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Environmental and technical aspects of the utilisation of tannery sludge as a raw material for clay products

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Abstract

This paper is a report on the results of a feasibility study on the immobilisation of tannery sludge by producing a ceramic product. The main purpose of this work was to test the clays used in the manufacture of a ceramic that could incorporate tannery sludge. The raw materials, tannery sludge and clay, were mixed together in different proportions. The ceramic specimens were characterised with respect to water absorption, porosity, linear shrinkage and transverse rupture strength. Leaching tests, in accord with the Brazilian and German regulations, were done on ceramic bodies made with different additions of sludge. In order to evaluate the possibility of air contamination during the firing process, preliminary studies of air emissions were carried out The mechanical properties of the samples evaluated were similar to those specified for ceramic bricks. All the leaching tests have shown that the main sludge contaminant i.e. chromium, could be immobilised within a finished ceramic product. The studies of air emissions have shown that zinc and chlorine are mainly collected from gas emissions and hence are not immobilised by the ceramic system. The study shows that the properties of the ceramic materials produced are acceptable for applications such as bricks for the building industry. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Bricks; Composites; Recycling; Sludge; Waste materials

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1. Introduction

The major leather production centres in the world are found in Mexico, Brazil, Japan, South Korea, China, India and Pakistan. Korea, Japan and Italy import hides from countries which have a large meat production industry i.e. USA, Australia, and the European countries. Whereas the South American countries, for example Argentina and Brazil, process their own hides. The leather industry is prevalent in Brazil, especially in the South, 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. The low efficiency of the chemical operations and the organic substances from the skin cause a significant pollution hazard. For example the chemical processes, performed in chemical reactors called tumblers consume a large amount of water and chemicals, most of which ends up as wastewater.[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 a good mechanical resistance, an extraordinary dyeing suitability and a better hydrothermic resistance in comparison with hides treated with vegetable substances. Chromium salts also have a high rate of penetration into the interfibrillar spaces of the skins. This results in a saving in terms of production time and a better control of the process. Unfortunately only a fraction of the chromium salts used in the tanning process react with the skins. The rest of the salts remain in the tanning exhaust bath and are subsequently sent to a depuration plant where the chromium salts end up in the sludge.[3]

A chemical precipitation technique is usually required to remove chromium and chemical oxygen demand from wastewater before it is allowed to go for biological treatment. This precipitation technique creates a sludge. The sludge from a tannery consists mostly of oil, grease and also magnesium, calcium and chromium hydroxides

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precipitates plus inert solids, and debris from hide.[4] A typical composition for wastewater treatment sludge from Italian tanneries is given in Table 1. The presented data are percentages of sludge from a biological treatment plant after dewatering.[5]

In the Federal State Rio Grande do Sul, in south Brazil it is estimated that each hide generates an average of 7.5 kg of sludge.[6] Fourteen million hides are treated each year[7] in Rio Grande do Sul.

The order of priority in waste management and treatment is (1) prevention, (2) reduction, (3) re-use, (4) recycling and recovery, (5) thermal treatment for certain types of waste and (6) landfill. The most common way to manage solid waste is by disposing of it on controlled land sites.[8] Because of the amount of chromium compounds and other pollutants this sludge is considered as toxic and hazardous. The American[9] and the Brazilian[10] regulations consider that chromium and chromium compounds are hazardous constituents in waste materials. The German[11] regulations list tannery sludge as a hazardous waste under code 14402. Tannery sludge is also included in the European Waste Catalogue[5] under code 04 01 06.

Regulations about solid wastes are becoming more and more restrictive and the disposal of hazardous waste on land sites may cease to continue. Landfilling of wastes with high organic content and toxic substances is increasingly coming under pressure in European States. Council Directive 1999/31/EC on the landfill of waste, adopted in 1999, is expected to have a considerable impact on trends to re-use and to re-cycle rather than to landfill. It lays down that by July 2003 States from the European Community shall have established a national strategy for the reduction of biodegradable waste going to landfills. This strategy should include reduction measures such as recycling, composting, biogas production or materials/energy recovery.[5]

Studies to minimise the amount of tannery waste, plus the treatment and possible exploitation of waste products are very important.[8] To avoid the high cost of dumping, sludge can be processed by hydrometallurgical methods to recover chromium, or thermally treated to reduce the volume to be disposed of. The problems associated with each of these processes is that they in turn generate other problems.

Table 1
Typical composition for wastewater treatment sludge in Italy[5]

	Minimum wt.%	Maximum wt.%
Water content	55	75
Organic matter	40	75
Inorganic matter	25	60
Organic carbon	21	38
Ammonium	0.1	1.6
Nitrogen (organic)	1.3	7.0
Substance extractable with CH_2Cl_2	0.06	0.4
Phosphorus	0.01	0.06
Chromium III	0.8	5.0
Aluminium	0	5.0
Iron	0.6	12
Calcium	1.0	15
Sulphur (total)	0.7	7.0

One problem observed by tanners during the recycling of chromium by dissolution from the sludge is the poor quality of the chromium due to the presence of organic lipolytic components, metals and other impurities.[3] Furthermore hydrometallurgical processes are associated with the generation of additional effluent.

The thermal treatment of sludge involves incineration, gasification, and pyrolysis as a means of disposal, whilst also recovering energy from waste.[5,12] Emission limits into the air may have an influence on the quality of sludge that is allowed to be incinerated and also on the cost of abatement of gaseous emissions[5,13] The residues of the process still have to be disposed of, but this is more easily achieved than with untreated sludge. Before the incineration of waste from tanneries, toxic releases such as chrome (VI), PCDD/F due to halogenated organic compounds, PAH have to be taken into consideration.[5]

Solidification is another process that has been considered as an alternative solution to the disposal of sludge containing heavy metals. In this process waste materials are mixed with various binding media to obtain a new product with improved physical properties. Recent papers have reported on the use of solidification, stabilisation and vitrification processes to recycle different wastes such as low-level debris,[14] radioactive wastes,[15] red mud from aluminium extraction[16] and zinc hydrometallurgy,[17] incineration ashes,[18–20] steel plant fly ash,[19–22] coal ash[23] and post-cupric-slag.[24]

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. Immobilisation within a cement-matrix does not require expensive thermal treatments to render hazardous waste inert and in a stable form.[17] Various authors[25,26] have studied the solidification of tannery wastes with cement. The final product is resistant to aggressive environmental agents and can be safely stored in landfill sites. This process is, however, experiencing increasing opposition in many European countries because the durability of cement mixtures is not proven. Therefore, the cement-mix containing hazardous wastes is not re-usable especially in the building industry. Ceramic and glass technologies are considered to be the most versatile for rendering hazardous waste inert because they destroy organic matter, immobilise regulated heavy metals in a stable matrix and are able to convert complex chemical compositions into useful materials with potential for market exploitation.[17]

2. Objective

This paper reports the results of a feasibility study on the immobilisation of tannery sludge by transforming it into a ceramic product. The main purpose of this work was to test the use of clays in the formation of a ceramic body that could incorporate tannery sludge.

The general criterion on the formulation of ceramic bricks and tiles is to mix a plastic component, usually a clay with a founder and a non-plastic material, that will form the basis of the final structure of the product. Tannery sludge can be incorporated into the ceramic mass as the non-plastic component. The incorporation of tannery sludge into ceramic products would help to disperse the waste in a useful and inert form. The manufacture of clay products in Brazil is as high as 60 million tons per year which could justify the process.

3. Experimental procedure

3.1. Raw materials

Tannery sludge was supplied by a leather factory in Rio Grande do Sul which produces 27 m^3 of sludge per day. The factory has a filter press system and after the filtration process the sludge contains 75% moisture. Samples of the sludge were dried at a temperature of 105 °C until the net weight was constant. The sludge was also studied by Ferreira,[7] who intends to use it for agriculture processes. Ferreira[7] characterised the sludge by chemical analysis and these results are presented in Table 2. Comparing these values with the values from other authors[5] (Table 1), it can be seen that the analysed elements are of the same magnitude.

Table 2
Chemical composition of the tannery sludge used in this work[7]

	Wt.%
Organic carbon	6.51
Nitrogen total	0.98
NH^{4+}	0.42
$NO_3 + NO_2$	0.682
Phosphorus total	0.20
Potassium total	0.01
Calcium total	2.00
Magnesium total	0.024
Sulphur total	1.33
Copper total	1.90
Zinc total	11.2
Iron total	0.63
Manganese total	26.2
Sodium total	0.84
Chromium total	0.81
Cadmium total	0.0138
Nickel total	1.50
Lead total	1.50

The composition of the base-clay material used in this work is shown in Table 3.

3.2. Formulation of the ceramic specimens

The raw materials, tannery sludge and clay, were mixed together in the ratios shown in Table 4. Pure clay was used as a standard comparison with the results. Moreover a CaO-containing formulation was also tailored because of the sulphur emission as later explained.

The raw materials were dried mixed and ground in a ball mill for 24 h. The ceramic bodies were moulded into 8×20×60 mm^3 bars using a hydraulic press (pressure: 20 MPa). A 10 wt.% polyalcoholvinylic (PVA) water solution was added to the mixture as plasticizer agent. After forming, the specimens were dried out in an oven for 24 h at 110 °C and then fired at 1000, 1100 and 1180 °C respectively for 2 h in a muffle furnace.

3.3. Characterisation of specimens: technological properties

The ceramic specimens were characterised with respect to water absorption, porosity, linear shrinkage and transverse rupture strength. Water absorption and porosity were measured using the Archimedes method in accord with standards ASTM C-373/94 (porosity)[27] and ASTM C-134/95 (apparent density).[28] The linear shrinkage was determined by the difference in the length

Table 3
Chemical composition of the clay

SiO_2	69.86
Al_2O_3	13.94
Fe_2O_3	5.75
K_2O	2.60
MgO	1.09
TiO_2	0.63
P_2O_5	0.21
CaO	0.12
Na_2O	0.12
MnO	0.08
Loss of mass by heat	6.31

Table 4
Samples of ceramic masses with tannery sludge

Samples	Raw materials (wt.%)		
	Clay	Dried sludge	CaO
S1	100	0	0
S2	90	10	0
S3	80	20	0
S4	70	30	0
S5	81	9	10

of the test bar before and after firing (ASTM C210/95).[29] The mechanical strength was determined by a four-point bend test using an ATS Universal Machine, according to specification ASTM C-773/88.[30]

3.4. Characterisation 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. Gas emissions during the firing process should be monitored to evaluate the possibilities of atmospheric pollution particularly with respect to a new process.

Leaching tests were performed on ceramic bodies produced at 1180 °C with different additions of sludge. There are no specific leaching tests for monolithic materials within the Brazilian regulations. The Brazilian tests used were the leaching and solubilisation tests (NBR10005[31] and NBR10006[32]) used to classify wastes.

The batch-leaching test procedure according to NBR1 000531 is analogous to the American Extraction Procedure Toxicity Test.[33,34] The procedure uses deionised water as extractor fluid. The pH of the water is adjusted to 5.0 by the addition of acetic acid. The quantity of added water is 16 times the amount of the sample. In this work samples of 100 g were taken and crushed to a particle size of less than 9.5 mm. The sample with water were agitated for 24 h. After this period the solid and liquid constituents are separated by filtration. The lixiviate was chemically analysed and the results were compared to the maximum values cited in the Brazilian specification of wastes (NBR10004[10]). According to this procedure a waste is classified on a scale ranging between hazardous and non-inert.

The solubilisation test (NBR10006[32]) 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 250 g of sample with a particle size of less 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 analysed and the element concentrations were compared to the values from specification NBR10004.[10]

The characterisation of materials produced with wastes requires the composition of the solution obtained from a leachability test to be known. The ceramic products were tested with the German method (DIN 38414-S4)[35] so as to compare the results obtained. This is because there is not an internationally accepted specific leachability test.

The German procedure uses a sample, which contains (at least) 100 g in a dry condition. 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 dosed and placed in a rotatory agitator for 24 h. After this period the solid constituent was separated by filtration. In this work the element concentration in the lixiviate were compared to the values found in specification NBR10004,[10] and in the German regulation TA-Abfall.[11] The element concentration was also compared with the waste classes of the German Federal State Nordrhein Westfallen.[36]

In order to evaluate the possibility of air contamination during the firing process, preliminary studies of air emissions were conducted. This investigation was done using 100 g of the sample to be fired. The sample was introduced into a quartz reactor inside a muffle furnace. The reactor had two holes: air was drawn over the sample via the first hole and heated air was collected from the second hole using vacuum apparatus. The collected air was washed in a conical flask with deionised water. The air was collected during heating from ambient to 1180 °C at a rate of 150 °C per hour and held at temperature for 2 h. The duration of the test was 10 h. After the experiment the water was analysed to estimate air emission. Fig. 1 shows a schematic diagram of the equipment used.

4. Results and discussion

4.1. Technological properties of ceramic bodies

Water absorption as a function of firing temperatures is shown in Fig. 2. From this figure it can be seen that the water absorption increases when the percentage of sludge in the sample is greater. Water absorption decreases with the increase in the firing temperature. The results also show that for a firing temperature of 1180 °C and for samples without any addition of sludge (sample 51) the water absorption is almost zero.

Experiments done by Vieira et al.[37] on the sintering of rock wastes have shown an increase of amorphous silica with sintering temperature. This increase gave the conclusion that this phase serves as a binder by lodging into the spaces between the granules of the material, and is the reason for the decrease in water absorption. From the studies undertaken on water absorption as a function of thermal treatment, the authors[37] have observed that absorption decreases significantly when the temperature during the treatment is greater than 1100 °C, i.e. after the formation of the amorphous phase. The presence of amorphous silica could also explain the results of this work with respect to the firing temperature and the fact that added sludge displaces the silica content of the samples.

The results obtained from the determination of total porosity as a function of firing temperature (Fig. 3) are

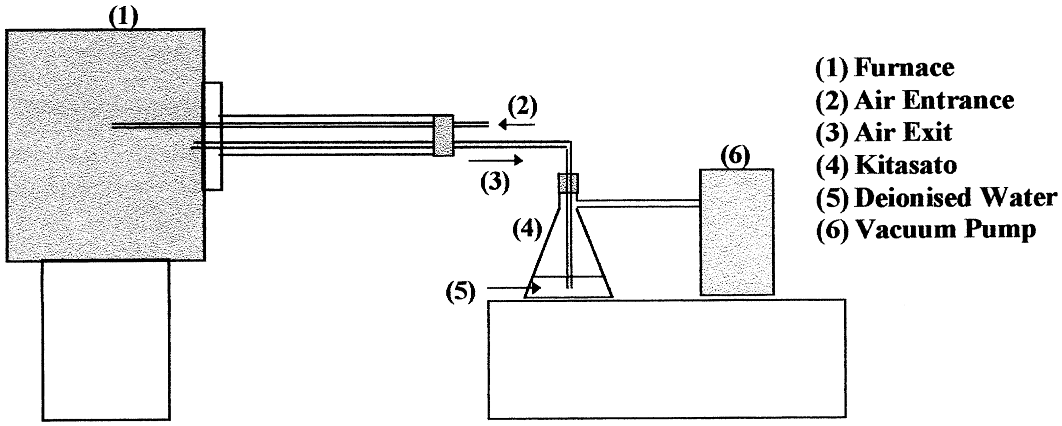

Fig. 1. Equipment used for evaluation of gas emissions during the firing of the ceramic samples.

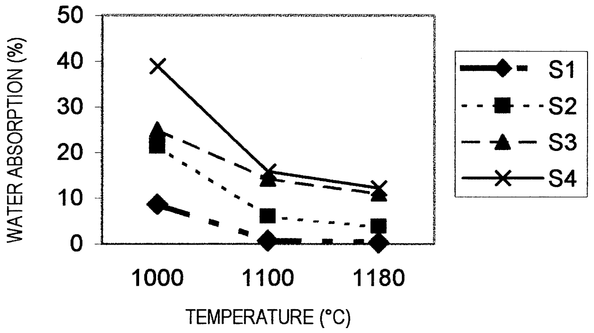

Fig. 2. Water absorption of ceramic samples as function of tannery sludge content and firing temperature.

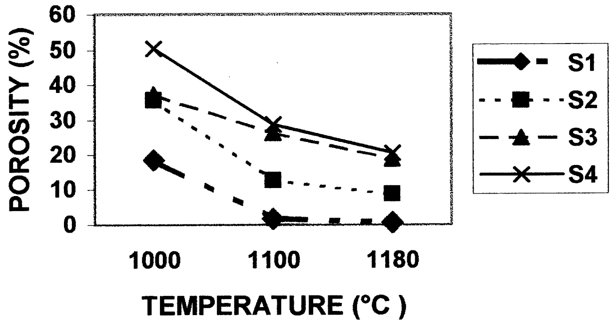

Fig. 3. Apparent porosity of ceramic samples as function of tannery sludge content and firing temperature.

very similar to that of water absorption. Sample Si (pure clay) shows a total porosity that is almost twice that of the open porosity and was determined by water absorption. For these samples the open and the closed porosity have almost the same value.

The apparent densities as function of tannery sludge content and firing temperature are shown in Fig. 4. These results show that the densification of the samples increases with the firing temperature. As would be expected sample S1 shows the greatest densification.

The linear shrinkage of ceramic samples as function of tannery sludge content and firing temperature is shown in Fig. 5. The maximum shrinkage occurred between 1100 and 1180 °C. These results are related to the densification of the samples. The sample containing 30% sludge (S4), with the smallest densification, showed the greatest linear shrinkage at these temperatures.

The results of the four-point bending testing of the ceramic samples as function of tannery sludge content and firing temperature are shown in Fig. 6. The bending strength increases with the firing temperature and is related to the porosity of the material. The material in the pores between the ceramic granules of the material is also responsible for the increase in the mechanical behaviour of the samples. The samples that had the highest porosity (S3 and S4—Fig. 3) had a lower

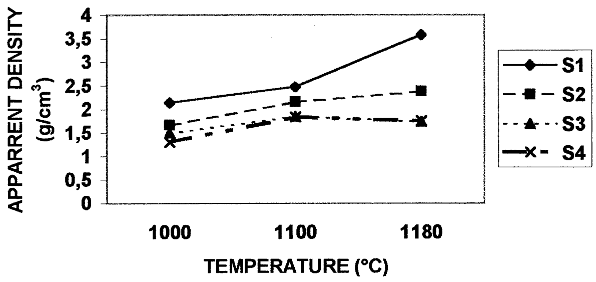

Fig. 4. Apparent density of ceramic samples as function of tannery sludge content and firing temperature.

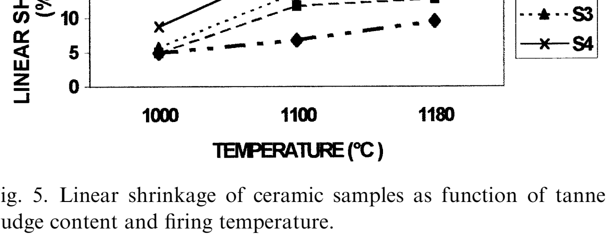

Fig. 5. Linear shrinkage of ceramic samples as function of tannery sludge content and firing temperature.

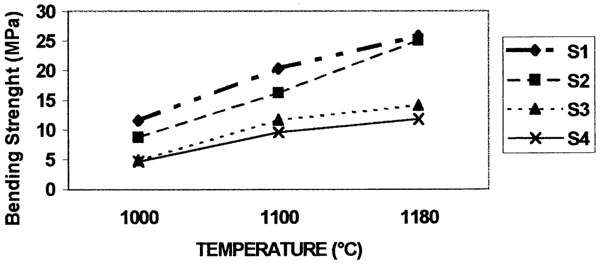

Fig. 6. Mechanical resistance of ceramic samples as function of tannery sludge content and firing temperature.

mechanical strength. Porosity also has an influence on the mechanical properties of the material. The bending strength of the samples reached a maximum of 25 MPa for samples S1 and S2 sintered at 1180 °C.

There is a good correlation between all the properties tested. The mechanical strength is greatest after firing at a temperature in excess of 1100 °C. At these temperatures the contraction of the samples and linear shrinkage increase, also the porosity decreases. The sintering process is the main cause of this behaviour.

The evaluated mechanical properties of the samples are similar to those specified for ceramic bricks.

4.2. Leaching characteristics

Tables 5 and 6 show the results of leaching and solubilisation tests of samples S1, S2 and S4 sintered at 1180 °C in accord with the Brazilian standards NBR10005[31] and NBR10006.[32] The results in the tables can be compared to the Brazilian standards from NBR10004.[10]

First leaching of as received clay and of the ceramic product (with the addition of tannery sludge) was carried out. The results were compared with the maximum permissible concentrations of pollutants in the lixiviates. It can be seen from Table 5 that the leaching of these products generates a lixiviate that does not exceed the set limits for hazardous wastes in Brazil.

A solubilisation test was done with identical samples and Table 6 shows that samples S1 and S2 could be considered as being inert according to the Brazilian regulations. The solution generated on the test with

Table 5
Concentration of elements in the lixiviates obtained from the leaching procedure according to the Brazilian Regulation NBR10005[31]

Element	Maximal concentration (mg l^{-1}) to consider a waste non hazardous according to NBR10004[10]	Lixiviate concentration (mg l^{-1})		
		Sample S1	Sample S2	Sample S4
Total chromium	5.0	<0.02	<0.02	<0.02
Lead	5.0	<0.04	<0.04	0.04
Silver	5.0	<0.01	<0.01	0.01
Fluoride	150.0	1.0	0.07	0.009
Mercury	0.1	<0.0001	0.0004	0.0005
Barium	100.0	0.11	<1	<1

Table 6
Concentration of elements in the solutions obtained from the solubilisation procedure according to the Brazilian Regulation NBR10006[32]

Element	Maximal concentration (mg l^{-1}) to consider a waste inert according to NBR10004[10]	Lixiviate concentration (mg l^{-1})		
		Sample S1	Sample S2	Sample S4
Total chromium	0.05	<0.02	<0.02	<0.02
Lead	0.05	<0.05	<0.05	0.08
Iron	0.3	0.06	0.03	0.03
Nitrate	10	<0.1	<0.1	0.1
Sulphate	400	1.8	15	0.8
Chlorine	205	5.05	0.62	0.76
Sodium	200	1.4	0.44	0.53
Barium	1	0.03	<1	<1
Copper	1	<0.02	<0.02	<0.02
Manganese	0.1	<0.01	<0.01	<0.01
Aluminium	0.2	<0.2	<0.2	<0.2
Zinc	5	0.16	<0.1	<0.1
Silver	0.5	<0.01	<0.01	<0.01
Fluoride	1.5	<0.02	0.02	0.02
Calcium carbonate	500	2.01	4.1	11.0
Mercury	0.1	<0.0001	0.0004	0.0005

sample S4 exceeded the limits for lead. This would be considered to be a non-inert product. A slightly higher concentration of lead in lixiviates of leather wastes was also observed by Fernandez-Sempere et al.[8] The use of 30% sludge in the formulation of the ceramic product would not guarantee a good immobilisalion for lead.

The low chromium impacts, which proved to be less than the demands, have shown the success of the immobilisation of the waste. Filibeli et al.[26] have also studied the immobilisation of chromium with a mixture of tannery sludge and cement.

In order to evaluate the results with respect to a different regulation, a leaching test was carried out according to specification DIN 38414-S4[35] for samples S1, S2 and S4. The German standards for Nordrhein-Westfalen[36] and the limits stated in TA-Abfall[11] were used as a reference. The standards for Nordrhein-Westfallen[36] have set 6 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, 2 and 3. The TA-Abfall[11] standard sets the limits up to which a waste is classed as non hazardous. Table 7 shows the results of these experiments.

The results show that according to the German regulations cited in TA-Abfall,[11] the ceramic specimens made with pure clay (S1) and containing 10–30% tannery sludge (S2 and S4) can be considered as non hazardous. The regulations applied in the German Federal State of Nordrhein Westfallen show that the ceramic material (with or without sludge) would be considered as class 3 because of the phenol concentration. The concentrations of the other elements are all smaller than the limits set in disposal class 1.

Comparing the three tests (NBR10005, NBR10006 and DIN 38414-S4) it can be seen that the highest lead concentrations were reached in the solution obtained after the NBR10006 test. Because this test is a 7-day test, this behaviour could be explained by the diffusion time necessary to dissolve the lead specimens. López[38] has studied the behaviour of lead during different leaching tests. The author has observed that time is an important parameter when lead compounds are present in a leachable waste. Because lead was found to be leachable with sample S4 (containing 30% of sludge), it would be advisable to use ceramic materials that contain less than 30% of sludge in the raw material.

4.3. *Air emissions*

Before the preliminary evaluation of the atmospheric emissions, the gas generated during the firing of sample

Table 7
Concentration of elements in the lixiviates obtained by the leaching procedure according to the German Regulation DIN38414-S4[35]

Element	Maximal concentration (mg l^{-1})				Lixiviate concentration (mg l^{-1})		
	Nordrhein-Westfalen[36]			TA-Abfall[11]	Sample S1	Sample S2	Sample S4
	Disposal class						
	1	2	3				
pH	6.5–9.5	5.5–12.0	5.5–12.0	4–13	5.2	5.4	5.8
Conductivity (μS/cm)	40,000	300,000	–	100,000	15.49	4.69	32.7
TOC	–	–	–	200	1.68	0.84	1.26
Phenol	0.0005	0.1	20	100	0.10	0.29	0.13
Antimony	0.01	0.1	1.0	–	<0.001	<0.001	<0.001
Arsine	0.04	0.1	1.0	1	<0.001	<0.001	<0.001
Barium	0.1	1.0	5.0	–	<1	<1	<1
Lead	0.04	0.5	2.0	2	<0.05	<0.05	<0.05
(Bore boron?)	1.0	1.0	10.0	–	0.04	0.02	0.02
Cadmium	0.005	0.05	0.5	0.5	<0.01	<0.01	<0.01
Total chromium	0.05	1.0	10.0	–	<0.02	<0.02	0.03
Chromium VI	–	0.1	–	0.5	<0.01	<0.01	0.03
Copper	0.1	1.0	10.0	10	<0.02	<0.02	<0.02
Iron	0.2	2.0	–	–	<0.03	<0.03	0.05
Manganese	0.05	1.0	–	–	<0.01	<0.01	<0.01
Nickel	0.05	0.5	10.0	2	<0.02	<0.02	<0.02
Zinc	0.1	5.0	10.0	10	<0.01	<0.01	<0.01
Mercury	0.001	0.005	0.05	0.1	<0.1	<0.1	<0.1
Fluoride	1.5	5.0	20.0	50	<0.02	0.02	0.02
Ammonium	0.08	4.1	–	1000	0.06	<0.02	0.25
Chloride	200	–	–	10,000	0.90	0.13	2.9
Cyanide	0.05	0.5	20.0	1	<0.004	<0.004	<0.004
Sulphate	–	–	–	5000	1.6	0.6	2.3
Nitrate	11.3	22.6	–	30	<0.1	<0.1	<0.1

Table 8
Chemical analysis of gas washing solutions after firing of the ceramic samples

Element	Concentration (mg l^{-1})			
	Deionised water	Sample S1	Sample S2	Sample S5
Chloride	0.1	4.3	71	60
Sulphate	0.1	<0.1	29	368
Nitrate	<0.1	<0.01	<0.1	<0.1
Aluminium	0.2	0.8	<0.2	<0.2
Barium	<1	<1	<1	<1
Lead	<0.05	<0.05	<0.05	<0.05
Copper	<0.02	<0.02	<0.02	<0.02
Total chromium	<0.02	<0.02	<0.02	<0.02
Hexavalent chromium	<0.001	<0.01	<0.01	0.017
Cadmium	<0.01	<0.1	<0.01	<0.01
Iron	<0.03	<0.03	<0.03	<0.03
Manganese	<0.02	<0.01	<0.02	<0.01
Sodium	<0.02	<0.1	<0.02	<0.02
Zinc	<0.01	0.05	1.1	0.63

batch S2 (containing 10% sludge) was washed. The washing solution was then analysed and the results presented in Table 8. Pure deionised water was also analysed. Pure clay was fired in order to establish a standard to compare with the results. During the firing of the samples a pungent smell of sulphur was in the laboratory. To avoid this problem a formulation containing 10% CaO, that would react with sulphur to form $CaSO_4$, was evaluated. This formulation could then be incorporated into the ceramic.

The results show that zinc and chloride are more likely to be collected from gas emissions than to be immobilised by the ceramic system.

Because of the great increase in sulphate concentration, as recorded by the gas analysis during the firing of sample S5, it was assumed that $CaSO_4$ had formed within the formulation. However, the addition of CaO can also result in a higher concentration of hexavalent chromium in the washing solution. At high temperatures ($T > 600$ °C) in the presence of oxygen and CaO, trivalent chromium oxidises to hexavalent chromium according to the reaction:[39]

$$2CaO + Cr_2O_3 + 3/2O_2 \rightarrow 2CaCrO_4$$

Because hexavalent chromium is much more soluble than trivalent chromium, there is a risk that this form of chromium would be present on the lixiviate of the solution.

The results presented here are just indicative of the gas emissions. Further studies will be carried out in order to evaluate these emissions and the possible treatment of them.

5. Conclusions

The present study was conducted to develop and to characterise a clay product with the addition of tannery sludge as a raw material. The feasibility in the use of this material was demonstrated. The technological properties are compatible with those specified for ceramic bricks. The environmental characterisation of the product indicate that a material containing 10% tannery sludge can be used safely. The previous results of the environmental compatibility of the process show that there are emissions of sulphur compounds, as well as zinc and chloride compounds.

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