VALORIFICAREA DEȘEURILOR DIN PIEI CHAMOIS PENTRU REALIZAREA UNOR MATERIALE DE CONSTRUCȚII UȘOARE PE BAZĂ DE MORTAR

VALORIZATION OF CHAMOIS LEATHER WASTE FOR OBTAINING OF CEMENT-BASED LIGHTWEIGHT BUILDING MATERIALS

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This paper presents the influence of some fractions obtained from alkaline hydrolysis of Chamois leather dust resulted from the buffing operation, on the physical and mechanical characteristics of a new type of cement-based lightweight building materials. The average molecular weight of the hydrolysis product and the changes in the characteristic peaks of IR spectral bands shows the obtaining of a polypeptide mixture after the chemical treatment. Hydrolysis products and solid residues were used in a series of mortar recipes; the obtained results indicate an improvement of the main physical and mechanical characteristics of mortar, such as water absorption, flexural and compressive strength, compared to the reference mix.

Lucrarea de față prezintă influența unor componente de reacție rezultate ca urmare a hidrolizei alcaline a deșeurilor din pulberi de piei Chamois provenite de la operația de șlefuire, asupra caracteristicilor fizico-mecanice ale unui nou tip de material de construcții ușoare pe bază de ciment. Masa moleculară medie a produsului de hidroliză și modificările survenite în picurile caracteristice ale benzilor spectrale IR, indică obținerea unui amestec polipeptidic după tratamentul chimic realizat. Produsele de hidroliză și reziduurile solide au fost folosite într-o serie de rețete de mortar; rezultatele obținute indică o îmbunătățire a principalelor caracteristici fizico-mecanice ale mortarului, cum ar fi absorbția de apă, rezistența la încovoiere și compresiune, în comparație cu rețeta convențională de mortar.

Keywords: *Lightweight mortar, chamois powder, alkaline hydrolysis, polypeptide by-products, compressive strength, flexural strength.*

1. Introduction

Over the last decades, a sharp increase in the amount of waste generated by various industrial sectors as well as due to population growth, has been noticed; it is estimated that the global amount of solid waste released into the environment in 2025 will be around 19 billion tones [1]. In this context, the leather processing industry is known as an important source of environmental pollution, due to the large amount of waste generated as a result of using a large number of chemicals and water-intensive processes. Thus, it is known that processing of one ton of raw skins results in 20-80 m^3 wastewater with a chromium content of 100-400 mg/L, sulfides, fat and other solids of 200-800 mg/L along with pathogenic pollutants. The manufacturing processes result in 250 kg of finished leather and 750 kg solid wastes, of which 500 kg are skin wastes, which contain protein components (gelatin), and 250 kg are tanning and finishing wastes [2].

Nowadays, all these rawhide and tanned leather wastes are processed in order to obtain products designed for bio-fertilizers [3, 4], biofuels [5, 6], filtering materials for sewage water treatments [7], or auxiliary agents for the obtaining of new building materials [8-11]. So far, few materials are known as feasible concrete substitutes, due to concrete outstanding mechanical and physical resistance to environmental conditions, which justifies its use as a basic material in constructions.

In this respect, the common formulations for concrete contain a binder component on the basis of cement paste and/or a natural or synthetic polymer. Lately, the recipes for obtaining materials with outstanding thermal and acoustic properties include different organic wastes [12].

Many building materials such as concrete, bricks, paving tiles, building materials with cellular structure etc. are usually produced from natural resources. In this context, lately there is a growing concern regarding the replacement of these natural resources with wastes as such or resulted from processing of organic materials such as wool, hair, feathers, cellulose fibers, synthetic fibers, natural and synthetic rubbers etc. for the development of

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new types of materials with different applications in building construction [13]. These new types of materials are considered as composite materials and present substantial advantages in terms of investment and manufacturing costs, thermal and acoustic insulation properties, and physical and mechanical resistance, compared to the classical construction materials.

Given the above considerations, this paper is dealing with the effects produced by the use of mixtures based on chamois leather wastes and hydrolysis products on the physical-mechanical properties of concretes obtained using such mixtures, in order to subsequently use them in different applications.

2. Experimental

2.1. Materials

The experiments were conducted using the following materials: Chamois leather waste from S.C MESSY DANNY DAY, with the following characteristics: total ash: 11.8 %; extractable fats (in trichloroethylene): 9.8 % [UNI EN ISO 4048 2000]; water soluble matter: 4.8 %; and pH: 10.5; Chemical reagents and chemical auxiliaries such as: trichloroethylene, NH_4OH, NaOH, distilled water; Sand sorts 0.1-1 mm and sort 0.3-3 mm; The basic mix of mortar, CEM I 42.5 R type (Romania); Superplasticizer Power Flow type to adjust the workability and viscosity of mortar mixture.

2.2. Working method

As a first step, alkaline hydrolysis of Chamois leather waste resulting from the buffing operation, was carried out at laboratory scale, under the following controlled parameters: autoclaving in a batch reactor equipped with a vapor condenser and pressure automatic control at 3 atm, in a solution of ammonium hydroxide (NH_4OH) with pH=10, at 120^{o}C for 10 hours.

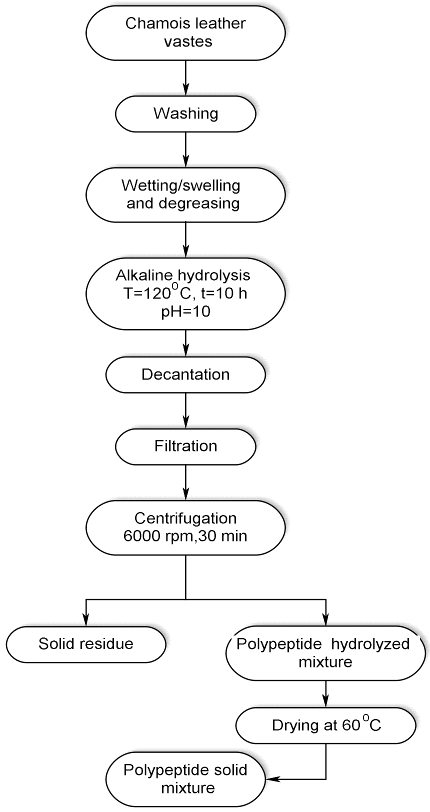

Fig.1 -The sequences of operations for obtaining the collagen hydrolysate by alkaline hydrolysis /*Fluxul tehnologic de obținere a hidrolizatelor de colagen prin hidroliză alcalină*.

Thus, 250 g of Chamois powder waste was subjected to a wetting/swelling and degreasing process with a non-ionic surfactant/trichlorethylene (1:5 wt/wt) mixture at 20^{o}C, for 24 hours, and then was dried in a thermo-regulated oven at 60^{o}C followed by cooling to 20^{o}C. Subsequently, the degreased product was placed in a batch reactor equipped with a stirring system and subjected to a hydrolysis process under the above-mentioned conditions. The resulting mixture was cooled to 20^{o}C, and then separated by centrifugation at 6000 rpm for 30 min. The process flow for obtaining the hydrolyzed polypeptide mixture is shown in Figure. 1.

Table 1

Variants of mortar recipes / *Variante de rețete pentru mortar*

Mortar indicative	Cement %	Water %	Degreased Chamois waste powder **%**	Peptide-solid mixture **%**	Solid residue %	Sort I Sand %	Sort II Sand %	Super Plasticizer %
R1	22.25	15	6	-	-	17.25	39.5	-
R2	22.25	15	4	-		17.25	39.5	2
R3	22.25	15	-	-	-	17.25	39.5	6
R4	22.25	15	-	3	3	17.25	39.5	-
R5	22.25	15	-	6	-	17.25	39.5	-
R6	22.25	15	-	-	6	17.25	39.5	-
R7-Reference miix	22.25	15	-	-	-	20.25	42.5	

a b c

Fig. 2 - Different products resulted from the Chamois leather waste processing: a. Degreased Chamois waste powder; b. Polypeptide-based Chamois waste hydrolysate; c. Solid residue / *Diferite produse rezultate din procesarea pieilor Chamois: a. Pudră degresată din deşeu Chamois; b. Polipeptidă din deşeu Chamois hidrolizat; c. Reziduu solid.*

Several fraction with narrow ranges of molecular weights were separated from the hydrolysate mixture using dialysis membranes SpectraPor type 3 (3.5 kDa), manufactured by Spectrum Laboratories Inc., Canada and also hydrolysis yield was determined.

In a second stage, the degreased Chamois powder and the hydrolysis product (Fig. 2) were used as additives for different variants of mortar recipes, a reference mix being also considered, as is presented/given in Table 1.

In laboratory experiments, a reference mix (R7) containing cement of CEM I 42.5 R type, grade I sand (0.1-1), grade II sand (0.3-3) and water was used as reference mortar. Other mortar recipe variants included different admixtures based on Chamois leather powder, product resulting by hydrolysis and viscosity regulator in a total concentration of 6% relative to the total weight of the mixture were made (R1-R6 variants -Table 1). Each mortar variant was prepared by mixing the component in a mixer, after which they were casted in rectangular (70x70x210 mm) or cubic (70x70x70mm) metal molds and deposited on a shaking table BEZ type for de-aeration (according to SREN-1015-11). The mortars have shown a good workability due to the use of superplasticizer. The samples thus obtained were stored at a temperature of 20^{o}C ± 2^{o}C and a relative humidity of 95% ± 5% for 28 days using an Environmental Chamber JTH 63, after which tests were carried out for determine some physical characteristics (density and water absorption), and also mechanical properties: flexural strength (Rf), using Michaelis Frühling apparatus and compressive strength (Rc) using Via De Nicola (Italy) apparatus, in accordance with actual standards (SREN 12390/2009).

3. Results and discussions

3.1. Characterization of hydrolysis products

The alkaline treatment is usually performed for the hydrolysis of proteins with an average molecular weight of 30 kDa and produces random breaking of the macromolecular chain into smaller peptides (about 40% of the total number of peptide bonds are splitted) with an average molecular weight between 2 and 5 kDa and polypeptides in the form of ammonium salts.

The mean molecular weight determined with the type 3 dialysis membrane was 3500 Da and hydrolysis yield related to total protein (according to relation 1), was 55,66%, indicating the existence of both a mixture of polypeptides and a residue that were later used in the preparation of mortar recipe for masonry.

$$Hydrolysis\ Yield\ \% = \frac{Collagen\ hydrolisate\ mass(g)}{Mass\ proteic\ substance\ of\ Chamois\ waste} X100 \quad (1)$$

3.2. FTIR spectral analysis of the hydrolysis compounds

In order to study the degree of hydrolysis of collagen matrix in an alkaline medium, FTIR analysis both of the hydrolysis compound and chamois leather powder as control sample was performed using a Spectrometer Digilab SCIMITAR series FTS 2000 with ZnSe cristals, 500 ÷ 4000 cm^{-1} range.

The spectra in Figure 3, show absorption bands at 1653-1662 cm^{-1} (1655-1690 cm^{-1} according to database) due to stretching vibration of C=O bond (amide I, a sensitive marker of the peptide secondary structure,) and at 1538-1552 cm^{-1} (1510 -1580 cm^{-1}), characteristic of N-H bond vibrations (amide II). The spectrum of hydrolyzed sample shows a slight shift of the Amide I band. The Amide III is illustrated by the complex absorption bands at 1200-1350 cm^{-1} corresponding to NH - CH bonds and provides information about the secondary structure of the collagen, the nature of the polypeptide chain, and also on the type of intermolecular bonds, such as hydrogen bonding. The range of absorption bands at 3460-3600 cm^{-1}, corresponds to Amide A band associated with the free N-H stretching vibration

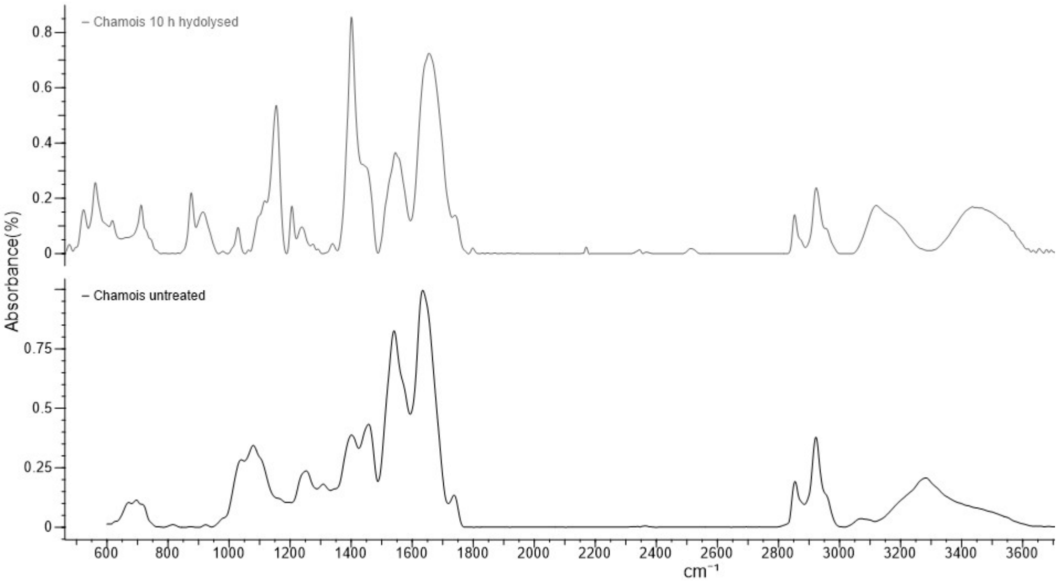

Fig. 3 - FTIR spectra recorded for chamois leather waste and hydrolyzed product/*Spectre FTIR pentru deșeuri de piele Chamois și pentru produsul hidrolizat*

Table 2

Data by FTIR analysis of hydrolysis product / Date obținute din analiza FTIR a produsului de hidroliză

Sample	Amide I		Amide II		Amide III		Amide A		A_I / A_A Ratio
	ν_1 cm^{-1}	*A*	ν_2 cm^{-1}	*A*	ν cm^{-1}	*A*	ν cm^{-1}	*A*	
Chamois waste	1654	22,53	1541	17,89	1251	4,5873	3450	14,18	0,301
Hydrolyzed product in NH_4OH	1654	22,92	1544	8,954	1238	3,17	3435	0,96	0,0201

(Figure 3). It can be seen a shift in the absorption band at 3460 cm^{-1} for the hydrolyzed sample. Data of FTIR analysis are summarized in Table 2.

Some information related to hydrolysis advance can be assessed by semi-quantitative relationships calculated using FTIR spectra, such as A_I/A_A ratio (ratio of absorbance of amide band I to amide A,) correlated with structural stability; the lower the ratio, the more advanced the degree of fragmentation. A_I/A_A ratio obtained for chamois leather is 0,301, which indicates structural stability of the collagen matrix due to stable and strong crosslinking bridges. This ratio in turn decreases for alkaline hydrolysates to a value of 0,020 indicating a strong fragmentation of the collagen matrix (Table 2).

3.3. *Physical and mechanical properties of mortar samples*

For each type of mortar, the results from the tests carried out for physical and mechanical characteristics determination depending on recipe variant and waste content are shown in Figure 4.

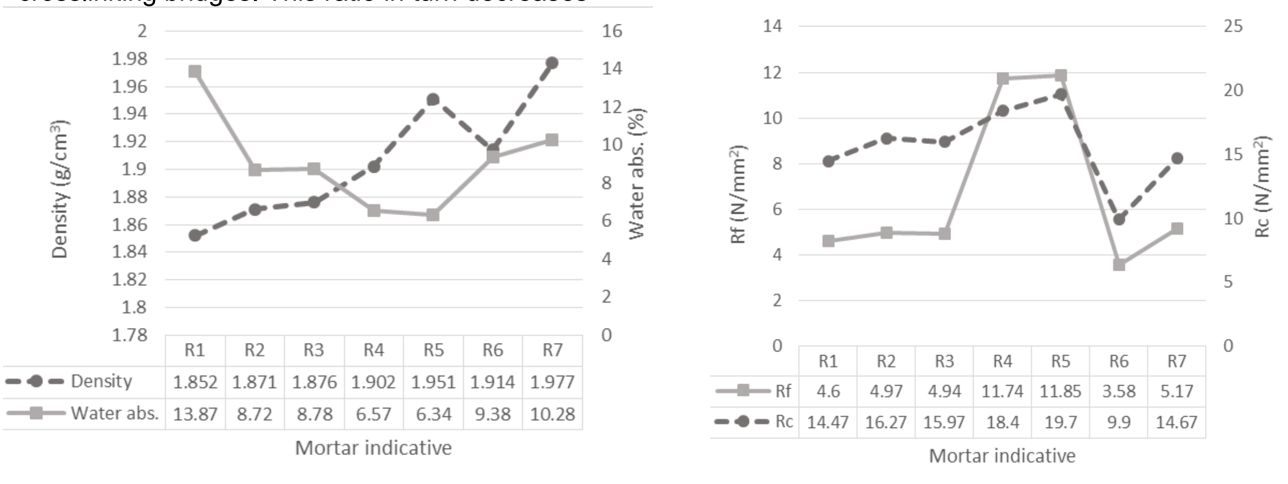

Fig. 4 - Physical and mechanical characteristics of the mortars depending on the recipe variant. / *Caracteristicile fizico-mecanice ale mortarelor în funcție de varianta de rețetă.*

Table 3

New variants of mortar recipes / *Noi variante de rețetă pentru mortar*

Mortar indicative	Cement %	Water %	Hydrolysate %	Residue %	Sand Sort I %	Sand Sort II %
R4b	22.25	15	4	4	16.75	38.0
R4c	22.25	15	5	5	16.25	36.5
R5b	22.25	15	8	-	17,0	37.5
R5c	22.25	15	10	-	17.25	35.5

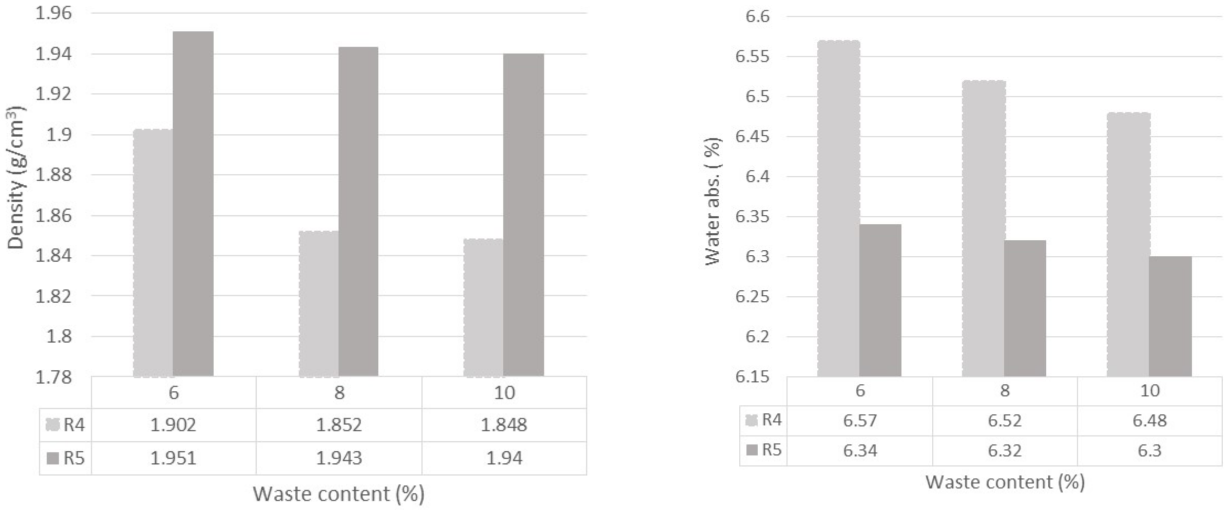

Fig. 5 - Physical characteristics of the mortars depending on the waste content /*Caracteristicile fizice ale mortarelor în funcție de conținutul de deşeu.*

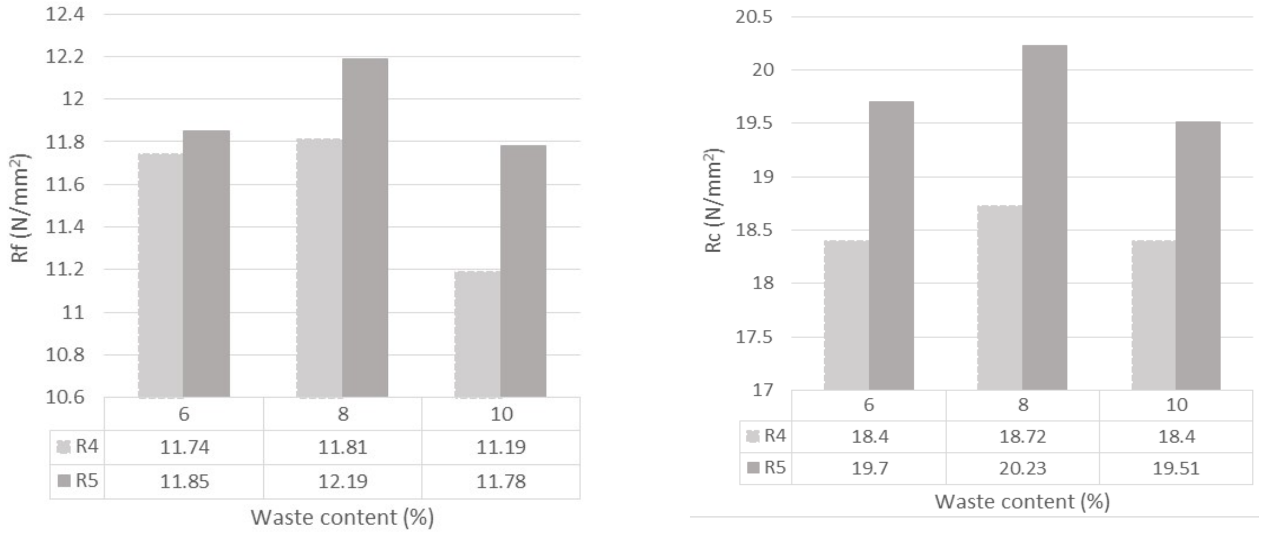

Fig. 6 - Mechanical characteristics of the mortars depending on the waste content. / *Caracteristicile mecanice ale mortarelor în funcție de conținutul de deşeu.*

Analyzing data in Figure 4 we can see:

- Density values for all variants of the recipe are characteristic for masonry mortar; there are no significant differences in density values for the mortar variants.
- R4 and R5 recipes containing hydrolyzed product and residue or hydrolyzed product only presents the lowest absorption of water, and also the best values for flexural and compressive strength respectively. This could be due to the formation of additional physical links between the components of the mixtures, due to an increased number of functional groups in the hydrolyzed product, which increases the average values of the physical-mechanical characteristics.

Proceeding from the results above, new experimental variants were taken into account in order to obtain mortar, by changing the concentration of the hydrolyzed components in the formulation of R4 and R5 between 6% and 10%, relative to the total weight of the mixture, as can be seen in Table 3.

The new samples thus obtained were subjected to the same physical-mechanical tests as the initial tests, the results being shown in Figure 5 and Figure 6.

According to this new data it can be seen that the best values in terms of physical-mechanical behavior were obtained for R5 recipe that contains the hydrolysis product in a concentration of 8%. R4 version containing hydrolysate product and residue shows a similar behavior to R5 variant, however with lower values, but higher than R7 (reference mix).

Mechanical characteristics could be also influenced by the cement/sand ratio, which varies for the different compositions: 0.3545 for R7, 0.396 for R1-R6, 0.42 for R5b (which had the best properties), aspect to be investigated.

4. Conclusions

- Alkaline hydrolysis of the chamois leather waste has provided two products of the reaction (a mixture of the polypeptide and a residue) as evidenced by chemical and physical analyzes (average molecular weight and changes in the characteristic peaks of the IR spectra).
- Leather waste and by-products resulting by hydrolysis were used as admixtures in mortar compositions, obtaining different variants of mortar that can be included in the class of masonry mortars as indicated by the density values.
- The recipe variants that included hydrolysate and residue (R4b) and hydrolysate only (R5b), with a total concentration of admixtures of 8%, led to the best values of water absorption and mechanical characteristics of mortars.
- The above results show that by-products resulting by hydrolysis can be successfully used as auxiliaries for the production of some types of cement-based lightweight building materials (e.g. in obtaining paving tiles or decorative bricks).
- The proposed method results in new value-added products based on Chamois leather waste, with potential applications in building materials.

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