Characterization of avian eggshell waste aiming its use in a ceramic wall tile paste

(Caracterização de resíduo de casca de ovo visando seu aproveitamento em revestimento cerâmico poroso)

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Abstract

In Brazil, the food industry generates every year huge amounts of avian eggshell waste, and a critical question is to find an adequate use for this waste. The aim of this work is to determine the chemical, mineralogical and physical characteristics of a nonprocessed avian eggshell waste sample, as well as to investigate its use in wall tile paste. The sample was analyzed regarding to chemical composition, X-ray diffraction, morphology, particle size analysis, density, organic matter, soluble salts, and thermal analysis. The results indicated that the eggshell waste sample rich in $CaCO_3$ can be used as an alternative raw material in the production of wall tile materials.
Keywords: characterization, eggshell, waste, recycling, ceramic tile.

Resumo

No Brasil a indústria alimentícia gera enormes quantidades de resíduo de casca de ovo galináceo todo ano, e uma questão crítica é estabelecer um uso adequado para este resíduo. O objetivo deste trabalho é estudar as características química, mineralógica e física de uma amostra de resíduo de casca de ovo natural, bem como avaliar sua utilização em revestimento cerâmico poroso. A amostra de resíduo de casca de ovo foi caracterizada com relação à composição química, difração de raios X, morfologia, análise de tamanho de partícula, massa específica, matéria orgânica, sais solúveis e análise térmica. Os resultados mostraram que o resíduo de casca de ovo rico em $CaCO_3$ *pode ser usado como uma matéria-prima alternativa na produção de revestimento cerâmico poroso (azulejo).*
Palavras-chave: *caracterização, casca de ovo, resíduo, reciclagem, revestimento poroso.*

INTRODUCTION

In recent years, special attention has been devoted to industrial sectors that are sources of pollution of the environment [1, 2]. The industry produces large volumes of solid wastes, which can end up in rivers, lakes, and coastal waters. The disposal of these wastes is a very important problem, which can cause risk to public health, contamination of water resources and polluting the environment. A topical area of great importance related to the waste processing and recycling approach is the proper characterization of the material [2].

In Brazil, a large number of food plants are constantly accumulating substantial quantities of avian eggshell waste. According with the Brazilian Association of Food Industry about 120,000 ton. Of avian eggshell waste are generated annually. This natural solid waste, although non-hazardous, is directly disposed in the environment. As a consequence, an huge problem of pollution is generated. In addition, it can attract rats and worms due the organic protein matrix, resulting in a problem of public health [3].

Wall tile is a ceramic material primarily composed of clays, carbonates, and quartz [4]. The wall tile materials according to the Brazilian tile standard NBR 13818 [5] are included in group BIII, in which the water absorption should be above 10%. In addition, the wall tiles present properties such as high dimensional stability and high porosity.

The aim of the current study was to characterize an avian eggshell waste sample, determining chemical and mineralogical compositions and physical characteristics. The potential of use of this waste as a ceramic raw material for wall tile was also examined.

MATERIALS AND METHODS

The raw waste material used in the present work was an avian eggshell waste sample, which was collected from a food plant localized at Campos dos Goytacazes-RJ (Brazil). The waste sample was pulverized, homogenized and classified by sieving (< 100 mesh; 75 μm ABNT).

X-ray powder diffraction analysis of the sample was done using Cu-Kα radiation and 1.5º (2θ)·min^{-1} scanning speed in a conventional diffractometer (URD-65, Seifert). Crystalline phases were identified by comparing the intensities and positions of Bragg peaks with those listed in the Joint Committee on Powder Diffraction Standards (JCPDS) data files.

The chemical composition of the eggshell waste powder sample was determined by X-ray fluorescence. The loss on ignition (Loi) of the calcined sample at 1000 ºC was determined according with % Loi = $(A_i - A_f)/A_i$ x 100, in which A_i is the weight of the dry sample at 110 ºC and A_f is the weight of the calcined sample at 1000 ºC, during 1 h. Other relevant parameters such as organic matter content, pH, cation exchange capacity and soluble salts content were also determined.

The particle size analysis of the waste powder sample was determined by the combination of sieving and sedimentation standardized procedures. The density of the sample was determined by pycnometry. Plasticity tests were performed according to standardized procedures.

The morphology and texture of the eggshell waste powder particles were examined by scanning electron microscopy (DSM 962, Zeiss).

TG/DTA experiments were carried out on the waste powder sample using a thermal analyzer (SDT-2960 Simultaneous TGA-DTA, TA Instruments), under air atmosphere from room temperature up to 1150 ºC at a heating rate of 10 ºC/min.

In this work a wall tile paste was formulated [6] from a mixture of red plastic clay, avian eggshell waste and commercial quartz. The composition of the mix used was as follow: red clay 70 wt.%, eggsshell waste 15 wt.% and quartz 15 wt.%.

The raw materials were mixed and homogenized using a laboratory mill. After adjusting the moisture content to 7%, the ceramic powder was held in a dissecator for 24 h to homogenize it moisture content.

Rectangular specimens (11.5 cm x 2.5 cm) were prepared by uniaxial pressing using a steel die at 35 MPa, and dried at 110 ºC for 24 h. The green pieces were sintered in a fast-firing laboratory kiln at 1150 ºC of maximum temperature using a fast-firing cycle (~ 60 min). The following properties were determined in accordance with the standard procedures: linear shrinkage, water absorption, apparent density, apparent porosity, and flexural strength. The sampling size used was of five specimens. The sintered microstructure was observed by SEM.

RESULTS AND DISCUSSION

X-ray diffraction patterns of the avian eggshell waste sample are shown in Fig. 1. The sample presented all diffraction peaks that are characteristics of calcite ($CaCO_3$). Calcite presents rhombohedral structure, and is the thermodynamically most stable form of $CaCO_3$ at room temperature [7].

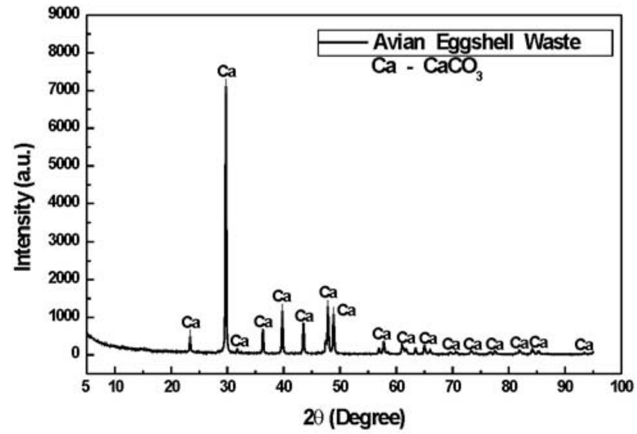

Figure 1: X-ray diffraction pattern for the eggshell waste sample.
[Figura 1: Difratograma de raios X da amostra de resíduo de casca de ovo.]

As Table I illustrates, the chemical composition of the avian eggshell waste sample shows that calcium oxide (CaO) was the most abundant component. The high amount of calcium oxide is associate the presence of calcium carbonate, which is the main component of avian eggshell [8, 9]. The sample also contained only small amounts of P_2O_5, Na_2O, SrO, SiO_2, MgO, Cl, Al_2O_3, Fe_2O_3, and NiO reporting less than 1.5% of the total composition. Thus, the eggshell waste sample can be considered from a chemical viewpoint a pure relatively natural carbonate-based material, as well as its composition is very similar to the calcitic calcareous [10]. In addition, it was also observed that the loss on ignition for waste sample was found to be 47.8%. This high value of Loi is caused mainly by decomposition of the calcite with formation of CaO and carbon dioxide (CO_2).

Some important physical and chemical characteristics of the eggshell waste sample are shown in Table II. The waste

Table I – Chemical composition of the eggshell waste sample (wt.%).
[Tabela I – Composição química da amostra de resíduo de casca de ovo (% em peso).]

CaO	50.7
SiO_2	0.09
Al_2O_3	0.03
MgO	0.01
Fe_2O_3	0.02
Na_2O	0.19
P_2O_5	0.24
SrO	0.13
NiO	0.001
SO_3	0.57
Cl	0.08
Loi	47.8

Loi = loss on ignition

sample presented density of 2.47 g/cm^3, which is within the range to calcium carbonate materials. The sample also presented low hygroscopic moisture content (1.1%), low soluble salts content (in water) and low cation exchange capacity (9.52 meq/100 g). The pH (in water) of the eggshell waste sample is 8.3, which is a weak alcali. The organic matter for eggshell waste sample was found to be 5.36%, which is in agreement with the literature [11]. The organic matter in the eggshell is in the form of shell membranes and matrix. In addition, this result also suggests that the presence of organic matter contributed for the high value of Loi (Tab. I).

Table II - Characteristics of the eggshell waste sample.
[Tabela II - Características do resíduo de casca de ovo.]

Real density, g/cm^3	2.47
Hygroscopic moisture, %	1.1
pH (H_2O)	8.3
Cation exchange capacity, meq/100 g	9.52
Content of soluble salts, ppm	
K	12.0
Ca	50.2
Mg	12.0
Al	0.0
H + Al	0.0
Na	21.0
Organic matter, %	5.36
Organic carbon, %	3.11
S – SO_4 content, ppm	39.0

The thermal behaviour of the eggshell waste sample was analyzed in DTA/TG experiments. The results are summarized in Table III. The results show the presence of three thermal events. The first event (~ 51 ºC) is endothermic and is attributed to the removal of physically adsorbed water on the particles of the waste powder. The second event (~ 324.0 ºC) is exothermic, and related to decomposition of organic matter. The third event (~ 765.3 ºC) is endothermic, and was caused by decomposition of calcium carbonate according to

$$CaCO_3 \text{ (calcite)} \rightarrow CaO \text{ (calcium oxide)} + CO_2 \uparrow \text{ (carbon dioxide)} \quad (A)$$

Table III - Results of thermal analysis of the eggshell waste sample.
[Tabela III - Resultados de análise térmica da amostra de resíduo.]

Thermal event	DTA (ºC)	Mass loss TG (%)
Endothermic	51.0	1.2
Exothermic	324.0	5.2
Endothermic	765.3	40.2

The thermal events are accompanied by an intense process of mass transfer in the eggshell waste sample, resulting in a total mass loss during heating of 46.6%. This result is in accordance with the loss on ignition (Tab. I). It was also verified that the mass loss related to the exothermic event is in accordance with the organic matter content (Tab. II). A reasonable semi-quantitative estimation of the $CaCO_3$ present in the eggshell waste sample can be done by integrating the thermal gravimetric analysis and X-ray diffraction results. The mass loss in the temperature range 750 – 1000 ºC corresponds to the proportion of CO_2 evolved from the sample. Then, the amount of $CaCO_3$ of the eggshell waste sample used in this work is given by $CaCO_3$ % = wt.% (750 – 1000 ºC) / 44. From the TG results in the Table III, the amount of $CaCO_3$ in the eggshell waste sample is 91.36 %. In fact, the eggshell is a thin protective coat composed of approximately 95% calcium carbonate, primarily in the calcite crystal form [8, 9, 11].

The particle size distribution curve of the eggshell waste is shown in Fig. 2. The sample presented large particle size distribution varying between 2 and 900 µm. Some characteristic diameters representative of the distribution curve are D_{10} = 3.6 µm, D_{50} = 61.5 µm and D_{90} = 437.5 µm, whose curvature coefficient is 23.5 and uniformity coefficient is 2.1.

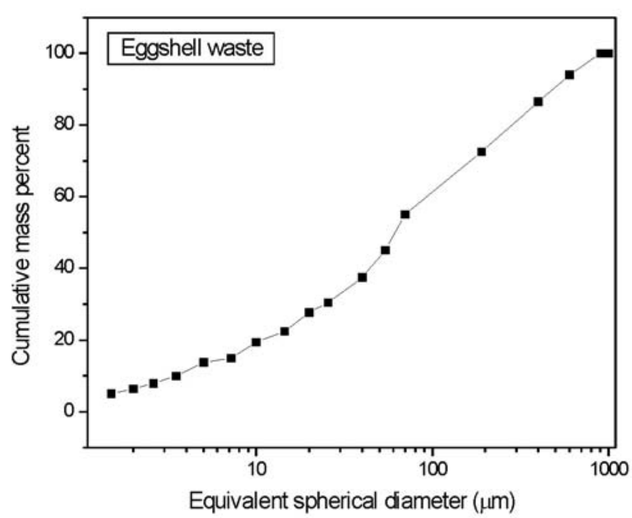

Figure 2: Particle size distribution of the eggshell waste.
[Figura 2: Distribuição de tamanho de partículas do resíduo de casca de ovo.]

Some attempts were done to determine the plastic properties (plastic limit and plasticity index). As expected, the experiments showed that the eggshell waste sample can be considered as a non-plastic material.

Morphological aspects of the eggshell waste sample particles are outlined in Fig. 3. As observed the eggshell waste powder particles have irregular shape, resulting of the comminution process used. In addition, a wide particle size range was observed, which is in accordance with the results obtained of the particle size analysis (Fig. 2). The scanning

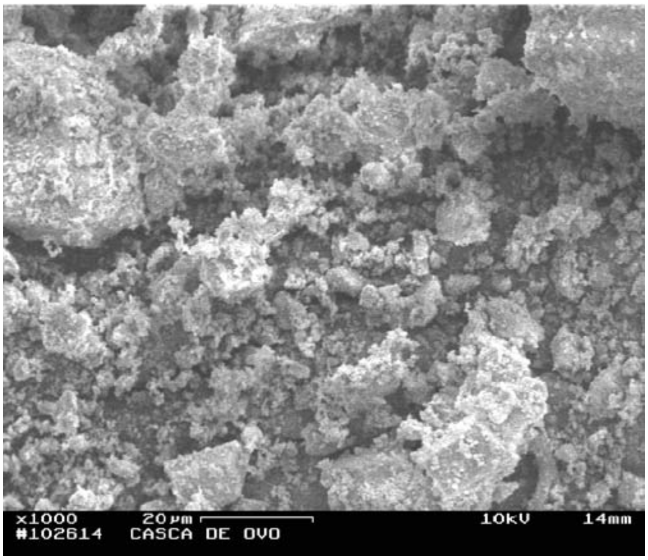

Figure 3: Overview of the eggshell waste sample.
[Figura 3: Aspectos morfológicos do resíduo de casca de ovo.]

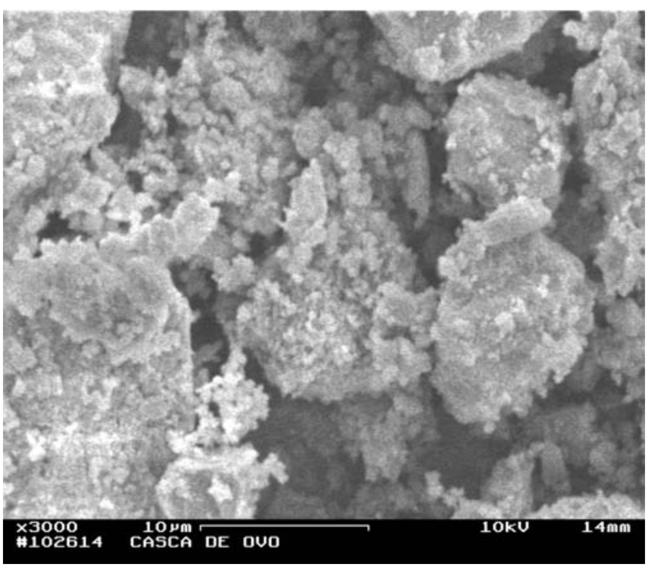

Figure 4: Morphological details of the eggshell waste sample.
[Figura 4: Detalhes morfológicos do resíduo de casca de ovo.]

electron micrograph of Fig. 4 shows the high porosity of the eggshell powder particles. In fact, the eggshell contains a significant amount of gas exchange pores [9].

The avian eggshell waste sample is basically consisted of calcium carbonate in the form of calcite ($CaCO_3$). Then, the eggshell waste material can be of immense interest as a ceramic raw material. In this context a triaxial composition for wall tile material was formulated using the eggshell waste in substitution to the traditional carbonaceous material. The physical-mechanical properties determined for the clay-eggshell waste-quartz formulation sintered at 1150 ºC are reported in Table IV. As can be observed the specimens exhibited low firing shrinkage (1.44%), which was well within the acceptable limit for industrial production of wall

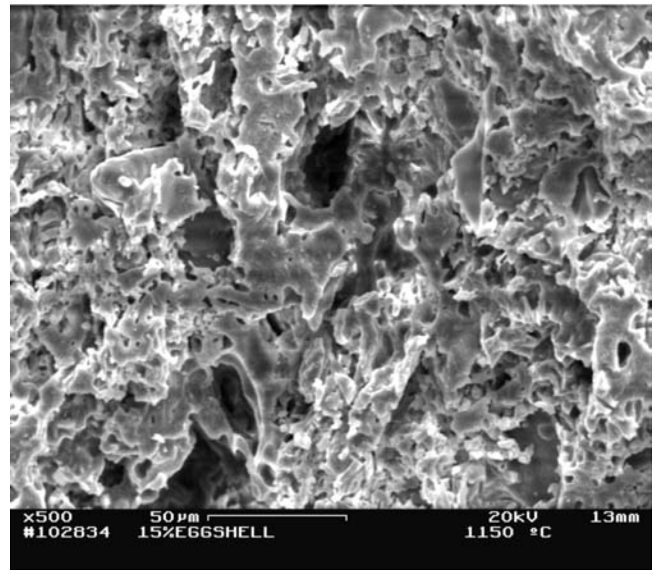

Figure 5: Microstructure of the specimen sintered at 1150 ºC.
[Figura 5: Microestrutura da amostra sinterizada em 1150 ºC.]

Table IV - Properties of the fired specimens at 1150 ºC.
[Tabela IV - Propriedades das amostras queimadas em 1150 ºC.]

Linear shrinkage, %	1.44 ± 0.15
Water absorption, %	22.72 ± 0.41
Apparent porosity, %	37.53 ± 0.47
Apparent density, g/cm^3	1.65 ± 0.95
Flexural strength, MPa	15.29 ± 1.09

tile materials. The water absorption of the specimens is 22.72% indicating their conformity to NBR 13818 Brazilian standard (group BIII – WA > 10%) [5]. The specimens also presented high apparent porosity, which was influenced by the decomposition of the calcium carbonate with evolution of CO_2 outside the structure of the specimens. The effect of the carbonate decomposition is clearly observed in the fractured surface of the sintered specimen as shown in Fig. 5. The microstructure is dominated by the high porosity connected with dense zones, and is very similar to the microstructure of eggshell waste-free wall tile materials [4]. The apparent density of 1.65 g/cm^3 is typical of wall tile materials, which provides less weight / m^2. In addition, the specimens (thickness < 7.5 mm) presented value of flexural strength (15.29 MPa) in conformity to wall tiles according to NBR 13818 Brazilian standard.

CONCLUSIONS

The avian eggshell waste sample studied in this work is chemically constituted basically by calcium oxide (CaO), and is more pure than traditional carbonate based materials used in ceramic industry. Results of X-ray diffraction showed that the crystalline phase present in the waste sample is calcium carbonate in the form of calcite ($CaCO_3$). TG measurement indicated high total mass loss (46.6%), which was caused mainly by evolved CO_2 and organic matter decomposition. The eggshell waste powder consists of porous irregular particles, whose size ranges from 2 to 900 μm. The results also showed that the eggshell solid waste in form of powder can be regarded as an interesting raw material for manufacture of single-fired ceramic wall tile materials. In addition, the use of eggshell waste in wall tile formulations is an excellent alternative for material reuse and waste recycling practices.

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