# USE OF WASTES FROM THE PEANUT INDUSTRY IN THE MANUFACTURE OF BUILDING MATERIALS

NANCY QUARANTA<sup>1, \*</sup>, MARTA CALIGARIS<sup>1</sup>, GISELA PELOZO<sup>1</sup>, ANDREA CÉSARI<sup>1</sup> & ADRIÁN CRISTÓBAL<sup>2</sup> <sup>1</sup>Universidad Tecnológica Nacional. Facultad Regional San Nicolás, Argentina. <sup>2</sup>INTEMA-CONICET, Universidad Nacional de Mar del Plata, Argentina. \*CIC Researcher

## ABSTRACT

Most of the national peanut production, estimated at 900,000 tons per year, is processed in several cities in the central area of Argentina. The third part of this amount corresponds to the shells, which are separated in the peanut selection and processing plants. In this work, the possibility of using peanut shells as raw material for the manufacture of ceramic materials for the civil construction industry is studied. There are precedents on the use of biomass residues in different building blocks, mainly with the aim of generating lightweight ceramics. With this objective, ceramic pieces were obtained from green bodies manufactured with mixtures of commercial clay and different percentages of ground and dry residue. After a drying period, the samples were heat treated following curves similar to those used in the ceramic industry. The raw material used, clay and peanut shells, were characterized with different techniques, such as XRD, SEM and DTA-TGA. The DTA-TGA analysis shows that the organic material added is burned in a wide temperature range, between 300 °C and 550 °C. Thus, the sintering process of the bricks is performed without cracking or shattering. This test also shows that after the heat treatment, the waste material eventually incorporated into bricks (ashes) is less than 3%. The obtained products have good physical and mechanical properties, with acceptable values of porosity, modulus of rupture, permanent volumetric variation and weight loss on ignition. Keywords: construction materials, peanut shells, waste

## **1 INTRODUCTION**

Most of the national peanut production, estimated at 900,000 tons per year, is processed in several cities in the central area of Argentina.

The Argentine peanut sector is composed of 25 companies. Most of them are in the province of Córdoba, the world's southernmost region for the production of peanut. Around 30 localities of the interior of this province support their economies with the peanut agroindustry as the only significant source of employment. These companies play a very important role in the life of their communities by helping to sustain the functioning of schools, police, firefighters, hospitals and road consortiums, which also allows a high retention of young people in the area of origin. Figure 1 shows the location of the province of Córdoba in Argentina and the participation of its different departments in the production of peanuts [1].

From the industrialization of the peanut different products appear, but the third part of the peanut production corresponds to the shells, which are separated in the selection and processing plants. The usual disposal of peanut shells is the incineration or use as fuel in boilers. When the shells are burned in open air significant impacts are caused. On the one hand, large amounts of CO<sub>2</sub> and micro particles in suspension (fumes) are produced, but on the other hand, the soil is rendered unusable and the degradation of the burning area is caused.

Peanut shells in the province of Córdoba constitute an abundant waste material with no market value, but with a potential use in building materials.



Figure 1: Participation in the production of peanut in the province of Córdoba.

There are precedents on the use of this type of residues of biomass in construction bricks, mainly in order to generate lightened ceramic matrices. Thus, the addition of grape and cherry seeds [2], olive stone and sunflower seeds [3], olive stone and wheat straw [4], durian shells and coconut fibres [5], residues from tea production [6], pineapple fibres [7], olive stones, barley and apricot stone [8] and residues from the brewing and ground coffee industry [9] as pore formers has been studied, with the aim of generating lightweight ceramics.

Peanut shells have been studied to produce biofuels, such as bioethanol [10]. Cellulose nanofibres were isolated from these shells and used as a reinforcing material in composite materials [11]. These shells were used as a biosorbent for the removal of Pb (II), Cu (II) and Cr (III) ions [12, 13] and have also been studied as raw materials for the preparation of activated carbon [14–17], along with other lignocellulosic materials of this type, for their low cost and availability.

In this work, the possibility of using peanut shells as raw material in the manufacture of ceramic materials for the civil construction industry is studied.

# 2 MATERIALS AND METHODS

The dried shells and the commercial clay were characterized by scanning electron microscopy (SEM) with X-ray electron dispersive analysis (EDS), X-ray diffraction (XRD) and differential and thermogravimetric thermal analysis (DTA-TGA). The calorific value of the waste was obtained by a LECO AC-350 calorimeter pump, according to ASTM D-5865 standard.

SEM analyses were performed with Philips SEM 515, with an X-ray detector (EDAX-Phoenix). The XRD patterns of these powders were obtained with PANalytical X'Pert PRO equipment, with CuK $\alpha$  radiation ( $\lambda = 1.5406$  nm). The operating conditions were 40 kV and 40 mA. The TGA-DTA essays were conducted on a Shimadzu DTA-50 analyser TGA-50 with YC-50 WSI.

Porous ceramic pieces were obtained from green bodies made with mixtures of commercial clay and 5%, 10% and 15% in volume of ground and dry residue.

The pieces have been formed by uniaxial pressure of 25 MPa, with addition of 8% in weight of water, into moulds of 70mm × 40mm × 18mm. After a drying period, the samples were thermally treated at 950 °C following heating curves similar to those used in the ceramic industry. Samples with 15% of added waste were also treated at 1,000°C. The compact bodies were characterized with different techniques: porosity, permanent volumetric variation (PVV), weight loss on ignition (LOI) and mechanical properties, among others.

The porosity of samples was determined according to Standard IRAM 12510.

The modulus of rupture (MOR) was obtained on an Instron Model 1125 machine, with a maximum capacity of 10,000 kg. The speed of the test was 0.5 mm/min.

From now onwards the samples will be referred to as follows:

- P0: sample of clay without waste, to be used as a reference, treated at 950°C
- P5: sample with 5% added waste, treated at 950°C
- P10: sample with 10% added waste, treated at 950°C
- P15: sample with 15% added waste, treated at 950°C
- P15B: sample with 15% added waste, treated at 1,000°C

# **3 RESULTS AND DISCUSSION**

Table 1 shows the semiquantitative chemical analysis by EDS of the shells and clay used, expressed as percentage of the elements.

The calorific value determined for this waste material was 4413.8 kcal/kg. With the same procedure, values between 6,400 and 7,700 kcal/kg have been obtained for coal. The calorific value of the waste is considerably lower than that obtained for the fuel currently used in most coal-fired plants.

Figure 2 shows several exothermic peaks in the DTA curve that have been assigned to the combustion decomposition of the biopolymers present in the biomass. A first broad peak with maximum at 316 °C, assigned to hemicellulose (H), which has a shoulder at 333 °C probably corresponding to the cellulose (C) present. Another intense fine peak at 407 °C followed by several small peaks, up to a temperature of 500 °C is observed. This zone corresponds to the lignin (L) presence. As the polymeric structure of these compounds becomes more complex, the combustion-decomposition temperatures are higher.

This thermal behaviour corresponds to that observed in the TGA curve. In this curve, the steps corresponding to the loss of mass of the sample can be observed as the temperature increases.

A first step up to 200 °C corresponding to the loss of adsorbed gases and water is observed. Then an abrupt decrease in weight up to 321 °C, with a slope change at 272 °C, which corresponds to the wide peak assigned to H-C. Finally another step, softer than the others, up to 500 °C. From the curve, the composition percentages of the sample, which are presented in Table 2, can be estimated.

	С	0	Na	Mg	Al	Si	Fe	S	K	Ca
Outer shell	54.0	44.7	_	0.4	_	0.1	_	0.2	0.4	0.2
Red peel	66.4	32.5	_	0.1	_	_	0.2	0.2	0.4	0.2
Clay	24.9	33.6	1.1	1.3	7.5	21.7	6.9	-	2.5	0.5

Table 1: EDS analyses of the raw materials.



Figure 2: DTA-TGA analysis of peanut shells.

Table 2: Composition of the peanut shells.



Figure 3: X-ray diffraction diagrams of peanut shells' ashes.

The DTA-TGA analysis shows that the incorporated organic material is burned in a wide temperature range, between 300 °C and 550 °C. This is important to ensure that the sintering process takes place without crack formation in the brick. This test further indicates that after the heat treatment, the residual material that will eventually be incorporated into the bricks (ashes) is less than 3%.

The X-ray pattern obtained from these ashes is shown in Figure 3. The presence of diffraction peaks assigned to the eckermannite phase  $((NaCa)_3(MgAl)_5Si_8O_{22}(OH)_2)$ ,

pdf 23-0663), calcium phosphate ( $Ca_3(PO_4)_2$ , pdf 09-0348), calcium oxide (CaO, pdf 48-1467) and magnesium oxide (periclase, MgO, 75-1525) is observed.

Figure 4 shows the particle size distribution of the clay and the peanut shells used for obtaining the bricks.

Figure 5 presents the sintered compacts obtained. It can be observed that these products have a homogeneous coloration throughout the sample. The sample with 15% of biomass presents a low degree of sintering at this treatment temperature. The increase in porosity is observable to the naked eye.

Figure 6 shows the optical microscopies of the samples. It is possible to observe a greater presence of pores as the amount of peanut shells added is greater. The shape of the produced pores is not round but elongated, similar to the shape of the particles of peanut shells added. In the Sample P15 a lower degree of sintering is observed, and the presence of elongated pores or microcracks are observed.

These samples have also been observed by SEM. The micrographs taken for Samples P0 and P15 are presented in Figure 7. It can be observed that the supposed elongated pores in the OM analysis are actually internal microcracks, generated in the brick matrix on 15% of ground shells.

Figures 8 and 9 present the porosity values and the PVV of the samples, respectively. The porosity of the samples increases as the residue addition increases. The porosity of the P0 sample is 19.2%. The PVV is greater as the amount of residue in the sample increases to P10. Sample P15 presents a PVV similar to P10.

Figures 10 and 11 present the LOI and the MOR of the samples, respectively. Sample P15 is the one with the highest weight LOI, as expected from the composition of the samples.

The results show that the flexural strength decreases as the amount of biomass residue added to the sample increases, although the greatest decrease is observed between Samples







Figure 5: Samples without shells and with 5%, 10% and 15% waste.



Figure 6: Optical microscopies of the samples. Magnification: 50X.



Figure 7: SEM micrographs of Samples P0 and P15.



Figure 8: Porosity of the samples.







P10 and P15. This may be due to the lower degree of sintering observed at P15. This value for Sample P0 is 8.3 MPa.

As mentioned above, in the materials and methods section, a new sample called P15B with a heat treatment at 1000 °C was made, due to the lower degree of sintering observed in the Sample P15 treated at 950 °C. This new sample presents a higher degree of sintering than P15, with more defined edges and less apparent porosity to the naked eye.

The obtained results from the characterization essays for this sample are: 25.12% for porosity, 8.10% for PVV, 10.81% for LOI and 9.10 MPa for MOR.

Indeed, the porosity of this sample is lower than that presented by P15, at the expense of a greater volumetric variation. As expected, the weight LOI is similar, since all biomass matter burns at both temperatures. The high value obtained for P15B for flexural strength is remarkable, even higher than the sample prepared without addition of residue that presented a value of 8.3 MPa.

The temperature of 950 °C has been established taking into account the composition of the clay used for this work as the necessary temperature to achieve sintering. When adding the different percentages of residual biomass to the mixtures, the final composition does not vary practically with respect to the original, except in the contribution of 3% of ash corresponding to the residue. Evidently, the effect of the presence of the organic material between the clay particles decreases the contact between them and the achieved degree of sintering is lower. The use of a higher temperature, 1,000 °C, causes a higher volumetric shrinkage during firing and a higher degree of sintering is achieved, with the consequent decrease of the samples porosity. This process implies a greater expenditure of energy.

## 4 CONCLUSION

In this work, the possibility of using peanut shells as raw material for the manufacture of ceramic materials for the civil construction industry is studied, and a high feasibility of using this residue as a pore former in ceramic bodies is determined.

The products obtained with 5% and 10% of added residue and treated at 950 °C have good physical and mechanical properties, with acceptable values of porosity, MOR, permanent volume variation and weight LOI. The porosity of the samples increases as the initial residual biomass content increases.

The sample with 15% of peanut shells presents a low degree of sintering at this treatment temperature. Another sample with 15% of residual biomass was prepared and treated at 1,000°C. It presented good characteristics, higher sintering degree and high flexural strength.

In this case, an economic balance is needed, regarding the use of less quantity of waste using less energy, or more percentages of residual biomass with a higher energy expenditure.

## ACKNOWLEDGMENT

The authors thank the National Agency for Scientific Promotion and the Scientific Research Commission of the Buenos Aires Province for the financial support for the development of this work.

# REFERENCES

- [1] Giuliano, F., Encadenamiento productivo del maní. Chapter 15 in *El balance de la economía argentina*, 2006.
- [2] Barbieri, L., Andreola, F., Lancellotti, I. & Taurino, R., Management of agricultural biomass wastes: Preliminary study on characterization and valorisation in clay matrix bricks. *Waste Management*, **33**, pp. 2307–2315, 2013. https://doi.org/10.1016/j.wasman.2013.03.014
- Bories, C., Aouba, L., Vedrenne, E. & Vilarem, G. Fired clay bricks using agricultural biomass wastes: study and characterization. *Construction and Building Materials*, 91, pp. 158–163, 2015.

https://doi.org/10.1016/j.conbuildmat.2015.05.006

- [4] Aouba, L., Bories, C., Coutand, M., Perrin, B. & Lemercier, H., Properties of fired clay bricks with incorporated biomasses: Cases of Olive Stone Flour and Wheat Straw residues. *Construction and Building Materials*, **102**, pp. 7–13, 2016. https://doi.org/10.1016/j.conbuildmat.2015.10.040
- [5] Khedari, J., Suttisonk, B., Pratinthong, N. & Hirunlabh, J., New lightweight composite construction materials with low thermal conductivity. *Cement & Concrete Composites*, 23, pp. 65–70, 2001.

```
https://doi.org/10.1016/s0958-9465(00)00072-x
```

- [6] Demir, I., An investigation on the production of construction brick with processed waste tea. *Building and Environment*, **41**, pp. 1274–1278, 2006. https://doi.org/10.1016/j.buildenv.2005.05.004
- [7] Chan, C., Effect of natural fibres inclusion in clay bricks: physico-mechanical properties. *International Journal of Civil and Environmental Engineering*, **3**(1), pp. 51–57, 2011.
- [8] Techniti, S., Anastasiadou, K., Vamvuka, D. & Gidarakos, E., *Investigating the recycling of agricultural biomass waste in construction materials*. Third International Conference on Industrial and Hazardous Waste Management, Creta, Grecia, 2012.
- [9] Eliche-Quesada, D., Martínez-García, C., Martínez-Cartas, M.L., Cotes-Palomino, M.T., Pérez-Villarejo, L., Cruz-Pérez, N. & Corpas-Iglesias, F.A., The use of different forms of waste in the manufacture of ceramic bricks. *Applied Clay Science*, 52, pp. 270–276, 2011.

```
https://doi.org/10.1016/j.clay.2011.03.003
```

- [10] Polachini, T.C., Sato, A.C.K., Cunha, R.L. & Telis-Romero, J., Density and rheology of acid suspensions of peanut waste in different conditions: An engineering basis for bioethanol production. *Powder Technology*, **294**, pp. 168–176, 2016. https://doi.org/10.1016/j.powtec.2016.02.022
- [11] Wang, B. & Li, D., Strong and optically transparent biocomposites reinforced with cellulose nanofibers isolated from peanut shell. *Composites: Part A*, **79**, pp. 1–7, 2015. https://doi.org/10.1016/j.compositesa.2015.08.029

- [12] Tasar, S., Kaya, F. & Özer, A., Biosorption of lead (II) ions from aqueous solution by peanut shells: equilibrium, thermodynamic and kinetic studies. *Journal of Environmental Chemical Engineering*, 2, pp. 1018–1026, 2014. https://doi.org/10.1016/j.jece.2014.03.015
- [13] Witek-Krowiak, A., Szafran, R.G. & Modelski, S., Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent. *Desalination*, 265, pp. 126–134, 2011.

https://doi.org/10.1016/j.desal.2010.07.042

- [14] Zhang, S., Tao, L., Jiang, M., Gou, G. & Zhou, Z., Single-step synthesis of magnetic activated carbon from peanut shell. *Materials Letters*, **157**, pp. 281–284, 2015. https://doi.org/10.1016/j.matlet.2015.05.117
- [15] Georgin, J., Dotto, G.L., Mazutti, M.A. & Foletto, E.L., Preparation of activated carbon from peanut shell by conventional pyrolysis and microwave irradiation-pyrolysis to remove organic dyes from aqueous solutions. *Journal of Environmental Chemical Engineering*, 4, pp. 266–275, 2016. https://doi.org/10.1016/j.jece.2015.11.018
- [16] Zhang, S., Tao, L., Zhang, Y., Wang, Z., Gou, G., Jiang, M., Huang, C. & Zhou, Z., The role and mechanism of K<sub>2</sub>CO<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> in the preparation of magnetic peanut shell based activated carbon. *Powder Technology*, **295**, pp. 152–160, 2016. https://doi.org/10.1016/j.powtec.2016.03.034
- [17] Xue, W., Zhao, H., Yao, J., Li, F. & Wang, Y., Esterification of cyclohexene with formic acid over a peanut shell-derived carbon solid acid catalyst. *Chinese Journal of Catalysis*, 37, pp. 769–777, 2016. https://doi.org/10.1016/s1872-2067(15)61076-2