PHYSICO-CHEMICAL ANALYSIS OF THE CASHEW NUT PRODUCTION WASTE AIMING THEIR USE IN CEMENT COMPOSITES

ANÁLISE FÍSICO-QUÍMICA DA CINZA DA CASCA DA CASTANHA DE CAJU VISANDO SUA APLICAÇÃO EM MATERIAIS CIMENTÍCIOS

SOFIA ARAÚJO LIMA[1]

JOÃO ADRIANO ROSSIGNOLO[2]

HOLMER SAVASTANO JUNIOR[3]

JULIANO FIORELLI[4]

ABSTRACT

Ashes have a prominent place among the agroindustrial wastes, as they result from the energy generation process. Most ashes have pozzolanic activity, and may be used as a cement replacement material, resulting in less energy waste and low cost composite. The present paper investigates the physical and chemical properties of cashew nut shell ash (CNSA) by the following measurement tests: chemical analysis, bulk density, specific mass, leaching and solubilization process, X-Ray diffraction (XRD), scanning electron microscopy (SEM) and specific surface area (BET). A low content of silicon (SiO_2) was observed by means of the chemical tests and heavy metals were found in the analysis of the CNSA solubilized extract. These results will be important for the determination of the pozzolanicity of CNSA in a next stage, as well as the development of a new product for civil building reducing the solubilization of the CNSA in the environment.

Keywords: Cashew nut ashes; Agroindustrial waste; X-Ray diffraction; SEM; Surface area.

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[1] Federal University of São Carlos- UFSCAR, São Carlos, SP, Brazil.

[2] São Paulo University - FZEA/ USP - Pirassununga, SP, Brazil.

RESUMO

As cinzas tem um lugar de destaque entre os resíduos agroindustriais, tal como resultam do processo de geração de energia. A maioria das cinzas podem apresentar atividade pozolânica, podendo ser utilizado como material de substituição do cimento Portland, resultando em menos desperdício de energia e compostos de baixo custo. O presente trabalho investiga as propriedades físicas e químicas da cinza da casca da castanha de caju (CCCC) por meio de análise química, densidade, massa específica, lixiviação e solubilização, difração de raios-X (XRD), microscopia eletrônica de varredura (MEV) e área de superfície específica (BET). Um baixo teor de silício (SiO_2) foi observada por meio dos testes químicos e metais pesados foram encontrados na análise do extrato solubilizado CCCC. Estes resultados serão importantes para a determinação do pozolanicidade da CCCC, em uma nova fase da pesquisa, bem como o desenvolvimento de um novo produto para a construção civil reduzindo o descarte da CCCC no meio ambiente.

Palavras-chaves: Cinza da casca da castanha de caju; Resíduos agroindustriais; Difração de raios-X; MEV; Superfície específica.

INTRODUCTION

The concern with the world energy scene has stimulated the search for renewable energy sources to reduce the consumption of fossil fuels, exhaustible and highly polluting, and to encourage the use of sustainable products in according to existing environmental standards. Loss of diversity, increasing the temperature, decrease the production of food and other problems, are some consequences of the global heating, and that may brake the human development, in economic or social scale. The search for alternative materials, the development of less polluting materials or the use of raw materials, the reuse of solid waste and the reduction of emission of carbon dioxide are some measures necessary for the current world scene.

Agroindustrial by-products, such as wastes or ashes, have been studied for use as fuel, fertilizers and soil stabilizers. The building construction, for its high consumption of raw materials, has been the largest potential market for recycling. Many researches are found in literature, which have been developed with agroindustrial wastes (SILVA & SOUZA, 1995).

Ashes are by-products generated by industrial or agroindustrial processes due to the back of some wastes to the same process. The rice husk ash may be used as an example. The husk of rice is burned to obtain energy, which generates the rice husk ash, another by-product.

According to JOHN et al. (2003), any plant predominantly siliceous, which can be produced in the amorphous state and with appropriate fineness, can be used as mineral admixture. Its reactivity may depend on the chemical composition.

In this article, it will be presented the assessment of physical and chemical characteristics of the rind of the cashew nut (ARCN) for use as mineral admixtures in Portland cement matrices. The results will be important to determinate the pozzolanic potential of ARCN in samples of mortar, in a next phase of studies.

EXPERIMENTALS

Wastes of cashew nut production

The cashew tree belongs to the *Anacardiaceae* family, genus *Anacardium L.,* species *Anacardium occidentale L*. The cashew tree occupies an important position among the tropical fructiferous trees on account of the growing commercialization of its main products: the (cashew) nut, the cashew nut shell liquid (CNSL), and the cashew ‘‘apple’’ (Figure 1).

FIGURE 1 – Cashew: nut and apple (yellow)

The plant is found in Central America, Africa, Asia and India, Vietnam and Brazil stand out as the largest producers of cashew nut (70% of the world production).

The cashew culture is one of the main agronomic activities in Northeast Brazil; almost the whole production is concentrated in the states of Ceará, mainly, and also Piauí and Rio Grande do Norte. Most of the production of the cashew nut and CNSL is destined for exportation (SANTOS et al. 2007). The rinds of cashew nut (wastes of nuts' production) are burned again during the heating process (Fig. 2), and in boilers, they'll generate heat for shelling other nuts. The ARCN is the waste collected from the boiler grid, resulted from burning of the rind of nuts. This waste is used as composts in plantings of cashew and a little part of it is dumped in landfill sites (LIMA, 2008).

FIGURE 2 – Rinds of cashew nuts after burning on LCC: non-uniforms pieces

The ARCN represents approximately 5% of initial weight of cashew nut, and because the production increasing in cashew's plants, the generation of ashes might achieve 15.000 tons per year. Until now few researchers were made with ARCN , even if other objectives different from civil building. One of them has used ARCN as stabilizer of soils on the production of adobes. This research, according to the authors, still needs further study (LIMA et al., 2004).

The ash used in these assessments was donated by the company CIONE, located in Fortaleza, Ceará, Brazil.

METHODS

To determine the physical and chemical characteristics of the ARCN were executed the following tests.

Chemical analysis

The method used for chemical analysis was the quantitative analysis. Some elements were determined in a optical emission spectrometer with plasma, except for potassium and silicon, which were determined by atomic absorption spectrometer, with flame, model Spectra The 640 , The brand Varian (IT AQ-158 revision 009).

Determination of specific and bulk densities

The test for specific density of the ARCN was made following the recommendations of standard NM23 (MERCOSUR, 2000), using kerosene as solvent and 45g of dry material. The bulk density analysis of ARCN was carried out in accordance with the standard NBR7251 (ABNT, 1982). The only change was in relation to the container, which was amended in this search for one of 3.0 litre. This change was needed because the characteristic of the ARCN, which is not a aggregate, but a material in powder.

Analysis of leached and solubilized extract

In analyses of leaching and solubilization of samples of ARCN were determined possible contaminants and/or heavy metals contained in the material. These data have a great relevance in the assessment of the needing of stabilization/solidification of this waste.

The test was carried out following the specifications of standards NBR10004, NBR10005, NBR10006 and NBR10007 (ABNT, 2004).

X-Ray Diffraction analysis

This technique was used in the sample of dust from ARCN. The aim was to obtain the predominant crystalline materials, and to observe the presence of ash in amorphous phase. It was used an XRD Brand RIGAKU ROTAFLEX, model RU200B. The conditions for carrying out analysis were: Radiation: Cu K á; Voltage: 50Kv; Current: 100mA; Scanning with step of 0.02° 2 θ; Scanning time: 2°/min; Interval of scanning: 3 to 100°(2 θ).

Determination of specific surface area

The method BET (Brunauer-Emmet-Teller) was chosen for analysis of specific surface area of the ARCN. The sample was milled in a mill of metal balls for 1 (one) hour (LIMA et al., 2007).

Scanning Electron Microscope analysis

The technique of Scanning Electronic Microscopy (SEM) was used in the analysis of particles of the ARCN. The sample was milled in a mill of metal balls for 1 (one) hour (LIMA et al., 2007).

RESULTS AND DISCUSSION

Chemical analysis

The results of chemical analysis of the ARCN are presented in Table 1. The main elements found were Potassium (K_2O), Magnesia (MgO) and Silicon (SiO_2), in that order. The level of silicon (SiO_2 - 12.17%) was below the recommended level by other researches (CINCOTTO, 1988; JOHN et al., 2003; PRUDÊNCIO JR. et al., 2003) to present pozzolanic reactivity.

TABLE 1 - Chemical composition of ARCN

Compound	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	K_2O	MgO	P_2O_5	TiO_2	MnO	Ingnition loss	Total
Mass Percent (%)	12,17	1,37	3,06	2,15	6,54	24,79	16,34	10,05	0,087	0,29	17,90	94,74

It was also observed the high quantities of magnesia (MgO - 16.34%), sodium (Na_2O - 2.15%), and potassium (K_2O - 24.79%), in the ARCN.

These elements, known as alkali, may hurt the performance of products made of cement (NEVILLE, 1997).

The standard NBR12653 (ABNT, 1992) limits the amount of equivalent material of Na_2O in pozzolanic materials by 1.5%. The calculation of the equivalence of Na_2O also takes into consideration the content of Potassium, through the equation "$Na_2O + 0.64\ K_2O$" (MEHTA & MONTEIRO, 1994).

For this formula the amount of alkali available in the ARCN was 18.02%, which may limit its use in low levels of cement Portland replacement.

Specific density and bulk density

The specific density value was obtained by the average of two consecutive tests, and obtained the value of 2.23 g/cm^3. The result of the bulk density of the ARCN was obtained by the average of three consecutive tests, and obtained the value of 0.56 g/cm^3.

Contamination levels

For the analysis of leaching and solubilized extracts of ARCN according to NBR10005 e NBR10006 were found various heavy metals. The results of the solubilization analysis had presented values above of the allowed limit for some chemical substances in accordance with the Index G - Standards for Solubilization Test.

Tab. 2 presents such substances, found in the ARCN solubilized extract. Although the results well above of the limit presented for the solubilization analyses, the results of the leaching had not presented values above of the limit allowed for the group of the Inorganic components, according to Index F - Maximum Limit in the Extract gotten in the Leaching Analysis. The results of the leaching assay are determinative in relation to the classification of a residue into "Dangerous" in (Class I) or "Not dangerous" (Class II).

TABLE 2 - Chemical elements found on the solubilized extract of ARCN and the standard limits of NBR10004

Compound	Unit	Result	Limit on the extract (mg/L)
Cadmium	mg Cd/L	**0,570**	0,005
Plumb	mg Pb/L	**1,390**	0,010
Chlorine Ion	mg Cl^-/L	**950,000**	250,000
Chromium	mg Cr/L	**3,090**	0,050
Phenol	mg	**0,042**	0,010
Iron	mg Fe/L	**1,680**	0,300
Nitrates	mg N/L	**75,000**	10,000
Silver	mg Ag/L	**0,620**	0,050
Sodium	mg Na/L	**12175,000**	200,000
Manganese	mg Mn/L	**0,210**	0,100

Although the high levels of heavy metals and phenol in the solubilized extract, the ARCN may be classified as “Not Dangerous Residue - Class II - Not inert”. The residues with such classification might be biodegradable, burnable or soluble in water.

One of the causes of contamination by heavy metals may be due to the use of pesticides in cashew. The pesticides might be absorbed by the rind of nut and may not have been fully eliminated during the process of nut production.

The studies with heavy metals in ecosystems have shown high concentrations of these elements in many areas near urban industrial complex and also in the areas of hightec agriculture. In these regions the soil have been polluted with Pb, Cd, Ni, Hg, As and other heavy metals (ALLOWAY, 1995). The increase of abnormal concentrations of these elements in the soil of such areas is atmospheric deposition and the application of fertilizers, corrective, pesticides, irrigation water, waste organic and inorganic (RAMALHO & AMARAL SOBRINHO, 2001). It is known that cadmium, plumb, chromium, and other substances derived from pesticides are harmful to human health (ABMC, 2007).

The origin of Phenol can be attributed to the cashew nut shell liquid (CNSL), The CNSL is a compound aggressive to human health, dark and very viscous, extracted from the cashew nut shell. It is known that the shell of nuts still have CNSL even after burned and separated from the kernel. The process of burning, from which it originated the ARCN, may not have completely eliminated the Phenol (SILVA, et al, 2004).

According to AGOSTINI-COSTA (2000) the phenolic lipids, main components of the CNSL, have properties which produces dermatitis when in contact with the skin. The main components are the anacardic acids, derived from salicylic acid, followed by cardols, derived from resorcinol, and lower levels of cardanols. The CNSL usually contains cardanol (60-65%), cardol (15-20%), polymer material (10%), e methyl-cardol traces (CARIOCA et al., 2005).

It should be noted that the ARCN is currently used as fertilizer in the planting of cashew nuts, or dumped in landfill sites without any consideration of his handling of the danger to human health. The presence of humidity in contact with the ARCN, causing solubility of the material, can be highly harmful to the soil and groundwater. Some of the soluble substances present in the ash are potentially carcinogenic and toxic to human health. This warning may be reported also to the other agroindustrial ashes researched as cement Portland or natural sand replacement.

X-Ray Diffraction analysis

For the ARCN difratogram it’s possible to see a halo, characteristic of the presence of amorphous material, between the angles 25º e 35º 2θ(Fig. 3).

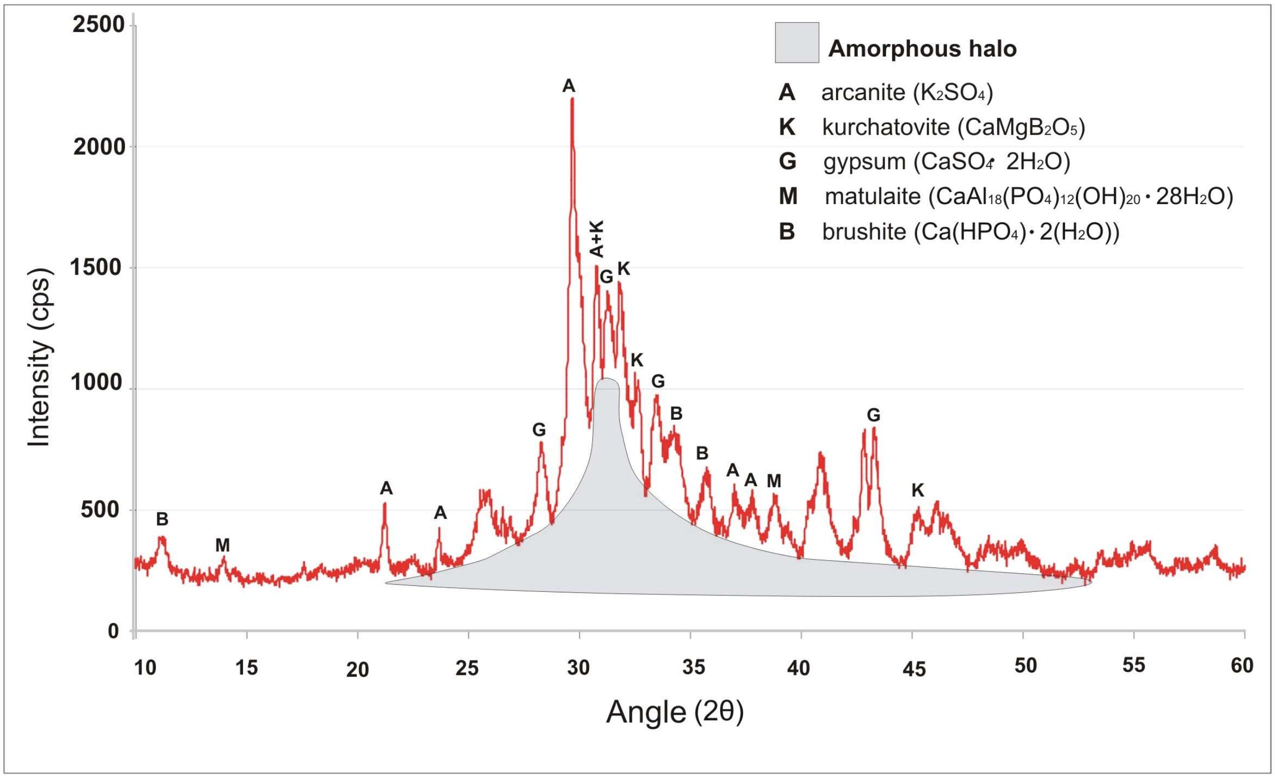

FIGURE 3 - X-Ray Diffraction of ARCN

For the analysis of ARCN difratogram it's possible to determine predominant elements, the mineral Arcanite (K_2SO_4 - potassium sulphate), peak identified approximately in the angle 30º2θ.

The other compounds found are formed, predominantly, by chemical species Potassium (K), Phosphorus (P) and Calcium (Ca), main constituents of the ARCN, according to the chemical analysis. The potassium sulphate is commonly used in potassium-based fertilizers. The potassium sulphate was also found in samples of ARCN originated by the burning of bagasse of peduncle cashew (SANTOS et al., 2007). This mineral may have been resulted from fertilizers used in the cashew plant. Potassium sulphate, even with higher cost, is recommended for use in various cultures as a substitute for potassium chloride - KCl (MASCARENHAS et al., 1994).

BET Surface Area

The results of BET Surface Area analysis are presented on Tab. 3.

TABLE 3 - Surface area of ARCN

Sample	Pre-treatment	Area (cm^2/g)	External Surface Area of particle (cm^2/g)	Internal Surface Area of Pores (cm^2/g)
Raw ARCN	milling	17.230	11.740	5.496

The BET method is widely used to determine the specific area of solid materials with different sizes of pores. It is known that a limitation on the BET method is the fact that it can only be applied to samples porous if they have open pores that can be filled by the gas used (ODLER, 2003).

It was observed that over than 30% of the surface of specific particles of ARCN are composed for internal pores. This feature may explain the increased demand for water and loss of workability of mortar, when there is the replacement of cement (Portland cement high early strength, CP V ARI) by ARCN above 10% (LIMA, 2008).

SEM Analysis

Fig. 4 shows the images obtained by Scanning Electronic Microscope. The particles of ARCN have different sizes, about 10 ìm to 75 ìm. These particles have lamellar aspect, with overlapping layers and small particles adhered to the surface, forming grains of various sizes and formats.

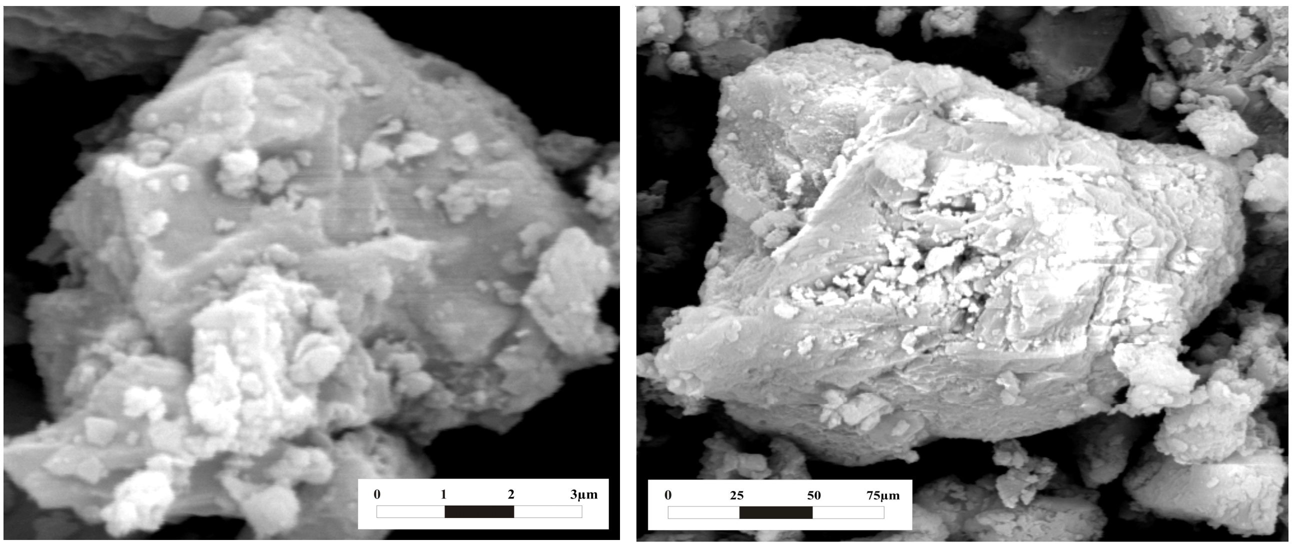

FIGURE 4 - Scanning electron micrograph of ARCN

CONCLUSIONS

It was observed by chemical analysis of the ARCN a low content of silica (SiO_2) present in the sample, which restricts its use as pozzolanic material. Moreover, high levels of alkali and magnesium oxide found also limit the use of high levels of ARCN in cementitious matrices. In relation to the levels of contamination, the analysis of soluble extract of the ARCN has presented various types of heavy metals and phenol. It should be noted that the ARCN is currently used as fertilizer in the planting of cashew nuts without any consideration of the danger to human health. The presence of humidity in contact with the ARCN, causing solubility of the material, can be highly damaging to soil and groundwater. The substances present in ARCN are potentially carcinogenic and toxic to human health. The results obtained by the tests have indicated the possibility of using the ACRCN in cementitious matrices in low levels of replacement. In a next step of testing, therefore, it will be examined samples with varying levels of Portland cement replacement by ARCN. It will be possible to determine the range of replacement without damage to the mechanical properties of the matrix.

ACKNOWLEDGEMENTS

The authors acknowledge FAPESP, for financial support; CIONE (Mr. Gerardo Aguiar); the Laboratory of Civil Building, the Laboratory of Sanitation, the Laboratory of Scanning Electronic Microscope and the Laboratory of X-Ray Analysis, all of them belonged of School of Engineering of Sao Carlos from University of Sao Paulo, Brazil.

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