

# **BIOCERAMIC COMPOSITE: HEN'S EGG SHELL CHARACTERIZATION AND MAIN APPLICATIONS**

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## **ABSTRACT**

The chicken eggshell is a bioceramic composite which constitutes a solid waste material whose final disposal is complex and expensive. Brazil generates significant amounts of eggshell residue. This work aimed to characterize the eggshells of white, red and backyard hens and indicate their technological potential as raw material for ceramic products manufacturing. The eggshells were crushed, ground, sifted in a ABNT number 80 sieve and subsequently analyzed by X-rays fluorescence (XRF), X-ray diffraction (XRD) and thermal analyses (DTA and TGA). Through XRF it was observed that the main constituent of eggshell is calcium oxide (CaO), with different percentages between the eggshell types. XRD analysis indicated that the chicken eggshells used in this work are mainly composed of CaCO<sub>3</sub>. DTA and TGA demonstrated that the thermal decomposition of the chicken eggshells occurs in three events: water removal; decomposition of organic matter; and decomposition of CaCO<sub>3</sub> in CaO and CO<sub>2</sub>. By reviewing the literature, it was verified that chicken eggshells have important applications since they can be used in biomedicine, civil construction, food industries and as soil nutrients. As a result, it is possible to conclude that the chicken eggshell is rich in CaCO<sub>3</sub> and can be easily calcined to obtain CaO.

**Key words:** Hen's eggshell. characterization and applications. bioceramic composite.

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## **INTRODUCTION**

Everyday, millions of tons of eggshell waste are produced worldwide as a result of the large egg production. In Brazil, according to the Brazilian Institute of Geography and Statistics (IBGE, 2017), the production of chicken eggs is increasing and in the first quarter of 2017 it reached the 788.26 million dozens, representing an increase of 4.1% in comparison with the first quarter of 2016, which was considered a production record year since records started by the government agency in 1987.

Chicken eggshell is a bioceramic composite rich in calcium carbonate ( $\text{CaCO}_3$ ) and its use is suggested as an alternative to produce other substances of social and industrial interest, contributing to the valuation of the discarded residue (RODRIGUES and ÁVILA, 2017).

Re-use of egg shells can reduce the risk of microbiological contamination in the environment and its respective disposal costs, it can also provide raw materials to replace  $\text{CaCO}_3$  extracted from non-renewable sources, such as limestone, and the production of other by-products from the CaO obtained by the calcination process (OLIVEIRA et al., 2013). Limestone, the main source of  $\text{CaCO}_3$ , has become scarce, and for this reason companies have sought new sources of this compound for its replacement as a raw material for  $\text{CaCO}_3$  (RODRIGUES and ÁVILA, 2017). Currently, most commercially available eggs come from laying hens raised in the intensive farming system (confined in cages), with the most noticeable variation of these being the coloring of the eggshells (classified in white and red). Whilst the eggs designated as backyard are of high value and come from laying hens raised in freedom in an extensive or semi-extensive system (MILBRADT et al., 2015). At present, there is an increasing need for environmental sustainability in the world and, therefore, this study aims at chemically characterizing eggshells from farm chicken, white and red color, as well as backyard and determining through review of the literature, possible applications of this residue with the purpose of stimulating its reuse and consequently, its value.

## MATERIALS AND METHODS

### Materials

The materials used were chicken eggshells obtained through the donation of household residue from staff and students of the Federal Institute of Espírito Santo (IFES), Vitória campus. The eggshells were washed and separated according to the marketed classification of eggs and identified by the acronyms: white eggshells (COB), red eggshells (COV) and backyard eggshells (COC).

### Methods

The eggshells were initially ground in a blender and subsequently sterilized in a 20-liter horizontal digital Stermax autoclave, in a 45 min cycle at 122°C to obtain a contamination-free material. The eggshells were then milled in a Marconi MA500 ball mill at 249 RPM for 12 hours to obtain a fine powder. After grinding, the eggshell powders obtained were sieved in an ABNT No.80 sieve (aperture of 0.177 mm) for limiting particle size. The initial and the obtained material are shown in Figure 1.

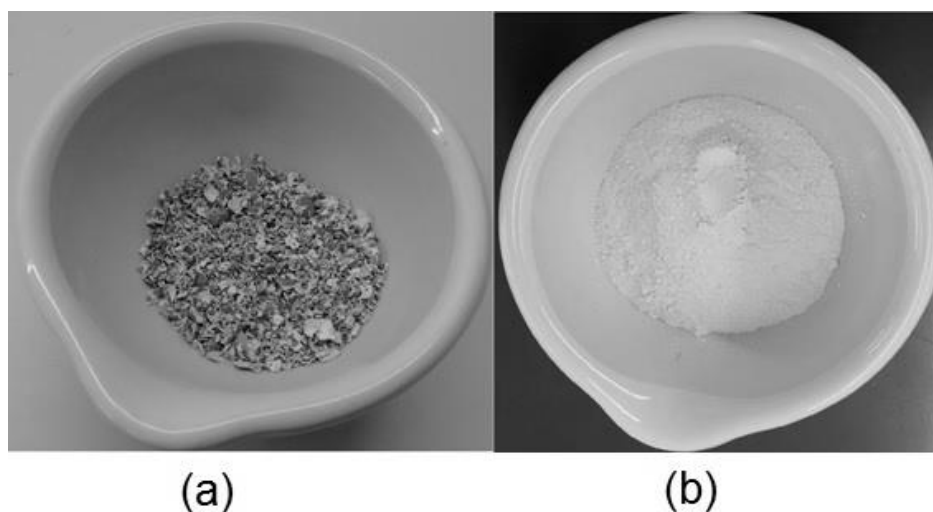


Figure 1 – Chicken eggshells (a) initial; and (b) powder obtained after milling and sieving.

Samples of the powder obtained from each type of eggshell were used to perform chemical composition tests by X-ray fluorescence (FRX), identification of phases present by X-ray diffraction (XRD) and thermal analysis by differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

The objective of the tests was to characterize the chemical constituents of the eggshells and to evaluate the constitution of the three different types of chicken eggshell analyzed in this study.

The X-ray diffraction analysis allowed the mineral identification of a powder through the characterization of its crystalline structure. This experiment was carried out in the characterization laboratory of the IFES Vitória campus using a Bruker X-ray diffractometer model D8 Advance with Cu ( $\lambda_{k\alpha}$ ) incident radiation operating at 40kV/20mA current. The samples were measured in a  $2\theta$  range: 20-50° in continuous scan mode at a speed of 1°/min with step size of 0.02° at room temperature (23°C). Software with an auxiliary PDF 4 database was used to analyze the results.

X-ray Fluorescence spectrometry is an analytical method for determining the chemical composition of the studied material. This stage was performed by means of a SHIMADZU equipment model EDX-720 belonging to the Laboratory of Characterization of the Academic Unit of Materials Engineering (UAEMa) of the Federal University of Campina Grande (UFCG).

The study of the relationship between a sample property and its temperature, while the sample is heated or cooled in a controlled manner, is known as thermal analysis, which was performed in this work by the Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) techniques.

The differential thermal analyses were performed on the BP Engenharia equipment, model RB 3000 at a heating rate of 10°C/min. Calcined alumina was the standard used, at a temperature of 1000°C. The results were obtained by measurements of temperature differences between the sample and the standard material through the continuous process, via endothermic and/or exothermic reactions that occurred during heating. The same parameters used for DTA were used to perform the thermogravimetric analysis of the samples, where the mass of the samples was measured and the variations were recorded as a function of the process temperature. These changes occur due to loss of water or CO<sub>2</sub>, oxygen gain, burning of organic matter, etc.

Finally, a search of scientific articles was carried out with the term "chicken eggshell" as keyword in the main database of the Periódico CAPES portal. A table containing some applications for the reuse of chicken eggshells was made from the selected articles.

## RESULTS AND DISCUSSION

The X-ray diffraction patterns for the three types of chicken eggshell analyzed are shown in Figure 2.

The analysis indicated that the types of chicken eggshells studied (white, red and backyard) consist mainly of calcium carbonate, which is demonstrated by the correspondence of the sample peaks with those of the calcite standard ( $\text{CaCO}_3$ , whose crystallographic data sheet used was ICDD-PDF n° 01-085-1108), results similar to those found in the literature (CÔRREA et al., 2015; TOMASELLI, 2014).

The chemical compositions of the three types of chicken eggshells were obtained by X-ray Fluorescence and are shown in Table 1.

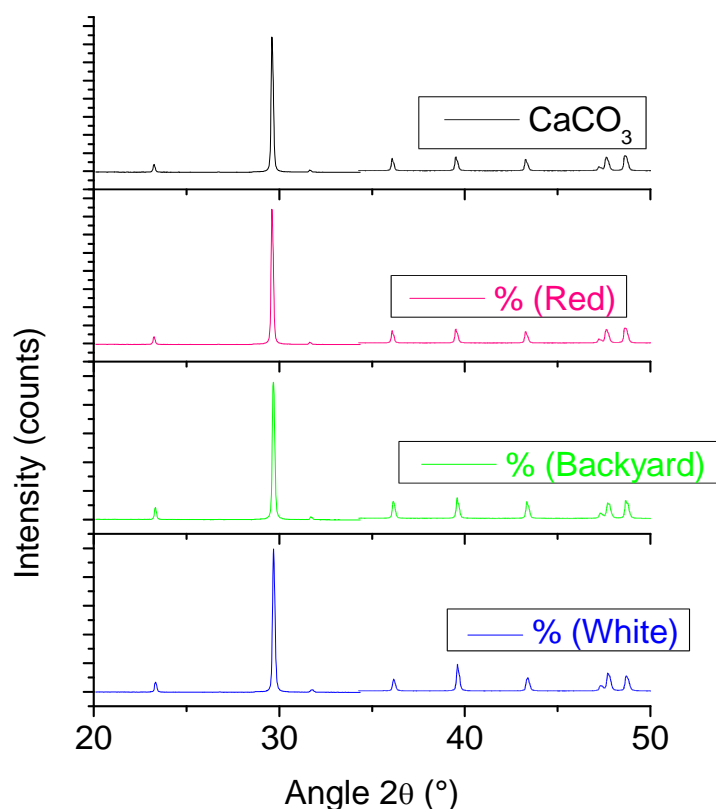


Figure 2 - White, red, and backyard egg shell diffractograms consistent with the calcite pattern ( $\text{CaCO}_3$ ).

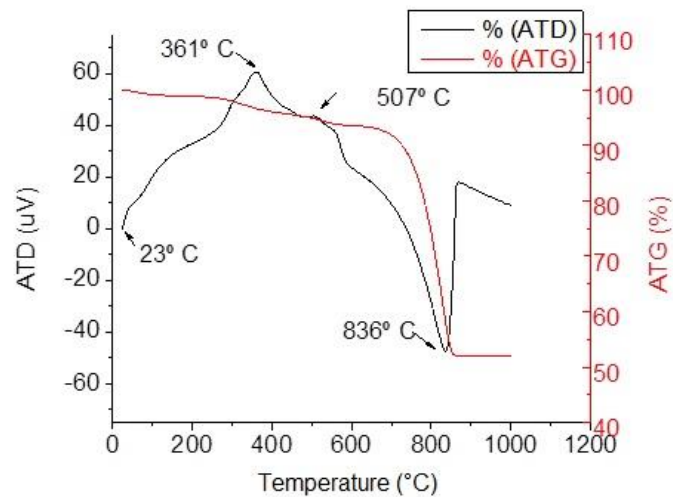
**Table 1** - Chemical composition of the analyzed eggshells.

<b>Composition</b>	<b>Backyard (%)</b>	<b>Red (%)</b>	<b>White (%)</b>
CaO	92.823	94.672	90.760
P <sub>2</sub> O <sub>5</sub>	2.383	2.198	2.437
SO <sub>3</sub>	2.456	1.165	3.934
SiO <sub>2</sub>	0.363	0.242	0.474
MgO	1.179	1.084	1.303
K <sub>2</sub> O	0.311	0.202	0.327
SrO	0.246	0.437	0.571
Al <sub>2</sub> O <sub>3</sub>	0.238	N/D	N/D
CuO	N/D	N/D	0.194

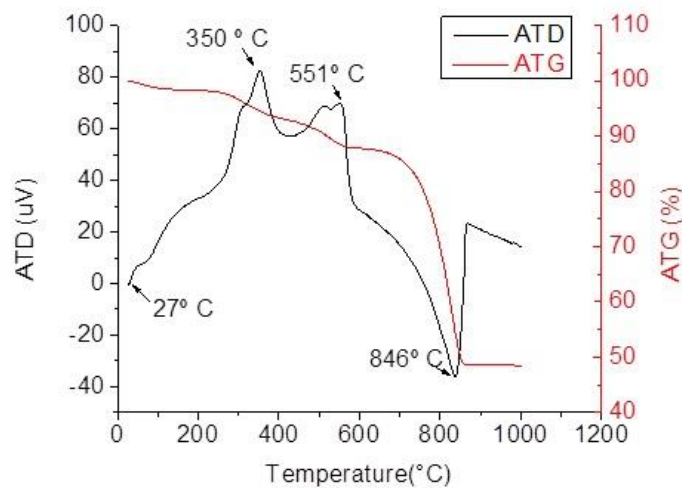
Among the elemental oxides analyzed, it can be observed that calcium oxide is the largest constituent of chicken eggshells, with a small difference in the percentages among the three types analyzed. The difference between CaO contents for each type of egg is due to hen's food. The TGA and DTA curves for all the samples (Figure 3) show that there were three stages of eggshell decomposition (white, red and backyard), which comprise the phases of dehydration, loss of organic matter and decomposition of the calcium carbonate (CaCO<sub>3</sub>) into calcium oxide (CaO) and carbon dioxide (CO<sub>2</sub>).

In the COV powder, occurred a water removal with around 2% mass loss between 23 and 361°C (Figure 3 (a)). Next, organic matter decomposition, with a 6% mass loss (totaling 8% of mass loss from the beginning of the process) is observed at a temperature range of 362 to 507°C. The most significant drop occurred in the third stage, where a mass loss of 41% occurred (totaling 49% mass loss from the beginning of the process) between 508 and 836°C, related to CaO generation and CO<sub>2</sub> release from the CaCO<sub>3</sub> decomposition. The COB powder reactions (Figure 4 (b)) were similar to those of the COV powder, namely: removal of water with mass loss of approximately 5% between 27 and 351°C; decomposition of the organic matter with 7% mass loss at a temperature range of 352 to 551°C (totaling 12% of mass loss from the beginning of the process); and decomposition of CaCO<sub>3</sub> into CaO with CO<sub>2</sub> release between 552 and 855°C and 39% of mass loss, reaching a total of 51% since the beginning of the process.

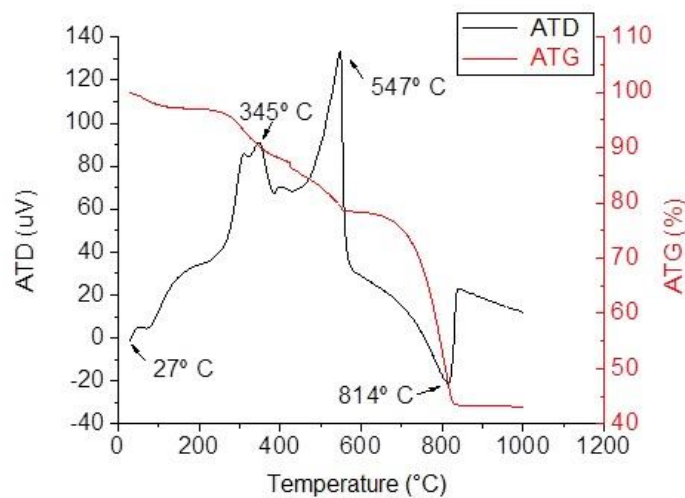
In the COC powder (Figure 4 (c)), water removal occurred between 27 and 345°C, with an approximate mass loss of 4%, while the organic matter decomposition occurred between 346 and 547°C, with around 18% of mass loss (22% of mass loss from the beginning of the process). The CaCO<sub>3</sub> decomposition into CaO and CO<sub>2</sub> generated 35% of mass loss between 548 and 814°C, for a total loss of 57% in this process. The difference between COV, COB and COC mass loss is due to the eggshells chemical composition.



(a)



(b)



(c)

Figure 3 - DTA and TGA curves of chicken eggshell samples: (a) red (COV); (b) white (COB); and (c) backyard (COC).



Traditionally, eggshells are destined to landfills (TOMASELLI, 2014). However, there are initiatives dedicated to changing this scenario by using calcium carbonate, the largest constituent of chicken eggshell, for applications such as pH correction of acid soils, organic fertilizer, raw material for chemical reactions, food supplement and other purposes (RODRIGUES and ÁVILA, 2017; CÔRREA et al., 2015; TOMASELLI, 2014; OLIVEIRA et al., 2013; FRANÇA et al., 2015; VILAR et al., 2010; GOMES et al., 2012; OLIVEIRA et al., 2012; NAVES et al., 2007; MAGALHÃES et al., 2011).

Through the investigation of the database, it was possible to identify that several authors have developed studies based on proposed uses of chicken eggshell residues. The following table (Table 2) contains the title of the works found with their respective author and a summary of their proposal for the reuse of chicken eggshells.

**Table 2** - Applications for chicken eggshell.

<b>AUTHORS</b>	<b>ARTICLE TITLE</b>	<b>CHICKEN EGGSHELL APPLICATIONS</b>
M.G. Tomaselli (2014)	Synthesis and characterization of hydroxyapatite obtained from chicken eggshell.	Hydroxyapatite production.
B.M.C. França, B. S. M. Domingos, R. B. Ribeiro, G. Silva (2015)	Effects of the addition of eggshells on the mechanical and corrosive behavior of reinforced concrete.	Reuse of egg shell residues as additive in reinforced concrete.
J.S.Vilar, A. U. O Saba-Srur, R. G. Marques (2010)	Chemical composition of chicken eggshell powder.	Eggshell powder for use as a source of calcium in multimixtures in Brazil.
A. S. Rodrigues, S. G. Ávila (2017)	Chemical characterization of chicken eggshell and use as a source for the production of calcium compounds.	Use of chicken eggshell as a source for the production of calcium compounds.

D. A. Oliveira, P. Benelli, E. R. Amante (2013)	Valorization of Solid Residues: Eggshells as Raw Material in the Development of New Products.	Calcium for human consumption; Eggshell powder as fertilizer, animal feed and/or heavy metal removal; Calcium carbonate as fertilizer, animal feed and/or removal of heavy metals with separation of the shell membrane; Purified calcium carbonate; Hydroxyapatite production; Protein hydrolyzate from the shell membrane; Protein concentrate from the shell membrane.
L.C. Gomes, B. C. Di Lello, J. B. Campos, M. Sampaio (2012)	Synthesis and characterization of calcium phosphates from chicken eggshell.	Use of the chicken eggshell as the initial precursor for the synthesis of calcium phosphates.
T. H. A. Côrrea, R. S. T. Manhães, J. N. F. Holanda (2015)	Conversion of gallinaceous eggshell residue into calcium phosphate-based biocement.	Conversion of gallinaceous eggshell residue into ceramic biomaterial.
R.A. Oliveira, P. A. B. Freitas, M. J. B. Cardoso, R. C. Barbosa, M. R. O. Pinto, M. V. L. Fook (2012)	Synthesis and characterization of chitosan composite with calcium carbonate extracted from eggshell for possible wound healing applications.	Composite made from eggshell and chitosan for wound healing applications.
M. M. V. Naves, D. C. Fernandes, C. M. M. Prado, L. S. M. Teixeira (2007)	Food fortification with egg shell powder as a calcium source	Food fortification

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B. G. Milbradt, A. L. H. Muller, J. S. Silva, J. R. Lunardi, L. I. G. Milani, E. M. M. Flores, M. G. K. Callegaro (2015)	Eggshell as source of calcium for humans: mineral composition and microbiological analysis.	Eggshell as a source of calcium for humans.
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M.C. Magalhães, A. Ribeiro, M. Quina, C. Cameira (2011)	Treatment and agricultural valorization of eggshell.	Use of eggshell as alkalizing agent for soil.
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## CONCLUSIONS

The DRX results led to the conclusion that regardless of the type,  $\text{CaCO}_3$  is the main constituent in chicken eggshells, and that the percentages of the different constituents vary for each type (via FRX). Using thermal analysis (DTA and TGA) it was verified that it is possible to obtain CaO from the  $\text{CaCO}_3$  decomposition when subject to temperatures above  $820^\circ\text{C}$ .

The bibliographical research demonstrated that chicken eggshells have important applications from the industrial and social point of view, since they can be used in several industries such as biomedical, civil construction, food and agriculture.

With the possibility of obtaining CaO from chicken eggshells and using it as a precursor in chemical reactions in several areas, this residue becomes a valued byproduct with high economic potential and of sustainable characteristics, since the CaO obtained from the decomposition of limestone is removed from nature and considered a finite good.

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