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Pore size distribution and porosity influence on Sorptivity of ceramic tiles: From experimental data to fractal modelling

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ABSTRACT

The Sorptivity is a coefficient very important to characterize porous materials. It is associated to principal properties such as mechanical durability, thermal and electrical conductivity, etc. In this work, the Sorptivity coefficient of several systems of porous ceramics has been measured following the experimental procedure. In different situations, this very simple test could be not performed; in cultural heritage or during an optimised industrial process. Major reasons for this inability include that it would demand great quantitates of materials impossible to withdraw from the protected building, as well as the experimental test can last for several days, which reduces the possibility to correct/improve the industrial production process. In this regards, being very useful to have analytical formulas in order to calculate Sorptivity coefficient, an Intermingled Fractal Units model has been proposed. Starting from its capability to reproduce entirely the pore size distributions of porous materials, IFU is used to simulate water absorption process and to estimate the Sorptivity coefficient. The obtained results are in good agreement with experimental data and others two models predictions. This fact allows considering IFU model as a future tool for design materials and to predict their service life.

1. Introduction

Porous ceramics are materials extensively used in several fields of industrial and civil engineering. The importance of these materials is owing to their remarkable properties. Indeed, the most important characteristics of porous ceramics include low density [1], relatively low mass [2,3], low thermal conductivity [4,5], resistance to chemical attack [6,7], high temperature as well as thermal cycling [8–11], high specific surface area and high permeability [12–14]. These peculiarities make them appropriate for numerous applications such as filters and membranes [15,16], fuel cell electrodes [17,18], catalyst supports for biomaterials [19], piezo-electric materials [20], acoustically and thermally insulating bulk media [21].

Regarding coarse and traditional porous ceramics (bricks and roof tiles) production, it represents an important segment of industry as well as remarkable economical business. According to the final report on European ceramics manufacturing, particularly bricks and roof tiles, by the Centre of European Policy Studies in 2014, the production value of the EU's bricks and roof tiles industry in 2012 was worth 5.5 billion of euros [22]. 68% of this fabrication is covered by Germany, France, Italy and the UK. The large application of these materials is primarily due to low-cost of their raw materials and the standardised production processes, which substantially follow the traditional procedure used for thousands years. The natural selected clays are mixed with water to obtain right plasticity, which can be shaped, dried and heated at 900–1050 °C. The relative properties of these porous ceramics depend on each of these production stages. Generally, bricks and roof tiles are characterised by high strength, wear resistance, long service life, chemical inertness, non-toxicity, electrical, heat and fire resistance as well as specific porosity [4,23–25].

The porosity is very important characteristic for ceramic materials. For example, mechanical behaviour and durability depend on the presence of the voids into the microstructure. Indeed, on the one hand, porosity decreases the surface resistance and consequently the mechanical strength of ceramic material. On the other, the effect of the movement of water through porous microstructures, such as chemical attack by acid-rain, dissolution processes, freeze thaw-cycles, salt crystallisation, are in function of pore volume fraction [26]. Moreover, these phenomena modify the porous microstructure and consequently the pore size distribution increasing weathering kinetic.

In this context, in order to predict the service life of porous ceramics as construction and building materials, it is very important to study their water capillary absorption. The parameter,

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which defined capillary absorption, is the Sorptivity coefficient (S). It is calculated as water volume absorbed per unit surface area per square root time. The experimental test is explained in the Italian Guideline NORMAL 20/85 [27]. Although, it is very simple to perform in laboratory, it needs large number of samples to provide a statistic validation of the fine result. This fact is in contrast when the studied materials are from cultural heritage. In these cases, the types of sample, which can be withdrawn, are only small and irregular and they do not have appropriate shape and dimensions required for measuring capillary absorption speed. Moreover, water absorption experimental test can last for long time (sometimes days, maximum 7 days). This aspect may be relevant during fabrication, where possible change in different steps of industrial process must be done rapidly in order not to compromise the production.

Owing to these reasons, a branch of porous ceramics research is focused on the development of analytical procedure for calculating indirectly the Sorptivity coefficient.

In this regard, several models capable of correlating Sorptivity to materials' microstructure and fluid properties have been proposed. Generally, they considered open porosity, average pore size, tortuosity, specific surface areas, bulk density, surface tension, contact angle and viscosity [28,29]. However, their capacity to predict water sorption is associated only to a particular class of materials, while for other materials, the application of the same model brings remarkable errors differing from the experimental data by even an order of magnitude [29].

Such deviations between experimental data and model predictions may be ascribed to the over-simplification of the microstructure representation. The analytical expressions are formulated in the function of total open porosity, average pore size and tortuosity, but they do not take into account the entire pore size distribution and pore size range. These last aspects deserve greater attention because sorption phenomenon is highly influenced by microstructure morphology [29,30]. For example, water capillary rise is slower in thinner pores than in larger, while the heights of water rise are inversely proportional to pore size [28].

Although the average pore size, average surface area, pore volume fraction are important parameters, but they may only provide a rough characterisation of complex porous microstructure of ceramic materials. A complete representation can be achieved by reproducing pore size distribution. In order to obtain this result, it is necessary to have available a geometric and mathematical model.

In this context, Fractal geometry may be an excellent choice. The revolutionary concepts and methods of Fractal geometry have been formalised in 1970s by Benoit Mandelbrot [31]. Fractals are geometrical figures, constructed by iteration process (theoretically unlimited), in which every part is similar to general feature. The principal characteristic of fractals is the non-integer dimension (D_f). Unlike Euclidean geometry, every geometrical aspects (shapes, number of repeated objects, etc.) can be described analytically using the fractal dimension (D_f) [32] in fractal geometry.

Fractal figures have been known since ancient times in art. However, they are not unrelated to natural human experience. Indeed, fractal peculiarities have been found in great number of organic and inorganic forms of nature as well as in different microstructures of natural or manmade materials [31,32]. This fact has been considered significant for understanding, describing and forecasting different physical properties and relative macroscopic behaviour.

For example, in cement and concrete materials, relationship between surface complexity and kneading water have been correlated to fractal dimensions of different microstructures indicating that kneading water is only responsible for the swelling of the structure without modifying the pore surface [33]. Another research demonstrated that high irregularity of hydrated cement pastes surfaces have fractal characteristics and can be associated to anomalies in vapour sorption experiments to determine surface area [34].

Moreover, starting from fractal modelling, a general model of porous medium was applied for predicting capillary pressure for the geyser rock [35]. The heterogeneity of this rock-type has been evaluated quantitatively considering the values of fractal dimension [35]. Cai and his group carried out an important application of fractal geometry in order to explain physical phenomena of porous materials. Spontaneous imbibition of wetting liquid into porous media has been described with an analytical fractal model finding a good agreement with experimental data [36–39].

Recently, an Intermingled Fractal Units (IFU) model, based on the capability to reproduce porous microstructure, has been formalised to understand relationship between structure and properties such as thermal conductivity, elastic behaviour, water movement into the microstructure of various classes of materials: cement and concrete [40], ceramics [41,42], earth based materials [43,44] and stones [45–47].

Although IFU model is composed of fractal figures, but it is able to reproduce also non-fractal pore size distributions. This fact makes it a good simulator of every different microstructure. After replication of pore size distribution, a series of mathematical expressions are applied for calculating physical properties.

In this paper, an IFU modelling procedure has been proposed in order to predict Sorptivity coefficient of porous ceramic materials used for producing roof tiles. This approach enables evaluating water absorption without the necessity to have large quantities of materials and with considerable saving of time. The experimental tests are performed on ceramics from Industrie Cotto Possagno SpA (Possagno, Treviso, Italy). In order to validate IFU model, the calculated Sorptivity coefficient has been compared with experimental data and with the results calculated by two other models. The Sorptivity predicted values by IFU model are better in agreement with experimental data than the others models' estimations reported in Scherer et al. [28] and Raimondo et al. [29].

2. Materials and methods

This research examines four series of porous ceramics provided from Industrie Cotto Possagno SpA. The series named A, B, C, and D consist of some clays, sand, carbonates mainly calcium carbonate, feldspars in different amount. The green samples were fired into an industrial oven with a heating cycle of 60 h cold to cold, and the

Table 1
Chemical composition of the samples A, B, C and D.

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	MnO	K_2O	Na_2O	P_2O_5	L. I. 1050 °C
A	48.13	17.88	2.52	10.08	2.50	4.82	0.10	2.70	1.50	0.10	9.50
B	52.95	16.90	1.35	7.30	3.09	5.20	0.10	3.24	1.55	0.10	8.30
C	49.87	17.46	2.50	9.49	2.50	4.78	0.10	2.82	1.33	0.10	9.06
D	53.62	16.37	1.40	7.58	3.36	5.01	0.10	3.15	1.50	0.10	7.76