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Characterization of a chromium-rich tannery waste and its potential use in ceramics

M.A. Abreu, S.M. Toffoli *

Department of Metallurgical and Materials Engineering, Polytechnic School, University of São Paulo, Av. Prof. Mello Moraes 2463, 05508-970 São Paulo, SP, Brazil

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Abstract

Leather industries which promote hide stabilization by the conventional chrome-tanning process are a major source of pollution because of the resultant chromium-rich wastes. In this work, an extensive characterization of such a chromium-rich waste sludge is presented, regarding its chemical composition (XRF), crystalline phase contents (XRD), organic carbon content (TOC), thermal behavior by thermogravimetry (TG) and differential scanning calorimetry (DSC), as well as its stability under chemical attack (the concentration of important ions in the leachates being determined by capillary electrophoresis) and when submitted to temperatures as high as 1100 °C, in air. The material showed the tendency to produce some undesirable, and previously non-detected hexavalent chromium when exposed to high temperatures, but after washing off the soluble salts and the elimination of the organic matter by firing, the resultant material was succesfully tested as a ceramic pigment in a conventional glaze composition usually employed in the ceramic tile industry.

Keywords: Leather; Chromium; Waste; Pigment

1. Introduction

The leather industry is a major economical segment in Brazil. Its production has been increasing over the past years, achieving around 44 million hides in 2006. Such production represents 20% of the global world market that is about 215 million hides per year, and is spread throughout several states within the country. In the year of 2007, 34.6 million hides were exported, comprising 78% of the leather production in Brazil [1].

Sundar et al. [2] observed that more than 90% of the global production of leather is through chrome-tanning process. Basegio et al. [3] estimated that each hide generates an average of 7.5 kg of chromium waste, therefore causing the generation of about 330 000 tons of chromium waste per year in Brazil alone. These numbers indicate that the conventional method employed for tanning lead to significant material losses and serious environmental concerns.

The discovery of chrome tanning is attributed to Knapp, in 1858. Three decades later, chrome-tanned leathers were produced in commercial scale by Augustus Schultz, of New York, in 1884. Only after World War II this process was greatly improved, when the use of basic chromium sulfate became an established practice [2,4].

According to Thorstensen [5] and Basegio et al. [3], tanning is the key process that renders the stabilization of hides or skins against wet heat, enzymatic degradation and thermo-mechanical stress. These properties may be obtained through treatments with mineral-tanning agents like basic salts of chromium, aluminum, or zirconium, and organic-tanning agents like vegetable tannins, aldehydes, etc. The choice of the tanning methods and materials depends chiefly on the properties required in the finished leather, the cost of the alternative materials, and the type of raw material. Chromium salts are the most widely used tanning substances for the excellent properties attained by the leather (e.g., good mechanical resistance of the hides), along with simplicity of operation, an extraordinary dyeing suitability and better hydrothermic resistance in comparison with hides treated with vegetable substances.

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* Corresponding author. Tel.: +55 11 3091 2260; fax: +55 11 3091 5243.
E-mail address: toffoli@usp.br (S.M. Toffoli).

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Chromium salts have a high rate of penetration into the interfibrillar spaces of the skins. In spite of that, only a fraction of the salts used in the tanning process yields the desired reaction with the skins. This happens because of the limited access to reactive sites for the tanning molecules, and/or the presence of low affinity species in the tanning materials. The rest of the salts remain in the tanning effluents and are subsequently sent to a treatment plant where the chromium salts end up in the waste [2].

Therefore, the tanning process is responsible for the generation of large quantities of chromium waste, which may also contain organic matter, and salts such as chlorides, sulfates and carbonates, as well as ammonia, detergents, emulsifiers, bactericides, fungicides, coloring agents, skin proteins, hair, fat, and other components. Besides the chromium contents, such varied and complex composition usually characterizes this waste as a potentially toxic material, so that it should be correctly disposed of in a manner not to cause adverse effects on the surrounding land, water, and the local flora and fauna [4,6–8].

Chromium is the second most abundant inorganic groundwater contaminant at hazardous waste sites [9]. It was observed that Cr(III) readily oxidizes to Cr(VI) when typical oxidation conditions are present [4,10]. The toxicity of Cr depends primarily on its chemical form. Trivalent chromium compounds are much less toxic than those of hexavalent Cr, since hexavalent chromium is known to be very mobile and hazardous to human health through inhalation, skin contact, and ingestion, being highly toxic, carcinogenic and mutagenic to living organisms, even when present in very low concentrations in water [11,12].

In the treatment plants, before biological treatment of the tanning process wastewater, it is necessary to remove chromium by a chemical precipitation technique. This is carried out usually using calcium hydroxide, generating chromium hydroxide, which is separated by filtration. In spite of the fact that the industry is constantly looking for efficient and innovative routes for chromium recovery or reuse, large amounts of such wastes are still released to the environment, throughout the world, every year. One possible, cost-efficient recovery process of chromium from the waste, is the redissolution of the $Cr(OH)_3$ with sulfuric acid, with the formation of basic chromium sulfate (BCS), $Cr(OH)SO_4$ [2,13–16].

Other approaches suggest the use of the wastes in processes other than tanneries themselves. Kowalski and Gollinger-Tarajko [17] propose the use of chromic wastes from different processes to substitute natural raw materials in the production of chromium compounds. Other studies include processes such as waste volume reduction by thermal treatment, the processing of the wastes by hydrometallurgical methods to recover chromium, as well as studies involving land treatment, encapsulation, solidification, stabilization, and vitrification processes to transform the wastes into cementitious agglomerates, ceramics, glasses, glass-ceramics and pigments [3,18–21].

The main purpose of this work is, besides presenting the initial characterization of the chromium tannery waste, discuss its treatment by washing and firing, aiming at the extraction of the soluble salts and the elimination of the organic matter, so that the chromium-rich, resultant material, could be suitably used as a ceramic pigment. Chromium bearing materials, specially chromium oxide, Cr_2O_3, are well known for resulting in strong green coloration in ceramic glazes for the ceramic tile industry and may also be used in the container glass industry. For these applications, the presence of soluble salts and organic matter of the tannery sludge is undesirable because, particularly in the case of glazes, they can leave superficial imperfections such as pores or cracks, resultant from their volatilization or decomposition.

2. Experimental

2.1. Materials

Chromium tannery waste was supplied by a leather industry from the city of Franca, São Paulo State, Southeastern Brazil, which is a major leather and shoes production center in the country. The sludge is obtained by precipitation of the tanning solution with $Ca(OH)_2$. Samples for study here presented were dried in a laboratory oven, at 105 °C, from the as-received material, until attaining constant weight. After that, the dry material was characterized.

For the preliminary application test as a pigment, a commercial monoporous transparent frit (FMTM) was also used. The frit was supplied by Johnson Matthey Ceramic Industry (Mogi Guaçú, Brazil).

2.2. Methods

The characterization and test of the chromium tannery waste followed four steps: (a) an initial characterization of the chromium waste, resulting in the material named (Cr NLAV); (b) extraction of the salts present in the chromium waste, resulting in the material called (Cr LAV); (c) oxidation study of the chromium ions (Cr LAV/ *T*, °C; *t*, h); and (d) performing a preliminary technological test. These experimental steps are detailed below.

2.2.1. Initial characterization of chromium waste (Cr NLAV)

Representative samples of the chromium tannery wastes were dried in air for 1 week, and thoroughly mixed to attain homogeneity. The initial characterization was carried out employing the following techniques:

- X-ray fluorescence (Philips TW1480), to determine the chemical composition of the sludge and the frit.
- Total organic carbon content (TOC), at 1400 °C, in helium gas, using a LECO CNS analyzer. The sample was previously treated with hydrochloric acid (10%) to remove carbonates and soluble sulfates.
- Differential scanning calorimetry (DSC) and thermogravimetry (TG) were used to study both qualitative and quantitative changes of the waste upon heating [17]. The test was carried out from room temperature to 1200 °C, under

a 100 mL/min air flow as the purge gas, with a heating rate of 10 °C/min, in a simultaneous TG/DSC TA equipment, model STA 409, with alpha-alumina as the reference material.

- X-ray diffraction (XRD), in a Philips X'Pert MPD instrument, using Cu Kα radiation, at 40 kV and 40 mA, at a scanning rate of 1° (2θ) per second, from 1 to 90° (2θ), to determine the crystalline phase content of the waste. The following samples were analyzed: chromium tannery waste, as-received (Cr NLAV) and after firing at 550, 1000, and 1100 °C, for 1 h; chromium waste after washing (Cr LAV); chromium waste after washing and firing (Cr LAV/700 °C, 1 h); salts of chromium waste; commercial Cr_2O_3 pigment; and the monoporous transparent frit.

When working with a chromium-rich material, it is very important to determine the amounts of the chromium ions in their several valence states. In particular, it is of paramount importance to detect the presence of Cr(VI) ions in the waste of the leather industry, as they have high solubility in water and have deleterious effects on the human health. Therefore, after the initial characterization of the waste, and in order to determine the amounts of Cr(VI) present, the samples were submitted to the Diphenylcarbazide Colorimetric Tests, carried out by two different methods: (a) qualitative test, and (b) quantitative test.

a) Qualitative test: two samples (around 5 g) of chromium waste were collected, one from the as-received material (Cr NLAV), and another after firing at 1000 °C/1 h. The samples were mixed with 200 mL of concentrated hydrochloric acid (2 N) in a magnetic stirrer for 2 h. For comparison purposes, a sample containing only the acid and distillated water was also tested. After that period, the color of the supernatant liquid was observed. The presence of Cr(VI) is revealed with the addition of 2 mL of a diphenylcarbazide indicator solution. Hexavalent chromium reacts with 1.5-diphenylcarbohydrazide (s-diphenylcarbazide) in an acidic medium to produce a reddish-purple color. The intensity of the color formed is proportional to the hexavalent chromium concentration [16,22].
b) The same kind of samples were used to determine the presence of Cr(VI) with the help of a photometric method, based on ASTM D1687-02-2007 [23], for Cr(VI) concentrations between 0.01 and 0.5 mg/L. A HACH spectrophotometer model DR2010, with absorption band at 540 nm, was employed. This test method covers the determination of dissolved hexavalent chromium in waters. However, it has been successfully used with leaching and effluent waters. For the solubilization of chromium waste, a sample (2 g) from the non-washed material (Cr NLAV) was attacked with concentrated nitric acid (3 mL), after which it was placed in a volumetric flask (100 mL) and submitted to the colorimetric test method.

2.2.2. *Chromium waste salts extraction (Cr LAV)*

Since the main purpose of the study here reported was to consider the tannery waste to be used in ceramic materials processing, in special for ceramic glaze pigments, the presence of soluble salts should be carefully considered. The presence of chlorides, sulfates, and carbonates in the waste can generate defects on the glaze surface during firing, because of their dissociation and subsequent elimination through the glaze surface. Another problem associated with such dissociation is the potential damage its products could cause to the firing furnace at high temperatures, since they could chemically attack the refractory lining of the kiln.

Therefore, the chromium waste had to be washed to accomplish the removal of the salts. This was carried out adding 100 g of the dry sample to 1.4 L of distilled water. The samples were then shaken by rotational agitation for 6 h, at room temperature, after what the samples were vacuum filtered in paper filter. The retained material was washed with distilled water until qualitative tests did not show the presence of chlorides and sulfates in the extracting water, what was determined by simple colorimetric analytical tests employing silver nitrate and barium chloride, respectively.

The presence of hexavalent chromium, Cr(VI), was determined by the diphenylcarbazide qualitative colorimetric method. On the other hand, due to experimental availability, quantitative analysis of the leaching solution was performed by the non-usual technique of capillary electrophoresis.

The water soluble fractions were identified, for each liter, as A, B, C, D, and E. The extraction solution A identifies the initial solution after the rotational agitation for 6 h, whereas solutions B, C, D, and E are the subsequent filtered water extract solutions. The characterization of the washing waters were realized qualitatively and after that, the quantification of important ions (Cl^-, SO_4^{-2}, Na^+, Cr^{3+}, Cr^{6+}) was carried out by capillary electrophoresis. After filtering, the waste sample was dried at 110 °C for 24 h and identified as Cr LAV.

Capillary Electrophoresis: electrophoresis is the separation of charged molecules based on differential migration in an electric field. The original concept was developed by Tiselius [24], for which he received a Nobel Prize in 1948. Later on, capillary electrophoresis (CE) was introduced by Jorgenson and Lukacs [25], and differs from the original Tiselius' technique for the introduction of an electrolyte filled capillary. CE encompasses a number of characteristics quite suitable for the simultaneous analysis of small ions such as high efficiency and resolving power, speed, full automation, impressively high peak capacity, short analysis time and a variety of injection-based pre-concentration schemes and detection modes [26,27].

The characterization of the tannery waste leachate solutions by capillary electrophoresis, was performed in a Beckman Instruments equipment model HP^{3D} CE (Agilent Technologies), equipped with a filter-carrousel UV detector, fused-silica capillaries (ϕ = 75 μm, 48.5 cm total length, and 200–300 nm detection), with samples injected at a 50 bar pressure for 9 s, under a capillary temperature of 25–30 °C.

2.2.3. *Oxidation of the chromium ions*

Besides the presence of several inorganic salts, the use of chromium waste as a ceramic pigment raises another concern: the presence of organic components, basically originary from the animal's little scraps of skin and body hair [4]. A material suited to be used as a ceramic pigment should present very small (if any) amounts of organic materials. Therefore, to achieve an industrial use of the waste, it should undergo a thermal treatment at temperatures high enough to eliminate all organic contents (>550 °C). However, the exposition of chromium ions of lower charges to high temperatures may result in an increase of the higher charge chromium content, particularly the much undesired hexavalent chromium.

Firstly, tests were carried out firing samples of the chromium waste in the non-washed state (Cr NLAV) at 550, 1000, and 1100 °C per 1 h, as well as in the after washing state (Cr LAV) at 700 °C and 1150 °C. The temperatures of 700 °C (complete elimination of the organic matter), and 1150 °C (typical firing temperature of industrial ceramic tiles) were investigated regarding the presence of Cr(VI) for 1, 3, and 6 h, in a muffled laboratory furnace.

In these samples the technique used to determine Cr(VI) in the extract's waters after filtration/vacuum washing was capillary electrophoresis. A small sample weight was necessary to run the tests (0.2–0.5 g), so that less volume of the final washing solutions could be obtained. Initially, 50 mL of distillated water was added to the solid sample. After 1 h agitation in magnetic stirrer, the material was filtered, and the retained material was washed with distillated water until complete removal of soluble Cr(VI), what was verified with the diphenylcarbazide colorimetry test.

To investigate the morphology characteristics of the washed samples, the material was observed in a scanning electron microscope (Philips XL30 instrument with a coupled X-ray dispersive energy analyzer (EDS)). The analyzed sample was the Cr LAV material, after firing at 700 °C, for 2 h.

2.2.4. *Preliminary technological test*

The performance of the treated waste as a ceramic material was preliminary investigated in a technological test. The washed material after thermal treatment was incorporated into a glassy matrix. The observed characteristics of the final glaze material were: development of color, brightness, opacity, texture, and also chemical stability. A sample of the (Cr LAV/700 °C, 2 h) material was mixed to a commercial transparent frit and other components usually present in a ceramic glaze composition, and it was fired in a pilot ceramic kiln. For a basis of 100 g of solids, that is, 92 g of FMTM frit and 8 g of kaolin, 15 g of the treated chromium waste (15 wt.%), 45 g of water, and 0.2 g of CMC (suspensor agent) were mixed. The materials were ground and mixed in a ball mill for 30 min. The suspension must have about 1.75–1.80 g/cm^3 and residue <1.5 wt.% (#325). This suspension is used to prepare fusion buttons after drying at 80 °C/2 h. The buttons were fired at 1100 °C, in a cycle of only 35 min, from cold to cold, simulating the industrial firing of ceramic tiles.

Several leaching tests may be found in the literature, to determine the chemical stability of the final glaze [22,28–30]. In this paper, the procedure of leaching the buttons to determine the possible presence of Cr(VI) was based on the Brazilian standard NBR10005 [31]. The identification of the presence or not of Cr(VI) in the leachate was performed by capillary electrophoresis. The samples were crushed to particle sizes less than 1 mm (ASTM #18), and attacked by a 0.5 N acetic acid solution as the extractor fluid (pH 4.93 ± 0.05), for 12 h, at room temperature, under mechanical stirring (90 RPM). After that, the material was filtered and then washed until negative qualitative test of Cr(VI) with diphenycarbazide solution. The lixiviate was chemically analyzed by capillary electrophoresis to estimate Cr(VI), whereas the total chromium concentration, Cr$_{total}$, was obtained by Atomic Absorption Spectrophotometer.

3. Results and discussion

3.1. *Characterization of the waste*

The chemical composition of the as-received waste is given in Table 1. The XRF analysis showed the presence of 21.8 wt.% Cr_2O_3. This result is not far from the 26.0 wt.% reported by Panswad et al. [14], for tanneries in Thailand. Besides chromium, it reveals the large amount of organic matter and the presence of the elements which are added to the original tanning solution. The chemical analysis revealing ions like chlorine and sulfur suggests the likely presence of sodium chloride, and sodium or calcium sulphate salts. The TOC analysis of the chromium waste showed the presence of 6.0 wt.% organic carbon, 3.7 wt.% of sulfur, and 1.1 wt.% of nitrogen. This test indicates organic carbon level only, since the inorganic carbon (e.g., from carbonates) is removed before running the TOC test.

The results of the thermal analyses are showed in Fig. 1. The small endothermal DSC peak around 109 °C shows a physical water weight loss from the beginning of the test, due to the residual adsorbed water content of the chromium waste, as well as to the dehydration of calcium sulphate ($CaSO_4{\cdot}2H_2O$), present after the precipitation process. The DSC curve also

Table 1
Chemical composition of the chromium tannery waste and the frit, by X-ray fluorescence.

OXIDE	Cr NLAV (wt.%)	Frit FMTM (wt.%)
SiO_2	0.93	54.30
CaO	7.15	13.26
MgO	1.87	1.31
Al_2O_3	0.16	11.32
Fe_2O_3	0.16	0.21
B_2O_3	–	2.26
Cr_2O_3	21.80	–
ZnO	–	11.28
K_2O	–	4.67
Na_2O	5.57	–
MnO	–	–
P_2O_5	0.36	–
ZrO_2	–	0.10
Chloride	5.95	0.06
SO_3	11.50	0.09
Moisture	9.57	–
L.O.I.	34.70	1.00
Total	99.72	99.86

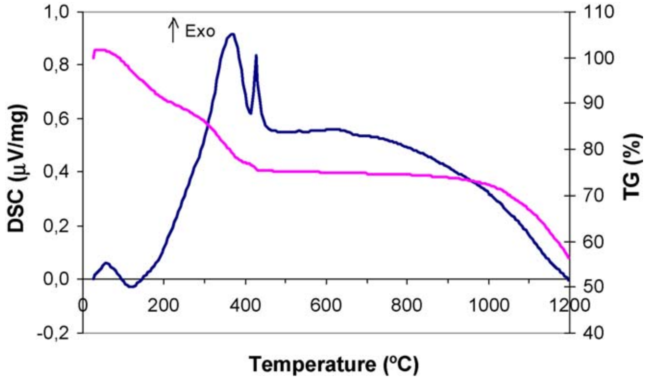

Fig. 1. DSC and TG curves of the chromium tannery waste (Cr NLAV).

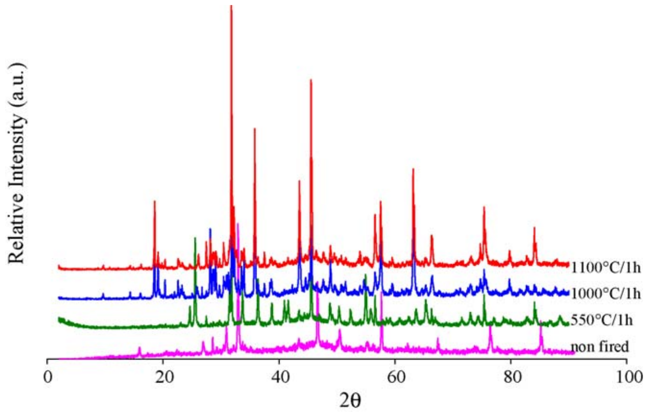

Fig. 2. XRD patterns of chromium waste: as-received (Cr NLAV), and fired at 550, 1000, and 1100 °C for 1 h.

exhibits the characteristic exothermal behavior of the organic matter burnout present in the waste, showing two peaks, around 365 °C and 427 °C, which, in turn, are associated to a significant weight loss, of about 25 wt.%, in the TG curve. Along with the organic matter burnout, other decompositions should also be expected, such as the dehydroxilation of chromium hydroxide (III) and alkaline chromium sulfate. For temperatures higher than 430 °C there is no significant weight loss up to around 900 °C, after what there is a significant weight loss of almost 20% in the range 900–1200 °C, possibly due to melting and evaporation of sodium chloride and other soluble salts, as well as because of the decomposition of the carbonates (releasing CO_2), and the possible formation and/or reorganization of new compounds (magnetite, chromates and ferro-aluminates) associated with weight loss, indicated by the curves in Fig. 2.

The XRD curves are shown in Figs. 2 and 3. Fig. 2 shows the curves for chromium waste, non-washed, before extraction of salts (Cr NLAV), in the as-received state, as well as after calcinations for 1 h at the temperatures of 550, 1000, and 1100 °C. The pattern of the non-fired chromium waste indicates the presence of the crystalline phases of salts, mainly sodium chloride and hydrated calcium sulfate, which was formed during the precipitation of the chromium waste from the reaction between basic chromium sulfate and calcium hydroxide. The material calcined at 550 °C exhibits peaks that can be attributed to calcium sulfate, $CaSO_4$ (anhydrous), and small peaks of two types of chromium oxide, Cr_2O_3 (JCPDS N.38-1479 and 06-0504). For the material calcined at the temperature of 1000 °C, other structures appear, particularly the spinel $MgCr_2O_4$, and possibly the spinels $MgFeAlO_4$ and $(Fe,Mg)(Al,Cr,Fe)_2O_4$, although they might be expected in very small amounts due to the small iron and aluminum contents (Table 1). At 1100 °C, the XRD curve does not show the presence of peaks associated with pure chromium oxides.

If the XRD curve of the as-received waste (Cr NLAV) showed the marked presence of sodium chloride and possibly other salts, the washed waste (Cr LAV) did not show any defined crystalline structures (Fig. 3). Chromium waste after washing and firing at 700 °C (Cr LAV/700 °C, 1 h) exhibits peaks mainly assignable to Cr_2O_3 (JCPDS 38-1479 and 06-0504) while there are also other small peaks, attributed to calcium sulfate, $CaSO_4$. For comparison purposes, the XRD curve for commercial chromium oxide is also shown in Fig. 3. It shows the main peaks of the crystalline phase scholayte, JCPDS 38-1479, and also the chromium oxide JCPDS 06-0504. Finally, Fig. 3 also shows the XRD curve for the transparent monoporous frit (FMTM), which confirmed its expected amorphous form.

The qualitative and quantitative diphenylcarbazide colorimetric tests of the non-washed chromium waste (Cr NLAV) did not identify the presence of any hexavalent chromium. This is an important result, because it shows that in the tannery industry process, no hexavalent, toxic and hazardous, chromium, is formed. These results are in agreement with the results obtained by Scaief [13], Fernández-Sempere et al. [22] and Font et al. [28]. On the other hand, for the calcined sample (Cr NLAV/1000 °C, 1 h) the solution showed a reddish-purple color, which was determined, by the spectrophotometer measurement, to represent a concentration of 100 mg Cr(VI)/g of fired chromium waste. The presence of sodium ions favors the oxidation of the Cr(III) to sodium chromate during firing. Therefore, the firing process causes the oxidation of part of the chromium in the waste, making it important to proceed the evaluation of the oxidation behavior of the chromium ions.

3.2. *Chromium waste salts extraction*

The amounts of the main ions present in the water extraction solutions of the (Cr NLAV) material are shown in Table 2. The results showed the gradual elimination of the soluble salts present in the chromium waste, and no presence of either Cr(III) or Cr(VI) in any stage of the process, what agrees with the results obtained in the dyphenylcarbazide colorimetric tests.

In order to determine the total amount of soluble salts in the original waste, all the five extraction solutions were mixed together and completely dried. Comparing the weight of the dry material with the initial amount of waste, the total amount of soluble salts represented 43.85% of the original waste. These results also show that, for the particular particle size distribution of the studied waste, the salt extraction by room temperature water is not a very efficient process, since it

Table 2
Main species present in the water extract solutions, by capillary electrophoresis, of the washing process of the chromium waste (Cr NLAV).

Water extract solutions	Color solution	Cl^- (g/L)	SO_4^{2-} (g/L)	Na^+ (g/L)	Cr(III) (g/L)	Cr(VI) (g/L)
Distilled water	Transparent	nd	nd	nd	nd	nd
A	Yellow	7.36	6.56	14.50	nd	nd
B	Transparent	1.58	3.09	3.82	nd	nd
C	Transparent	0.51	2.26	1.07	nd	nd
D	Transparent	0.36	0.85	0.34	nd	nd
E	Transparent	0.20	0.99	nd	nd	nd
Total		10.01	13.80	19.70	nd	nd

nd: non-detected.

demands great quantities of water and/or long exposition times. Therefore, other extraction conditions should be investigated if this waste is to be industrially considered. However, it should be pointed out that the presence of organic matter possibly makes the solubilization of the salts more difficult. Walsh and O'Halloran [4] observed that much of the chromium in a tannery effluent remained stably bound to organic ligands like proteins.Fig. 4 shows the chromium waste appearance after washing and firing at 700 °C for 1 h. The material exhibits a strong green color after the treatment. As already indicated, in weight terms, the Cr NLAV material contains, in round numbers, 44% of soluble salts. Upon calcining, this material looses more 27 wt.%, therefore yielding 29 wt.% of material, after washing and firing the original chromium waste.

3.3. Oxidation of the chromium ions

The washed material was studied after calcining at two selected temperatures: 700 and 1150 °C, chosen because the former is a temperature high enough to decompose and eliminate the organic matter, whereas the latter is a typical reference temperature for firing industrial ceramic tiles. Table 3 depicts the amounts of chromium ions in the lixiviate, by capillary electrophoresis, for samples calcined at these two temperatures for three different soaking times: 1, 3, and 6 h.

These results show that the quantity of hexavalent chromium Cr(VI) increases with increasing firing temperature. For both firing temperatures, in the initial hours, the amount of Cr(VI) increases. On the other hand, for longer periods of time, the Cr(VI) concentration seems to come back down. The formation during firing, of other oxides containing trivalent chromium, could be one explanation for this behavior, and was confirmed by the X-ray diffraction analysis, which showed the increasing presence of stable structures like the spinel magnesio-chromite $MgCr_2O_4$, and maybe smaller amounts of $(Fe,Mg)(Al,Cr,Fe)_2O_4$, for increasing temperatures.

For comparison purposes, the same leaching procedure used to measure Cr(VI) in the above mentioned samples, was

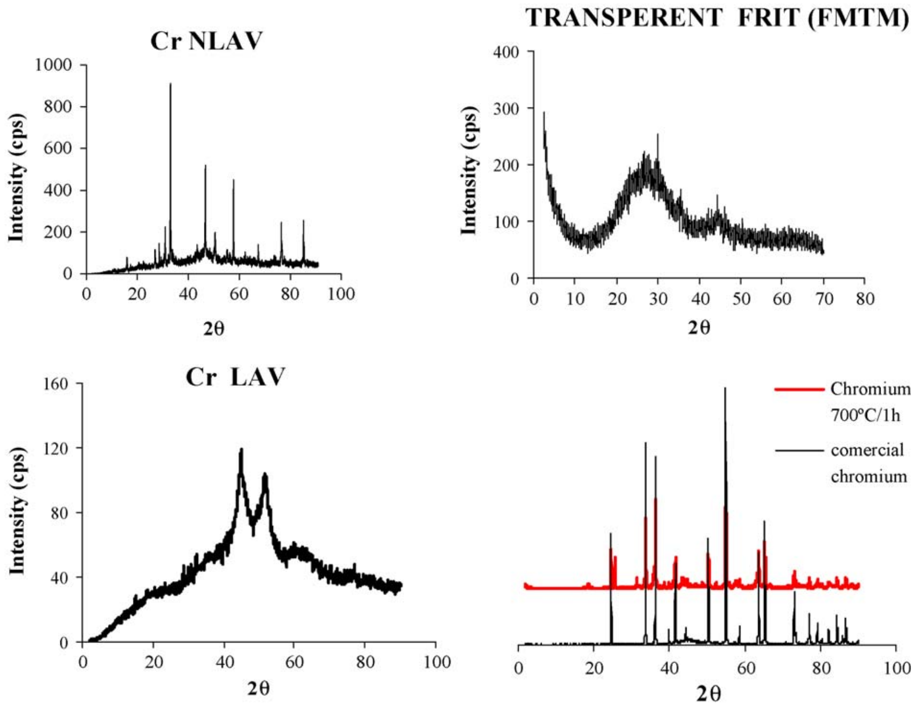

Fig. 3. XRD curves of: as-received, non-washed chromium waste (Cr NLAV); washed (Cr LAV) waste, transparent frit FMTM, and the Cr LAV material after firing at 700 °C/1 h compared to commercial chromium oxide (Cr_2O_3).

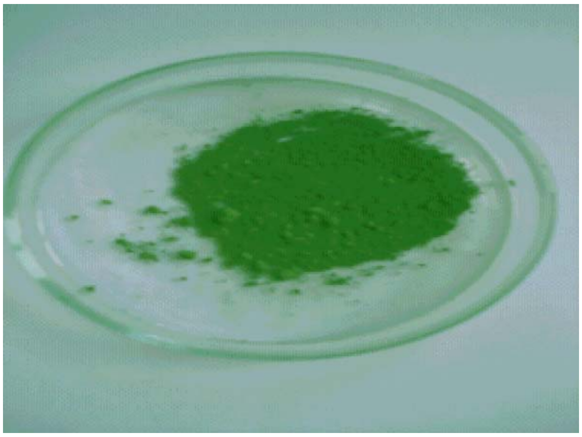

Fig. 4. Chromium waste after washing and firing at 700 °C for 1 h.

Table 3
Influence of the temperature and firing time on the concentration of hexavalent chromium, Cr(VI), in the lixiviate, by capillary electrophoresis.

Sample	Concentration Cr(VI) (mg/g)		
	1 h	3 h	6 h
Cr LAV, 700 °C	10.4	23.9	17.2
Cr LAV, 1150 °C	58.2	68.7	41.6

employed to determine the leaching behavior of a commercial chromium oxide (Cr_2O_3), fired at 700 °C for 1 h, and also at 1100 °C for 1 h. The capillary electrophoresis measurements resulted in the Cr(VI) amounts of, respectively, 0.038 and 0.037 mg/g. Therefore, calcining commercial chromium oxide does not influence the oxidation state of the chromium. This is probably due to the stable crystalline form of such oxide, the hexagonal rombohedral structure, corundum type, practically not allowing lixiviation by acids, alkalis and alcohols [19]. Comparing these results with the ones given in Table 3, the need of firing the washed waste together with some particular additives (like other selected raw-materials) should be indicated, allowing the formation of chromium containing stable structures, so that the oxidation of the chromium ions would be impeded or reduced [21]. This way, a stable chromium containing ceramic pigment could be obtained.

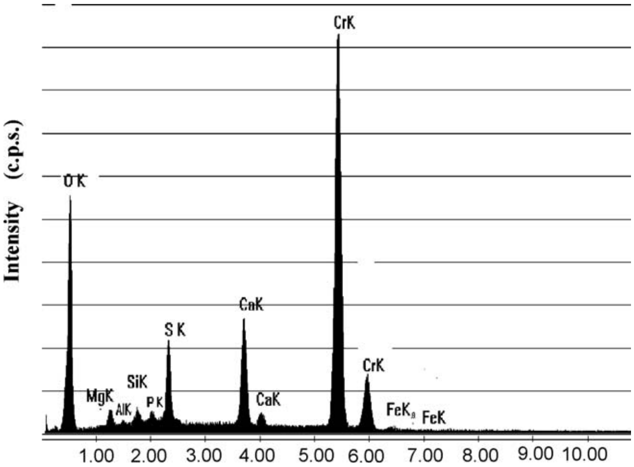

Fig. 6. EDS spectrum of washed chromium waste fired at 700 °C for 2 h (Cr LAV/700 °C).

Micrographs of the chromium waste particles after washing and firing (Cr LAV/700 °C, 2 h) are shown in Fig. 5. They show that the sample has a wide particle size distribution, and particles with varied morphology, exhibiting mostly round, not angular, shapes. The EDS analysis (Fig. 6) indicates that the material is constituted mainly by chromium, with smaller quantities of Ca, S, Mg, and minor amounts of Fe, Si, Al, and P. The analysis does not show the presence of any sodium or chloride, revealing that the washing step was efficient in removing such ions from the original, as-received, waste.

3.4. Preliminary technological test

In order to evaluate the potential behavior of the waste as a ceramic pigment, a preliminary test was performed, mixing calcined Cr LAV to a commercial transparent frit, used in ceramic tile glazes. Fig. 7a shows the sample buttons obtained with such mixtures. The button on the left in Fig. 7a is composed of the glaze composition without any waste addition, whereas the button on the right is the glaze composition containing 15 wt.% of waste. Both were fired at the same time, at 1100 °C, in a pilot kiln where the firing conditions simulate the industrial thermal cycle (35 min of total cycle, with 3 min at the top temperature). It can be noticed that the waste + frit

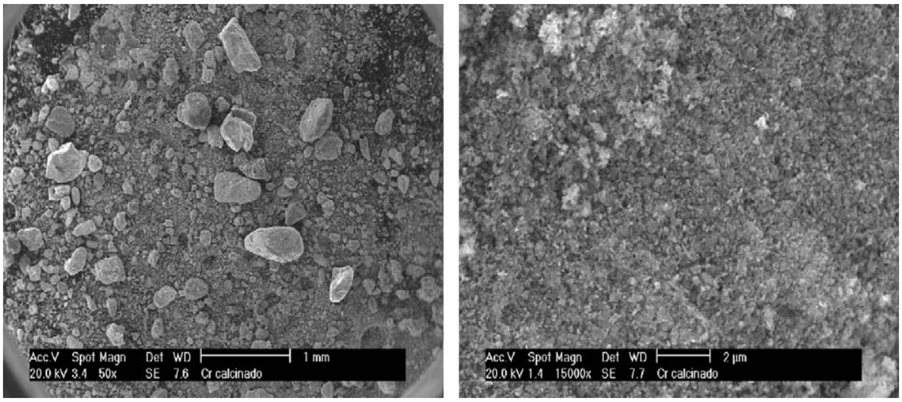

Fig. 5. Secondary electron, SEM micrographs of chromium waste washed and fired (Cr LAV/700 °C, 2 h). Left: 50×; right: 15,000×.

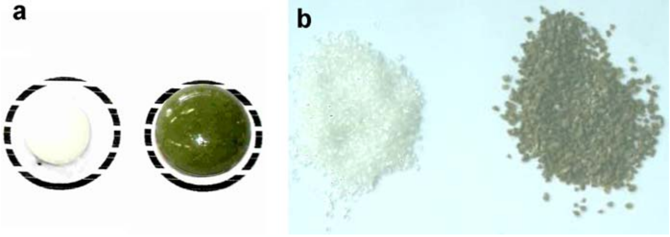

Fig. 7. (a) Fusion buttons: on the left, pure glaze composition, and frit FMTM + 15 wt.% (Cr LAV/700 °C, 2 h), on the right. (b) The same materials, crushed to particle sizes less than 1 mm, for the lixiviation process.

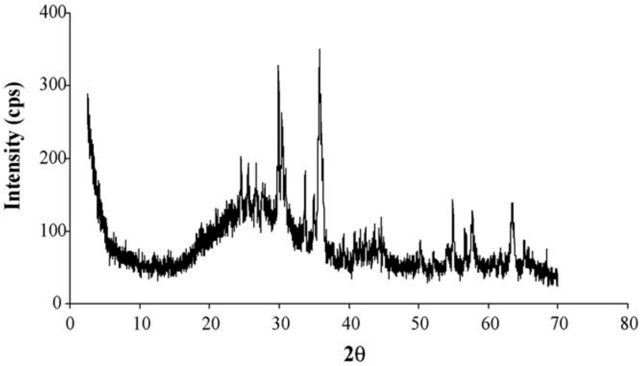

Fig. 8. XRD pattern of the fusion glazed button frit FMTM + 15 wt.% (CrLAV 700 °C/2 h), fired at 1100 °C/35 min cycle.

material developed a strong green, bright color, with good superficial texture, compared with the visual appearance (white, shiny) of the pure glaze composition button, showed on the left hand side of Fig. 7a. The buttons were then crushed to particle sizes less than 1 mm to undergo a lixiviation test (Fig. 7b).

In order to comply with current regulations in Brazil, a low leachability of hazardous components from glaze matrix must be achieved. Thus, the particulate material showed in Fig. 9 (right) was submitted to a lixiviation test according to the procedure given by Brazilian standard NBR 10005 [31]. The water extract of the crushed button containing waste had its total chromium concentration determined by means of atomic absorption spectrometry. The result, 0.4 mg/L, is less than the upper limit of 5 mg/L given by the Brazilian standard NBR 10004 [32], which sets the acceptable levels of hazardous components present in the leachates obtained by the NBR 10005 [31] procedure.

Table 4
Cr(VI) concentration in the leachate by capillary electrophoresis, expressed in terms of the extraction solution volume, and of weight of glaze.

Material	Cr(VI) (mg/L) at extraction solution	Cr(VI) (mg/g) glaze
Frit FMTM	nd	nd
FMTM + 15% (Cr LAV/700 °C, 2 h)	<0.1000	<0.0023

nd = non-detect.

Table 4 shows the results for the hexavalent chromium content in the extration solutions. Standard NBR 10004 [32] sets the limit for total chromium only, not specifying a limit for the Cr(VI) concentrations. However, in his paper, Makdisi [10] quotes the California Code of Regulations, which classifies Cr(VI) levels in sludges or solids as hazardous waste, as being 0.5 mg/g (Total Threshold Limit Concentration (TTLC)). Therefore, the experimental results reported in the present paper, showing lixiviation levels with acetic acid 0.5 N for 12 h, could be considered satisfactory. On the other hand, the results are not to be considered surprising, since glassy matrices have been successfully used for the immobilization of hazardous and toxic materials for quite some time.

Summarizing, the results here obtained indicate that, despite the lack of Brazilian regulation regarding lixiviation levels specifically for ceramic tile glazes, up to 15 wt.% of the washed and calcined chromium waste might be used as a green pigment in ceramic enamels and glazes, for the resultant material comply with the broadened current legislation.

Fig. 8 shows the XRD pattern for the button containing the waste. It can be identified the presence of a few short peaks over a typical, amorphous band relative to the silicate vitreous phase. These peaks are mainly assignable to chromium oxides, Cr_2O_3 (JCPDS 38-1479 e 06-0504), and zinc chromite, $ZnCr_2O_4$ (JCPDS 22-1107). This latter spinel is formed because of the considerable amount of zinc in the frit FMTM (Table 1). It is important to observe that if the firing cycle were longer, there would be sufficient time for the crystalline phases to grow

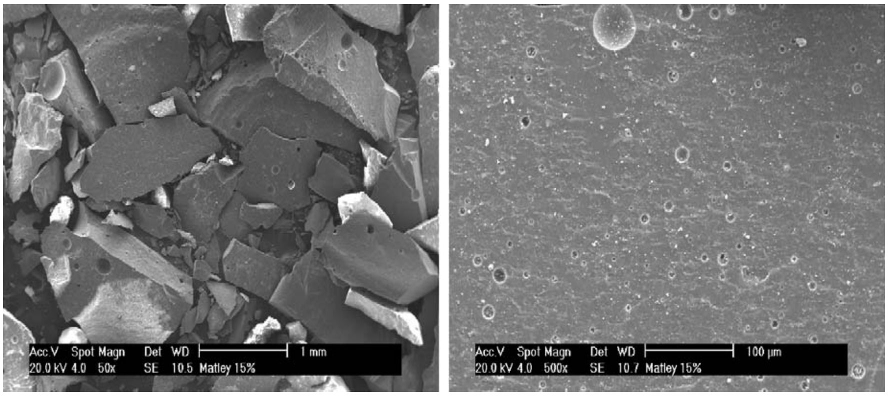

Fig. 9. SEM micrographs of the crushed glaze composition button containing chromium waste, under two magnifications. Left: 50×; right: 500×.

bigger and/or in greater number, causing the peaks to be more pronounced.

Fig. 9 shows SEM pictures of the crushed button containing waste (Fig. 9, right) under two magnifications. The particles morphology exhibit irregular angular edges, typical of the fracture of glassy materials, and the presence of also typical spherical pores, always to be expected due to the fast firing cycle.

4. Conclusions

A chromium-rich, toxic waste, generated by the tanning process of leather was studied in terms of its composition, stability of the chromium ion, and potential use as a ceramic pigment for the glass and ceramic industries. The preliminary characterization did not show the presence of hexavalent chromium ions in the as-received material, but exposition to temperature, although necessary for the removal of the undesirable organic matter, indeed caused the formation of Cr(VI) ions. Moreover, a washing step of the as-received material is also necessary, in order to remove soluble salts which may cause defects in the glazes upon firing. To overcome or, at least minimize, the oxidation tendency of the chromium ions under temperature, the mixture of the washed waste with selected raw-materials prior to the firing step is indicated.

The incorporation of the waste, after washing and firing, into a ceramic tile glaze formulation yielded good results in aesthetic terms (color tone, texture, and brightness) and in terms of the stability of the chromium in the glass matrix.

Therefore, a potential alternative use for a present industrial waste was identified, which might imply in the reduction of the amount of waste disposal and also the consequent reduction in the use of chromium bearing raw-materials by the ceramic and glass industries. A more detailed study regarding the use of the treated waste as a ceramic pigment is under way and the results will soon be published elsewhere.

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