

Production of materials with alumina and ashes from incineration of chromium tanned leather shavings: Environmental and technical aspects

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Abstract

The leather tannery industry produces a significant amount of solid and hazardous wastes. Chromium-containing wastes like tanned shavings used to be incinerated in order to recover energy. The incineration process generates ashes that must be disposed of. This paper is a report on the results of the evaluation of technological properties and environmental compatibility of products made of alumina and ashes from incinerated chrome tanned shavings. The raw materials, tannery ashes and alumina were mixed together in different proportions. The ceramic bodies were molded using a hydraulic press and fired with a heating rate of 100 K/h until 1400 °C for 4 h in a muffle furnace. The ceramic specimens were characterized regarding physical, mechanical and thermal properties. Leaching tests, according to Brazilian, German and Dutch regulations, were performed on ceramic bodies containing different additions of ash. Results show that the ceramic materials produced are acceptable for refractory applications.

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1. Introduction

Most Brazilian leather industries are located in the south part of the country, in the Federal State Rio Grande do Sul, where more than 50% of Brazilian leather is produced. In the tanning industry raw skin is transformed into leather by means of a series of chemical and mechanical operations [1,2]. Chromium salts (in particular chromium sulphate) are the most widely used tanning substances today. Hides that have been tanned with chromium salts have improved mechanical resistance, extraordinary dyeing suitability and better hydrothermal resistance in comparison with hides treated with vegetable substances. Chromium salts also have higher rate of penetration into the interfibrillar spaces of the skins. This results in savings in terms of production time and better control of the process [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 exact specifications and open the fiber structure, in order to improve the response to subsequent chemical processing. This operation is called shaving and 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 [4]. Since each tannery industry processes 1500 hides every day, the daily generation of shavings is about 6 tonnes [5] and these shavings must be disposed of.

In Brazil almost all shavings are land filled. However, regulations about solid wastes are becoming more and more restrictive and the disposal of hazardous wastes on land sites may cease to continue. In the European State, the pressure over land filling of wastes with high organic content and toxic substances is continuously increasing [6].

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Studies to minimize the amount of tannery waste, their treatment and possible exploitation of waste products are very important. According to Rivela et al. [7] the tanned wastes like shavings can be utilized with or without the presence of chromium. The direct application includes the manufacture of bonded leather, leather boards, fibrous sheets grafted with acrylates, insulators and building materials.

Considering the great volume of generated shavings, 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 of. 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 the chromium due to the presence of organic lipolytic components, metals and other impurities [3]. The thermal treatment of wastes involves incineration, gasification and pyrolysis as a means of disposal, while also recovering energy from waste [8]. Before the incineration of waste from tanneries, toxic releases such as chrome(VI), PCDD/F due to halogenated organic compounds and PAH have to be taken into consideration [6].

Solidification is another process that has been considered as an alternative solution to the disposal of wastes containing heavy metals. In this process, waste materials are mixed with various binding media to obtain a new product with improved physical properties [9]. Different papers have reported the use of solidification, stabilization and vitrification processes to recycle different wastes such as low-level debris [10], radioactive wastes [11], red mud from aluminum extraction [12] and zinc hydrometallurgy [13], incineration ashes [14–16], steel plant fly ash [15,17,18], coal ash [19] and post-cupric-slag [20]. From these studies it can be seen that technologies involving the transformation of wastes into cementitious agglomerates, ceramics, glasses or glass–ceramics have acquired economical importance. Immobilization within a cement-matrix does not require expensive thermal treatments to transform hazardous waste into inert and stable residues [13].

Several authors [21–23] have studied the solidification of tannery wastes with cement. Filibeli et al. [22] have studied the solidification of tannery sludges with high chromium content. The sludge was mixed with cement and some additives as fly ash or sand. After 28 days there was a great reduction on chromium and sulphate concentrations, showing their immobilization in the cementitious phase. The final product is resistant to aggressive environmental agents and can be safely stored in landfill sites. On the other hand, a study of Wang and Vipulanandan [23] about chromium immobilization in cements showed that mixing K_2CrO_4 with cement in concentrations of 0.5, 2 and 5 wt% resulted in a process efficiency of 80%. The immobilization capacity of cement depends on the oxidation state of chromium. Cr^{3+} is more effectively incorporated, while Cr^{6+} is not immobilized in the hydrated phases of cement [24]. Therefore, this process is experiencing increasing opposition in many European countries, because the durability of cement mixtures is not proven and the cement-mix containing hazardous wastes is not reusable, especially in the building industry.

Table 1
Chemical composition of alumina APC 2011 (wt%)

Na ₂ O	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃
0.14	99.78	0.06	0.02

Ceramic and glass technologies are considered to be the most versatile for rendering hazardous waste inert because they destroy organic matter, immobilize regulated heavy metals in a stable matrix and are able to convert complex chemical compositions into useful materials with potential for market exploitation [13]. Nevertheless, the direct use of chrome shavings as raw material for the ceramic industry is also associated to air pollution. So, wastes should be previously thermal treated in a system with good air pollution control, in order to recover energy. The incineration of these wastes results in chromium-rich ash. This is a potential source of chromium oxide, which could be used in the refractory materials production.

The main purpose of this work was to evaluate the immobilization of chromium present in ashes from the incineration of leather shavings with the use of alumina, aiming to produce a refractory material. The technological properties of the obtained product were also evaluated.

2. Materials and methods

2.1. Raw materials

Raw materials from this work were alumina type APC 2011 from ALCOA and ash from the incineration of chromium tanned leather shaving (ACS). A leather factory in Rio Grande do Sul supplied tannery shaving. The shaving was incinerated on a pilot plant with fixed bed, at a temperature of 800 °C [25].

The composition of the alumina APC 2011 from ALCOA is shown in Table 1.

Table 2 shows the chemical analysis of ACS. Such analysis was performed at Activation Laboratories Ltd., Canada. The chromium content of the sample was 29.4%. From this total content, 2.5% is hexavalent chromium [26], determined according to DIN 63.314 standard.

Table 2
Chemical composition of ASC (ash from the incineration of chromium tanned leather shaving)

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

Table 3
Samples of ceramic masses with ash from the incineration of chromium tanned leather shavings (ASC)

Sample	Raw materials (wt%)		
	ASC	Cr ₂ O ₃	Alumina
A1	2	0	98
A2	5	0	95
A3	10	0	90
A4	20	0	80
A5	30	0	70
5% Cr ₂ O ₃	0	5	95

2.2. Formulation of the ceramic specimens

The raw materials, ASC and alumina, were mixed together in the ratios shown in Table 3. Moreover, a formulation with 5% pure Cr₂O₃ and 95% alumina (sample 5% Cr₂O₃) was also tailored to compare the results with the formulation with 10% ash (similar concentration of Cr₂O₃).

The raw materials were dried mixed and ground in a ball mill for 24 h. A 10 wt% polyalcoholvinyllic (PVA) water solution was added to the mixture as plasticizer agent. The mixture was then graded according to size in a mesh #20 (850 μm) sieve. The ceramic bodies were molded into 8 mm × 20 mm × 60 mm bars using a hydraulic press (pressure: 20 MPa). After forming, the specimens were dried at room temperature for 24 h and at 110 °C in an oven for 24 h more. The samples were then fired with a heating rate of 100 K/h until 1400 °C and held at this temperature during 4 h.

2.3. Characterization of specimens: technological properties

The ceramic specimens were characterized in terms of porosity, linear shrinkage and transverse rupture strength, refractoriness and refractoriness under load. Porosity was measured using the Archimedes method according to ASTM C-373/94 [27] standard. The linear shrinkage was determined by the length difference of the test bar before and after firing [28]. The mechanical strength was determined by a four-point bend test using an ATS Universal Machine, according to ASTM C-773/88 [29] specification. The refractoriness of the samples was determined according to two physical test methods: pyrometric cone equivalent [30,31] and refractoriness under load [32,33].

Table 4
Pyrometric cones experiments

Experiment	Temperatures used on experiments (°C)	Orton cones used on experiments	Typical deformation temperature of Orton cones (°C)
1	1366	11	1315
		12	1326
		13	1346
		14	1366
2	1506	15	1431
		16	1473
		17	1485
		18	1506
3	1549	19	1528
		20	1549

Pyrometric cones are designed to deform at certain moments during firing. According to the Brazilian Standard NBR 10358 [34], the produced material can be considered refractory if its refractoriness is similar or higher than the one presented by cone 15 ($T = 1431$ °C) without any deformation. The pyrometric cones were submitted to a heating rate of 150 K/h until temperatures of 1366, 1506 or 1549 °C were reached. Reference pyrometric cones were Orton type. Table 4 shows the parameters used on the pyrometric cones tests.

To evaluate the use of the new refractory material on industrial furnaces it is important to determine the refractoriness under load. This experiment determines the deformation of the refractory material when submitted to a constant load (2 kgf/cm²) with rising temperature. In this work a refractory brick was used as a basis for the samples. Another refractory brick weighting exactly 2 kg was placed over the samples. The testing samples had an area of 1 cm², resulting in a uniaxial force of 2 kgf/cm². A constant heating rate of 150 K/h was used until a maximal temperature of 1550 °C was reached. Fig. 1 shows how the experiment was performed.

2.4. Characterization of specimens: environmental compatibility

In order to comply with current regulations in Brazil, a low leachability of hazardous components from the ceramic matrix must be achieved. Leaching tests were performed on ceramic bodies produced at 1400 °C with a holding time

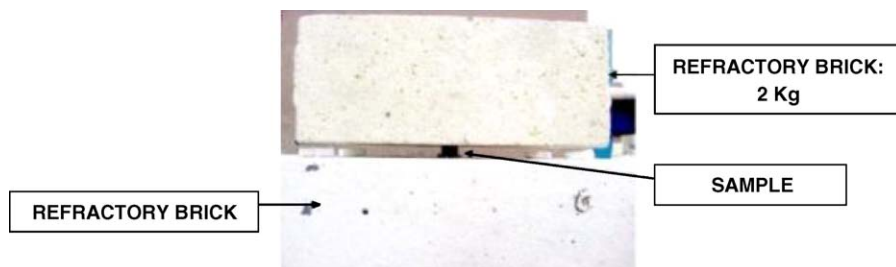


Fig. 1. Refractoriness under load experiment.

of 4 h. The Brazilian tests used were the leaching [35] and solubilization tests [36], which are used to classify wastes.

The batch-leaching test procedure described by NBR 10005/1987 is analogous to the American Extraction Procedure Toxicity Test [37,38]. Deionised water is used as extractor fluid in this procedure. The pH of the water is adjusted to 5.0 by the addition of acetic acid. In this work, samples of 100 g were taken. The green samples were cut in cubes and sieved to a size smaller than 9.5 mm. After drying at 100 °C and firing at 1400 °C, the samples were placed in a recipient with water and stirred for 24 h. The quantity of added water is 16 times the sample weight. After this period the solid and liquid constituents are separated by filtration. The lixiviate was chemically analyzed and the results were compared to the maximum values cited in the Brazilian specification of wastes [39]. According to this procedure a waste is classified on a scale ranging between hazardous and non-inert.

The solubilization test [36] is a tank-leaching test used to classify a waste on a scale between non-inert and inert. The procedure uses deionised water without any pH correction and the liquid/solid ratio is 4:1. In this work, samples of 250 g with a particle size smaller than 9.5 mm were mixed with 1 L of deionised water. After mixing for 5 min, the material was left in the bottle for 7 days. After this period the solid and the liquid constituents were separated by filtration. The liquid constituent was analyzed and the elements concentrations were compared to the values specified in the NBR 10004/1987 standard.

Because there is no leachability test accepted worldwide, the ceramic products were also tested according to the German method [40], in order to compare the obtained results. In the German method, samples weighting at least 100 g in a dry condition are used. The sample with a particle size smaller than 10 mm was introduced into a 2 L bottle and 1 L of deionised water was added. The bottle was closed and placed in a rotary stirrer for 24 h. After this period the solid constituent was separated by filtration. In this work, the elements concentrations in the lixiviate were compared to the values found in specification NBR 10004 [39], and in the German regulation TA-Abfall [41]. The elements concentrations were also compared with the waste classes of the German Federal State Nordrhein-Westfallen [42].

Since there are no specific Brazilian regulations concerning leaching tests for monolithic materials, the method adopted in Holland was applied. The NEN 7345/9 [43] is a tank-leaching test that intends to evaluate the effect of diffusion processes on a leaching system. Two samples of 50 mm × 100 mm were prepared, so this test could be used. The samples were placed on a recipient with deionised water. The water volume is five times the sample weight. The water should be acidified with HNO₃ 0.1N to pH 4. The leaching solution is changed eight times during the experiment: after 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days. In each change the pH and the conductivity were measured. The samples were not washed or dried between changes of solution. Cr was analyzed in each leaching solution.

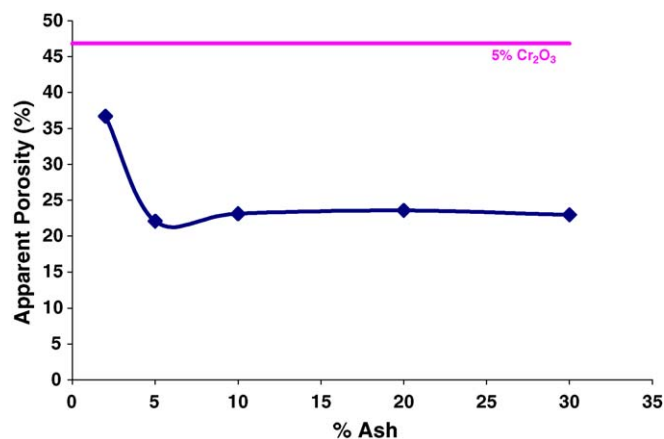


Fig. 2. Apparent porosity as a function of ash content compared to pure Cr₂O₃.

3. Results and discussion

3.1. Physical and mechanical properties of ceramic bodies

Both apparent porosity and mechanical resistance as a function of ash content on the formulations are shown in Figs. 2 and 3. Comparisons with pure Cr₂O₃ are also shown.

As can be seen from Figs. 2 and 3, there is a decrease in the apparent porosity and an increase in the mechanical resistance with higher ash content in the alumina formulation. Densification increase, resulting from the probable vitreous phase formation caused by ash addition, could explain these results. Since the vitreous phase formation occurs when fluxes such as Na₂O are present, and the formulations with higher ash content have higher flux content, a more intense densification is expected. This behavior was also verified in the linear shrinkage, as shown in Fig. 4.

Comparing the results obtained with 10% ash and 5% Cr₂O₃, which has the same amount of Cr₂O₃ in the formulation, it is possible to see that there is no similarity between them. This is probably also associated to the presence of fluxes

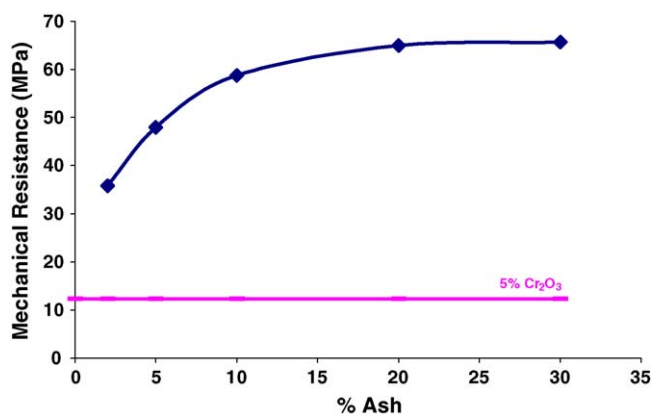


Fig. 3. Mechanical resistance as a function of ash content compared to pure Cr₂O₃.

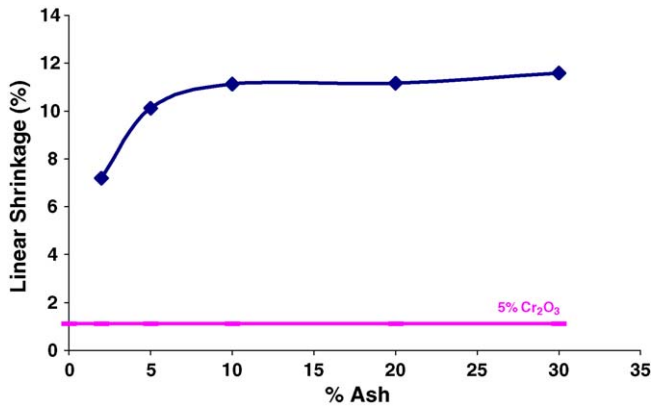


Fig. 4. Linear shrinkage as a function of ash content compared to pure Cr₂O₃.

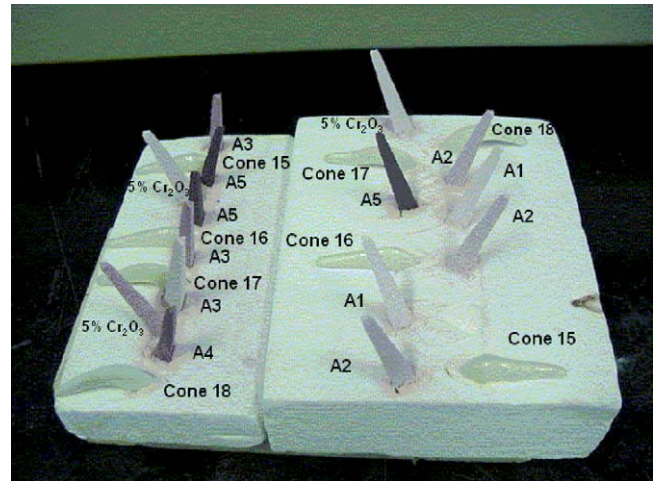


Fig. 6. Pyrometric cone test— $T = 1506\text{ }^{\circ}\text{C}$.

in the ash, causing the formation of vitreous phases in the product.

3.2. Pyrometric cone evaluation

Fig. 5 shows the results obtained on the pyrometric cone test carried out at 1366 °C with cones 11–14, as well as cones made with formulations A1 (2% ash), A2 (5% ash) and A5 (30% ash).

In Fig. 5 it is possible to observe that the cone made with ash-containing formulations showed no deformation at all. Only the standard cones deformed during firing. Fig. 6 shows the test performed at 1506 °C with cones 15–18, and cones made with formulations A1 (2% ash), A2 (5% ash), A3 (10% ash), A4 (20% ash) and A5 (30% ash). Likewise previous test (at 1366 °C), only standard cones suffered significant deformation. The same results were observed at 1549 °C, with cones 19 and 20 being compared to formulations A1 (2% ash), A2 (5% ash) and A4 (20% ash) (Fig. 7).

The resistance of all cones formulated with alumina and ash to the temperatures evaluated shows that the vitreous phase that causes densification of the ceramic specimens still has a high

viscosity, avoiding the deformation. The oxide mixture on formulations, chromium oxide – associated to the hardening of the vitreous phase – and fluxes, brings a favorable equilibrium: high densification with high deformation temperature.

3.3. Refractoriness under load

Fig. 8 shows the results of refractoriness under load at the temperature of 1550 °C. There was a decrease in the refractoriness under load with the ash content, varying from 4 to 6% of deformation with ash contents of 5 and 10% deformation to ash content of 30%. This result is probably associated to the fluxes present in ash.

3.4. Environmental compatibility

In order to get higher confidence levels of the results obtained in the environmental compatibility tests, a statistical approach was used. For that, the error related to the test repeatability was calculated using *t*-Student method [44] with a confidence level of 90%. The following equation was used, for a number of samples

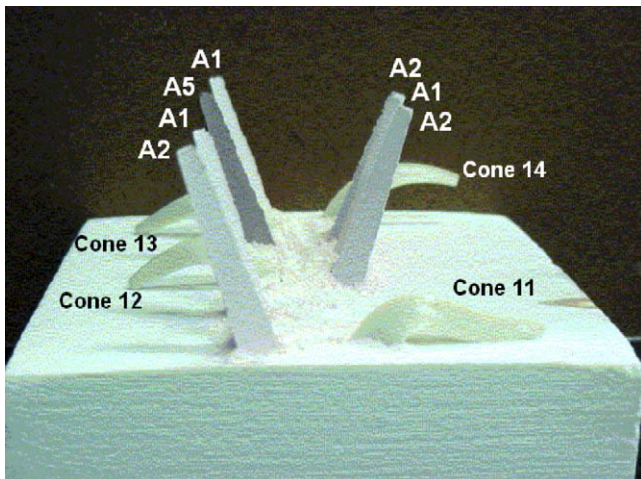


Fig. 5. Pyrometric cone test— $T = 1366\text{ }^{\circ}\text{C}$.

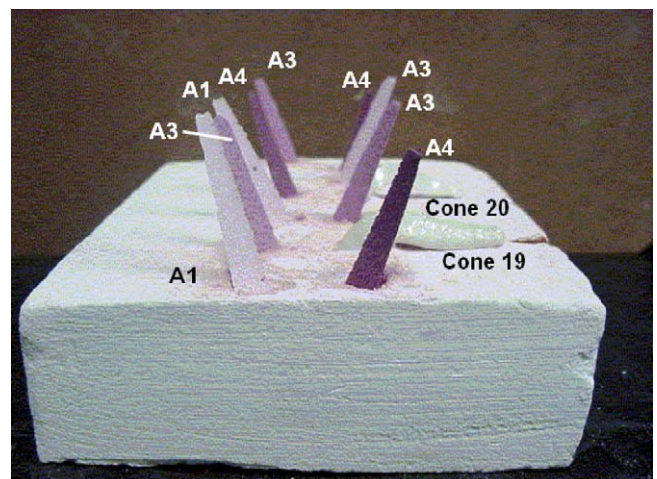


Fig. 7. Pyrometric cone test— $T = 1549\text{ }^{\circ}\text{C}$.

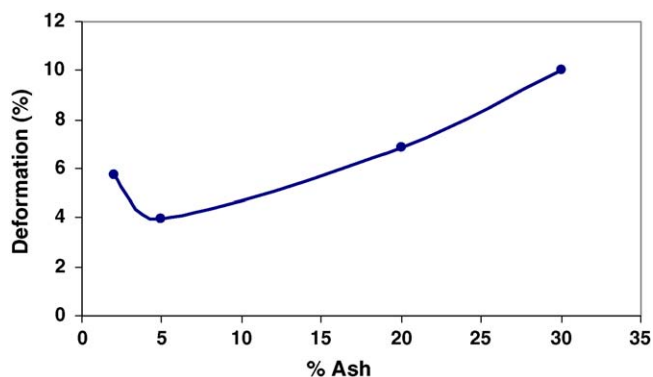


Fig. 8. Refractoriness under load at the temperature of 1550 °C.

lower than 30:

$$C\%E_{\text{repeatability}} = t_{\alpha/2} \cdot \frac{S}{m}$$

where $C\%E_{\text{repeatability}}$ is the repeatability error for a confidence level of $C\%$, $t_{\alpha/2}$ a function of the desired confidence level, S the samples standard deviation and m is the number of samples.

Tables 5 and 6 show the results of leaching and solubilization tests done according to the Brazilian regulations NBR 10005 [35] and NBR 10006 [36] on samples A1–A5 and 5% Cr_2O_3 , fired at 1400 °C.

The results show that all elements from samples were lixiviated in concentrations smaller than the concentrations established on NBR 10004 [39]. However, the sample containing 5% Cr_2O_3 had higher chromium content than the value permitted in the Brazilian regulation, meaning that this would be classified as a hazardous waste. Table 6 shows the results of solubilizations tests carried out with the same formulations.

Elements/ions barium, lead, cadmium, copper, iron, manganese, zinc, silver, mercury, fluoride, cyanide and nitrate were also evaluated; however, results laid down below the equipment detection limits, which are far smaller than the maximum concentration determined by NBR 10004 Standard [39].

The solution generated on the solubilization test with all samples exceeded the limits for chromium. This would be considered to be a non-inert product. According to the Brazilian regula-

tions, the use of ash in the formulation of ceramic products would not assure a good immobilization of chromium. However, it is possible to see that the chromium from ash is less soluble than the chromium that comes from formulation with pure Cr_2O_3 .

In order to evaluate the results concerning a different regulation, a leaching test was carried out according to specification DIN 38414-S4 [40] for samples S1, S2 and S4. The German standards for Nordrhein-Westfalen [42] and the limits stated in TA-Abfall were used as a reference. The standards for Nordrhein-Westfalen [42] have set six different classes for disposal. Disposal class 1 corresponds to inert wastes and classes 5 and 6 correspond to hazardous wastes. In this work the samples were compared to disposal classes 1–3. The TA-Abfall [41] standard sets the limits up to which a waste is classified as non-hazardous. Table 7 shows the results obtained in these experiments.

The results show that according to the German regulations cited in TA-Abfall [41], the ceramic specimens made with ash or pure Cr_2O_3 can be considered as non-hazardous. The regulations applied in the German Federal State of Nordrhein-Westfalen show that the ceramic material would be considered as class 3 because of chromium, copper and phenol concentration. The concentrations of the other elements are all smaller than the limits set in disposal class 1. Antimony, arsine, barium, lead, cadmium, copper, iron, manganese, nickel, zinc, mercury, fluoride, ammonium, cyanide and nitrate were also evaluated, but none of them was detected in the lixivate.

In order to evaluate the role of diffusion of elements in monolithic samples, leaching experiments according to NEN 7345 were made. The obtained results in terms of chromium concentration in the lixivate are shown in Table 8.

The results show that there was no significant chromium lixiviation in all ash-containing samples. The conditions of the test, with bigger samples with smaller surface area, seem to have a great influence on chromium lixiviation. Again, the chromium solubilization for the sample containing Cr_2O_3 was higher, demonstrating that this formulation does not have the conditions to a good chromium immobilization. Nevertheless, diffusion does not seem to be the most important leaching mechanism, since the chromium solubilization decreases with the experiment time, indicating that it is surface process.

Table 5

Concentration of elements in the lixivates obtained from the leaching procedure according to the Brazilian regulation NBR 10005/1987

Element	Maximal concentration (mg L^{-1}) ^a	Lixivate concentration (mg L^{-1})					
		Sample A1	Sample A2	Sample A3	Sample A4	Sample A5	Sample 5% Cr_2O_3
Chromium	5.0	0.69 ± 0.0067	0.18 ± 0.005	0.07 ± 0.003	0.07 ± 0.0018	0.11 ± 0.005	0.11 ± 0.0056
Fluoride	150.0	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cadmium	0.5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Lead	5.0	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Barium	100.0	<1	<1	<1	<1	<1	<1
Silver	5.0	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mercury	0.1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

^a Consider a waste non-hazardous according to NBR 10004.

Table 6
Concentration of elements in the solutions obtained from the solubilization procedure according to the Brazilian regulation NBR 10006/1987

Element	Maximal concentration (mg L ⁻¹) ^a	Lixivate concentration (mg L ⁻¹)					
		Sample A1	Sample A2	Sample A3	Sample A4	Sample A5	Sample 5% Cr ₂ O ₃
Total chromium	0.05	0.34 ± 0.009	0.7 ± 0.017	2.2 ± 0.0505	0.237 ± 0.003	0.24 ± 0.0034	60 ± 1.68
Sodium	200	1.23 ± 0.035	9.1 ± 0.168	19 ± 0.337	2.5 ± 0.034	4.6 ± 0.16	16 ± 0.67
Aluminum	0.2	<0.02	0.48 ± 0.017	2.43 ± 0.097	<0.02	<0.02	<0.02
Calcium carbonate	500	0.019 ± 0.0005	0.019 ± 0.0016	0.052 ± 0.00097	0.023 ± 0.0025	0.022 ± 0.0009	82 ± 1.68
Sulphate	400	0.54 ± 0.009	1.2 ± 0.034	17 ± 0.67	0.33 ± 0.0097	0.33 ± 0.0034	280.33 ± 0.973
Chloride	250	0.014 ± 0.0003	0.23 ± 0.0084	0.052 ± 0.00097	0.014 ± 0.0005	0.018 ± 0.0007	3.1 ± 0.033

^a Consider a waste inert according to NBR 10004/1987.

Table 7
Concentration of elements in the lixivates obtained by the leaching procedure according to the German regulation DIN 38414

Element	Maximal concentration (mg L ⁻¹)				Lixivate concentration (mg L ⁻¹)					
	Nordrhein-Westfalen			TA-Abfall	Sample A1	Sample A2	Sample A3	Sample A4	Sample A5	Sample 5% Cr ₂ O ₃
	1	2	3							
pH	6.5–9.5	5.5–12	5.5–12	4–13	7.1 ± 0.16	7.5 ± 0.16	8.4 ± 0.17	7.4 ± 0.17	6.8 ± 0.16	7.6 ± 0.16
Conductivity (µS/cm)	40.000	300.000	–	100.000	33.6 ± 0.16	34.3 ± 0.16	65.4 ± 0.17	33.6 ± 0.16	31.5 ± 0.16	104.4 ± 0.17
TOC	–	–	–	200	<3	<3	5 ± 0.17	8.067 ± 0.19	<3	<3
Phenol	0.0005	0.1	20	100	0.024 ± 0.001	0.003 ± 0.0001	0.002 ± 0.001	0.002 ± 0.001	<0.01	0.005 ± 0.0003
Bore	1.0	1.0	10.0	–	<0.01	<0.01	0.02	0.03	0.01	0.02
Total chromium	0.05	1.0	10.0	–	0.2 ± 0.0033	0.31 ± 0.016	1.2 ± 0.0017	0.15 ± 0.0016	0.18 ± 0.016	16 ± 0.505
Chromium(VI)	–	0.1	–	0.5	0.15 ± 0.006	0.29 ± 0.016	1 ± 0.034	0.12 ± 0.0017	0.18 ± 0.016	0.011 ± 0.0009
Chloride	200	–	–	10.000	0.95	0.75 ± 0.016	0.8 ± 0.017	0.82 ± 0.016	1.2 ± 0.084	2.2 ± 0.16
Sulphate	–	–	–	5000	1.1 ± 0.016	1.6 ± 0.016	6.8 ± 0.17	1.4 ± 0.033	1.3 ± 0.033	90 ± 1.68

Table 8

Concentration of elements in the lixiviates obtained by the leaching procedure according to the Dutch regulation NEN 7345

Time (days)	Total chromium concentration (mg L ⁻¹)					
	A1	A2	A3	A4	A5	5% Cr ₂ O ₃
0.25	<0.02	0.11 ± 0.0026	<0.02	0.04 ± 0.001	<0.02	12 ± 0.033
1	<0.02	0.09 ± 0.0032	<0.02	0.03 ± 0.0001	<0.02	4.10 ± 0.337
2.25	<0.02	0.04 ± 0.0016	<0.02	0.03 ± 0.00168	<0.02	2.57 ± 0.098
4	<0.02	<0.02	<0.02	<0.02	<0.02	1.60 ± 0.016
9	<0.02	<0.02	<0.02	<0.02	<0.02	0.48 ± 0.018
16	<0.02	<0.02	<0.02	<0.02	<0.02	0.04 ± 0.002
36	<0.02	<0.02	<0.02	<0.02	<0.02	0.03 ± 0.0016
64	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

4. Conclusions

The present study was conducted to develop and to characterize a refractory product with the addition of ashes from incinerated chrome tanned shavings in alumina. The feasibility of the use of these ashes as raw material was demonstrated. The increase of ash content decreases the apparent porosity and increases the mechanical resistance and the linear shrinkage of samples. All samples have shown refractoriness higher than the one presented by cone 15 ($T = 1431\text{ }^{\circ}\text{C}$). In this case the technological properties are compatible with those required for refractory products. However, the increase in ash content causes a deleterious effect on the refractoriness under load and further studies should be made to evaluate the limits of use in this case. Concerning the environmental compatibility of ceramic bodies, the results of leaching and solubilization tests according to the Brazilian regulations NBR 10005 and NBR 10006, to the German regulation DIN 38414, and to the Dutch regulation NEN 7345 showed that the lixivate generated by leaching of these products did not exceed the set limits for hazardous wastes. Nevertheless, the concentration of copper, chromium and phenol in several samples exceeded the limits in a way that the product could be considered non-inert.

Results obtained in this work showed both technological and environmental trends and possibilities of this kind of ceramic waste processing.

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