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Nitrogen Porosimetry on Ancient Ceramics

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Abstract

The present work introduces nitrogen porosimetry as an alternative–additional method of characterizing ancient ceramic materials. Analysis of the pore structure of such materials in the micro- and mesopore region may give useful information, which can, either independently or if related to results produced by other conventional methods, give helpful hints for the determination of their origin and time of production. Several samples coming from the neolithic cave of Diros as well as from Lefkanti (Greece) have been studied by means of nitrogen porosimetry. Although no definite conclusions can be drawn out of this investigation, the results seem promising. © 1998 Elsevier Science Limited. All rights reserved

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Introduction

Ceramic materials are prepared from ceramic powders or clays that are mixed with water, formulated in shapes and annealed in high temperatures. Ancient ceramists were preparing their ceramic pots from raw materials that were available at the place of construction. Since the chemical and physicochemical characteristics of a ceramic material depend on the composition of the raw materials and the annealing conditions, the characteristics of ancient ceramics produced at the same place at a certain period of time should be similar.

Archeologists, based on the determination of such characteristics, define the place and time of construction of ancient ceramics. For instance, the place of production can be indicated by possible existence of certain chemical elements in the sample's chemical composition, while its production time can be determined by determining the content of a certain radioactive element[1] or by nuclear activation techniques.[2]

One of the most important physicochemical characteristics of a ceramic material is its porous structure. In modern ceramics, the pore space can be either interparticle (space between the powder particles) or intraparticle [space within the grains, Fig. 1(a)]. The initial (before annealing) interparticle space depends on the particle size distribution of the raw powder as well as on how closely packed the grains are. During annealing, the interparticle space is diminishing due to aggregation of the particles. The ceramic particles, if heated at high temperatures, begin to melt on their outer surface and thus they get attached to each other as shown in Fig. 2, simultaneously reducing the interparticle space. This results in an overall shrinkage of the material which can be used as means of evaluating the quality of annealing. The aggregation process can also influence the intraparticle pore space by blocking the ends of the small capillaries ending on the outer surface of the particle and making these capillaries inaccessible to any gas or vapour.

The same observations are also valid for ancient ceramics. Since it can be considered, as mentioned before, that ancient ceramic materials coming from a certain place and time should be produced from similar raw materials and annealed under similar conditions, it is possible that the pore structure characteristics of such materials can indicate their age and origin. Additional complexity in those studies arises from the fact that the current porous structure of an ancient ceramic may not only be a function of its production conditions but also a function of the conditions that this was maintained over the years. Indeed, some of the most archeologically important samples have been maintained buried in several depths and under different humidity conditions, for many centuries.

The pores in porous materials are classified in three categories according to UIPAC, depending on the magnitude of their width: micropores (less

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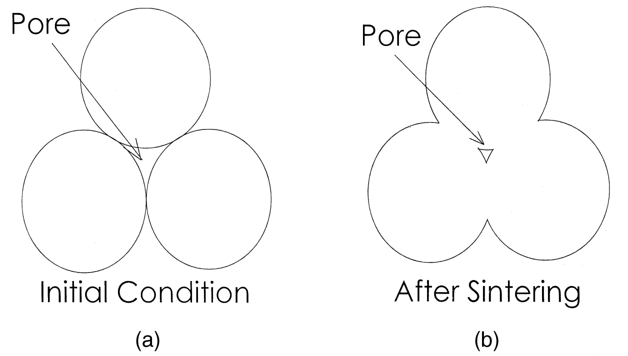

Fig. 1. Interparticle pore space between the grains of ceramic powders, (a) before and (b) after annealing.

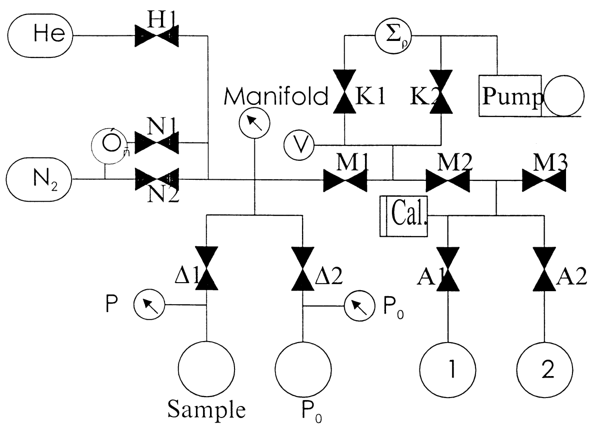

Fig. 2. Nitrogen porosimeter.

than 20 Å), mesopores (between 20 and 500 Å) and macropores (more than 500 Å).[3]

Several techniques have been developed for characterizing the porous structure of porous materials depending on the category in which they are classified. Macropore structures are mainly characterized by means of mercury porosimetry. This technique seems appropriate for characterizing samples of ancient pottery. The main disadvantage of this method is that the sample is destroyed after one experimental cycle. One of the most important techniques for characterizing micro- and mesoporous structures is the nitrogen porosimetry. The porous sample is equilibrated at several nitrogen relative pressures, P/P_o, at the liquid nitrogen temperature (77 K), and the amount adsorbed, V_s, at each relative pressure is calculated volumetrically. The resulting curve (V_s versus P/P_o) is the adsorption isotherm, appropriate analysis of which provides valuable information concerning the sample's porous structure. Nitrogen porosimetry has never been applied before in studying the pore structure of ancient ceramic materials. It can provide independent measurements, not related in any way with the conventional timing methods of ancient materials.

In this work we present nitrogen porosimetry measurements on ancient Greek ceramics. Our intention is to investigate whether this technique and the information provided can be useful in characterizing ancient ceramic materials concerning their time and place of production.

Materials and Archeological Background

In the present study, nine samples of ancient ceramics were tested with nitrogen porosimetry. The samples named S (S1, S2, S4, S21, S27, S29), come from the neolithic Diros cave in south Peloponesos, Greece. The age of this cave has been determined by one of the authors by means of the concentration of radioactive carbon found in flame traces (ashes). It was found that the cave was inhabited from 4300 BC until 2180 BC. The samples treated in this work are recovered from different parts of the cave, and were found buried at several depths. They were maintained over the years mixed with ashes (the ones used for the determination of the age of the cave) and under high humidity conditions. They were selected for this study because they are some of the oldest ceramic materials that can be found in Greece, and thus they are of great historical and archeological importance. Our intention was to investigate the existence of similar characteristics in those materials.

The three samples named L (L1, L2, L3) come from a big ceramic pot found in the archeological region Lefkanti, in central Evia, Greece. According to estimations of archeologists, Lefkanti flourished in the 'Dark Ages' period, that is between 1100 BC and 750 BC. As implied by the term 'Dark Ages', very little is known about this period of Greek history. The ceramic materials found there are considered a very important source of information about this period. The ceramic pot considered in this study was relatively big, and its thickness was approx. 2 cm. Sample L1 was taken from the outer part of the pot, sample L2 from the middle and sample L3 from the inner part. Those three samples were measured in order to investigate whether or not the sintering process results in uniform pore structure on the whole range of the ceramic structure.

Nitrogen Porosimetry Measurements

The samples were brought in powder form through grinding. The grinding process affects the sample in a scale no smaller than microns. Since nitrogen porosimetry technique studies pores with radius is within the mesopores range, the grinding process does not effect the results of the analysis.

The adsorption measurements were performed by means of an Autososrb Quantachrome Nitrogen porosimeter, presented in Fig. 2. The samples were initially outgassed at the temperature of 120°C. The adsorption–desorption isotherms were analyzed by means of the quantachrome software. The parameters evaluated from the adsorption isotherms are the specific surface, by means of the BET method, the constant C of BET theory, the mean pore radius and the pore volume.

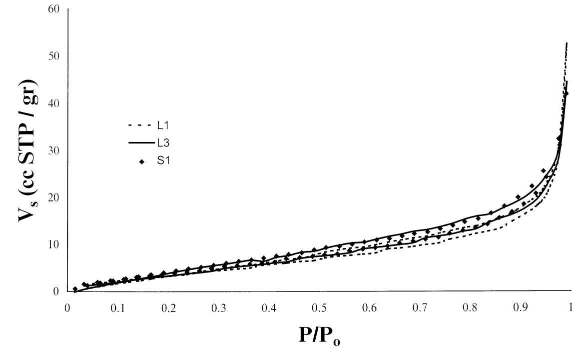

Fig. 4. Nitrogen adsorption–desorption isotherms for two of the Lefkanti samples compared with one sample from Diros.

Results and Discussion

Figure 3 presents three characteristic adsorption isotherms corresponding to samples S1, S21 and S27 of Diros cave. As can be observed all three isotherms have similar shapes. Isotherms of this shape are produced by samples that contain slit-like pores—typical for clay based materials—and are classified as type II.[3]

A very important observation is that all isotherms present a hysteresis loop. That means that for a certain region of nitrogen relative pressures the amount adsorbed during desorption is higher than the corresponding amount during adsorption. This can be attributed to two factors:[4,5] (a) *Single pore thermodynamic hysteresis*. That means that the relative pressure at which capillary condensation occurs in a single pore during adsorption is different than the one that this pore empties during desorption, due to thermodynamic reasons. (b) *Network constriction effects*. If a pore is surrounded by smaller pores, during desorption it will not 'empty' at the relative pressure predicted by Kelvin equation, because the vapour has no access to the outer surface. By the time that pressure becomes low enough for the smaller surrounding pores to empty, the bigger pore empties with them.

Since, as concluded from the shape of the isotherms, the pores in our samples are slit-like, thermodynamic hysteresis can be neglected, because no such phenomena appear in pores of that shape.[3] Thus the hysteresis loop can only be attributed to network constriction effects. This fact indicates that these samples actually contain pores in the mesopore region that can be analyzed by means of nitrogen porosimetry.

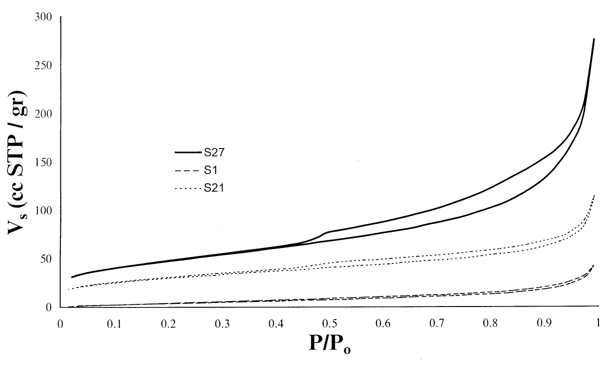

Fig. 3. Nitrogen adsorption–desorption isotherms for three characteristic Diros samples. The isotherms of the rest of the Diros samples 'lay' between the isotherms corresponding to samples S1 and S27.

As can be observed from Fig. 3, significant differences concerning the amount adsorbed are present among Diros samples. Sample S27 adsorbs almost five times as much as sample S1. The isotherms of the rest of Diros samples lay within the 'band' determined by S1 and S27, and they all show similar characteristics. It is also important that these differences are of almost the same magnitude throughout the whole range of equilibrium relative pressures. This indicates that these samples should have similar pore size distributions but different porosities.

Figure 4 presents isotherms corresponding to L1 and L3 Lefkanti samples and the isotherm of S1 Diros sample in comparison. It is obvious that the isotherms of Lefkanti samples are very similar. These samples also have similar specific areas and total pore volumes, as shown in Table 1, where all the specific surface and total pore volume values for all samples tested are summarized. This result shows a very important feature from the ceramist point of view. This is that the person who made this specific pot understood the importance of uniformity of raw materials as well as for the firing procedure. Clearly the raw materials were carefully

Table 1.

Samples	*Pore volume (cc gr^{-1})$\times 10^{-2}$*	*BET Area (m^2 gr^{-1})*	*C (BET)*
L1 (outer)	8·16	15·66	12·7
L2 (middle)	6·89	18·29	8
L3 (inner)	6·94	17·14	7·54
S1	6·47	17·99	12
S2	8·39	29·44	17
S4	14·13	73·6	140
S21	17·6	104·9	206
S27	12·65	70·55	148
S29	7·9	44·54	96

selected and the furnace to fire such a big item cannot have been trivial.

Although Lefkanti samples present differences from most of the Diros samples, this is not confirmed for samples S1 and S2. This hampers us from being able to draw a clear conclusion concerning those differences. It is clear though that maintenance conditions could be one of the most important reasons responsible for the similarities between L and S1–S2 samples. Indeed, the conditions under which an ancient ceramic material is maintained over several centuries can affect the active adsorption sites on its outer surface, changing its tendency to adsorb nitrogen molecules. This tendency is depicted by the C value of BET approximation. The C values calculated for all the samples tested are also presented in Table 1.

Low C values normally lead to calculations of low specific surface values. This is because specific surface is calculated via the number of molecules required for forming an adsorbed monolayer on the sample's surface. Low adsorption tendency results in low estimation of this number and thus in low specific surface values. This fact is confirmed in the results presented in Table 1. In our case though, both these values concerning samples S1 and S2 may be misleading, if the amount of nitrogen adsorbed is strongly influenced by the physicochemical conditions of the surface developed over the years. Chemical analysis of the samples and particularly of the samples' surface exposed to the adsorbate could give some helpful hints towards estimating the influence of this aspect. Unfortunately, such an analysis cannot be currently curried out due to technical difficulties concerning the samples' availability.

An essential factor for drawing significant results out of this investigation is the comparison of our results with results from 'control' ceramics with very well known chemical composition and porous structure. This idea is facing the difficulty of deciding what characteristics an appropriate control sample should have. Since those characteristics cannot be easily specified, a wide range of control samples must be produced and characterized. Some of the most important parameters for investigation are the chemical composition, raw material grain size distribution, temperature and duration of firing, etc. Another essential point is finding the appropriate conditions for technical aging of the materials under different temperature and humidity conditions. In order all these aspects to be investigated, a very wide range of standard ceramics must be produced. This study is currently in its very early stages.

Conclusions

Nitrogen porosimetry has been applied to ancient ceramic materials for the first time. The results obtained show small but not negligible differences between the samples tested. Unfortunately, a very small amount of chemical and archeological data concerning those ceramics is currently available, and thus a not quite clear interpretation of porosimetry data can be performed. Nevertheless it is clear that analysis of ancient ceramics by nitrogen porosimetry can be proven an important tool towards the determination of the place and time of production.

Since the amount of samples incorporated in this work was relatively small due to technical reasons, this study will be continued and expanded to more recent and even modern ceramics. This investigation is already in progress and some primary results will be presented in a forthcoming paper.

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