# Industrial Tanned Leather Waste Embedded in Modern Composite Materials

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*The aim of this study is to demonstrate that tanned waste leather can be successfully incorporated in cement matrix and the resulted composite material can be proposed as construction material. The composite leaching tests for total chromium (maximum concentration registered = 2.76 mg/kg), which is the most used tanning agent, shown low levels in leachate lower than maximum allowed concentration MAC for non-hazardous waste (MAC = 10 mg/kg). The study proposes a new environmentally friendly recycling method for tanned leather waste.*

*Keywords: leather, waste, recycling, composite material*

In the European Union the concept of sustainable development covers all the environmental fields including the appropriate waste management. The leather industry production and processing sector generates high quantities of tanned leather waste, whereby, an important amount reaches the municipal landfills.

Leather industry is one of the most important industries of the European economy and in Asia is the largest amount of generated waste from leather processing [1, 2]. Romania have an important tradition in leather processing, leather products representing 41% of all industrial uses for this material. The leather industry use only 80% of the rawhide material, the processing waste representing 20%. From 1,000 kg of tanned leather is obtained 600 - 700 kg of solid waste and 40-50 $m^3$ of wastewater [2].

Even the leather waste is framed into the European Waste Catalogue as a non-hazardous waste, because of the high concentration of heavy metals founded in waste leather scraps, leads to a real environmental risk. Therefore, because of the chromium content, it's important to not discard the industrial leather waste in nature or to store it in open dump landfills; it is indicated to manage it properly through recycling and recovery thereof or by storage in compliant landfills. The open dump landfills generate impact and risk to the environment and public health, due to lack of facilities and poor exploitation [3, 4]. The waste from tanneries must be handled and stored so as to avoid leakage, odor problems and air emissions [5].

In the tannery process, generally, as tanning agent are used trivalent chromium (III) compounds. The processed leather waste has a major impact on human health and environment because of the chromium content. In certain tanning processes the added chromium (III) in the leather may be transformed by oxidation in chromium (VI) [6] which is considered a prioritary/ hazardous substance [7-9]. In the Regulation 301/2014 was considered that an unacceptable risk to human health appears in the case of chromium (VI) concentrations equal to or greater than 0.0003 % by weight in leather goods and articles containing parts of leather that comes into contact with the skin [6].

Some leather products may contain traces of hexavalent chromium (Cr VI), and it may appear as a contaminant, in the following situations: ►after UV exposure (at over 80°C) the fat-liquoring acids is possibly to lead to the oxidation of Cr III; ► in the process of the storage of fat-liquored leather at 35% humidity; ►in the shoe production, the use of alkaline glues may contribute to the formation of Cr VI [10]. Also, the forming of chromium VI compounds, appears in the collagen subunits crosslink tanning processes, destined to increase leather's resistance to mechanical action and heat [6]. There are numerous studies on tanned leather waste treatment for recycling and recovery [11-16], etc.). Most of these studies are related to the extraction of chromium from waste and its reuse in the tanning process [11].

For leather processing, the reference documents for best available techniques (BAT - Best Available Techniques) are covered by the Directive 2010/75/EC [17]. In the European legislation, as well as in the Romanian one, the waste from the leather industry, fur and textiles are listed and coded under Chapter 04 *Wastes from the leather, fur and textile industries* [18, 19]. It must be noticed that the leather waste, containing chromium salts *isn't framed as hazardous waste*; this waste is coded at code 04 01 08: *waste tanned leather (blue sheeting, shavings, cuttings and buffing dust) containing Chromium.* Only the codes marked with an

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asterisk (*) are considered as a hazardous waste [19, 20]. The purpose of this study was to demonstrate the recycling possibility of the industrial tanned leather waste by incorporate it in cement matrix, obtaining thus a composite material, safe for the environment.

This study is a new approach in recycling leather waste methods. The industrial tanned leather waste, comes from leather uppers industry. The used method for achieving the composite is an ecological recovery method, with low energy consumption and low costs.

## Experimental part

The research was structured in four parts: obtaining the composite material; analytical measurements (with determination of heavy metals from leather, sand and composite leachate); mechanical strength tests and composite microstructure analyze.

### *Composite obtaining method*

For this study were prepared 5 composite samples by mixing brown dyed leather waste, after a milling operation, with sand, cement and water. A white Portland cement, type CEM II / AL 52.5 N normal curing [21] was used. The mixture was homogenised by stirring, afterwards the composition was casted in rectangular plastic molds. Thus, five sets of four samples each (2X2 cm) were manufactured. Samples were demoulded after 24 h, and prepared to perform the leachability tests.

### *Analytical measurements*

Total chromium analysis was made for a brown waste leather sample coming from upper industry and for the sand which was used to the preparation of the proposed composite material.

After demoulding, the samples were placed in solutions at four different *p*H (*p*H = 2-3 *p*H = 5-6 *p*H = 9-10, *p*H = 12), where pH was adjusted with concentrated $HNO_3$ and concentrated NaOH. The composite leaching tests (according to MO 95/2005 - 10 L/kg) [22], were performed at different conditions: sonication in the ultrasonic bath (type Elmasonic S 10) for 30 min , at 20-25 °C; 40-50 °C and 60-70 °C, at several *p*H (*p*H = 2-3, *p*H = 5-6, *p*H = 9-10, *p*H = 12).

The total chromium (without atomic speciation) analysis were performed by Atomic Absorption Spectrometer (ZEEnit 700, Analytic Jena), flame method.

### *Mechanical tests*

In order to verify the possibility of using the obtained composite as construction material, flexural and compressive strength mechanical tests were performed.

The mechanical resistance of the obtained composite was verified with a Technotest device (Italy). The three standard samples 40 mm X 40 mm X 160 mm, had been made according to the standard SR EN 1015-11:2002 [21], were weighted and the density was calculate.

Fig. 1. Flexural and compressive strength mechanical tests, analyzed with a Technotest device (Italy)

After those, flexural and compressive strength mechanical tests were performed (fig. 1), according to the European construction standards [23].

For the flexural strength, the samples were placed in the device with the lateral side on the bending roll support and perpendicular to the longitudinal axis thereof. Flexural load was applied vertically, with a constant increase of 50 $N \cdot s^{-1}$ until fracture. For a standard test, tear must occur in a period of 30-90 s. The obtained prism halves were kept to be subsequently subjected to compression strength tests. It must be noticed that for comparison were made 3 sample sets with three different leather granulation: mixed smooth and large slices-Set 1, smooth slices –Set 2 and large slices Set 3.

### *Composite microstructure*

Composite microstructure was determined, by scanning the composite with the Scanning Electron Microscope (SEM) (Type Jeol – JSM – 5510LV) to investigate the homogeneity of the material.

## Results and discussions

### *Results for leachability tests*

Because there is no legislation to establish pollutants levels in leachate, for the composite materials with waste content, the obtained concentration values were compared with MAC from the legislation for waste acceptance to landfill [22]. The results of total chromium concentration from brown leather waste proved high values (13,459.30 mg/kg). The composite leachate analysis proved that only a small percentage of the total chromium from waste leather incorporated in the composite material, passed into the leachate, lower than the maximum allowed concentration (MAC) for the non-hazardous waste (MAC=10 mg/kg).

In figure 2 it can be seen the relation between the total Cr concentration and *p*H.

The higher values of the total chromium concentration were registered at alkaline *p*H = 12 (fig. 2). Author's studies shown similar behavior of heavy metals leaching from composite materials with waste content: lead concentrations were higher at *p*H = 12 [23, 24].

### *Results for mechanical tests*

In table 1, are presented the mechanical resistance tests results for the used standard samples. According to the specific standards in construction, the apparent density of

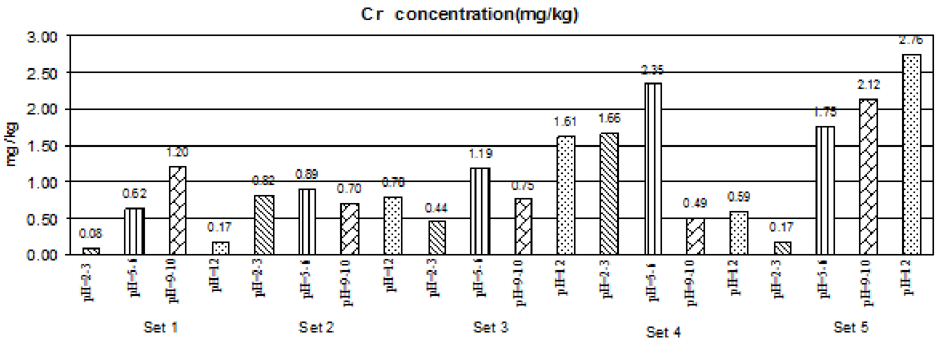


Fig. 2. Chromium concentration depending on *p*H

| Sample Set | $M_1$ [g] | $M_2$ [g] | $M_3$ [g] | Apparent density **1** [$kg \cdot m^{-3}$.] | Apparent density **2** [$kg \cdot m^{-3}$.] | Apparent density **3** [$kg \cdot m^{-3}$.] | **Average** apparent density [$kg \cdot m^{-3}$] |
|---|---|---|---|---|---|---|---|
| 1 | 442.30 | 440.70 | 432.90 | 1,728.00 | 1,721.00 | 1,691.00 | 1,713.00 |
| 2 | 436.8 | 434.1 | 432.5 | 1,706.00 | 1,696.00 | 1,689.00 | 1,697.00 |
| 3 | 442.3 | 440.70 | 443.2 | 1,728.00 | 1,721.00 | 1,731.00 | 1,727.00 |

**Table 1**
RESULTS FOR MASS AND APPARENT DENSITY FOR THE THREE STANDARD SAMPLES

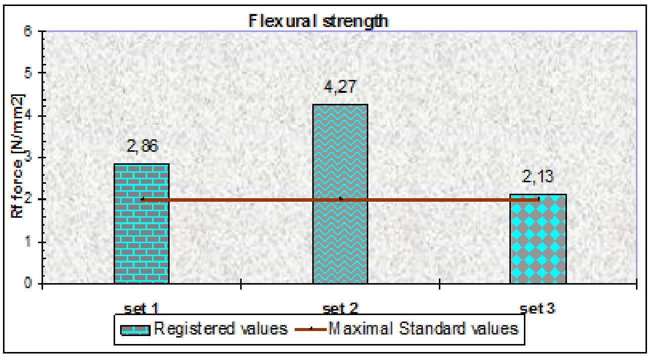


Fig. 3. Flexural strength results for the composite material

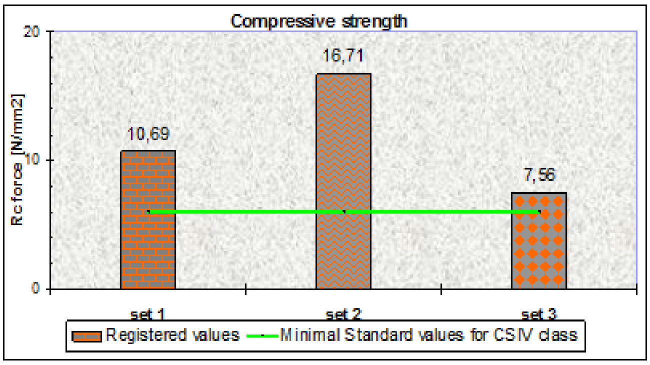


Fig. 4. Compressive strength results for the composite material

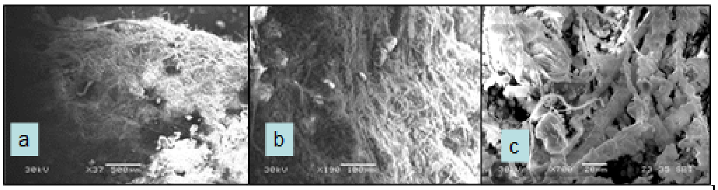


Fig. 5. Microscopic structure analyzed with SEM technique: a) set 1 b) set 2 c) set 3

dry mortars is used for comparison, along with other parameters for mortars classification. Thus for light mortars (plaster and masonry) the average for apparent density must be ≤ 1300 $kg \cdot m^{-3}$ [25, 26].

In table 1, can see that the apparent density (average) is higher than 1,300 [$kg \cdot m^{-3}$] which mean that the samples overdraws the light mortars.

Flexural strength, $R_f$, was also calculated by the following formula (according to SR EN 1015-11 /2002 [27]).

$$R_f = (1.5 \times P_f \times l)/(b \times d^2) \qquad (1)$$

where: $R_f$ = flexural strength [$N \cdot mm^{-2}$]; d = square section prism side [mm]; b = length of the sample [mm]; $P_f$ = applied load in the middle prism at breaking [N]; l = distance between supporting rolls [mm].

Standard device used for bending test [23], shown in figure 6, has the supporting rolls distance of 100 ± 5 mm and prisms have dimensions of 40 mm x 40 mm x 160 mm [28]. The average bending strength was calculated.

The results for the flexural strength (fig. 3) show values above mortars flexural strength standard values (0.2-2 $N \cdot mm^{-2}$) [26].

Compressive strength $R_c$ was calculated with the formula 2 (according to SR EN 1015-11 /2002 [27]) as follows:

$$R_c = F_c/A \qquad (2)$$

where: $R_c$ = compressive strength [$N \cdot mm^{-2}$]; $F_c$ = maximum load when prism is breaking [N]; A = 1600 = platters area [$mm^2$].

According to SR EN 1015-11 /2002 [27], the applied load to the prism sample was gradually increased, without shock, at a rate of 2400 ± 200 $N \cdot s^{-1}$, until breaking, when maximum load when prism was breaking $F_c$ [N], it was recorded.

Compressive strength test results and resistances were calculated according to the formula 2 and presented in figure 4.

The obtained results for the compressive strength tests entitled to classify the composite material in the $CS_4$ mortars class for plaster (≥ 6 $N \cdot mm^{-2}$) and in $M_7$ class for masonry (7 $N \cdot mm^{-2}$) [25, 26] (fig. 4).

The mechanical strength tests revealed that ▶ the flexural strength increase with the decreasing of the waste leather scrap size ▶ as well as the compressive strength.

The new environmental waste recycling approaches are applied in author's previous studies [29 - 31]. The results proved the various possibilities of hazardous waste recycling. These studies also came to sustain the present research.

*Results for microscopic structure*

Figure 5 shows the microscopic structure of the composite material.

From figure 5 it can observe that the composite behavior under mechanical stress was sustained by the SEM images, which shown that the thinnest leather scraps are, the more homogeneous composite structure was (set 2).

## Conclusions

The obtained results showed *a hazardous character of the leather waste*, due to the high levels of total chromium. The maximum allowed concentration (MAC) from the legislation, for the hazardous waste is MAC=70 mg/kg.

The proposed composite can be easy manufactured and the total chromium concentration in leachate has lower values than the MAC (10 mg/kg) for the non-hazardous waste in legislation.

The composite can be safely used for manufacturing of different decorative elements as mortar plaster.

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## References

1. CTC, Fourteenth Session of the leather and leather products industry panel, Wastes Generated in the Leather Products Industry, 13-15 dec 2000, on line: http://www.unido.org/fileadmin/import/userfiles/timminsk/leatherpanel14ctcwastes.pdf.

2. VISAN, S., CIOBOTARU, V., GHIGA, C., FLORESCU, M., COARA, GH., Recycling technology in the protein leather industry in industrial applications, research project under the National Program MENER (C202/2002-2005), 2002, on-line at: http://www.management.ase.ro/reveconomia/2004-special1/30.pdf.
3. LIXANDRU, B., Ecology and Environmental protection, 1-2, 1999, Editura Presa Universitarã, Timiºoara, Romania.
4. POPITA G.-E., VARGA I., GURZAU A., BENCE F., REDEY A., YUZHAKOVA T., HATEGAN R. M., POPOVICI A., MARUTOIU C., Environ. Eng. Manag. J., **12**, no. 10, 2013, p. 2031.
5.*** BAT, Decision 84 of 2013 laying down the conclusions on best available techniques (BAT) under Directive 2010/75 / EU of the European Parliament and of the Council on industrial emissions (Text with EEA relevance EEA) Celex number: 32013D0084, integrated Pollution Prevention and Control, reference document on Best available Techniques for leather tanning, Ministry of Agriculture, Water, Forests and Environment, 2013.
6. *** REGULATION 301, COMMISSION REGULATION (EU) No 301/2014 of 25 March 2014, amending Annex XVII to Regulation of the European Parliament and of the Council on the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) as regards chromium VI compounds, Official Journal of the European Union 90/1, 2014.
7.*** DIRECTIVE 60, Water Framework Directive, OJ L EU **327**, 2000, p. 193-264.
8.*** DIRECTIVE 105, Directive 2008/105/EC of the European Parliament and of the Council on environmental quality standards in the field of water policy, OJ L EU, **348**, 2008, p. 84-97.
9.*** REGULATION 1272, Regulation of the European Parliament and of the Council of 16 December 2008 on classification, labeling and packaging of substances and mixtures, 2008, p. 1907-2006.
10. KOLOMAZNIK, K., ADAMEK, M., ANDEL, I., UHLIROVA, M., J. Hazard. Mater., **160**, 2008, p. 514,
11. YILMAZ, O., KANTARLI, C., YUKSEL, M., SAGLAM, M., YANIK, J., Resour. Conserv. Recycl., **49**, 2007, p. 436.
12. ALPTEKIN, E., CANAKCI, M., SANLI, H., Fuel, no. 1, 2012, p. 214.
13. NOGUEIRA, F.G.E., CASTRO, I.A., BASTOS, A.R.R., SOUZA, G.A., CARVALHO, J.G., OLIVEIRA, L.C.A., J. Hazard. Mater., **186,** 2011, p. 1064.
14. FAMIELEC, S., WIECZOREK-CIUROWA, K., Technical Transactions, no.8, 2011, p. 43.
15. ZAINESCU, G., ALBU, L., DESELNICU, D., CONSTANTINESCU, R.R., VASILESCU, A.M., NICHITA, P., SIRBU, C., Mat. Plast., **51**, no. 1, 2014, p. 90.
16. PANTAZI, M., STEFAN, D.S., CONSTANTINESCU, R., ANGHEL, R., MEGHEA, A., VASILESCU, A.M., Rev. Chim. (Bucharest), **65**, no. 2, 2014, p. 233.
17. *** DIRECTIVE 75, Directive of the European Parliament and of the Council of 24 November, 2010, on industrial emissions (integrated pollution prevention and control) (Recast), OJ L EU, **334**/17, 2010.
18. DECISION 532, Commission Decision 2000/532/EC replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste, OJ L EU, **226**, 6.9.2000, p. 3-24.
19.*** GD 856, Government Decision regarding the evidence of waste management and approving the list of wastes, including hazardous waste, Romanian Official Monitor part I, no. 659, 2002.
20. *** DECISION 532, Commission Decision replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste, OJ L EU, **226,** 2000, 3.
21.*** LAFARGE, Cement Lafarge sheet, type CEM_II_A-L_52.5N_White, 2013, on line at http://www.lafarge.ro/CEM_II_A-L_52.5N_Alb.pdf (RO), accesed at 02/02/2015.
22. *** MO 95, Ministry Order for accepting and preliminary procedures for accepting waste at landfill and the national list for accepting waste at each type of landfill, Romanian Official Monitor part I, no. 194 bis 2005.
23. POPOVICI, A., POPITA, G. E., ROBA, C., RUSU, T., TOFANA, V., ROSU, C., J. Environ Prot Ecol, **14**, no. 4, 2013, p. 1703-1711.
24. POPOVICI, A., RUSU, T., TOFANÃ, V., VIOREL DAN, POPITA, G.-E., HATEGAN R., MÃRUTOIU C., Environ Eng Mang J,, **12**, no. 2, 2013, p. 1535.
25. *** SR EN 998-2 /2011, European Standard SR EN 998-2-2011, Specification for mortar for masonry – Part 2: Masonry mortar.
26. *** SR EN 998-1 /2011, European Standard SR EN 998-2-2011, Specification for mortar for masonry – Part 1: Plaster mortar.
27. *** SR EN 1015-11:2002, Tests methods for masonry mortars.
28. *** SR EN 1996-3 Eurocod 6: Design of masonry structures - Part 3: Simplified calculation methods for unreinforced masonry structures.
29. CORBU, O., POPOVICI A., POPITA, G.-E., RUSU, T., ROSU, C., PUSKAS, A., Proceedings of the 14th International Multidisciplinary Scientific GeoConference & EXPO – GeoConference on Nano, Bio And Green – Technologies For A Sustainable Future, SGEM, Albena, Bulgaria, ISBN 978-619-7105-21-6 / ISSN 1314-2704, 2014, p. 81-88, DOI: 10.5593/sgem2014B62.
30. POPOVICI, A., CORBU O., POPIÞA, G.-E., ROSU, C., PROOROCU, MARIAN, SANDU, A.V., ABDULLAH, M.M.A.B., Mat. Plast., **52**, no. 4, 2015, p. 588
31. NORDIN, N., ABDULLAH, M.M.A., TAHIR, M.F.M., SANDU, A.V., HUSSIN, K., International Journal of Conservation Science, 7, no. 1, 2016, p. 161

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