglomerate.

ensured that the particle size remained in the same fraction. As usual, the kinetic process due to the fast firing process is important for stoneware. The firing cycle does not favour equilibrium and not only quartz but also the feldspar and the Ni–Cr spinel that was already present in the calcined GW used in the mixtures only get partially dissolved in the liquid phase that develops in the composition during firing.

The partial substitution of feldspar by glass decreases the viscosity of the liquid phase as it was reported[29] and favours both the dissolution and the rearrangement processes. For this reason feldspar agglomerates were not so evident in G series samples as in P series samples.

The visual evaluation of the colour of the sintered samples showed that the colour changed from beige (formulations G00 and P00) to dark brown, the darkness increasing as the amount of incorporated galvanic waste increased. The colorimetric analyses of the porcelains quantified this observation and showed dependence between the galvanic waste addition and the CIELab coordinates changes, Fig. 7. The incorporation of recycled glass to the basic composition of the porcelain produced a slight whiteness in the final product. It was found that darkning observed
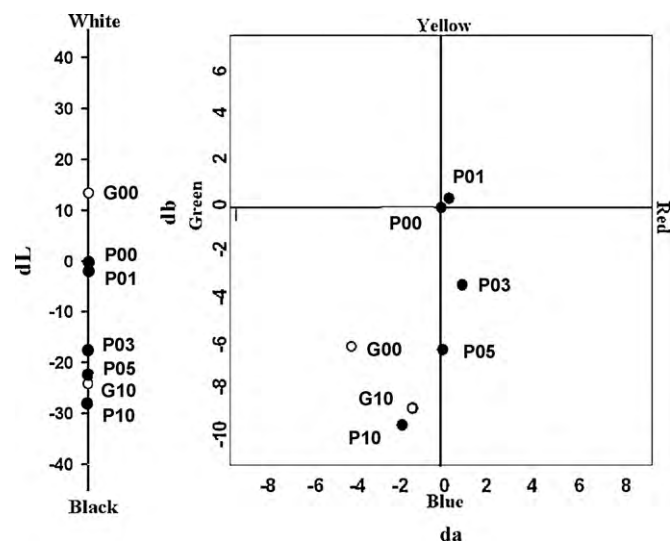
Table 3
Mechanical properties of stoneware porcelains.

Composition	σ_f (MPa)	Hv (GPa)
P00	49 ± 5	4.9 ± 0.3
P10	37 ± 2	5.8 ± 0.2
G00	55 ± 7	6.2 ± 0.2
G10	48 ± 3	5.6 ± 0.6

in the GW added series was independent of the presence of recycling glass. The incorporation of GW produced a marked displacement of the CIELab coordinates towards the blue. It should be noticed that the GW addition dominated the colour and minimized the base colour effect of the porcelain. Similar amount of GW produced a similar colour as resulted for G10 and P10 samples. The pre-calcination of the GW produced a reaction described above which turned out in the formation of the spinel which acts as crystalline pigments into the porcelain body. This fact is particularly relevant and adds to the previous reports on the production of pigments from waste raw materials by using conventional synthesis.[30] It is known that stoneware has higher added value when it is white and clear, because distinct aesthetic effects can then be produced by separate addition of different pigments or opacifiers. In this study it has been noticed that the incorporation of GW not only resulted in a valorization of the residue to produce new pigments useful in other applications, but also demonstrated that the residue could be directly incorporated in stoneware ceramic tiles, hence directly reducing its toxicity.

Table 3 summarizes the mechanical properties of some of the studied compositions. The table shows 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. The incorporation of galvanic waste decreased the modulus of rupture but the obtained values exceeded the 27.0 MPa industrial required standards,[31] so the porcelains can be used as tiles accordingly. The glass addition as fluxing agent, in G series samples, provides homogeneity to the glassy matrix that translates into the reinforcement of the material.[27] This behaviour could be associated to two reasons: (a) the decrease of the porosity as was observed by FE-SEM micrographs; (b) the presence of crystalline phases as spinel type particles which causes stress development in the glassy matrix.

The chemical resistance and stability under environmental conditions were studied by 7 days PCT-B test (ASTM 1285-02).[24] In Table 4 the ICP analyses of 7 days PCT-B test are presented. These results clearly show that the normalized elemental release of P00, P01, P03, P05, P10, G00 and G10 porcelains are significantly lower than the corresponding PCT specifications for Handford LAW borosilicate glass for nuclear waste disposal[32,33] (i.e. 2 g/m² for Si and Na and 0.08 g/m² for Cr). In the case of the Cr, Cu, Ni and Zn, the concentrations were below the lower detection limit of the ICP technique (<0.03 mg/l, <0.04 mg/l, <0.04 mg/l and <0.04 mg/l, respectively). The high resistance to chemical attack was related to the pigment formation of the GW with heavy metals into the glass matrix. The

Fig. 7. CieLab coordinates corresponding to sintered P00, P01, P03, P05, P10, G00 and G10 porcelains.

Table 4
Normalized elemental release (g/m^2) from galvanic waste (GW) and P00, P01, P03, P05, P10, G00 and G10 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	–	–	–	–
P01	0.078	0.086	0.294	$<1.1 \times 10^{-5}$	$<2.0 \times 10^{-5}$	$<3.8 \times 10^{-5}$	$<5.5 \times 10^{-5}$
P03	0.066	0.056	0.253	$<1.1 \times 10^{-5}$	$<2.0 \times 10^{-5}$	$<3.8 \times 10^{-5}$	$<5.5 \times 10^{-5}$
P05	0.081	0.066	0.327	$<1.1 \times 10^{-5}$	$<2.0 \times 10^{-5}$	$<3.8 \times 10^{-5}$	$<5.5 \times 10^{-5}$
P10	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	–	–	–	–
G10	0.060	0.052	0.231	$<8.5 \times 10^{-5}$	$<1.4 \times 10^{-4}$	$<2.9 \times 10^{-4}$	$<4.4 \times 10^{-4}$

spinel synthesis during the thermal treatment of the GW and the re-crystallization in the glass matrix during the stoneware sintering transformed the galvanic waste into crystals which showed chemical resistance. The fast firing process does not allow to the system to achieve the equilibrium conditions; this fact prevents the incorporation of metal cations in the glass and thus most of the GW formed crystal. This procedure allows to effective immobilization of up to 6 wt% of metals from galvanic waste, which represent 10 wt% of the as received GW, in a porcelain matrix. Most of the metal waste was transformed to crystalline phases which contributed to the colour of the matrix and showed high chemical resistance and standard stoneware characteristics, as low porosity and high modulus of rupture.

4. Conclusions

Porcelain stoneware having industrial compositions was processed in order to incorporate galvanic waste. The galvanic waste possesses an amount of gas forming species that must be eliminated by calcination before its incorporation in the stoneware tile. The calcined galvanic waste acted as pigment and the resulting colour coordinates increased linearly with the added GW content and spinel crystals were formed. The pigment remained stable during the sintering step of the stoneware because the fast firing process did not allow the complete dissolution of the cations in the glass. The incorporation of the galvanic waste with the crystallizations produced a rapid growth of the spinel type phase $NiCr_2O_4$.

The produced tiles showed (a) no volatilization of the heavy metal during the sintering step, (b) porosity and mechanical properties similar to those of commercial samples fulfilling the required standards for these materials. The higher chemical resistance of the tiles produced was attributed to the re-crystallization of the galvanic residues into the stoneware tile.

In addition the incorporation of galvanic waste constituted a colour change that makes possible the use of the calcined galvanic sludge as pigment for other applications. Hence this fact constituted an additional advantage to the galvanic waste, apart from its immobilization.

Acknowledgments

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