



Vitrification: An alternative to minimize environmental impact caused by leather industry wastes

T. Basegio*, A.P. Beck Leão, A.M. Bernardes, C.P. Bergmann

PPGEM - Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e de Materiais, Escola de Engenharia, Universidade Federal do Rio Grande do Sul, LACER - Laboratório de Materiais Cerâmicos, Av. Osvaldo Aranha, 99/705, 90035-190 Porto Alegre-RS, Brazil

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ABSTRACT

The main purpose of this work was the investigation of the immobilization of chromium ion present in the ash from the incineration of chromium-tanned leather shavings (ACS) by means of vitrified ceramic bodies. To achieve the immobilization samples were initially produced adding soda-lime glass to ACS. After that, new formulations were produced with the addition of pure oxides, TiO₂ and MgO, to the soda-lime glass and ACS sample. These samples were conformed by pressing and fired in an electrical furnace, at temperatures of 750, 800, 950 and 1000 °C.

The ceramic bodies were evaluated with respect to their physical properties and mineralogical composition by X-ray diffraction and energy dispersive spectroscopy (EDS) mapping. The chromium immobilization was characterized by leaching tests according to Brazilian Regulations (NBR 10005). The results confirmed the immobilization of the chromium ion within the allowed limits of Brazilian Regulations, NBR 10004 (5 mg/L), with the use of glass and vitrification/densification agents such as titanium and magnesium oxides.

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1. Introduction

The industrial development in the last two centuries has also led to serious environmental problems. The preoccupation and concern for the environment resulted in the adoption of systematic treatment processes for solid, liquid and gaseous waste during industrial production, in spite of the fact that the preservation of the environment and ecology are sometimes still considered as additional production costs and expenditure.

Undoubtedly, at present there is a general awareness related to the environment and inspection, and law enforcement by environmental protection agencies has become wide spread worldwide. The exportation of pollution is no longer permitted by means of environmentally unsafe technology or by the exportation of ecologically aggressive products. Motivated by such thoughts and vision, the industry now seeks new routes to control and reduce environmentally unsafe procedures by developing new appropriate technology aimed to eliminate/or treat industrial wastes in order to minimize risks to mankind and the environment.

The leather industry is inserted into this context. The major leather production centers in the world are found in Mexico, Brazil, Japan, South Korea, China, India and Pakistan. Korea, Japan

and Italy import hides from countries which have a large meat production industry, that is, the United States, Australia, and the European countries, whereas the South American countries, for example, Argentina and Brazil, process their own hides [1]. The leather industry is prevalent in Brazil, especially in the South, in the State Rio Grande do Sul, where more than 50% of Brazilian leather is produced [1].

According to the European Commission (EC) the quantities of solid waste produced by tanneries depend on the type of leather processed, the source of hides and skins, and the techniques applied [2]. On an average, at the end of the process, about 20% of the weight of the raw hides is (grain side) leather [2]. On the other hand, in Rio Grande do Sul, approximately 40% of the initial raw material is transformed into solid and liquid wastes [3].

In the tanning industry, raw skin is transformed into leather by means of a series of chemical and mechanical operations [4,5]. Chromium salts (in particular, chromium sulfate) are the most widely used tanning substances today. Hides that have been tanned with chromium salts have a good mechanical resistance, an extraordinary dyeing suitability and a better hydrothermal resistance in comparison with hides treated with plant substances. Chromium salts also have a high rate of penetration into the interfibrillar spaces of the skin, what represents a saving in terms of production time and a better control of the process [6].

In Brazil, approximately 90% of the leather industry uses chromium in hide processing, resulting in hazardous chromium

* Corresponding author. Tel.: +55 51 3308 3637; fax: +55 51 3308 3405.
E-mail address: basegio@ufrgs.br (T. Basegio).

wastes. The American [7] and the Brazilian [8] regulations consider that chromium and chromium compounds are hazardous constituents in waste materials. The German [9] regulations consider the wastes resulting from the leather and hide processing (group 14) to be hazardous. On the other hand, the European Commission (EC) recently rejected a call by some member states of the European Union (EU) to include tannery wastes containing chromium in the European Hazardous Waste List on the basis that the wastes did not possess the characteristics necessary for classification as a hazardous waste, except degreasing waste containing organic solvents without a liquid phase [2]. The wastes listing in the European Waste Catalogue [2] under group 04 01, are mainly from the leather and fur industry.

Disposal routes for trimmings, fleshings, splits and shavings differ from tannery to tannery, and depend on the available recycling facilities and the quantity of waste generated. Furthermore, economic feasibility of recycling depends on the demand for the by-products and the cost/revenue from recycling compared to disposal routes such as landfill. For example, in the United Kingdom, a large proportion of tannery waste is landfilled because tanneries are dispersed across the country and, in comparison to landfilling, communal waste treatment plants would not be economic. The landfill cost of wastes in the United Kingdom is significantly lower than other European countries due to the wide availability of landfills. Landfilling of raw wastes is not allowed in Germany [2]. In Italy, it is economically feasible to establish communal waste treatment plants as tanneries are situated together in large numbers (pools) [2]. In Brazil, such wastes are disposed off in controlled and semi-controlled industrial wastes landfills, maintained by the tanneries themselves [3].

Chromium-tanned leather sawdust, especially from the shaving operation, is considered the most problematic waste considering the great amount generated (4–8 kg/leather) [3].

Since tanned hides are too thick for most purposes, they are split using a machine similar to a horizontal band saw. After splitting, the thickness of the hides must be uniform all over the hide. This is achieved with a shaving machine used in the process line. The helical shaped cutting blades level the overall thickness to meet the exact specifications and open the fiber structure, in order to improve the response to subsequent chemical processing. This operation is called shaving, which results in the removal of small pieces of leather with a consistency similar to very coarse sawdust. In the Federal State Rio Grande do Sul, it is estimated that each hide generates an average of 4 kg of shavings [10]. Since each tannery industry processes 1500 hides every day, the daily generation of shavings is about 6 tons [11], which must be disposed off.

In this context, considering the nature of this waste and the big amount that is generated, the need for alternatives to its disposal and/or application becomes significant. Studies to minimize the amount of tannery waste, their treatment and possible exploitation of waste products are very important.

Considering the great volume of shavings generated, the direct use is not always possible. Therefore, to avoid the high cost of dumping, shavings can be processed to recover chromium, or thermally treated to reduce the volume to be disposed off. The issue associated with each one of these processes is the problems that they generate. One problem observed by tanners during the recycling of chromium by dissolution from wastes is the poor quality of chromium as Cr_2O_3 due to the presence of organic lipolytic components, metals and other impurities [6]. The thermal treatment of wastes involves incineration, gasification and pyrolysis as a means of disposal, while also recovering energy from waste [8]. Fluidized bed combustion, when optimized and controlled, can be an alternative for treatment and recycling of this kind of waste, as it reduces about 90–95% of the waste amount [3]. The chromium-rich ash gen-

erated in this process can be used as a raw material by different industrial segments [3].

Ceramic and glass technologies are considered to be the most versatile for rendering hazardous waste inert, as they destroy organic matter, immobilize regulated heavy metals in a stable matrix and are able to convert complex chemical compositions into useful materials with a potential for market exploitation [12].

According to Bernstein et al. [13], vitrification technology is the solution of choice to the problem of hazardous waste disposal containing substantial amounts of heavy metal and/or organic pollutants. This can be accomplished directly if the waste composition is suitable for vitrification; otherwise the batch composition can be adjusted using cheap raw materials, such as glass cullet as composition correctors [13]. Vitrification technology permits the recovery or reuse of vitrified material, because the toxic substances are inertized due to the destruction of the organic portion during the process and to the immobilization of the inorganic portion that may be chemically bonded to the highly durable gas network [13].

The positive aspects of this inertization technology using vitrification, are process flexibility (various types of wastes such as sediment and fly ashes can sometimes be treated without preliminary preparation); volume reduction (caused by mass fusion/vitrification); and the process cost that can be lower than their landfill disposal. In addition to this, vitrification is also attractive from an ecological point of view, eliminating landfills and at the same time producing glass that can be reused, giving aggregated value to the wastes.

The generic process to obtain ceramic materials aiming for the immobilization of wastes in vitrified structures (or structures with high amount of vitreous phase) is based on the incorporation of the wastes in masses rich in silica and/or fluxes. Glasses and crystalline silicates lexiviate very slowly under the action of water; therefore, the obtained materials are generally considered to be safe regarding final disposal and do not require secondary contention [3].

Barbieri et al. [14] have studied the use of alkaline and alkaline-earth silicate glasses and glass ceramics for the immobilization of municipal and industrial wastes containing heavy metals. The properties that a glass should exhibit, such as good melting behavior, homogeneity, durability, among others, are closely related not only to chemical composition but also to the kind and amount of raw materials used during the melting process.

By the vitrification technique it is possible to obtain monolithic glasses, which, by controlled thermal treatments, can be transformed into glass-ceramics, particularly wollastonite ($\text{CaO}\cdot\text{SiO}_2$), diopside ($\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$), anorthite ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) and iron oxides (Fe_2O_3 , Fe_3O_4). They could be used as coating materials with high chemical and mechanical resistance for building or thermo-mechanical applications [15].

Romero et al. [16], developed a new glass-ceramic by means of controlled vitrification of inorganic wastes from urban incineration. The major components of the raw material, which was from a Spanish domestic incinerator, were CaO , SiO_2 and Al_2O_3 . Nucleating agents such as TiO_2 , P_2O_5 and Fe_2O_3 were also present in reasonable amounts. They found that a relatively stable glass with a suitable viscosity could be obtained by mixing 65 wt.% of raw material with 35 wt.% glass cullet. The heat treatment resulted in a glass ceramic containing a number of crystalline phases, the most stable being clinoenstatite. The microstructure contained both fiber-like and dendritic crystals. The mechanical properties were acceptable for applications such as tiles for the building industry.

Pelino et al. [17], have studied the vitrification and chemical durability of glasses containing industrial wastes such as electric arc furnace dusts, zinc-hydrometallurgy wastes, drainage mud and granite mud. Batch compositions were prepared by mixing the wastes with glass, cullet and sand to force the final glass-forming

region of the $\text{SiO}_2\text{--Fe}_2\text{O}_3$ (CaO , MgO) system. Heavy metals such as Cr, Pb, Zn, Cu and Cd were immobilized and leaching tests confirmed the chemical stability.

Ferraris et al. [18], investigated the production glass–ceramic bodies from the bottom ashes of municipal solid waste incinerators that were subsequently used for tile production. Two different mixtures were used for tile production: (a) glass from bottom ashes plus corundum-based waste from aluminum foundry and (b) glass from bottom ashes plus kaolin-based waste from the kaolin ore extraction process. The sintered materials were found to be appropriate for building applications such as tiles, bricks, and so on. They exhibited bending strengths up to about 60 MPa and Young modulus of up to about 53 Gpa.

The vitrification of hazardous wastes is consolidating as an environment-compatible stabilization process because of the high chemical resistance of the vitreous products in environmental conditions [19].

The immobilization of ACS (ash from incineration of chromium-tanned leather shavings), by the incorporation in glasses or ceramics has a special attraction. Both glass and ceramics technologies are considered to be potentially interesting in the immobilization of hazardous wastes, since they are able to retain heavy metals in a stable matrix with a significant reduction of volume and convert complex chemical compositions into usable materials in the market.

However, the main concern in the use of a waste as secondary raw material in the formulation of a ceramic mass is its immobilization inside the ceramic body after transformations occurred during the ceramic process. The transference of the contaminants present inside the ceramic body to the environment depends on their ability to be lixiviated by water.

An ideal immobilization process turns the hazardous constituents into chemically nonreactive or stable compounds, in such a way that the waste can be safely reused or disposed off. To be totally effective, the treatment process must produce a final product with good dimensional stability, weather and mechanical resistance, and environment compatibility [20].

The efficiency of a treatment is usually evaluated by means of lixiviation tests. These tests measure the ability of a stabilized waste to release immobilized contaminants during the solidification–stabilization process. This is based on the comparison between a previously established standard and the lixiviate obtained from the exposition of the waste to a lixiviate agent.

The main purpose of this work was to investigate the immobilization of the chromium ion present in ash from incineration of chromium-tanned leather shavings (ACS) by means of vitrified ceramic bodies. This provides a solution for the hazardous solid wastes generated by the leather industry and minimizes the environmental impact caused by these industrial wastes.

2. Experimental procedures

2.1. Raw materials

The raw materials used in this work were: ash from the incineration of chromium-tanned leather shavings (ACS); soda-lime glass and analytical reagent grade oxides (TiO_2 and MgO).

The ash was obtained experimentally by the incineration of chromium-tanned leather shavings (ACS) using fluid bed combustion at 800°C [21]. The raw material was supplied by a leather factory from Rio Grande do Sul. The ACS was characterized in terms of its chemical, thermal and granulometric properties.

Table 1 shows the results of chemical analysis obtained for ACS, using ICP, by Activation Laboratories Ltd., Canada. The total amount of chromium oxide was 29.4% by weight. Analysis done by GREEN-

Table 1

Chemical analysis of ash obtained by the incineration of chromium tanned leather shavings (ACS).

Elements	Wt.%
Cr	29.4
Na	8.0
Al	1.5
Si	1.8
Fe	1.9
Ca	2.4
Ti	0.04
K	0.33
P	0.30
Mn	0.07
Mg	19.0
Loss of mass by heat	17.0

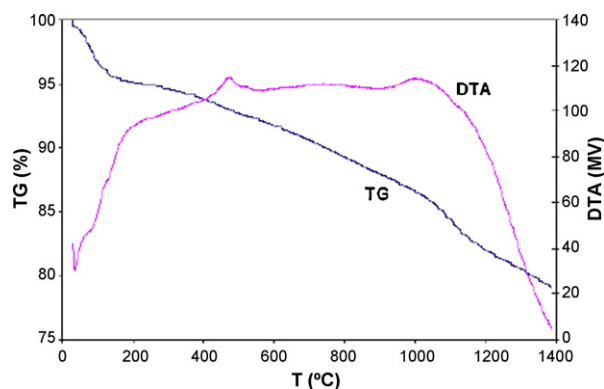


Fig. 1. Thermal analysis and gravimetric analysis (DTA/TG) of ash from the incineration of chromium tanned leather shavings (ACS).

LAB, Porto Alegre, RS, Brazil, showed that only 2.5% of the chromium was hexavalent. Fig. 1 shows the results of differential thermal analysis and gravimetric analysis (DTA/TG) obtained for ACS with a Harrop ST-736 thermobalance using a heating rate of 80 K/h and a maximum temperature of 1400°C .

The ACS sample exhibited a mass loss of about 20%. The exothermic peak around 500°C is probably due to the formation of calcium sulfate, anhydrite [22].

Granulometric analysis, obtained using a Cillas, Model-1180 equipment, indicated an average size of $7.94\ \mu\text{m}$ for the particles and values of D_{10} ($0.69\ \mu\text{m}$), D_{50} ($5.47\ \mu\text{m}$) and D_{90} ($19.23\ \mu\text{m}$).

The soda-lime glass used for the formation of the vitreous phase during the firing of the ceramic mass was obtained by dry grinding in a ball mill for 24 h. It was prepared from commercial glass used for bottles. Fire loss for the soda-lime glass was 0.035%. Table 2 illustrates the results obtained for the chemical analysis of the glass using X-ray fluorescence. Granulometric distribution obtained by

Table 2

Chemical composition of the soda-lime glass.

Oxide	Wt.%
Fe_2O_3	0.17
MnO	0.038
TiO_2	0.062
CaO	12.38
K_2O	0.92
P_2O_5	0.063
SiO_2	72.00
Al_2O_3	2.03
MgO	0.38
Na_2O	11.97

*Shimadzu XRF-1800 semi-quantitative analysis.

Table 3
Granulometric analysis of the oxides used.

Oxide	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	D_{avg} (μm)
Cr_2O_3	0.16	0.99	2.76	1.36
MgO	1.51	4.32	7.68	4.5
TiO_2	0.13	0.33	0.64	0.37

Table 4
Formulations for the vitreous ceramic bodies containing the ACS, glass, titanium oxide and magnesium oxide (weight percent).

Formulation	Glass powder (%)	ACS (%)	Oxide used (%)
100A	–	100	–
5T35G	35	60	5TiO ₂
5T65G	65	30	5TiO ₂
5T75G	75	20	5TiO ₂
5T85G	85	10	5TiO ₂
5Mg85G	85	10	5MgO
10Mg80G	80	10	10MgO

laser diffraction shows an average diameter of 28.50 μm and values of $D_{10} = 2.38 \mu\text{m}$, $D_{50} = 20.24 \mu\text{m}$ and $D_{90} = 68.46 \mu\text{m}$.

The oxides used as additives were of pure analytical reagent grade. The choice of MgO was based on their presence in the ash (ACS). On the other hand, TiO_2 , although present in small quantities in the ash, was chosen because of its characteristic fusion properties [23]. Pure chromium oxide (Cr_2O_3) was also used in the formulation of soda-lime glass mainly for comparison purposes. Table 3 shows the results obtained for granulometric analysis of the oxide employed using laser diffraction.

2.2. Formulation of the ceramic specimens

The glass and the ashes were sieved (no. 80 sieve—180 μm), homogenized under dry conditions for 15 min in a high-energy mill, using a proportion of 2:1 for the mass of the sample and the homogenizing balls.

First, formulations containing only ACS were produced (ash from the incineration of chromium-tanned leather shavings) and soda-lime glass. The soda-lime glass was added to the ACS in amounts of 40, 70, 80 and 90 wt.%.

Second, specimens were produced with TiO_2 and MgO additions, as shown in Table 4. The criterion used to define the formulations was the chemical composition of ACS, except for TiO_2 , which was chosen because it is an excellent flux.

The ceramic masses were humidified with an aqueous solution containing 10 wt.% polyvinyl alcohol (PVA) as a plasticizer agent. The ceramic bodies were molded into 20 mm \times 60 mm bars using a hydraulic press (pressure 20 MPa). After formation, the specimens were dried at room temperature for 24 h and subsequently in an oven at 110 °C for an additional 24 h in order to remove the humidity, if any. The samples were then fired at 750, 800, 950 and

1000 °C with a heating rate of 80 K/h and held at this temperature for 2 h. The firing conditions used were determined on the basis of pretests aiming to optimize firing time, densification and comparison of the different formulations with respect to chromium immobilization/mobilization in the ceramic bodies.

2.3. Characterization of the materials obtained

2.3.1. Immobilization/mobilization of chromium

The degree of immobilization of chromium in the vitreous ceramic bodies was evaluated by leaching tests. Also, the evaluation of gaseous emissions during firing of ceramic bodies was made. The aim of this evaluation was to verify if any chromium loss could occur by gaseous emission, in such a way that it could interfere in the immobilization evaluation by lixiviation tests.

The leaching test was performed according to the Brazilian technical standard test NBR 10.005 [24] which is similar to the American Extraction Procedure Toxicity Test [25]. This procedure uses demineralized water as an extractor fluid. The amount of water added was 16 times the amount of sample. In this study vitreous ceramic body samples, pressed while still green and weighing 100 g were used. They were crushed to a particle size of less than 9.5 mm subsequently dried in an oven at 110 °C for 24 h and fired under the conditions described earlier. The pH of the water was adjusted to 5.0 using acetic acid. The leaching test had a duration of 24 h, under stirring after which the solid and the liquid were separated by filtration. The lixivate was chemically analysed and the results were compared with the maximum values cited in the Brazilian wastes specification NBR10.004 [26]. According to this procedure, wastes are classified on a scale ranging between hazardous and non-inert.

Evaluation of gaseous emissions, generated during material firing, was performed with the aid of the apparatus shown schematically in Fig. 2 [3]. Specimens subjected to the firing cycle were placed in a quartz reactor inside an electrical oven. This reactor has an air intake (air from the atmosphere is blown over the specimens) and an air outlet (air from the burning atmosphere is collected under vacuum, with the aid of a Teflon diaphragm pump). The collected air was washed in a sequence of three gas washing bottles (500 ml each), which were immersed in an ice bath, in order to increase the solubility of gases in water. The first two bottles were filled with deionized water to ensure the caption of emissions. The third bottle (also called dry bottle) was empty in order to help process visualization, retain any condensation and avoid humidity reaching the vacuum pump. Air collection occurred during the whole process. Washing water was collected and the concentration of the elements present in the samples was determined by means of atomic absorption.

2.3.2. Physical and microstructure characterization

The ceramic specimens were characterized with respect to water absorption and linear shrinkage. Water absorption was

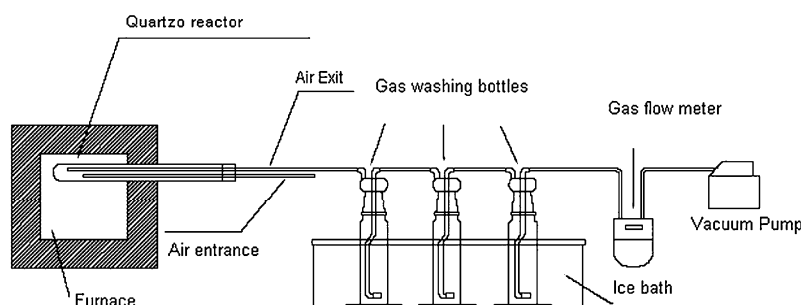


Fig. 2. Apparatus used to evaluate gaseous emissions generated during firing process.

measured by the Archimedes method, in accordance with ASTM C 373/94 [27], and the linear shrinkage was determined by the difference in the length of the test bar before and after firing, according to the ASTM-C326-03 [28].

The ceramic bodies were also sent for mineralogical and microstructural analyses. The mineralogical analysis of ACS and ceramic bodies was carried out by X-rays diffraction in a PHILIPS equipment model X-PERT MPD. This diffractometer uses an X-ray tube with Cu target and was operated at 40 kV and 40 mA in all measurements made in this work. A graphite monochromator was attached to the secondary optical system.

Microstructural analysis of the samples was made by the evaluation of present phases. Both optical microscopy (OM) and scanning electron microscopy (SEM) were used. The OM was an OLYMPUS BX51M, with a digital camera attached to it, while the used SEM was a JEOL JSM-5800 from the UFRGS Microscopy Center. An EDS microprobe, attached to the SEM, was used to punctual chemical analysis and mapping of chemical elements of interest in the ceramic body. Samples for both optical and electron microscopy were prepared by conventional grinding and polishing steps. Polishing was made with a suspension of alumina in water or diamond paste. A thin layer of carbon was sputtered on the surface of the samples, in order to obtain good electrical conductivity for SEM analysis.

3. Results and discussion

First, ceramic bodies with different additions of glass to ACS were obtained, as discussed earlier. From the lixiviation tests, it was possible to verify that glass additions to ACS increased total chromium lixiviation. The higher the glass addition, the higher the total chromium lixiviation, and it decreased for increasing firing temperatures. One explanation to this fact is related to the phases formed during formulations firing, and the ability of these phases to immobilize chromium in the ceramic body during the lixiviation process.

The presence of phases such as sodium chromate and/or dichromate were detected by means of X-ray diffraction for all ceramic bodies produced with glass additions to ACS. Thus, the increase in lixiviable phases, such as sodium chromates, from reactions of sodium, sodium–calcium glass and chromium from ACS would explain the increase in lixiviation for increasing content of glass in the ceramic bodies.

Weyl [23] substituted increasing amounts of CaO by Cr_2O_3 in different types of glass and verified that lithium glasses are better solvents for chromium oxide than sodium–calcium glasses (kind of glass used in this work). This solubility decreases with decreasing firing temperatures, causing a segregation from the chromium oxide vitreous structure to occur, forming thin plates of emerald color.

Assuming that the glass used in this work is not the most suitable one to immobilize chromium within the ceramic body structure, other immobilization agents were added to the formulations with ash and glass such as TiO_2 and MgO , in order to get deeper into this issue. Formulations with additions of these agents were prepared as follows: 10%, 20%, 30%, and 60% of ACS and 5% of TiO_2 and sodium–calcium glass: balance. The graph in Fig. 3 shows the chromium-corrected concentration in the lixiviation of those ceramic bodies as a function of firing temperature. In the same graph, data for formulation at 100°C are also plotted.

The chromium leaching from ceramic bodies produced with the addition of 5% of titanium and glass decreased from the firing temperature of 950°C , with a minimal chromium concentration on the leachate to the samples fired at the temperature of 1000°C (Fig. 3).

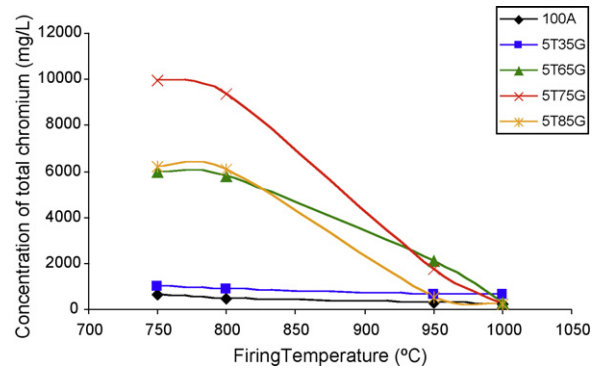


Fig. 3. Concentration of total chromium in the lixiviation of ceramic bodies produced from formulations 100A, 5T35G, 5T65G, 5T75G, and 5T85G as a function of firing temperature.

Fig. 4 shows the gresification curves of these ceramic bodies. It is observed that, the higher the glass addition, the lower the water absorption and the higher the linear shrinkage. Hence, the densification of the ceramic bodies is intensified, leading to a lower reactivity (surface area available for metal lixiviation), which favors the lixiviation phenomenon.

Table 5 shows the phases present in the ceramic bodies from formulation 5T85G for increasing firing temperatures. Fig. 5 shows the respective micrographs.

Fig. 5 shows a higher densification as temperature increases and glassing also occurs. A significant increase in chromium immobilization when compared to formulations with ACS and glass was expected, because of the more intense formation of vitreous phase caused by TiO_2 addition. This expectation was based on the results obtained for formulation containing glass and pure Cr_2O_3 and TiO_2 addition [3]. This is not observed in the data shown in Fig. 4. Formulations with glass and ACS had a minimum concentration of total chromium in the lixivium of 57 mg/L, for the formulation 90G (10% ACS + 90% glass) fired at 1000°C . For this temperature, the total chromium concentration in the lixivium for the formulation 5Ti85G (5% TiO_2 + 85% glass + 10% ACS) was 23 mg/L. On the contrary, the total chromium concentration in the lixivium for the formulation 5Cr5Ti (5% Cr_2O_3 + 5% TiO_2 + 90% glass) fired at 950°C was only 0.56 mg/L [3].

One possible explanation for this lies in the fact that, in this case, soluble phases are formed despite the addition of TiO_2 to the ACS. This occurs due to the presence of oxides in the ACS, such as Na_2O , which are also present in the glass, leading to an increased content

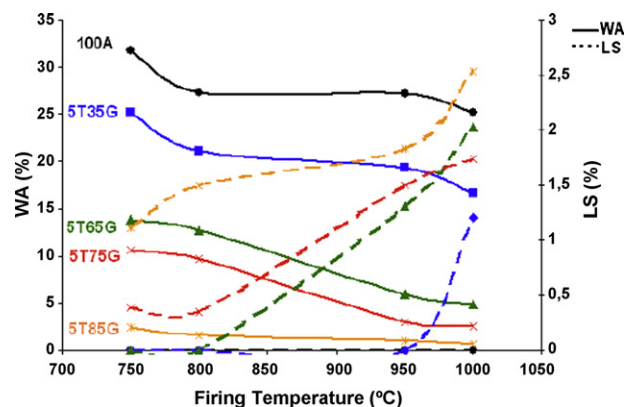


Fig. 4. Gresification curve (water absorption – WA and linear shrinkage – LS) as a function of firing temperature of formulations 100A, 5T35G, 5T65G, 5T75G, and 5T85G.

Table 5
Phases present in ceramic bodies made from formulation 5T85G for increasing firing temperatures.

Formulation	Firing temperature (°C)			
	750	800	950	1000
5T85G	Cristobalite	Cristobalite	Cristobalite	Cristobalite
	Quartz	Quartz	Quartz	Quartz
	Ca/Na silicate	Ca/Na silicate	Ca/Na silicate	Ca/Na silicate
	Rutile	Rutile	Rutile	Rutile
	Corundum	Corundum	Corundum	Corundum
	Eskolaite	Eskolaite	Eskolaite	Eskolaite
	Sodium chromate	Sodium chromate	Sodium chromate	Sodium chromate

of the corresponding ion in the formulation. As a consequence, oxidation to Cr⁶⁺ will be promoted through sodium chromate formation, leading to an increased leachability of chromium.

In fact, as can be seen in Table 5, the phase sodium chromate is present in ceramic bodies produced from formulation 5T85G (10% ACS + 5% TiO₂ + 85% glass) for all firing temperatures. This phase was detected in all ceramic bodies that had low efficiency in chromium immobilization in all the investigate formulations.

Fig. 6 shows the total chromium concentration in the lixiviation of ceramic bodies produced from formulations glass-ash and 5% MgO.

The high chromium lixiviation (819 mg/L) at 800 °C, as well as its drastic reduction for 950 °C, is shown in Fig. 6. This fact can be explained based on the phases formed in these firing temperatures. Table 6 shows the phases formed during firing of formulations 5Mg85G at different temperatures. At 800 °C, the phase sodium chromate appears, explaining the high lixiviation for this temperature. From 950 °C onwards, the phase sodium chromate is no longer present, and the chromium concentration in the lixiviate decreases to 23 mg/L. At 1000 °C, chromium concentration decreases to 2.4 mg/L, that is, about 10 times lower than those occurring at 950 °C. This decrease should be also associated to the higher densification of the ceramic bodies fired at this temperature, since the phase sodium chromate was not detected for both tem-

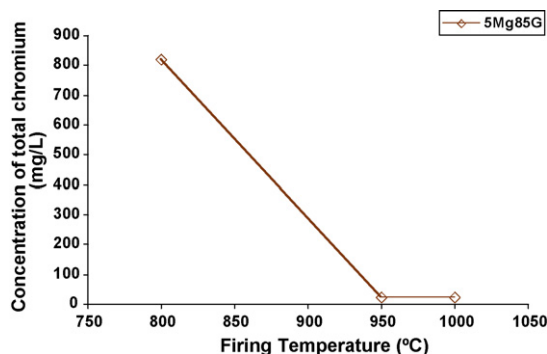


Fig. 6. Total chromium concentration in the lixiviation of ceramic bodies produced from formulations glass-ACS with addition of 5% of MgO as a function of firing temperature.

peratures. The gresification curve of ceramic bodies 5Mg85G as a function of firing temperature is shown in Fig. 7.

As can be seen from Fig. 7, the porosity was lower and linear shrinkage was higher at 1000 °C. Hence, a higher densification was obtained, lowering the surface area available for chromium lixiviation, thereby explaining the lower chromium lixiviation observed for this temperature.

Fig. 8 shows the total lixiviate chromium as a function of the percentage of MgO added to the formulation 90G, fired at 1000 °C. As can be observed, addition of 5% of MgO reduces the chromium lixiviation drastically. However, addition of 10% of MgO and firing at the same temperature leads to an increase in chromium lixiviation.

Table 6
Phases present in ceramic bodies produced from formulations 5Mg85G and 10Mg80G for increasing firing temperatures.

Formulation	Firing temperature (°C)			
	750	800	950	1000
5Mg85G		Quartz	Quartz	Quartz
		Corundum	Corundum	Corundum
	(did not sinter)	Aluminum phosphate	Aluminum phosphate	Ompacite
		Wollastonite	Ompacite	Eskolaite
		Clinoenstatite	Eskolaite	
		Ompacite		
	Eskolaite			
	Sodium chromate			
10Mg80G		Quartz	Quartz	Quartz
		Corundum	Corundum	Corundum
	(did not sinter)	Aluminum phosphate	Aluminum phosphate	Ompacite
		Wollastonite	Ompacite	Eskolaite
		Clinoenstatite	Eskolaite	
		Ompacite		
	Eskolaite			
	Sodium chromate			

Ompacite: NaMgAl(Si₂O₆)₂, Clinoenstatite: MgSiO₃.

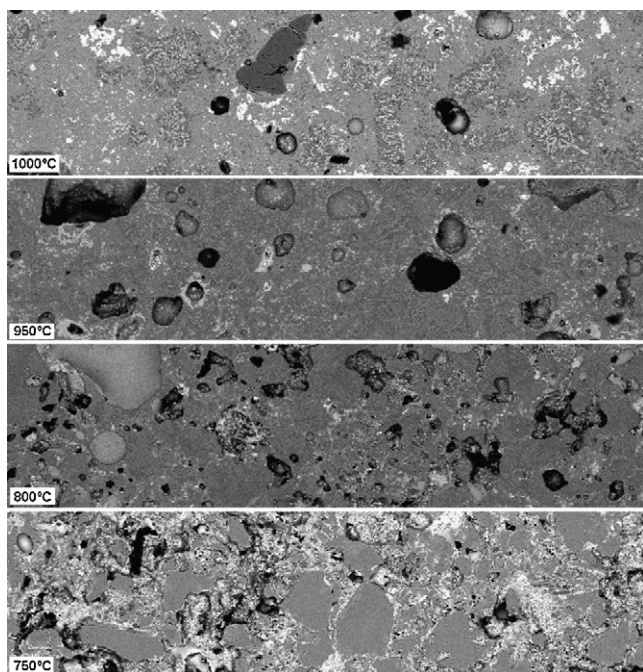


Fig. 5. Micrograph of ceramic bodies of formulation 5T85G with increasing firing temperatures.

Table 7
Image mapping of sample 5Mg85G fired at 800 °C.

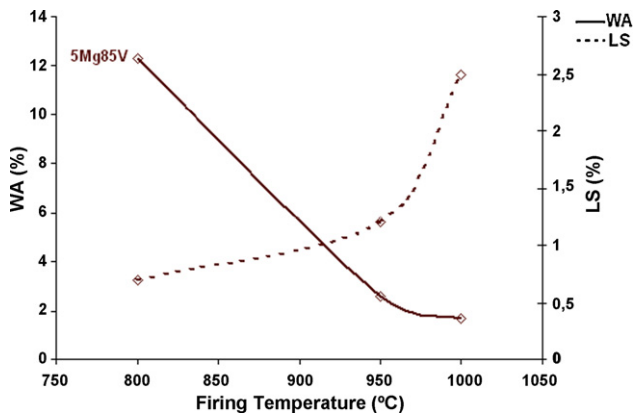
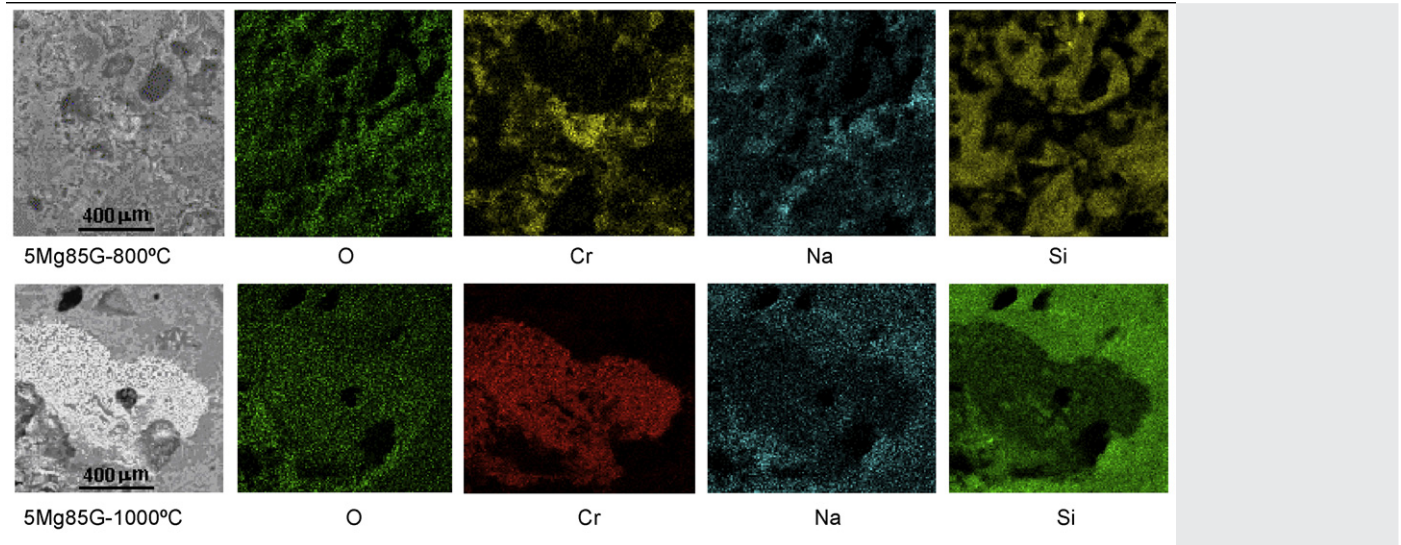


Fig. 7. Gresification curve (water absorption – WA and linear shrinkage – LS) as a function of firing temperature of samples glass-ACS with addition of 5% of MgO.

Water absorption and linear shrinkage for this ceramic body were 6.81% and 1.29%, respectively, indicating a significantly lower densification of this ceramic body when compared to those shown in the graph of Fig. 7. The higher solubility of ceramic body 10Mg80G would then be associated to its higher open porosity (water absorp-

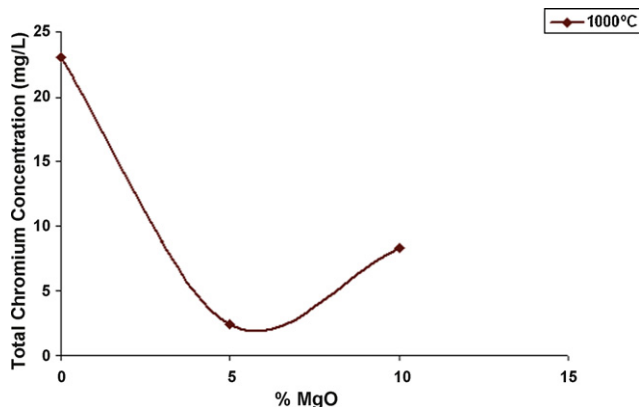


Fig. 8. Total lixiviate chromium concentration as a function of MgO percentage added in sample containing 10% ACS and fired at 1000 °C.

Table 8
Gaseous emissions evaluation of ceramic bodies 5Mg85G for firing temperatures of 750 and 1000 °C.

Samples	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	Cr _{total} (mg/L)
5Mg85G-750 °C	0.40	0.19	0.11	<0.02
5Mg85G-1000 °C	0.19	0.04	0.03	<0.02

tion), since the ceramic bodies 5Mg85G and 10Mg80G present the formation of the same phases on the evaluated temperatures (Table 6).

Table 7 shows the mapping of elements O, Cr, Na and Si of ceramic bodies 5Mg85G, for firing temperatures of 800 and 1000 °C.

From these mappings, a more homogeneous distribution of O, Na and Si in the microstructure of the ceramic body fired at 1000 °C can be observed. Cr is concentrated in one single grain (probably eskolaite). When comparing to the mapping of the sample fired at 800 °C, it can be verified that the distribution of Si and Cr are almost complementary to each other. This suggests that the higher densification of the ceramic body fired at the highest temperature is associated to the microstructure vitrification, in which both Cr and Si are not totally segregated.

Because of the immobilization of the chromium obtained for ceramic bodies of formulation 5Mg85G (10% ACS + 5%MgO + 85% glass), this formulation was submitted for the evaluation of gaseous emissions. The obtained results are shown in Table 8.

The chromium ion concentration was below the atomic absorption detection limits for all gaseous emissions during firing of ceramic bodies (Table 8).

4. Conclusions

The following conclusions can be drawn based on the results obtained in this work.

For formulations containing ash and glass, it was possible to obtain chromium ion immobilization, which comes from the ash of chromium-treated leather, when magnesium oxide was added as vitrification/densification agent. Samples were tested according to lixiviation procedure described by NBR 10.005 Standard and evaluated according to the maximum level established by NBR 10.004 Standard (5 mg/L).

- From gaseous emissions data, it was verified that there was no detectable chromium evolution by gas emissions during firing of ceramic bodies. Results of chromium ion analysis in washing gases were below the atomic absorption detection limits.
- The chromium immobilization in ceramic bodies was more effective for higher firing temperatures. Therefore, increasing firing temperatures decrease the open porosity by vitreous phase formation, leading to a decrease in chromium lixiviation.
- Addition of ACS to glass reduces water absorption and increases the linear shrinkage of ceramic bodies. Hence, there is a higher densification of ceramic bodies, reducing the contact area available for lixiviation. However, sole addition of glass to ACS increased chromium lixiviation of ceramic bodies, even if it is lower for increasing firing temperatures. This is due to increase in lixiviable phases, such as sodium chromate, from the reaction of sodium, calcium sodium glass, and chromium from ACS.
- Chromium lixiviation is directly related to the presence of sodium in the glass-containing ceramic bodies. The presence of Na₂O leads to the formation of sodium chromate, which is highly lixiviable. Addition of CaO also increases chromium lixiviation, but this increase is associated to a lower densification of ceramic bodies.
- Open porosity is not the only determining factor of lixiviation in ceramic bodies. However, a relationship between chromium lixiviation decrease at 950 °C and densification increase was evidenced. Thus, higher lixiviation is not only due to lower densification, but also by the presence of sodium.
- The chromium ion immobilization was poor for all investigated ceramic bodies that had the presence of sodium chromate in their constitution.
- The decrease in chromium lixiviation in ceramic bodies for the investigated firing temperatures is associated to a lower amount of phases with hexavalent chromium, and to a more closed microstructure and the presence of vitreous phase in the ceramic body.

References

- [1] T. Basegio, F.A. Berutti, A. Bernardes, C.P. Bergmann, Environmental technical aspects of the utilization of tannery sludge as a raw material for clay products, *J. Eur. Ceram. Soc.* 22 (2002) 2251–2259.
- [2] European Commission, Directorate-General JRC, Joint Research Centre, Institute for Prospective Technological Studies (Seville), Technologies for Sustainable Development, European IPPC Bureau, Integrated Pollution Prevention and Control (IPPC), Reference Document on Best Available Techniques for the Tanning of Hides and Skins, Final Draft/February 2003, <http://www.eippcb.jrc.es>.
- [3] T.M. Basegio, Imobilização do Ion Cromo de Cinzas da Incineração de Serragem de Couro em Corpos Cerâmicos Vitrificadas, Porto Alegre, Ph.D. Thesis, UFRGS, Brazil, 2004, 118 pp.
- [4] A. Cassano, E. Drioli, R. Molinari, Recovery and reuse of chemicals in unhairing, degreasing and chromium tanning processes by membranes, *Desalination* 113 (1997) 251–261.
- [5] A. Cassano, E. Drioli, R. Molinari, Saving of water and chemicals in tanning industry by membrane processes, *Water Res.* 4 (1999) 443–450.
- [6] A. Cassano, E. Drioli, R. Molinari, C. Bertolutti, Quality improvement of recycled chromium in the tanning operation by membrane processes, *Desalination* 108 (1996) 193–203.
- [7] Environmental Protection Agency, USA, 40 CFR, Chapter 1, Part 261, Identification and Listing of Hazardous Waste, App VIII, 1998.
- [8] Associação Brasileira de Normas Técnicas: NBR 10004, Resíduos: Classificação, 1987.
- [9] Bundesrat: Zweite allgemeine Verwaltungsvorschrift zum Abfallgesetz (TA-Abfall), GMDI 170, Germany, 1990.
- [10] D.D. Castilhos, Alterações Químicas e Biológicas Devidas à Adição de Resíduos de Curtume e de Cromo Hexavalente no Solo, Master Degree Thesis, UFRGS, Brazil, 1998.
- [11] S.A. Ferreira, Efeitos da Adição de Resíduos de Curtume e Carbonífero nas Plantas e no Solo, Master Degree Thesis, UFRGS, Brazil, 1998.
- [12] B. Rivela, C. Bornhardt, G. Vidal, R. Mendez, Towards a cleaner production in developing countries: a case study in a Chilean tannery, *Waste Manage.* 22 (2004) 131–141.
- [13] A.G. Bernstein, E. Bonsembiante, G. Brusatin, G. Calzolari, P. Colombo, R. Dall'igna, S. Hreglich, G. Scarinci, Inertization of hazardous dredging spoils, *Waste Manage.* 22 (2002) 856–869.
- [14] L. Barbieri, A.C. Bonamartini, I. Lancellotti, Alkaline and alkaline-earth silicate glasses and glass-ceramics from municipal and industrial wastes, *J. Eur. Ceram. Soc.* 20 (2000) 2477–2483.
- [15] A. Karamanov, M. Aloisi, M. Pelino, Sintering behaviour of a glass obtained from MSWI ash, *J. Eur. Ceram. Soc.* 25 (2005) 1531–1540.
- [16] M. Romero, R.D. Rawlings, J. Ma Rincón, Development of a new glass-ceramic by means of controlled vitrification and crystallisation of inorganic wastes from urban incineration, *J. Eur. Ceram. Soc.* 19 (1999) 2049–2058.
- [17] M. Pelino, A. Karamanov, P. Piscicella, S. Crisucci, D. Zonetti, Vitrification of electric arc furnace dusts, *Waste Manage.* 22 (2002) 945–949.
- [18] M. Ferraris, M. Salvo, F. Smeacetto, L. Augier, L. Barbieri, A. Corradi, I. Lancellotti, Glass matrix composites from solid waste materials, *J. Eur. Ceram. Soc.* 21 (2001) 453–460.
- [19] P. Piscicella, S. Crisucci, A. Karamanov, M. Pelino, Chemical durability of glasses obtained by vitrification of industrial wastes, *Waste Manage.* 21 (2001) 1–9.
- [20] J.L. Means, The Application of Solidification/Stabilization of Waste Materials, Lewis Publishers, Ohio, 1995.
- [21] R.R. Godolphim, Incineração em Leito Fixo de Resíduos de Couro *wet-blue*, Dissertação de Mestrado em Engenharia Química, UFRGS, 2000.
- [22] J.S. Chincón, Environmental impact of mineral transformations undergone during coal combustion, *Environ. Geol. Water Sci.* 18 (1991) 11–15.
- [23] W.A. Weyl, Coloured Glasses, 6th ed., Society of Glasses Technology, Sheffield, Reino Unido, 1999.
- [24] Associação Brasileira de Normas Técnicas: NBR 10005, Lixiviação de Resíduos Sólidos, set. 1987, 20 pp.
- [25] US EPA, Extraction procedure toxicity test, in: Stabilization/Solidification of CERCLA and RCRA Wastes. US EPA 625/6-89/022, US EPA, Cincinnati, Ohio, 1986.
- [26] Associação Brasileira de Normas Técnicas: NBR 10004, Resíduos Sólidos – Classificação, set. 1987, 63 pp.
- [27] ASTM C373-88 (2006): Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products.
- [28] ASTM C326-03: Standard Test Method for Drying and Firing Shrinkages of Ceramic Whiteware Clays.