

# Effect of concentration of starch in the properties morphological and structural of porous ceramic based on expansive clays

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**Abstract.** In this article is used the sacrificial material method to generate different porosities between 44.42% and 69.14% in ceramics based on expansive clays from San Jose de Cúcuta metropolitan area, Colombia, to analyze the effect of concentration of starch (porogenic agent) in the morphological and structural properties using calcium carbonate as a stabilizer. The porous ceramics was characterized by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy. Finally, the images were analyzed with the software Image J, Image Tool and Origin. The results showed that the weight concentration of starch has a relationship with the average pore size, the number of pores and the porous area of the samples where the percentage of porous area and the average pore size of the mixtures increases as starch is added due to the decay of the sacrificial material. The number of pores of the mixtures decreased by increasing the weight concentration of the starch due to the agglomeration of the starch.

## 1. Introduction

Currently porous bodies are used in the elaboration of filters, catalyst, preforms for pressure filtration processes, membranes, battery separators, membrane reactors, fuel cell electrodes, insulating materials, lightweight structural materials, biomedical applications, among others [1-2].

The elaboration of porous bodies depends on the properties required but the specific application, therefore there are different methods to incorporate porosity that is divided into three basic techniques: replica, sacrificial template and direct foaming [3]. However, there are some research that are using novel routes to generate porosity for example starch consolidation casting [4], freeze casting of nanoparticle suspensions [5], among others [6-7]. The sacrificial material method uses a porogenic agent (organic or synthetic), which decays by evaporation, pyrolysis, drying, or sintering.

A research of the use of sawdust for the preparation of porous bodies from kaolin for applications of catalytic substrates shows porosities between 28% and 67% [8], likewise starch has also been used due to its low cost and high availability [9].

The starch has a gelatinization process in which the amorphous phase is moistened and the crystalline phase is fused [10], likewise, it has been used on consolidation processes generating porosities between 23% and 70% with pore sizes from 10  $\mu\text{m}$  to 80  $\mu\text{m}$  [11].

In this research was used the induced porosity method to generate porous ceramics from different weight concentrations of expansive clays and corn starch, likewise analysis was performed to determine the relationship between the porous area, the average pore size, the number of pores and the



concentration of starch looking for an alternative use of expansive clays in the construction sector and the industry ceramic.

## 2. Methodology

For the elaboration of the porous ceramics expansive clays that were used, were extracted from San José de Cúcuta metropolitan area, Norte de Santander, Colombia, with coordinates 7°50'43.2" N, 72°29'24.7" W, these were characterized on the laboratories of "Centro de Investigación de Materiales Cerámicos (CIMAC)" and the "Laboratorio de Suelos y Pavimentos" of the Universidad Francisco de Paula Santander (UFPS)" and "Parque Tecnológico de Guatiguará, Universidad Industrial de Santander (UIS)". As for the corn starch and calcium carbonate, they were a commercial product.

The soils texture was characterized using granulometry by hydrometer according to INVE-123-07 standard [12]. Winkler diagrams were used to identify soil aptitude.

The mineralogical composition of clays was characterized by X-ray diffraction (DRX) with a BRUKER D8 Advance powder diffractometer using DaVinci geometry. The expansive soils classification [13-15], shows parameters to identify the potential expansion (See Table 1), classifying it as very high, high, middle, and low, according to its plasticity index, percentage of particles lesser than one micron and free expansion.

**Table 1.** Expansive soils classification.

Expansion potential	Plasticity index (%)	Particles lesser than one micron (%)	Free expansion (%)
Very high	>32	>37	100
High	23 - 45	18 - 37	100
Middle	12 - 34	12 - 27	50 - 100
Low	<20	<17	<50

Atterberg limits were determined based on INVE 125-07 [16] and INVE 126-07 [17]; the percentage of particles lesser than one micron was obtained from the granulometric by hydrometer; and the percentage of free expansion was done with a sample of 10 cm<sup>3</sup> passant clay sieve No. 40 that was poured into a test tube with 100 cm<sup>3</sup> of water, later it was calculated by the following Equation (1) [11].

$$F. E. = \frac{V - V_0}{V_0} * 100, \quad (1)$$

where, F.E. is the free expansion of the soil in percentage,  $V$  is the volume of the sample after expansion in cm<sup>3</sup> and  $V_0$  is the volume of the sample before the expansion that is equal to 10 cm<sup>3</sup>. Likewise, Rico, A., Del Castillo, H. (1977) [18], uses the correlation between the expansion potential and the plasticity index, that is used to classify the soils as shown in the following table (See Table 2).

**Table 2.** Soils classification.

P.I. (%)	Expansion potential (%)
10.0	0.4 - 1.5
20.0	2.2 - 3.8
30.0	5.7 - 12.2
33.4	7.7 - 16.4
40.0	11.8 - 25
50.0	20.1 - 42.6
Soils classification according to its expansion potential	
Very high	>25.0
High	5.0 - 25.0
Middle	1.5 - 5.0
Low	0.0 - 0.5

To achieve different porosities, seven compositions were used among clays, starch and calcium carbonate that were named as M1, M2, M3, M4, M5, M6 and M7, where M1 has the lowest weight concentration of starch and M7 has the highest weight concentration of starch (See Table 3).

**Table 3.** Mixtures of clay, starch and calcium carbonate compositions.

Mixtures	Clay (Wt%)	Starch (Wt%)	Calcium carbonate (Wt%)
M1	90	0	10
M2	85	5	10
M3	80	10	10
M4	75	15	10
M5	70	20	10
M6	65	25	10
M7	60	30	10

The clay (passant sieve No. 200), starch and calcium carbonate were mixed dry, also sodium silicate was used to deflocculates the mix, it assures the lesser quantity of distilled water on the mix process.

The homogenization was done with a mechanical head agitator DLAB® model OS20-S, with a speed 1300 rpm, for 5 minutes increasing progressively from 800 rpm per each mixture.

Later they were subjected to a drying process at room temperature during 12 hours' period to pour them manually in molds with the following average dimensions 5 cm wide, 10 cm long, and 1.5 cm high, then they were placed in a drying oven with forced circulation at temperatures of 40 °C and 60 °C for 30 min each one and 80 °C - 100 °C for 1 hour at each temperature.

Then heat treatment was applied, heating up to 400 °C, with a firing curve of 10 °C/min during an hour in order to eliminate the starch; later they were heated up with the same curve to 950°Celsius during another hour; then, they were cooled down to 80 °C, and finally, let to cool down to room temperature.

The samples were characterized with the scanning electron microscope (SEM) model FEI Quanta FG650, they were analyzed with the software Image Tool version 3.0 for the study of the average pore size, likewise the software Image J was used to determine the porous area and the 3D models, the elemental microanalysis was done with the energy dispersion spectral and the software Origin version 7.0.

### 3. Results

The soil had a content of clays of 77.2%, silts of 22.4% and sands of 0.4%, also shows the presence of Quartz (38.2%), Kaolinite (30.3%), Muscovite-2MI (26.7%), and in a smaller proportion Anatase (1.3%), Rutile (1.6%), Calcite (0.2%),  $\alpha$ -Hematite (0.6%), Cristobalite (1.1%), and Halloysite.

The clay presents a liquid limit of 50.1%, a plastic limit of 16.8, and a plasticity index of 33.4%, also has a percentage of particles less than one micron of 58.21%, and a free expansion percentage of 120%.

Considering these results and according to the soil classification [18] (See Table 2), the clay has a very high expansion potential.

Likewise, the expansion potential was correlated according to the classification by Rico A, *et al.* [18] and according to the results of the plasticity index, there is a high expansion potential.

The analysis of the SEM images shows an increasing percentage of porous area from 44.42% to 69.14%, and in the average pore size from 82.87  $\mu\text{m}$  to 3293.03  $\mu\text{m}$  (See Table 4), by increasing the concentration in weight of starch. Also, a decrease in the number of pores was observed, between 2197 pores and 57 pores.

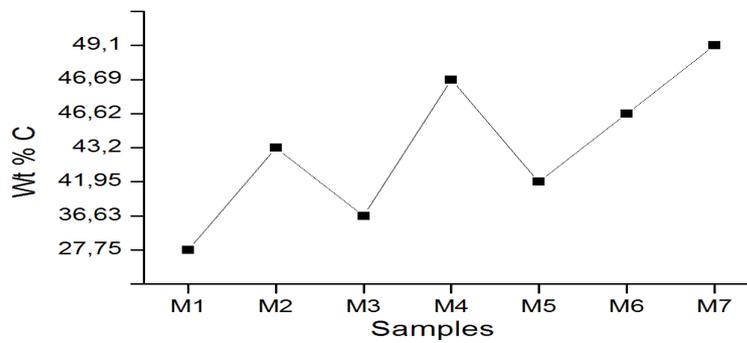
In Figure 1, Figure 2 and Figure 3, the percentages by weight of the elemental composition of carbon, aluminum, and silicon are presented respectively. From these it can be seen that as the concentration of starch increases in the sample, the carbon increases. Similar case can be seen with the concentration of clay, which when increasing in the sample, provides a higher concentration of silicon and aluminum.

A 3D representation of the images obtained by SEM, using Image J software, is presented in Figure 4. This shows the distribution of the porosity generated in the sample, which is mostly provided by starch during the sintering process. This morphology is corroborated with the data in Table 4, in which

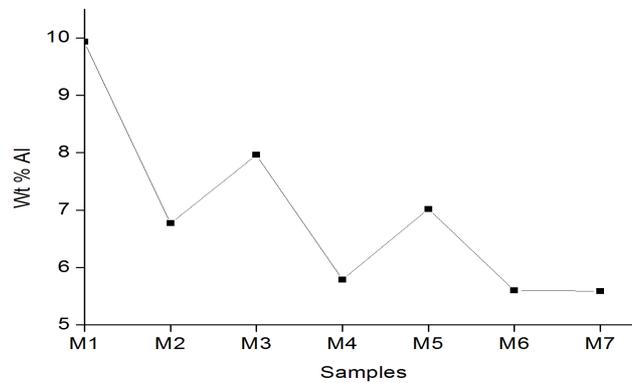
it can be seen that as the concentration of starch in the sample increases, the percentage of porosity increases.

**Table 4.** Percentage of porous area and average pore size of the samples.

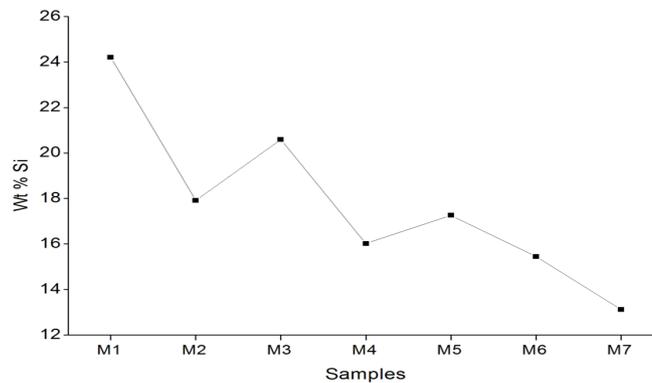
Mixture	Porous area (%)	Average size ( $\mu\text{m}$ )
M1	44.42	82.87
M2	54.48	176.55
M3	54.70	134.22
M4	58.46	371.99
M5	57.10	227.40
M6	61.61	3293.03
M7	69.14	580.20



**Figure 1.** Percentage by weight of carbon.



**Figure 2.** Percentage by weight of aluminum.



**Figure 3.** Percentage by weight of silicon.

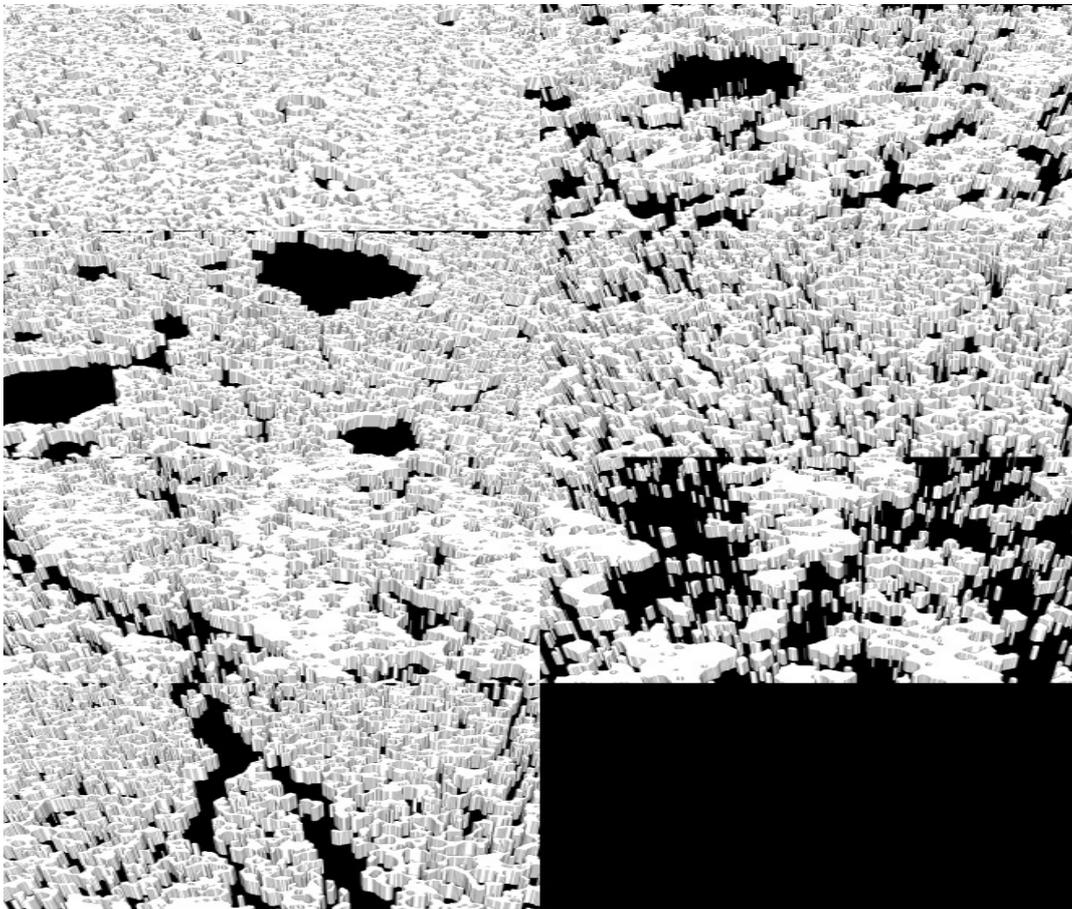


Figure 4. SEM of the 3D samples.

#### 4. Conclusions

The percentage of porous area and the average pore size of the samples increases as starch is added. This is due to the swelling of starch when it gels and the increase in the amount of material that disintegrates at the time of firing. The porous area and the average pore size of the samples have a direct relationship with the weight concentration of starch.

At chemical composition level an increase in the concentration in weight of the carbon is observed, that probably happened due to the increase of the organic matter that disintegrated. Likewise, the decrease in the amount of clay used in the mixes probably caused a decrease in the amount of silicon and aluminum. Sintered samples can be used for wastewater treatment and filtration processes.

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#### References

- [1] Zhengwei Y and Yuyi L 2015 Fabrication of porous alumina ceramics with Corn starch in an easy and low-cost way *Journal Ceramics-Silikáty* **59** 348
- [2] Gregorová E Zircová Z and Pasbst W 2009 Porous Ceramics made using potato starch as a pore-forming agent *Fruit, Vegetable and Cereal Science and Biotechnology* **3** 115
- [3] Hammel E Ighodoro E and Okolin O 2014 Processing and properties of advanced porous ceramics: An application-based review *Ceramics International* **40** 15351

- [4] Talou M and Camerucci M 2015 Processing of porous mullite ceramics using novel routes by starch consolidation *Journal of the European Ceramic Society* **35** 1021
- [5] Zhao J Li Y Wu Y Lv S and Lu K 2016 Microstructure of TiO<sub>2</sub> porous ceramics by freeze casting of nanoparticle suspensions *Ceramics International* **43** 14593
- [6] Li J Yuan W Deng C and Zhu H 2016 Porous SiC/SiCN composite ceramics fabricated by foaming and reaction sintering *Journal of the European Ceramic Society* **37** 1131
- [7] Matsunaga C Fukushima M Hyuga H and Yoshizawa Y 2017 Fabrication of porous silica ceramics by gelation-freezing of diatomite slurry *Journal of the European Ceramic Society* **37** 5259
- [8] Obada D Arhin D Dauda M Anafi F Ahmed A and Ajayi O 2016 Potentials of fabricating porous ceramic bodies from kaolin for catalytic substrate applications *Applied Clay Science* **132-133** 194
- [9] Gonzen T Stuart R Tervoort E and Gauckler L 2007 Macroporous ceramics from particle-stabilized wet foams *Journal of the American Ceramic Society* **90** 16
- [10] Menchavez R Rhamel C and Calgas M 2013 Starch consolidation of red clay-based ceramic slurry inside a pressure-cooking system *Materials Research* **17** 157
- [11] Lyckfeldt and Ferreria J 2013 Processing of porous ceramics by 'starch consolidation' *Journal of the European Ceramic Society* **18** 131
- [12] Instituto Nacional de Vías (INVÍAS) 2017 *Análisis granulométrico de suelos por tamizado, INVE-123* (Colombia: Instituto Nacional de Vías)
- [13] Dakshanamurthy V and Raman V 1973 A simple method of identifying an expansive soil *Soils and Foundations* **13** 97
- [14] W. G. Holtz and H. J. Gibbs 1956 Engineering properties of expansive soils *Transactions of ASCE* **121** 641
- [15] Tugas A Cakrawala M and Aditya C 2012 The effects of water contents on free swelling of expansive soil *International Journal of Civil & Environmental Engineering* **12** 13
- [16] Instituto Nacional de Vías (INVÍAS) 2017 *Determinación del límite de Atterberg de suelos, INVE-125* (Colombia: Instituto Nacional de Vías)
- [17] Instituto Nacional de Vías (INVÍAS) 2017 *Determinación del límite líquido de los suelos, INVE-126* (Colombia: Instituto Nacional de Vías)
- [18] Rico A and Del Castillo H 1977 *La ingeniería de suelos en las vías terrestres vol 2* (México: Limusa)