

## Incorporation of chromium residue from tannery in black and red clay



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### ABSTRACT

Brazil has a large amount of clay reserves scattered throughout the country, but due to environmental awareness, restrictive laws and conservation units there is a restriction of the availability of this mineral resource. In addition, ceramics are widely studied for waste encapsulation, aiming at cost benefit and sustainability. One of these residues is

chromium from leather tanning, it has polluting characteristics mainly because it contains Chromium (Cr)III. This work aimed to study the feasibility of incorporating tannery residue in ceramic materials, using different clays. For this, two types of clay were selected and incorporated 0, 1 and 2% of tannery residue with 8.03% of Cr, molded ceramic bodies, and then extruded. The bodies were dried and burned at temperatures of 900°C and 1050°C. The characterization of the raw materials showed through the limits of Atterberg that red clay is more plastic than black clay. In general, the results of incorporation of residues in red clay were better than in black clay. In fact, the red clay in the presence of tannery residue showed lower linear retraction, lower water absorption, less mass loss to fire and rupture tension. Thus, as for the addition of chromium, associated with temperatures of 1050° C it can be said that the ceramics made of red clay had their characteristics improved, without changing the plasticity parameters and the physicochemical properties of the tested ceramics. This study shows a feasibility for an ecologically more appropriate destination of tannery waste.

**Keywords:** Tannery Residue, Ceramics, Chromium.

## 1 INTRODUCTION

In the tanning industry, every process is carried out to curb the putrefaction of leather, with this procedure two types of effluents are generated, requiring the treatment of them for later use or disposal. One of them is generated in the first stage of leather tanning, it is rich in organic material The other effluent is generated through the last stage of the manufacture of *wet-blue* leather, it is in this step that the tanning process occurs through mineral tannants, and the Chromium salts are the most used worldwide.

Chromium waste, because it is a hazardous metal, has been much studied so that a correct disposal occurs so as not to generate any environmental problem. The sector that most releases this type of waste is the Tannery, specifically considering the amount of hazardous waste of chromium



salts, used in the tanning of the skins. These residues are released in the shavings of the skins, in powder (from the relower) and also in sludge (from the WWTP) (ABREU, 2006; NARDINO et al, 2015). The aggravating factor is due to factors such as inadequate disposal of waste, scarcity of dumping areas, high cost of maintenance and control of landfills (chemical analysis of sulfur, guarantee of soil impermeability) among others (COSTA, 2009).

Waste containing chromium falls under elements of Class I of ABNT (Brazilian Association of Technical Standards), and NBR (Brazilian Standards) 10004/2004 as highly hazardous, which presents risks to public health and the environment during its handling or disposal incorrectly (ABREU, 2006 ; PERON, 2008).

Studies involving the reuse of chromium have been carried out for various applications, for example, the production of basic chromium sulfate, manufacture of ceramic and glazed pigments, manufacture of bricks, porcelain tiles and refractories, among others. Aiming to minimize manufacturing costs of the materials in addition to incorporating chromium in the final products avoiding damage to the environment (Abreu et al 2006; Peralta et al, 2014). For a tannery with production of 2700 skins per day the amount of chromium sludge discarded will be 4500 Kg/month. This sludge could be incorporated into a pottery with production of 47000 ceramic blocks monthly, only in 4 days of production, if 1% of chromium residue was used in each block (OLIVEIRA, 2008).

Specifically in the environment, studies refer that there are three types of oxidation of the element being these: the "chromium 0, chromium III and chromium VI. Chromium III has natural occurrence in the environment, while chromium VI and chromium 0 are usually produced by industrial processes" (GIANNETTI, *et al* 2001).

According to Oliveira (2008), the chromium resulting from the industrialization of leather, presents itself in its trivalent form, chromium III, being relatively non-toxic compared to the hexavalent that is considered carcinogenic if ingested. Also according to Oliveira (2008), Freitas (2006) carried out the monitoring of three tanneries in the State of Mato Grosso do Sul, taking samples at all stages, either in the tanning or in the waste treatment plants, and no traces of hexavalent chromium (chromium VI) were found. It is also emphasized that due to the acidic or neutral pH, which is subjected to this element during the treatment processes, there is a high stability in remaining in a state of chromium III oxidation, making it feasible to reuse this residue without presenting toxicity in the final product.

An important problem of the ceramics sector has always been to be recognized as a great degrader of the environment. That is why entrepreneurs have been looking for sustainable techniques, opting for cleaner production, whether at the time of burning, seeking biomass products for the heating of furnaces or even in the search for eco-efficient methods, which enable a differential in their product in relation to the competition.



The technique involving the transformation of clay, is given by the fusion of silica with waste and other materials forming the ceramic material, obtaining a safe final product, making hazardous waste in manufactures with less toxicity and with added value (OLIVEIRA, 2008). According to Keller (1997), the use of chromium within the ceramic body, builds a reducing environment, avoiding the oxidation of chromium III in chromium VI, so the chromium is stabilized within the ceramic material.

This work aims to evaluate the feasibility of applying the waste with chromium salts after treatment in the WWTP (Effluent Treatment Station) from a tanning industry, incorporating it in ceramics, aiming at reducing the costs of disposing of chromium waste in industrial landfills and in environmental impacts because there is a decrease in the amount of clay used and avoids the incorrect disposal of chromium waste in non-legalized places.

## 2 METHODOLOGY

### 2.1 RAW MATERIALS

Clays and chromium residue were used for the manufacture of ceramic blocks. The chromium sludge comes from a WWTP of a Tannery in Rio Grande do Sul, Figure 1 shows the chromium residue before any procedure. The clays were collected in different potteries of the southern region of Rio Grande do Sul, one of them with dark coloration approaching the black color was collected in the region of Caçapava do Sul, the other clay with reddish color, was collected in the region of Bagé - RS.

Figure 1- Chromium residue from a tannery WWTP.



Source: authors

### 2.2 PREPARATION OF RAW MATERIALS

The clays were subjected to a drying procedure for 4 days with intense sun to lower their humidity, then they were detorted and sprayed in a hammer mill. The chromium residue was first dried in an oven for 5 hours at a temperature of 105 °C and then a ball mill was used for the granulometric reduction



### 2.3 CHARACTERIZATION OF RAW MATERIALS

The analyses of Atterberg limits for the two clays were performed in the same way. First, 200g portions of the samples were separated and passed in a 0.42 mm sieve. For the liquidity limit (LL) a portion of the sample was sieved, moistened with distilled water and mixed until a homogeneous mixture was obtained. The Casagrande apparatus (Solotest Brand) was used, in which the mass was placed in the apparatus, made a standard crack and the process was started by turning the crank so that the blows occurred (1/s) until closing the groove. A fraction of the sample was removed and stored in previously weighed and identified metal capsules, and then their weights were determined with the aid of the scale. This process was repeated 5 times with different moisture contents in the homogenized sample. After finishing the capsules were taken to the oven (105°C) for 24 hours and weighed again. At the plasticity limit (LP), approximately 5g of the moistened and homogenized sample was used. With the aid of a frosted glass plate, cylinders were made in the clay manually, comparing it with a jig of approximately 3 mm, until it was not possible to reach the diameter without it cracking. At this point the clay was also stored in capsules previously weighed and identified, then weighed to identify the mass of the sample. This process was repeated 5 times and taken to the oven at 105°C for 24 hours and weighed again. After this period, the Liquidity Limit (LL) and Plasticity Limit (LP) were defined. With the limits of liquidity and plasticity already defined it was possible to calculate the plasticity index through equation 1 (FIORI, 2009).

Eq 1:

$$IP (\%) = LL - LP$$

The granulometry was performed by sedimentation with the aid of a densimeter, using NBR 7181/84.

### 2.4 CHEMICAL COMPOSITION:

For the characterization of the chemical composition of the raw materials, S1 TURBOSD was used, which is based on energy dispersive X-ray fluorescence technology and uses an X-ray tube as an excitation source. The samples were placed in bags and weighed on an analytical balance, with an approximate amount of 10g each. Then the samples were placed in the device for reading

### 2.5 COMPOSITION OF ORGANIC MATTER AND CARBON IN CLAYS

Based on Benaci (2010), 1g of each clay was weighed and placed in an oven at 105°C for 3h and then weighed. Subsequently, it was taken to muffle for 2 hours at a temperature of 550°C and



weighed again. For the quantification in percentage of organic matter and carbon, equations 2 and 3 were used, respectively:

Eq 2:

$$(\%)M.O. = \left( \frac{(P_1 - P_2) * 100}{M} \right)$$

Eq. 3:

$$(\%)C.Total = \left( \frac{(P_1 - P_2) * 100}{M} \right) / 1,72$$

Where (%) M.O. is the amount of organic matter given as a percentage, (%) C. Total is the amount of carbon as a percentage in the sample, P<sub>1</sub> is the weight of the dry sample after the greenhouse, P<sub>2</sub> is the weight of the sample burned at 550°C and M the initial mass.

## 2.6 PRODUCTION OF SPECIMENS

Firstly, to proceed with the mixing of the raw materials it was necessary to determine the moisture of each of the clays, the samples were weighed before and after being placed in the oven, obtaining humidity of approximately 10%, the two mixtures were carried out in the same way. Then proceeded a homogeneous mixture, with incorporation of chromium residues and (1.0 % and 2.0%) in the clays, then water was added, adjusting the humidity rate to close to 27%, a control group was used, without the addition of chromium. The specimens were molded by extruder obtaining about 100 specimens of each specimen, all of which were identified manually.

## 2.7 BURNING OF SPECIMENS

The specimens were dried naturally for 5 days and then taken to the oven for 24 hours at a temperature of 110°C. The specimens then went to the muffle, with temperatures of 900°C and 1050°C. The heating rate was manually regulated, there was an increase of 50°C every 20 minutes until a temperature of 550°C then went to an increase of 100°C to every 30 minutes, up to the desired temperature. Figure 28 shows the post-burn specimens.



## 2.8 TESTS CARRIED OUT ON CERAMICS:

### 2.8.1 Loss of mass to fire (PF)

For the analysis of mass loss to fire, electronic scales with digital reading were used. The masses were weighed after remaining in an oven for 24 hours and cooled thus obtaining their dry mass. Likewise, they were weighed after burning in muffle with temperatures of 900°C and 1050°C, determining the burning mass. Thus, equation 4 was used to determine the PF.

Eq. 4

$$PF(\%) = \left( \frac{m_s - m_q}{m_s} \right) * 100$$

Where PF (%) is the percentage loss of mass to fire,  $m_s$  (g) is the mass of the specimen dried in the oven and  $m_q$  (g) is the mass of the specimen burned in the muffle.

### 2.8.2 Linear Retraction (RL)

A digital caliper was used for the linear retraction analyses. The length of the specimens was made after extrusion, after remaining in an oven for 24 hours and after burning in muffle with temperatures of 900°C and 1050°C determining the percentage of retraction of the specimen. Equation 5 was used to determine the RL.

Eq. 5:

$$RL(\%) = \left( \frac{C_s - C_q}{C_s} \right) * 100$$

Where RL (%) is the linear shrinkage given as a percentage,  $C_s$  (g) is the length of the specimen dried in the oven and  $C_q$  (g) is the length of the specimen burned in the muffle.

### 2.8.3 Apparent specific mass (MEA)

The apparent specific mass was obtained in triplicates, first the specimens were placed in water, as observed in Figure 29 and subjected to heating until the water boiled for 1 hour, and then they were immersed for 24 hours in the same container. Subsequently, the immersed weight ( $m_i$ ) was determined on a hydrostatic scale. Subsequently, using the electronic scale, the wet weight ( $m_u$ ) was recorded.



Finally, the specimens remained in an oven at 105°C for 24 hours, and after cooling they were weighed again, thus obtaining their dry mass ( $m_s$ ). Thus, the MEA was determined by equation 6.

Eq. 6:

$$MEA = \frac{m_s}{V_A}$$

Where MEA ( $\text{g}/\text{cm}^3$ ) is the apparent specific mass,  $m_s$  (g) is the dry mass of the sample and ( $\text{cm}^3$ ) is the apparent volume  $V_A$  of the sample.

#### 2.8.4 Water absorption (AA)

Water absorption was determined using the wet masses and dry masses found in the apparent specific mass, and using equation 7.

Eq 7:

$$AA(\%) = \left( \frac{m_u - m_s}{m_s} \right) * 100$$

Where AA (%) is the water absorption as a percentage,  $m_u$  (g) is the mass of the wet specimen, and  $m_s$  (g) is the dry specimen mass.

#### 2.8.5 Apparent porosity (AP)

To determine the apparent porosity, wet masses and immersed masses, found in the apparent specific mass, were used and applied in equation 8.

Eq. 8:

$$PA(\%) = \left( \frac{m_u - m_s}{m_u - m_i} \right) * 100$$

Where PA (%) is the apparent porosity given as a percentage,  $m_u$  (g) is the mass of the wet specimen,  $m_s$  (g) is the mass of the dry specimen,  $m_i$ (g) is the mass of the specimen immersed in water.



### 2.8.6 Flexural tensile strength (FRT)

To determine the flexural strength, 5 ceramics of each model were separated, with the specimens already burned, and through the flexometer the Flexural Rupture Stress was determined. It was necessary to provide the software with the width and height of the specimens and the distance used between the supports, being 80mm. Using the software of the equipment itself, the rupture stresses were determined, where it uses the parameters of equation 9.

Eq. 9:

$$\sigma = \frac{3.P.L}{2.b.h^2}$$

Where  $\sigma$  is the flexural strength (N/mm<sup>2</sup>), P is the load now of rupture (kgf), L is the distance between the supports (mm), b and h are the dimensions of the specimens at the base and height respectively (mm).

### 2.8.7 Leaching

The leaching was performed in duplicate, based on NBR 10005, in which, first, 100 g of each ceramic was ground with the aid of a pistil, until the crushed obey the rule of passant in mesh 9.5mm. Then solution No. 1 was made with the addition of 5.7 ml of glacial acetic acid to distilled water and added 64.3 ml of NaOH 1.0N and the volume was completed up to 1L, the pH was verified between  $4.93 \pm 0.05$ . An orbital agitator with a speed of 50 rpm was used for 24 hours. After rotation, the vials were removed from the equipment and the samples were centrifuged and filtered in vacuum. The filtrate was subjected to XRF in duplicates to quantify the chemical elements that were leached.

## 3 RESULTS AND DISCUSSION

### 3.1 CHARACTERIZATION OF RAW MATERIALS

#### 3.1.1 Analysis of Atterberg limits

The results of the Atterberg limits for the samples of the two clays, named as red clay and black clay, are shown in Table 1.





Table 1- Atterberg limits.

	Red Clay	Black Clay
LL(%)	43	40,5
LP(%)	16,3	19,3
IP(%)	26,7	21,2

The plasticity index (PI) of the different clays presented values of 26.7% and 21.2%, for the red and black clay respectively, according to Medeiros (2010), when the  $IP > 15\%$  the clays are considered highly plastic, so the red clay is more plastic than the black clay. The values of liquidity limits (LL) showed values of 43% for red clay and 40.5% for black clay. Regarding the plasticity limit (LP), which indicates the minimum amount of moisture that the clay must contain to be formed, the values were between 16.3% for red clay and 19.3% for black clay. According to Medeiros (2010), the values for the LT should be within the range of 30% to 60%, LP between 15% to 30% and IP 10% to 30%, showing that the results are within the range mentioned.

Table 2- Characteristics of clays.

	Red Clay	Black Clay
Mea (g/cm <sup>3</sup> )	2,677	2,598
Clay (%)	40	32
Silt (%)	25	30
Sand (%)	31	38

As can be seen in Table 2, the apparent specific masses are 2.677 g/cm<sup>3</sup> for red clay and 2.598 g/cm<sup>3</sup> for black clay. According to Vieira *et al* (2000), clay compounds are classified according to their granulometry, being  $< 2 \mu\text{m}$  clay, between 2 and 20  $\mu\text{m}$  silt and  $> 20 \mu\text{m}$  sand. Therefore the red clay is composed of 40% (clay fraction), 25% (silt) and 31% (sand), the rest of the 4% are boulders, in relation to black clay the values are 32% (clay fraction), 30% (silt) and 38% (sand).

### 3.1.2 Chemical composition

The chemical composition was performed by X-ray fluorescence (XRF), analyses were made of the red and black clays and also of the chromium residue from tannery, Table 3 presents the results obtained.

Table 3- Chemical composition by XRF of the different raw materials.

Element	Red Clay	Black Clay	Cr residue
Mg (%)	2,64	3,00	21,50
Al (%)	22,47	22,25	18,66
Si (%)	38,79	44,14	0,82
P (%)	-	-	2,52
S (%)	-	-	17,30
Cl (%)	0,07	0,07	2,86
K (%)	0,51	1,76	0,04



Ca (%)	0,05	0,35	27,10
Ti (%)	0,79	1,01	-
Cr (%)	-	-	8,03
Mn (%)	0,05	0,08	0,06
Fe (%)	5,39	6,31	0,19
Co (%)	0,26	0,34	
Zn (%)	-	-	0,01
Rh (%)	0,31	0,25	0,05
Cd (%)	0,13	0,10	-
Sr (%)	0,00	0,00	0,04

In relation to clays, they are basically composed of the same chemical elements, with variations mainly in the amount of silicon (Si), where black clay contains 44.14% and red 38.79%, iron (Fe) with 6.31% in black clay and 5.39% in red clay and potassium (K) with values of 1.76% in black clay and 0.51% in red.

It is possible to verify that the residue from tannery has about 8.03% of chromium (Cr), which was expected due to the tannin used being the chromium salts, it is also possible to observe 18.66% of aluminum (Al) and 17.3% of sulfur (S) due to the aluminum sulfate used to lower the pH, there is 27.10% of calcium (Ca) due to lime added in the treatment, 21.50% of magnesium (Mg) is perceived perhaps due to clay minerals that can be a hydrated magnesium compound.

### 3.1.3 Composition of organic matter and carbon in clays

Table 4 shows the organic matter and carbon contents in the different clays.

Table 4 shows that the percentage of carbon varied from 0.86% and 2.92% for red and black clay respectively, the organic mass was 14.79 g/kg for red clay and 50.15 g/kg for black clay. The red clay is characterized as a low amount of organic matter being below 2.5%, while the black clay contains a high content of organic matter with a value higher than 5%.

Table 4 - Organic matter and carbon contents in clays.

Types of Clays	(%) Total Carbon	(%) Organic Mass	Organic Mass (g/kg of soil)
Red Clay	0.86 ± 0.14	1.48 ± 0.23	14.79 ± 2.34
Black Clay	2.92 ± 0.14	5.02 ± 0.25	50.15 ± 2.49

## 3.2 PHYSICO-CHEMICAL PROPERTIES

### 3.2.1 Water absorption (AA)

Table 5 represents the water absorption at the different temperatures at which the specimens were burned and with the proportions of chromium residues incorporated in the different clays.



Table 5- Water absorption of the specimens at different firing temperatures, proportions of chromium residue and clay types.

Temp. Burning (°C)	% Residue	AA (%) Red Clay	AA (%) Black Clay
900	0	16,52 ± 0,14	16,41 ± 0,37
	1	16,81± 0,33	17,03± 0,30
	2	16,70± 0,11	16,83± 0,11
1050	0	14,19± 0,14	15,07± 0,52
	1	14,14± 0,38	15,07± 0,56
	2	13,58± 0,21	14,90± 0,33

Comparing the two types of clay at the same temperature and percentage, it is not possible to verify the increase or decrease in the water absorption of the specimens due to the values of the standard deviation. It can also be observed that there was no gradient between the absorption of water with the increase in the addition of residue at the same temperature in any of the cases. In relation to each clay, in the same proportion and different temperature, it is suggested a lower water absorption when the temperature is increased from 900°C to 1050°C, this behavior was similar for the specimens manufactured with the two clays, results also found by Oliveira (2008) and Camargo (2005).

Comparing the limits specified in Santos (1989) and by the Ceramics Laboratory of ITP/SP, represented in Table 5, it is possible to observe that there was no restriction for any temperature in water absorption.

### 3.2.2 Linear Retraction (RL)

Table 6 represents the linear retraction at the different temperatures that the specimens were burned and with the proportions of chromium residues incorporated in the different clays.

Table 6- Linear retraction of the specimens in the different firing temperatures, proportions of chromium residue and clay types.

Temp. Burning (°C)	% Residue	RL (%) Red Clay	RL (%) Black Clay
900	0	0,78± 0,11	0,53± 0,12
	1	0,66± 0,23	0,36± 0,06
	2	0,70± 0,09	0,51± 0,13
1050	0	3,38± 0,34	2,60± 0,17
	1	3,13± 0,29	2,48± 0,19
	2	3,17 ±0,17	2,81 ±0,16

Relating the two types of clay, at the same temperature and percentage of residue, it is possible to verify a tendency of the specimens of the red clay to have greater linear retraction than the specimens manufactured with black clay.

In relation to each clay, at the same temperature and proportion of chromium residue, it is not possible to identify higher or lower values for the linear retraction of the specimens due to standard deviations



It is also observed that the linear retraction suggests an increase as it raises the temperature in both clays, when at the same temperature and addition of residue, comparing with Oliveira (2008), it is possible to perceive a behavior like the results acquired here.

### 3.2.3 Apparent porosity (AP)

Table 7 represents the apparent porosity data at the different temperatures that the specimens were burned and with the proportions of chromium residues incorporated in the different clays.

Table 7- Apparent porosity of the specimens at different firing temperatures, proportions of chromium residue and clay types.

Temp. Burning (°C)	% Residue	BP (%) Red Clay	BP (%) Black Clay
900	0	31,14± 0,22	29,83± 0,64
	1	31,51± 0,43	30,80± 0,21
	2	31,42± 0,16	30,52± 0,18
1050	0	27,95± 0,22	28,47± 0,29
	1	27,88± 0,48	28,63± 0,17
	2	27,04± 0,30	28,44± 0,46

Comparing the clays at the same temperature and amount of residue, it can be said that at the temperature of 900°C the specimens made with red clay appear to be more apparent porosity than the specimens made with black clay in all percentages. At a temperature of 1050°C, specimens made with red clay appear to have lower apparent porosity than specimens made of black clay. It can also be observed that specimens made of red clay appear to have a higher percentage of apparent porosity reduction than specimens made of black clay.

By relating each clay at the same temperature and different residue proportions, it is possible to verify that the apparent porosity values of the specimens are all within the same range due to the standard deviations. It is also noted that the specimens of the two clays, the apparent porosity tended to decrease with increasing temperature, compared to the same percentage of residue.

### 3.2.4 Apparent specific mass (MEA)

Table 8 represents the specific masses apparent at the different temperatures that the specimens were burned and with the proportions of chromium residues incorporated in the different clays.



Table 8 - Apparent specific mass of the specimens at different firing temperatures, proportions of chromium residue and clay types.

Temp. Burning (°C)	% Residue	MEA (g/cm <sup>3</sup> ) Red Clay	MY (g/cm <sup>3</sup> ) Preta clay
900	0	1,89± 0,003	1,82± 0,002
	1	1,87± 0,012	1,81± 0,006
	2	1,88± 0,003	1,81± 0,002
1050	0	1,97± 0,005	1,89± 0,020
	1	1,97± 0,015	1,90± 0,019
	2	1,99± 0,008	1,91± 0,011

Comparing the specimens made with the two types of clay, at the same temperature and percentage of residue it is observed that the red clay appears to have a greater apparent specific mass than the black clay.

With respect to the same clay and temperature, the specific masses apparent in the different proportions of residue were in the same range of values because of the standard deviations for the specimens.

Note that the apparent specific mass tends to increase as the temperature in both clays rises, relating the same clay to the same addition of residue.

### 3.2.5 Loss of mass to fire (PF)

Table 9 represents the loss of mass to fire at the different temperatures that the specimens were burned and with the proportions of chromium residues incorporated in the different clays.

Table 9- Loss of mass to fire of the specimens at different firing temperatures, proportions of chromium residue and types of clay.

Temp. Burning (°C)	% Residue	PF (%) Red Clay	PF (%) Black Clay
900	0	5,22± 0,12	6,99± 0,23
	1	5,35± 0,12	7,13± 0,14
	2	5,24± 0,11	7,53± 0,10
1050	0	5,61± 0,28	7,01± 0,07
	1	5,54± 0,17	7,51± 0,15
	2	5,71± 0,19	7,88± 0,16

It is possible to verify that the specimens made with the red clay appear to have a lower loss of mass to the fire than the specimens made with black clay, comparing the same proportion of residue with the same temperature.

Relating the same clay and temperature, with different percentage amounts of residue it is possible to say that due to the standard deviations it is not possible to identify an increase or decrease in the loss of mass to fire.



Comparing the same amount of chromium residue it is verified that when the temperature was increased from 900°C to 1050°C there was a greater tendency of mass loss to fire in the specimens in both clays.

### 3.2.6 Flexural tensile strength (FRT)

Table 10 represents the bending tensiles at the different temperatures that the specimens were burned and with the proportions of chromium residues incorporated in the different clays.

Table 10- Rupture stress at flexion of the specimens at different firing temperatures, proportions of chromium residue and types of clay.

Temp. Burning (°C)	% Residue	TR(MPa) Red Clay	TR(MPa) Black Clay
900	0	2,25± 0,18	6,39± 0,29
	1	2,75± 0,29	5,50± 0,19
	2	3,20± 0,17	6,00± 0,40
1050	0	2,50± 0,27	6,73± 0,39
	1	3,02± 0,16	5,59± 0,39
	2	3,66± 0,19	6,15± 0,46

It is possible to observe that the specimens made with red clay appear lower rupture stress than the specimens manufactured with black clay in all cases, relating the same addition of residue and the same temperature.

In the red clay specimens it can be verified that there was a tendency of increase of rupture stress both in relation to the increase of residue at the same temperature and the same amount of residue with the increase of temperature. In the black clay specimens, it is observed that when there is an increase in temperature there is a tendency to increase the rupture stress compared to the same amount of residue, but with respect to the same temperature with the addition of different residue, the highest rupture stress is presented when there is no addition of residue.

Now, comparing the heating with the same percentages of residue, in the specimens of the two clays, it is noticed that all three proportions appeared to increase the tensile strength of the flexion. Therefore, when using a temperature of 1050°C the quality of the bricks obtained is higher than when subjected to a burning temperature of 900°C.

The results of Oliveira (2008) and Camargo (2005) for rupture stress to flexion increased both relating to the same percentage of residue, and comparing with different amounts percentage of residue. Facing the results obtained in this work, it is observed that the same behavior occurred with the specimens of the red clay. In relation to the specimens of black clay only relating the temperature with the same amount of residue, obtained the same results.

Comparing the limits specified in Santos (1989) and by the Ceramics Laboratory of ITP/SP represented in Table 5, it is possible to observe that black clay can be used on any occasion. Already



the red clay can be used only for the manufacture of masonry bricks, the values for the clay without addition of residue were very close to the limits, being important to pay attention to the standard deviation, for the addition of 1 and 2% was obtained trend of increase in the rupture stress.

The specimens made with black clay when added chromium residue appeared to have their resistance reduced, this can be explained perhaps due to the formation of the so-called black heart, where it can be observed through figure 2.

Figure 2- Ceramic with black heart.



Source: Author

### 3.2.7 Leaching Analysis

The analyses performed through NBR 10005, with the use of XRF, can verify the chemical elements that were leached, through Table 11.

Table 1- Percentage of chemical elements leached in clays.

Element	Red Clay (%)	Black Clay(%)
Al	4,288±0,161	4,208±0,385
K	0,140±0,000	0,118±0,011
Cr	-	-
Mn	-	-
Fe	0,005±0,004	0,008±0,004
Ni	-	-
Cu	0,005±0,00	0,010±0,000
Zn	-	-
Se	-	-
Hg	-	-
Pb	-	-
Ag	-	-

It can be observed in Table 11, that the leached elements were, aluminum that presented values of 4.288% and 4.208% for the specimens manufactured with red clay and black clay respectively, it is observed 0.140% of potassium for the specimens manufactured with red clay and 0.118% for the black clay, the percentage of iron for the specimens manufactured with red clay was 0.005% and 0.008% for



the specimens made with black clay and finally copper presented 0.005% for specimens manufactured with red clay and 0.010% for black clay.

Regarding the maximum leachate limits of both NBR 10004 and the Department of Health and Environment (1989), Tables 6 and 7 respectively, it can be said that none of the elements exceeded the leachate limits.

#### 4 CONCLUSIONS

The characterization of the raw materials presented important information for the construction of the specimens. With Atterberg's limit analysis it can be verified that red clay is more plastic than black clay. The specimens manufactured with red clay showed lower rupture stress than black clay in all cases, relating the same addition of residue and the same temperature. In the red clay, the ceramic showed a tendency to increase the tensile strength of rupture when chromium residue was added. In the specimens manufactured with black clay the greatest rupture stress is presented when there is no addition of residue, that is, it is suggested that the addition of chromium residue reduced the strength of the ceramic. Regarding the maximum leachate limits of both NBR 10004 and the Department of Health and the Environment, it can be said that none of the elements exceeded the leachate limits.

Thus, it is concluded that it is possible to incorporate waste with chromium salts after treatment in the Effluent Treatment Station from the tanning industry in ceramics. Since in the specimens manufactured with red clay there was a tendency to increase the strength of the material, not reaching the minimum limits required for all materials, but for the masonry brick the values fit for use. This incorporation of the residue to the ceramic proves to be a good alternative for the final deposit of this material in a less polluting way to the environment.





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