EVALUATION OF THE POROSITY OF ORNAMENTAL GLAZED TILES BY NITROGEN ADSORPTION

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Abstract

The adsorption of nitrogen at 77 K has been carried out on samples of Portuguese ornamental glazed tiles (*azulejos*) from the XVIth to XXth centuries. Analysis of the results indicates that degradation is associated with the development of mesoporosity and an increase in specific surface area. It was found that impregnation of deteriorated tiles with Paraloid B-72 or with polyurethane was effective in blocking the porosity. Wacker OH, on the other hand, did not cause blocking of the pores but appeared to be deposited as a surface coating. It is concluded that the technique of low temperature nitrogen adsorption is very useful for characterising porosity, and its changes during degradation or after consolidation procedures, in a region of pore size where other techniques are inadequate.

Introduction

It is well known that porosity plays an important role in deterioration of stones, mortars and other building materials [1]. Among the more important consequences, are effects associated with capillary transport of water into and out of the internal pore structure which, on the one hand, results in a gradual alteration of the microstructure and, on the other hand, introduces soluble salts such as sulphates, nitrates and alkaline chlorides into the pore network. As a result of cyclic variations in humidity and dryness, the salts dissolve and recrystalize, thereby creating internal pressures high enough to break down the microstructure and, in this way, cause a further increase in the overall porosity. Consequently, one of the factors which should be taken into account when developing new protective and consolidation treatments is their effect on the pore structure. Characterisation of porosity is therefore an essential study to be undertaken when trying to understand the mechanisms of deterioration and to evaluate and predict the efficiency and the mechanism of the conservation treatment.

The information obtained about porosity depends on the experimental technique used [2-4]. In particular, different techniques are necessary to study different kinds of pores. With regard to pore size the classification used in this paper is that officially adopted by IUPAC [5]:

micropores- $d < 2$ nm
mesopores- $2 < d < 50$ nm
macropores- $d > 50$ nm

where d is the diameter of a cylindrical pore or the width of a slit shaped pore.

To evaluate macroporosity one of the more commonly used techniques is mercury porosimetry. The shape of the intrusion-extrusion curves can give some qualitative information about the kind of porosity and, in certain cases, it may also be possible to carry out a quantitative analysis in order to obtain pore size distribution curves.

In the case of micro and mesoporosity, techniques based on gas adsorption have proven to be very useful. In particular, outside of the conservation field, adsorption of nitrogen at 77 K is probably the most widely used method of characterisation of porous materials. The analysis of the experimental data (adsorption isotherms) by appropriate methods, such as BET and α_s methods [6], can provide information about the kind of porosity, the specific surface area and, in certain cases, pore size distributions and pore volumes.

In the field of conservation of works of art and monuments, mercury porosimetry is a widely used technique. On the other hand, nitrogen adsorption has been very little used. With regard to the characterisation of ornamental glazed tiles (*azulejos*) a few studies have been published [7-13], but only two in which nitrogen adsorption is used [9,11]. In one of these previous studies [11] we applied both techniques to characterise the porosity of XVIIIth century portuguese ornamental tiles in different states of deterioration and subjected to different modification procedures and it was found that nitrogen adsorption gave more valuable information than mercury porosimetry, as the results indicated that deterioration was associated with mesopores and not macropores.

This work has now been extended to include tiles from the XVIth to XXth century with the aim of evaluating in more detail the capacity of nitrogen adsorption to give information in a region of pore size which is involved in processes of deterioration, but where other techniques are insensitive.

Experimental

Samples of portuguese ornamental tiles from the XVIth to XXth centuries, from different locations and in different apparent states of conservation, were studied. The samples are designated by their centuries, for example, sample XVI referring to the sample from the XVIth century. In addition, a tile from the XVIIIth century in a particularly good state of conservation was also used and is designated Friso. Only the ceramic body of the tiles was used (without the glaze). The sampled material was ground (cut) in irregular shapes to a size of approximately 2 mm diameter.

Part of sample XVIII was used directly and part was immersed in deionised water for 7 days for desalination. The desalinated sample was divided in 4 parts: one was analysed (XVIII desal) and each of the remaining 3 parts impregnated with a polymer. The polymers used were:

Paraloid B-72 (PB72) 5 % in acetone
Wacker-OH (WOH) in the commercial concentration
Polyurethane (PU) 5 % in n-butyl acetate

Sample XVI was also studied before and after impregnation with Wacker-OH. Before impregnation, the samples were dried at 105°C for 24 hours and then exposed to air for at least 24 hours. For impregnation, the samples were half immersed in the solutions for 30 min, after which they were closed in Petri dishs for 2 weeks, before analysis.

Nitrogen adsorption isotherms at 77 K were determined on a conventional high precision manual volumetric apparatus with a Datametrics Barocel 572 for pressure measurement. Samples were outgassed at 110°C to remove physisorbed water, except the impregnated samples that were outgassed at 50°C. The total mass of sample used for each adsorption isotherm measurement was about 7 g.

Results and discussion

Nitrogen adsorption on tiles from different centuries

In Figure 1 are shown the nitrogen adsorption isotherms and corresponding α_s plots (using silica as standard) obtained on samples XVI to XX. Values obtained from the BET and α_s analyses of the isotherms are given in Table 1.

With the exception of the XX and XVII samples, all isotherms have an hysteresis loop of type H3 which indicates the presence of mesoporosity associated with slits between lamellar particles [5]. This is consistent with the shape of the α_s plots which show positive deviations from linearity at $\alpha_s > 1$, that is, in the multilayer region. The absence of hysteresis and the linearity of the

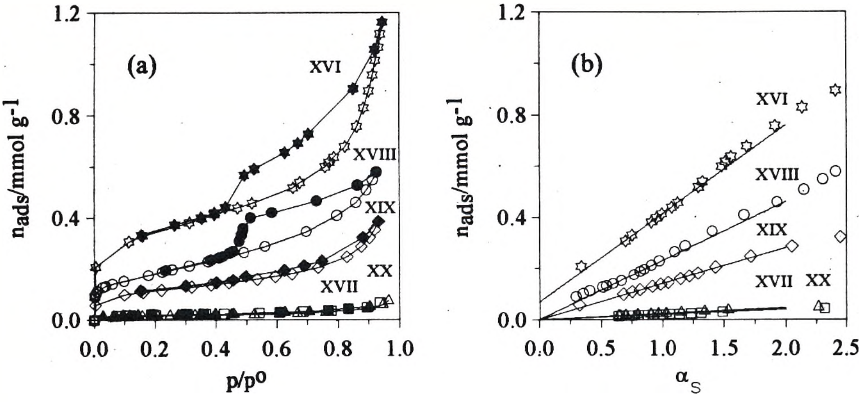

Figure 1 - Nitrogen adsorption isotherms (a) and corresponding α_S plots (b) on tiles of XVIth to XXth centuries.

α_s plot of XX and XVII samples indicate that these samples are non porous. The reasonable agreement between the BET and the α_s specific surface areas (A_S) for all samples except XVI indicates the absence of microporosity. On the other hand, with the XVI sample the BET area is higher than the α_s area. Furthermore, extrapolation of the α_s plot gives a positive intercept. Both of these features indicate the presence of microporosity, the corresponding value of pore volume being given in Table 1.

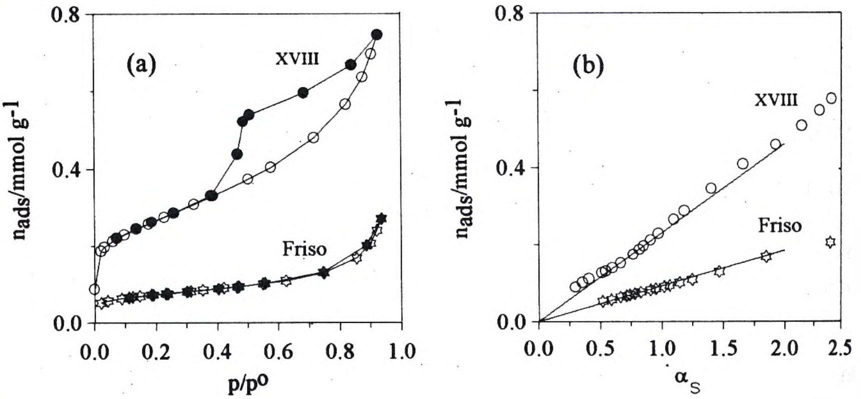

Figure 2 - Nitrogen adsorption isotherms (a) and corresponding α_S plots (b) on a degraded (XVIII) and a well preserved (Friso) tile of the XVIIIth century.

Table 1 - Results of BET and α_s analysis of nitrogen adsorption isotherms at 77 K determined on samples of portuguese ornamental tiles. C_{BET} = BET C constant. A_{BET} and A_S = specific surface area determined from BET and α_s plots. V_{mp} = micropore volume determined from α_s plot.

Sample	C_{BET}	A_{BET} m^2g^{-1}	A_S m^2g^{-1}	V_{mp} cm^3g^{-1}
XVI	121	28.3	22.1*	0.0024
XVI-OH	67	25.3	17.9*	0.0029
XVII	95	1.6	1.5	0
Friso	313	5.8	5.8	0
XVIII	126	14.5	14.7	0
XVIII desal	208	21.0	19.0*	0.0010
XVIII-OH	91	17.0	3.6*	0.0075
XVIII-PB	78	3.7	3.7	0
XVIII-PU	54	1.2	1.1	0
XIX	147	9.2	9.0	0
XX	188	1.3	1.3	0

*Value obtained from the linear region that doesn't pass through the origin, thereby corresponding to external surface area, excluding micropores.

In Figure 2 the nitrogen isotherms and corresponding α_s plots of sample XVIII are compared with results obtained on the Friso sample (also from the XVIIIth century but in a good state of preservation). The results indicate that this sample is non porous.

Consideration of the results presented in Figures 1 and 2 indicates that the appearance of hysteresis in the nitrogen adsorption isotherm is associated with the degradation of the tile. The more deteriorated is the tile, the higher will be its surface area and the more mesoporous and even microporous it will be. We can conclude, furthermore, that the development of micro and mesoporosity is not merely related with the age of the tile, but is more dependent on the technology of production and on the conditions to which tile was subjected during its life. It is particularly noteworthy that XVII century tile has apparently been maintained in an excellent condition, comparable with a tile from the beginning of the current century.

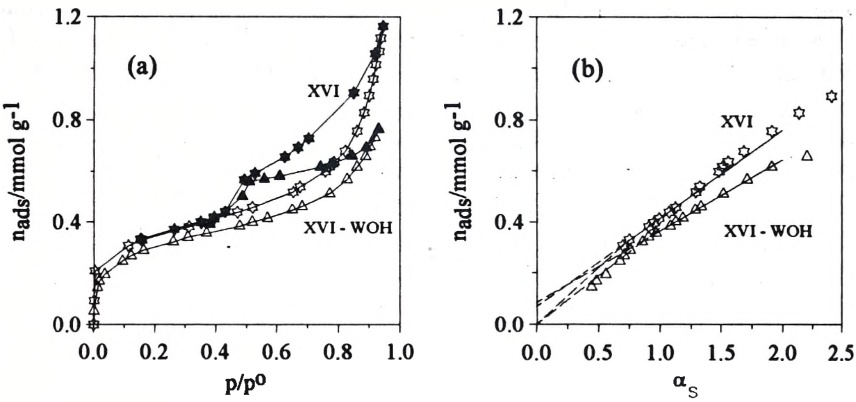

Figure 3 - Nitrogen adsorption isotherms (a) and corresponding α_S plots (b) on a XVIth century tile before and after impregnation with Wacker-OH.

Effect of impregnation with polymers

In Figure 3 are shown nitrogen isotherms and corresponding α_s plots of sample XVI before and after treatment with Wacker-OH. In Figure 4 are shown the results obtained with the XVIII sample (previously desalinated) and after consolidation with 3 different impregnants. Results of the BET and α_s analyses are given in Table 1. In all cases there is a large decrease in C_{BET} which indicates a lowering of the surface energy and is consistent with the deposition of a layer of polymer on the surface. There is also a decrease in the surface area, this being much more pronounced in the case of the PB72 and the polyurethane impregnation.

Impregnation with Wacker-OH produces similar changes with both tiles. Although the specific surface area decreases slightly, there is a more significant reduction in the adsorption at higher relative pressures. This, together with analysis of the shape of the α_s plots indicates that there occurs a narrowing of the wider pores which become narrower mesopores or even micropores, but without causing a significant blocking of the pore structure.

The effect of impregnation is more drastic with PB72 and polyurethane which suggests that in these cases there probably occurs pore blocking. For instance, it can be seen that in the case of sample XVIII, the total surface area available after impregnation with PB72 is similar to the external surface area (i.e. excluding micropores) obtained from the α_s plot for the sample impregnated with Wacker-OH.

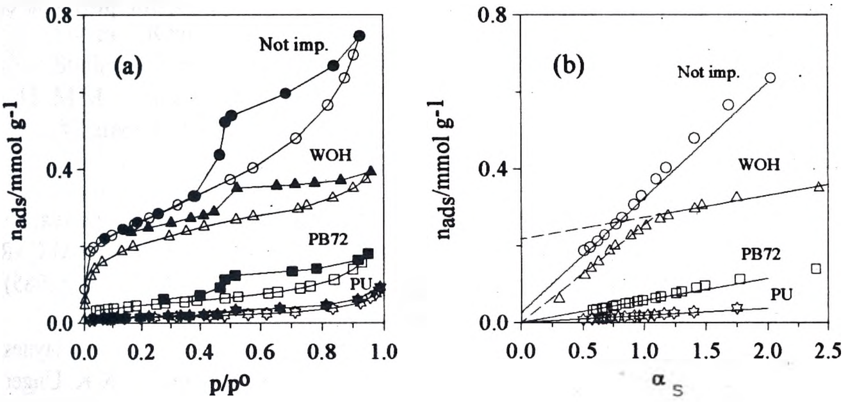

Figure 4 - Nitrogen adsorption isotherms (a) and corresponding α_S plots (b) on a XVIIIth century desalinated tile before and after impregnation with Wacker-OH, Paraloid B72 and Polyuretane (PU).

Conclusions

The results obtained indicate that degradation of tiles is associated with the development of a mesopore structure and sometimes microporosity. So, the values of specific surface area and the presence of an hysteresis loop in the isotherm can be used as a diagnostic for the degree of degradation.

With regard to impregnation with polymers, two sorts of processes were found: Wacker-OH was found to cover the pore walls leading to pore narrowing, while with PB72 and polyurethane pore blockage occurred.

Both degradation and impregnation cause alterations in pore structure in the range of pore size corresponding to mesopores and micropores, that is, in a range which is not easy to study using other techniques but which is ideal for gas adsorption measurements. So, the work presented here shows that nitrogen adsorption at 77 K is a very useful technique for characterising the porosity of tiles and for evaluating the effects of, on the one hand, degradation and, on the other hand, impregnation treatments.

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