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REUSE OF "CASSOSTREA VIRGINICA" OYSTER SHELLS TO OBTAIN A MORTAR BINDER FROM THEIR MILLING AND CALCINATION

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— Abstract—

Currently oyster shells "Crassostrea virginica" commercially exploited in Tabasco, represent a pollution problem. Because people after consuming the edible part of the scallop, discarded on the streets or in public places and even in landfills shells, causing bad aspect to the place, poor hygiene and spread of pests. Therefore, through this research it is to provide a solution to this problem of pollution and recycle this waste material for environmental purposes for construction. The shells were collected and selected in diffe-rent sizes and subjected to coarse grinding treatments with manual fracturing and dry grinding in a ball mill. Subsequently, these oyster shells were heat treated for calcining at 500, 700, 800, 900 and 1000°C. The powders obtained with the two treatments were separated with a vibrating table to perform the sieve analysis. Through analysis by X-ray diffraction (DRX), it was found that the powders are composed of CaO, $CaOH$ and $CaCO_3$. By these results the feasibility of using this waste oyster shells as a material for mortar used in the construction is proposed.

Keywords

Reuse oyster shells; Crassostrea virginica; cement mortar, Calcite.

Currently oyster shells of "Cassostrea virginica", which are commercially exploited in Tabasco, represent a pollution problem since after consuming the edible part of the oyster, which is the abductor muscle, people dump them into the streets or in public places causing unpleasant scenes, poor hygiene and the spread of pests. This project intends to provide a solution to this pollution problem and recycle this waste to obtain an environmental material for the purposes of construction. In Tabasco like in many coastal states, the consumption of oysters is increasing because they have been considered a gourmet product because of their taste, palatability, appearance and secondarily by some myths about its alleged "aphrodisiac" powers. However, this does not pose any problem for Tabasco as it is one of the main oyster producers and has contributed a high percentage of production at the national level. With statistical data released by SAGARPA CONAPESCA in 2013 there was production of 15, 402 Tons / year, being second only to Veracruz, which produces 19,422 Tons / year (CONAPESCA, 2015).

In addition, its capture and production is the main activity for the settlers in the coastal lagoons of the state. The problem subsists in when you do not know what to do with the inedible part of this marine product. This problem affects restaurants and the civilian population and their government authorities, since tons of them are generated and only a quarter is used for the reproduction of the adductor mollusk. The above is not exclusive of the state, but at the national level as well in other coastal states such as Tamaulipas, Veracruz and Campeche which are also affected by this same problem.

The disposal of the shells in these places generates considerable inconveniences, mainly due to its insolubility in the water and its resistance to biodegradation. One of the problems that most concerns the communities is the growth of the mosquito carrying dengue within the oyster shells, since it has an irregular and asymmetrical shape. The outer face is rough and dark, contrasting with the interior, which represents a smooth surface in a concave shape that allows water to be retained in it.

It has been found that shells contain high amounts of calcium carbonate, calcium oxide and calcium hydroxide- compounds which, at present, are used for their functional properties to perform various processes that are beneficial to humans, covering such varied fields as food, medicine (Ronge Xing, Yukun Qin, Xiaohong Guan, Song Liu, Huahua Yu, Pengcheng Li, 2013), agriculture, cosmetics, wastewater treatment (Yao-Xing Liu, Tong Ou Yang (Yong Sik Ok, Sang-Eun Oh, Mahtab Ahmad, Seunghun Hyun Kwon-Rae Kim, Deok Hyun Moon, Sang Soo Lee, Dong-Xing Yuan, Xiao-Yun Wu, Kyoung Jae Lim, Weon-

Tai Jeon and Jae E. Yang, 2010) and soils contaminated with heavy metals, among others (Yao-Xing Liu, Tong Ou Yang, Dong-Xing Yuan, Xiao-Yun Wu, 2011). This mollusc has been used by man in his diet since prehistoric times, as revealed by the remains of their shells found in caves and shelters inhabited by primitive peoples or in shells that have been located by archaeologists in different areas of the coast and are very important in the dating of dates for this science. The shells were a material used by prehispanic cultures, as can be seen in the Teotihuacan Temple, where they appear carved in stone along with the symbolic serpent, or by the Maya who, in the absence of limestone, built and lined up large cities using shells in combination with other materials such as clay.

In recent years, the scientific publications, patents and websites of some countries or companies have been conducting studies and exposing advances in the production, characterization and applications of oyster shell components (Yang, Yong Sik Ok, Sang-Eun Oh , Mahtab Ahmad, Seunghun Hyun, Kwon-Rae Kim, Deok Hyun Moon, Sang Soo Lee, Kyoung Jae Lim Weon-Tai Jeon, Jae E., 2010) (Shih-Ching Wua, b, Hsueh-Chuan Hsua, b, Yu -Ning Wuc, Wen-Fu Hoc, 2011). It has been found that the materials that are the product of calcareous species can be considered as natural hybrid materials, since they are constituted by organic and inorganic compounds. An example of a natural hybrid material is bone, whose hardness and stiffness have not been found in any synthetic material.

The advantage of these porous materials is that by removing the organic components, the size and shape of the pores can be accurately controlled, making them fire resistant, impermeable in construction and for environmental uses such as absorbing contaminating gases (Kai-Wen Ma, Hsisheng Teng, 2010). They also form very complex and orderly structures with good mechanical and chemical properties, making these hybrids ideal for applications in the modern fields of Biotechnology, Computer Science and Nanotechnology (BIN). Nanotechnology continually requires self-assembling structures, because it is very difficult to assemble devices made up of a few molecules. One way to make good use of crustacean waste would be to obtain a material based on calcium carbonate, for use in the preparation of a powder consisting of nanoparticles of $CaCO_3$.

Materials and methods

Oyster shells were collected in places where they are disposed as waste, washed and all of the collected shells were rinsed with potable water to remove some of the dirt and were selected in size between 7 and 10 cm in length. With manual shredding, the size of the shells was decreased and divided into two groups of samples; Samples for grinding and samples for calcination. The first group of oyster shells was subjected to milling in a ball mill for 30 minutes. To the second group, heat treatment was applied in a muffle with air atmosphere at 500, 700, 800, 900 and 1000 ° C. Granulometric analysis was done on the powders obtained in the two treatments using meshes with aperture size of 0.42 mm to 0.074 mm, with a vibration time of 20 minutes. The crystal structure was determined by the X-ray diffraction analysis of all powders subjected to the various treatments.

Presentation and discussion of results

Granulometric analysis of the two treatments

Figure 1. (a) Shows the percentage of retention per mesh made at different calcination temperatures. (B) Shows the percentage of retention per mesh of the oyster shells subjected to mechanical treatment.

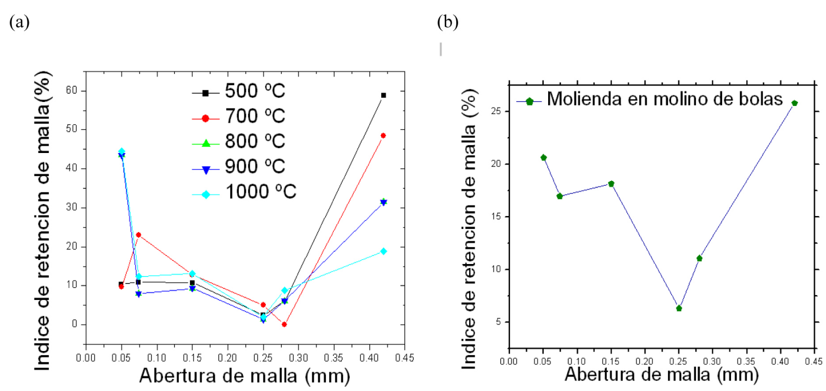


Figure 1 shows the granulometric analysis of the calcination (Figure 1a) and grinding treatments (Figure 1b) of the previously manually crushed oyster shells. Analyzing the graphs a and b of Figure 1, it is observed that with the heat treatment a greater decrease of the particle size is obtained as the calcination temperature increases, and a very fine powder with a particle size of about 74 µm is obtained. This treatment favors the use of oyster shells as a binder in the mortar used in the restoration process, as it has been reported that the historical mortar binders are composed of carbonates and silica of small sizes, which give it a hydraulic character and high strength (Elif U ğurlu Sagin, Böke Hasan, Nadir Aras, Şerife Yalçın, 2012).

Crystal analysis of the powders obtained

By means of the structural analysis, the crystalline structures present in each of the samples were analyzed and the diffractograms of Figures 2 and 3 were analyzed, which correspond to oyster shell powder with grinding treatment (Figure 2), and with thermal treatments (Figure 3). As you can see, all of the materials that were tested are highly crystalline and have a higher proportion of characteristic peaks of the rhombohedra type of CaCO3 , in the calcite phase with characteristic signals of 2θ = 29.34 °; 39.41; 43.16; 47,11º (according to PDF, No. 471743, JCPDS database).

Figure 2. Diffractogram of the oyster shell milled with ball mill.

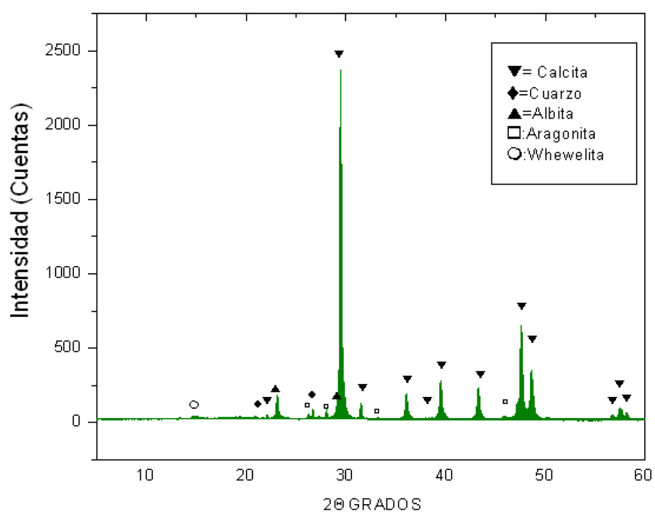
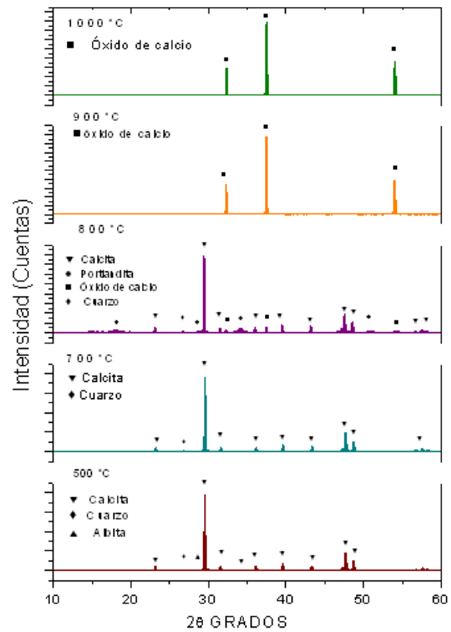


Figura 3. Difractograma de la concha de ostión tratada térmicamente.



In the case of powders from the untreated and manually ground oyster shells (Figure 2), it can be seen that in addition to calcium carbonate in the form of calcite (Shih-Ching Wu, Hsueh-Chuan Hsu, Yu- Ning Wu, Wen-Fu Ho, 2011), aragonite is also present which is another type of calcium carbonate but with a different crystalline structure (Zhuona Zhang, Yidong Xie, Xurong Xu, Haihua Pan, Ruikang Tang, 2012). When heat is applied to the aragonite that comes from mother-of-pearl (JE Parker, SP Thompson, AR Lennie, J. Potter and CC Tang, 2010) its crystal structure changes to calcite. This can be seen in the graph corresponding to the calcinated oyster shell at 500 ° C (Figure 3), in which the presence of aragonite is no longer detected and only calcite appears. In the case of the oyster shell powders which are heat treated from 500 ° C to 1000 ° C (Figure 3), it is observed that CaO or (quicklime) is obtained from 800 ° C. This is due to a decomposition reaction that occurs during the calcination process.

$$CaCO_{3(solido)} + Calor \rightarrow CaO_{(solido)} + CO_{2(gas)} \qquad Ecu. (1)$$

This reaction takes place above the decomposition temperature of the shell, that is to say at the temperature at which the Gibbs free energy standard of the reaction is zero. This results in a white or grayish white product (Kai-Wen Ma and Hsisheng Tengw, 2010). Such calcination reactions in an atmosphere of air lead to a mass loss of 45%.

On the other hand, when comparing the two types of treatments that were studied, it is concluded that with the mechanical treatment there are no favorable changes to obtain lime, which can be used as a mortar binder. Only the presence of calcite was detected, which is naturally present in oyster powder without any treatment and trace calcium oxalate monohydrate is detected as the mineral whewellite (Figure 2).

In the case of the thermally treated powder, the presence of aragonite can be found which upon the application of heat application changes its crystalline structure to calcite, as can be seen in the graph corresponding to the oyster shell calcinated at 500 ° C. The presence of aragonite is no longer detected and only calcite appears (Figure 3). The ideal temperature at which calcium oxide can be obtained as a material for use as a mortar binder is at 900 ° C, since the only thing that is achieved by calcinating the oyster shell at higher temperatures is the increase in alkalinity of the material.

CONCLUSIONS

The treatment that favors the use of the oyster shell as a mortar aggregate material for the restoration of old buildings is the heat treatment of the oyster shell at 900 ° C. At this temperature calcium oxide is obtained, which is a compound used in the construction industry. On the other hand, the shell which is calcinated at this temperature is easier to grind and has a particle size of 0.74 mm, which is able to adhere to the wet walls that are to be restored. The texture of the powder obtained with this heat treatment in this investigation is thinner and white, which favors the reflection of light, increasing the reflectance of visible light. It is for these characteristics that this material can be used as a mortar for the restoration of old buildings and archaeological sites, being the material used since ancient times and long before the discovery of Portland cement that is used today.

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