DESIGN OF A FUNCTIONAL CERAMIC TILE COATING WITH HUMIDITY SELF-REGULATING CAPABILITY

J. Castellano[1*], V. Sanz[1], J.J. Conejos[2], S. Vives[3], E. Sánchez[1]

[1]Instituto Universitario de Tecnología Cerámica (IUTC), Universitat Jaume I (UJI), Castellón, Spain

[2]Gimecons Construcciones y Contratas, S.L., Castellón, Spain

[3]Realonda, S.A., Onda, Castellón, Spain

ABSTRACT

This study was undertaken to design and fine-tune a coating with a humidity-regulating capability that could be incorporated into any type of ceramic tile. The design was based on different raw materials that are commonly used in the ceramic tile industry and that, appropriately combined, could develop, after the firing process, a pore structure capable of adsorbing and condensing humidity. A variant of one of the compositions was also designed. The ceramic compositions were characterised from a humidity regulation standpoint, determining the moisture adsorption and desorption curves of the test pieces formed from these compositions under isothermal conditions.

The porous nanostructure of the materials was verified to condition the humidity regulation properties. Humidity self-regulation is fundamentally due to surface adsorption and capillary condensation phenomena, which are related to the quantity of nanometre-sized pores, known as mesopores. The pore structure of the materials was characterised by mercury intrusion porosimetry.

The results show that one of the selected compositions, as well as the variant designed from that composition, exhibited a high humidity regulation capability that was preserved when the composition was incorporated as a coating on a standard ceramic tile body. In addition, these compositions also exhibited an excellent volatile organic compound (VOC) adsorption capability. This functionality was verified to be maintained in a wide range of firing temperatures. These results validate the technology developed for use in the manufacturing processes of any type of ceramic tile.

1 INTRODUCTION

The increase in home comfort and decrease in energy demand have led to the development of more hermetic interiors, with less ventilation and more thermal insulation. Lack of ventilation can give rise to the so-called sick building syndrome, which is characterised by environments with harmful humidity conditions for people and low air quality. Exposure to this type of degraded or unhealthy environments produces clinical symptoms in building occupants, such as headache, mucous membrane irritation, increased allergies, and even respiratory insufficiency [1]. Although humidity can be regulated through electrical devices, the development of passive technologies to regulate humidity and purify the air in interior spaces is of greater interest from an energy and environmental sustainability viewpoint.

It is in this context that functional ceramic tiles with humidity self-regulating capability are being developed. These tiles are characterised by their potential for controlling ambient humidity and reducing the concentration of gaseous pollutants such as volatile organic compounds (VOC). Ceramic materials and tiles with a humidity-regulating functionality were first developed in Japan, a nation highly sensitised to comfort, health, and environmental sustainability [2]. The main component determining the functionality of these products is allophane, an amorphous compound of silica and alumina, found in certain volcanic soils in Japan. Allophane exhibits, after a thermal treatment, a hierarchised pore microstructure with a great quantity of mesopores (small pores sized between 2 and 50 nm), which provide it with an innate ability to regulate humidity and adsorb organic compounds such as formaldehyde or toluene [3] [4]. However, the local occurrence of this mineral limits its use and makes it difficult to extend this technology beyond its country of origin.

Although various studies have been carried out on the humidity regulation capability of materials with high specific surface area and small pore size, no evidence has been found that ceramic tiles with a regulating functionality are being marketed beyond Japanese products. The most widely analysed porous materials of a ceramic nature are dolomite, zeolite, gibbsite, diatomite, sepiolite, and other clay minerals of the montmorillonite type in general [5] [6]. Most of these studies have focused on developing highly porous microstructures in the fired pieces.

Previous studies have shown that one of the major difficulties in integrating these porous materials in ceramic tile manufacturing processes is the loss or deterioration of the porous nanostructure after the firing cycle. Microstructural deterioration is related

to the effect of temperature on tile sintering, causing porosity to decrease and pore size to increase as a result of pore coalescence [7]. Thus, for such a material to be useful, it is necessary to preserve a porous nanostructure with a high quantity of mesopores after a cycle with maximum temperatures between 1100 ºC and 1200 ºC, which may not be self-evident.

Another important difficulty is obtaining tiles with the typical technical and aesthetic specifications for this type of product, while holding inside the desired porous nanostructure. The tile must have a design that matches current trends, while concurrently allowing water vapour to be exchanged with the environment. The practice adopted to date has been designing pore structures in the ceramic tile body, which gives rise to excessively porous tiles that do not meet the technical specifications required in many applications. A hitherto unexplored strategy consists of developing porous coatings that accommodate the humidity-regulating functionality, deposited on ceramic standard tile bodies, porous or not.

As a result of the above, the present study was undertaken to develop a technological innovation consisting of functional ceramic tiles with a humidity self-regulating capability, formulated with ceramic raw materials commonly used in Spain, in which the humidity regulation functionality was confined to a coating on a standard wall or floor tile body. Such tiles are characterised by their potential for controlling ambient humidity and reducing gaseous pollutant concentrations. For this, it was necessary to design a coating that had a hierarchised pore structure with a major presence of mesopores, in order to develop the desired functionality and preserve it after firing. The present study also sought to characterise and to verify the microstructural requirements in the fired tiles that would allow the humidity-regulating functionality of the coating to be optimised.

2 EXPERIMENTAL

2.1 MATERIALS AND SAMPLE PREPARATION

The study was carried out using different commercial ceramic materials with high porosity, which were likely to exhibit a moisture adsorption capability, the most noteworthy materials being detailed in Table 1 (references C1, C2, C3 and C4). These materials included a traditional wall tile composition that was used as reference standard, a clay raw material with a high percentage of carbonates, an industrial composition with 25–30% dolomite used for manufacturing faience ceramics and a spray-dried powder with aluminium oxide for advanced ceramics. Finally, a variant was developed, based on composition C4, in which the aluminium oxide content was optimised to improve its adsorbent properties. The table also lists the major components of each composition, identified by X-ray diffraction (D8 Advance, Bruker).

Reference	Description and use	Major components		
C1	Spray-dried powder for wall tiles	Calcite	Quartz	Kaolinite
C2	Clay for bricks and roofing tiles	Calcite	Dolomite	Quartz
C3	Spray-dried powder for faience	Dolomite	Quartz	Kaolinite
C4	Spray-dried powder for advanced ceramics	Gibbsite	Quartz	Kaolinite
C5	Variation of C4 with more Al_2O_3	Gibbsite	Quartz	Kaolinite

Table 1. *Porous ceramic materials considered in the study*

The powdered materials were used to obtain laboratory test pieces by uniaxial pressing, which were dried and then fired in an electric kiln according to a fast cycle to peak temperatures between 1020 and 1120 ºC in accordance with industrial practice.

2.2 CHARACTERISATION OF THE SAMPLES

The moisture adsorption and desorption tests were carried out in a climate chamber (HC2020, Heraeus Vötsch), keeping the temperature constant throughout the test and conveniently modifying relative humidity. First, the test pieces were placed inside the chamber, setting a temperature of 23 ºC and relative humidity of 50% for at least 16 hours to reach equilibrium. The pieces were weighed, obtaining m_0, and introduced again into the chamber; relative humidity was then raised to 90%, and the pieces were then re-weighed at increasing periods of time (m_t) for 24 hours. The amount of water adsorbed in every period of time was calculated as an incremental percentage in relation to m_0. Moisture desorption was then analogously determined, varying relative humidity from 90% to 50%, and then duly re-weighing the test pieces. The humidity-regulating capability (HRC) was determined from the mean amount of water adsorbed and released by desorption in a certain time (8 or 24 hours), expressed per unit mass (m_0) or sample surface area.

Pore microstructure was observed by sample analysis with a scanning electron microscope (Quanta 200 FEG, FEI Company), and pore size distributions were determined by mercury intrusion porosimetry, using an automated mercury porosimeter (AutoPore IV 9500, Micromeritics).

The adsorption capability of volatile organic compounds and gaseous pollutants was determined by Radiello passive samplers with two model substances of differing nature: formaldehyde and ammonia. The tests were conducted introducing samples of the materials to be tested in two receptacles of 20 L together with aqueous solutions of the pollutants to reach theoretical concentrations of 0.36 mg/m^3 (≈0.3 ppm) with formaldehyde, and 7 mg/m^3 (10 ppm) and 14 mg/m^3 (20 ppm) in the case of ammonia. Depending on the pollutant, samplers with different cartridges and appropriate analytical techniques were used. For formaldehyde, cartridges with 2,4-dinitrophenylhydrazine and analysis by high-performance liquid chromatography (HPLC) were used. In the case of ammonia, cartridges of microporous polyethylene impregnated with phosphoric acid were used, and the amount of ammonium was determined by visible spectrometry.

3 RESULTS AND DISCUSSION

3.1 EVALUATION OF THE HUMIDITY-REGULATING CAPABILITY OF THE SAMPLES

Figure 1 shows the moisture adsorption and desorption curves at 23 ºC of the test pieces fired at the temperatures indicated in brackets. The greatest adsorption corresponded to the pieces of composition C5, which underwent an increase in moisture content of about 7%. Sample C4 also adsorbed a significant amount of water, with increases in weight of about 2% in 24 hours. The remaining samples (C1, C2 and C3) exhibited much lower adsorption, so that their potential as materials with a humidity-regulating functionality was very limited, in particular that of reference standard sample C1, which exhibited zero regulation. The comparison in regard to process kinetics (curve slopes) showed that moisture desorption occurred at a faster rate than moisture adsorption: more than 60% of the total amount of water was adsorbed in periods of time of 8 hours, whereas more than 90% of the desorption process was completed in periods of less than 8 hours.

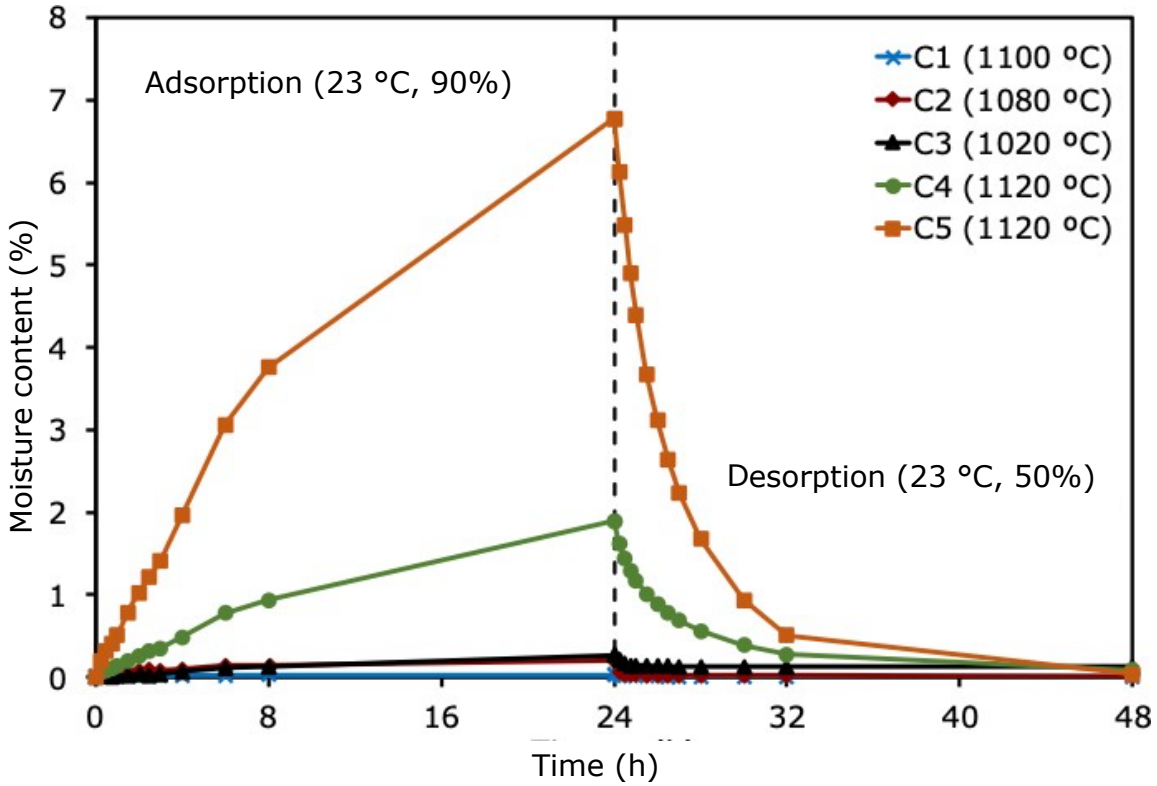

Figure 1. *Isothermal curves of moisture adsorption and desorption during 24-hour cycles for the samples fired at the temperatures indicated in brackets*

To determine the effect of temperature on humidity regulation, test pieces of composition C5 were fired at different temperatures, obtaining the results shown in Figure 2. The figure displays the humidity-regulating capability (HRC) of the samples fired at 1120 ºC, 1180 ºC, and 1200 ºC in cycles of 8 and 24 hours. The results are expressed as a percentage with relation to the initial product mass and they are compared with those corresponding to Japanese products based on allophane and sintered at lower temperatures [4]. It may be observed in Figure 2 that raising peak firing temperature lowered the humidity regulation capability, though the values still remained high at 1200 ºC compared with those of products with allophane. The material was therefore confirmed to maintain a notable regulation capability, even though sintering was performed according to a higher temperature cycle, as occurred in the case of porcelain tile.

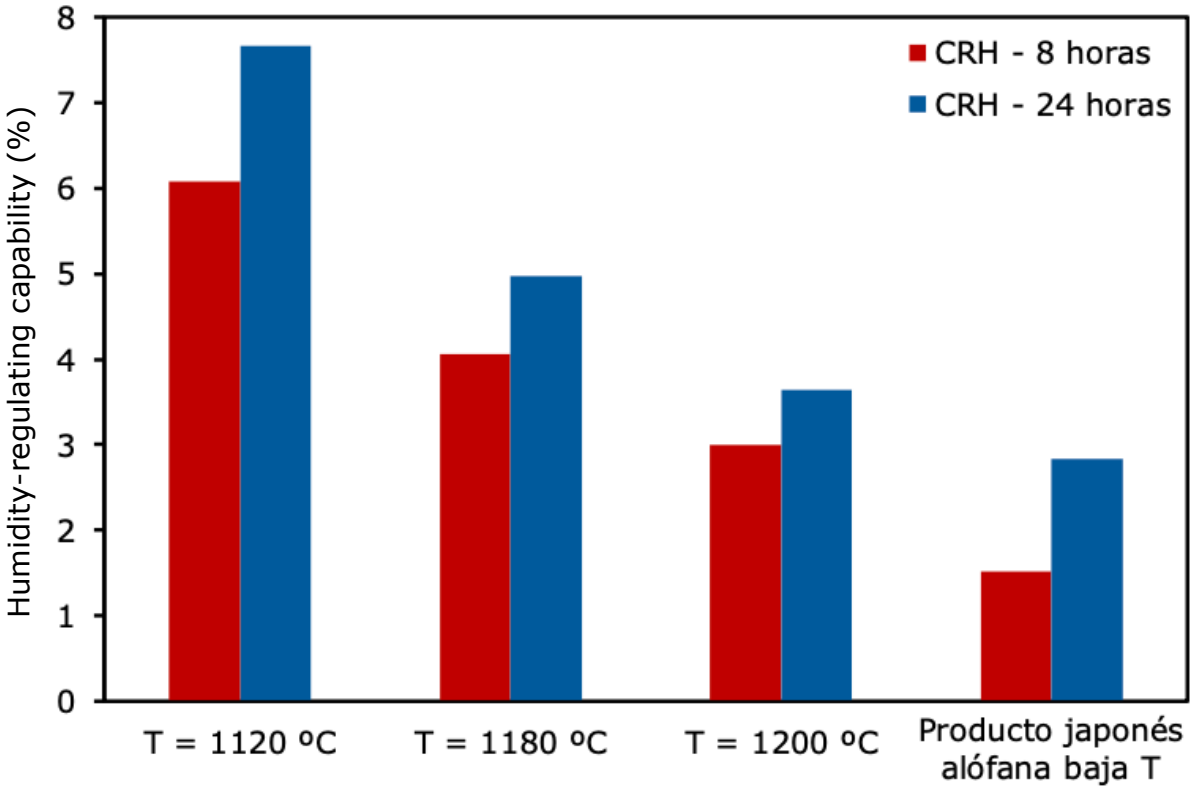

Figure 2. *Humidity-regulating capability (HRC) at different firing temperatures in comparison with a product based on allophane at low temperature*

3.2 PORE MICROSTRUCTURE AND RELATION TO HUMIDITY REGULATION

Pore microstructure conditions capillary condensation phenomena and water vapour diffusion inside a material, which determine humidity regulation. The microstructure of the materials was characterised by pore size distribution using mercury porosimetry, which yielded the results shown Figure 3 and Table 2. The graph in Figure 3 reveals the presence of small-sized pores, between 0.005 µm and 0.04 µm

(5–40 nm), in samples C4 and C5. These pores corresponded to the zone with mesopores (2–50 nm), which are responsible for the humidity regulation capability resulting from capillary condensation phenomena according to the Kelvin equation [8]. It was found, moreover, that humidity regulation did not depend on the porosity of the material, determined by total pore volume (V_p) and the percentage of open porosity (P), because sample C2 exhibited high values for these parameters (close to those of composition C5), but very limited humidity regulation according to Figure 1. It was therefore inferred that, to be able to control humidity with materials that had a self-regulating functionality, it was not enough to increase the total porosity of these materials. Rather, it was necessary to increase the quantity of small-sized pores or mesopores (2–50 nm).

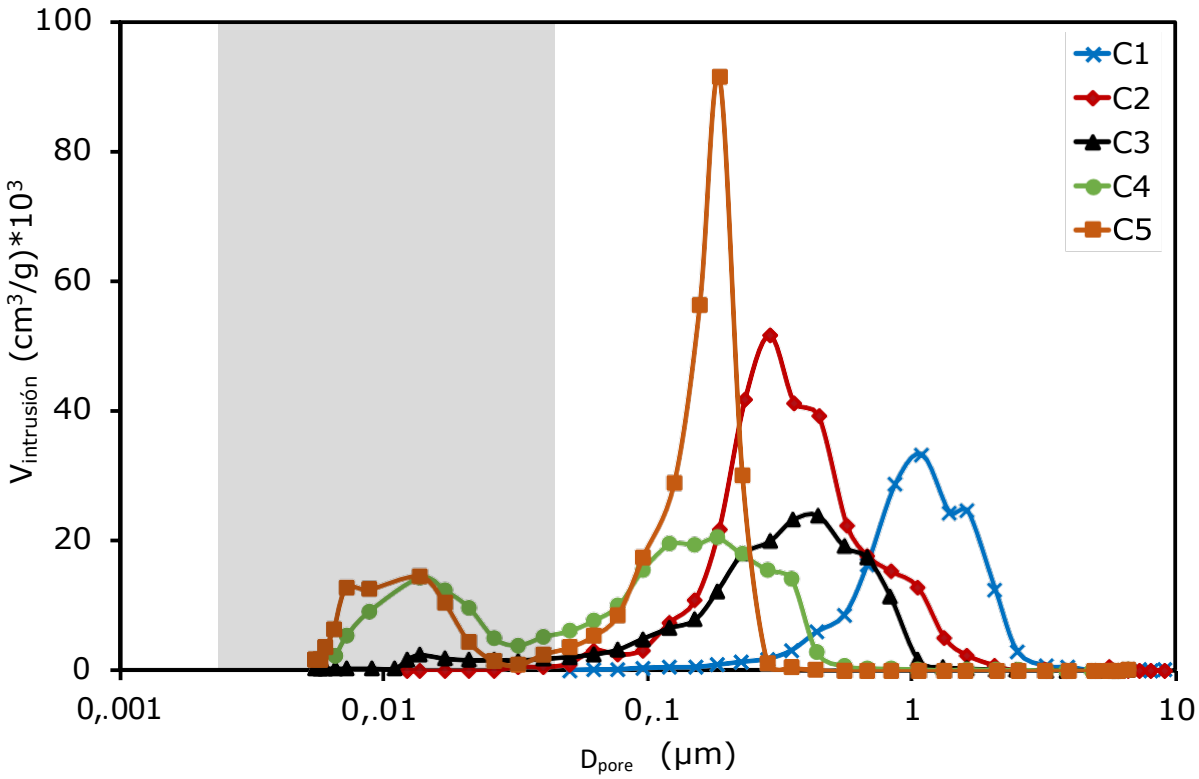

Figure 3. *Pore size distributions determined by mercury porosimetry (shaded mesoporosity region)*

Reference	d_{50}	V_p (cm^3/g)	P (%)
C1	1.20	0.188	33.7
C2	0.36	0.327	49.1
C3	0.37	0.202	38.8
C4	0.12	0.244	40.4
C5	0.16	0.364	51.7

Table 2. *Mean pore diameter (d_{50}), total pore volume (V_p) and percentage of open porosity (P) determined by mercury porosimetry*

Microstructure was analysed by scanning electron microscopy (SEM). The micrographs corresponding to a conventional porous wall tile body (sample C1) and a material with a humidity-regulating functionality (sample C4) are shown in Figure 4.

The images confirm the differences observed. Sample C1 exhibited a microstructure with rounded pores sized about 1 μm or more, typical of the sintered porous materials used in tile manufacture. The material with a humidity-regulating capability (micrograph on the right) exhibited a more complex, hierarchized microstructure, with small-sized pores and greater heterogeneity, displaying zones or groups particles in the form of plates or small thin slabs that housed, in their arrangement, small-sized (submicron) pores, which were much smaller than those observed in the figure on the left.

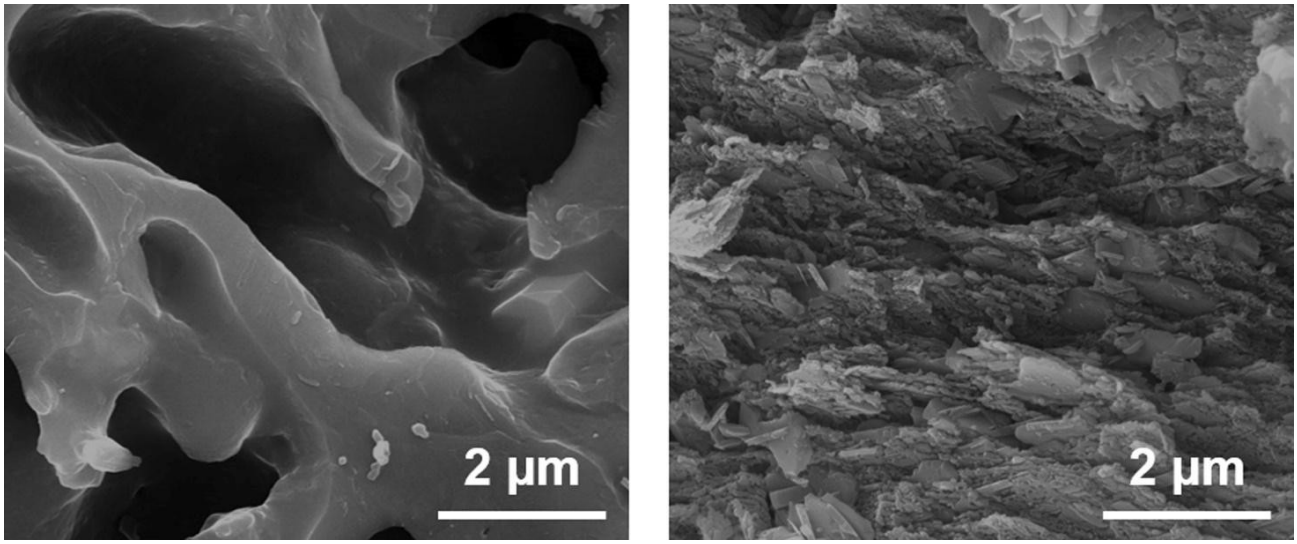

Figure 4. *SEM micrographs of a conventional porous wall tile body (left) and a material with humidity-regulating capability (right)*

3.3 INTEGRATION OF HUMIDITY-REGULATING MATERIALS IN CERAMIC TILES

After developing and characterising humidity-regulating materials, it was necessary to incorporate these materials into ceramic tiles in order to obtain the targeted functionality, while simultaneously maintaining product performance. To do so, two fundamental aspects needed to be considered: i) tile make-up must allow contact of ambient water vapour with the regulating material, even though the product is glazed and decorated and ii) product cost must be sufficiently competitive to allow implementation of the technology in common housing and building construction. In view of these two considerations, tiles were designed in accordance with the scheme in Figure 5. Thus, humidity-regulating tiles consisted of a traditional ceramic tile body on which a continuous layer was deposited as a functional coating that provided the product with a humidity-regulating capability. Decoration layers were then applied on the functional coating, avoiding complete surface sealing by discontinuous applications using inkjet technology in combination or not with other complementary techniques. These tiles were manufactured according to industrial practice. Figure 5 also shows a photograph of tiles obtained in industrial production.

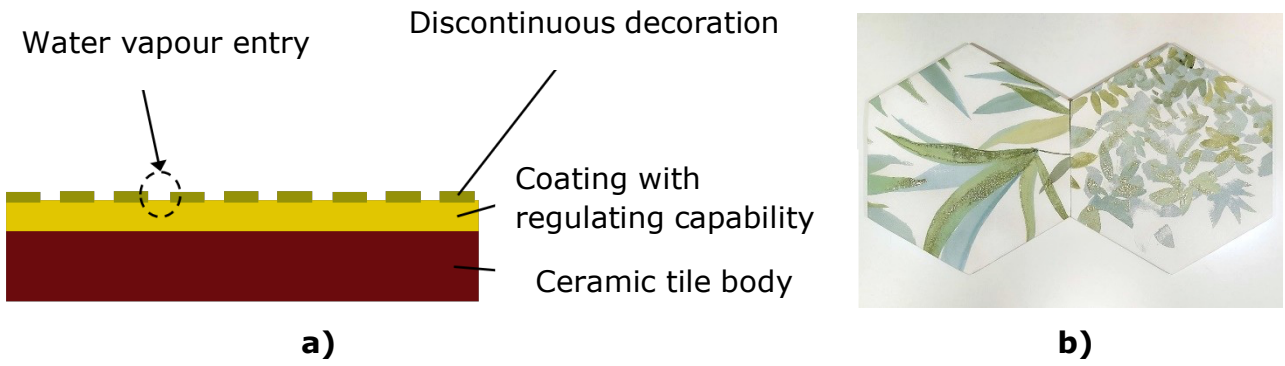

Figure 5. *a) Scheme of the make-up of tiles with a humidity-regulating functionality, b) Photograph of tiles obtained on an industrial scale*

Finally, with a view to validating coating functionality, the humidity-regulating capability and VOC adsorption of tiles prepared, as schematically illustrated in Figure 5, with porcelain tile bodies, fired according to the usual cycle at a peak temperature of about 1180 ºC, were determined. Figure 6 details the results obtained after the adsorption–desorption tests at 8h and 24h (Figure 5a), and the formaldehyde adsorption and ammonia adsorption (Figure 5b). In every case, the results were compared with those of commercial products. As may be observed, the designed tile exhibited an excellent humidity-regulating capability, much greater than that of a Japanese product with allophane (estimation made from commercial information). A much higher VOC adsorption capability than that of a porous commercial product (single-fired porous wall tile) was observed, with pollutant amounts that decreased by more than 90%. The results obtained confirmed the validity of the material formulated for the coating and the industrial tile design made.

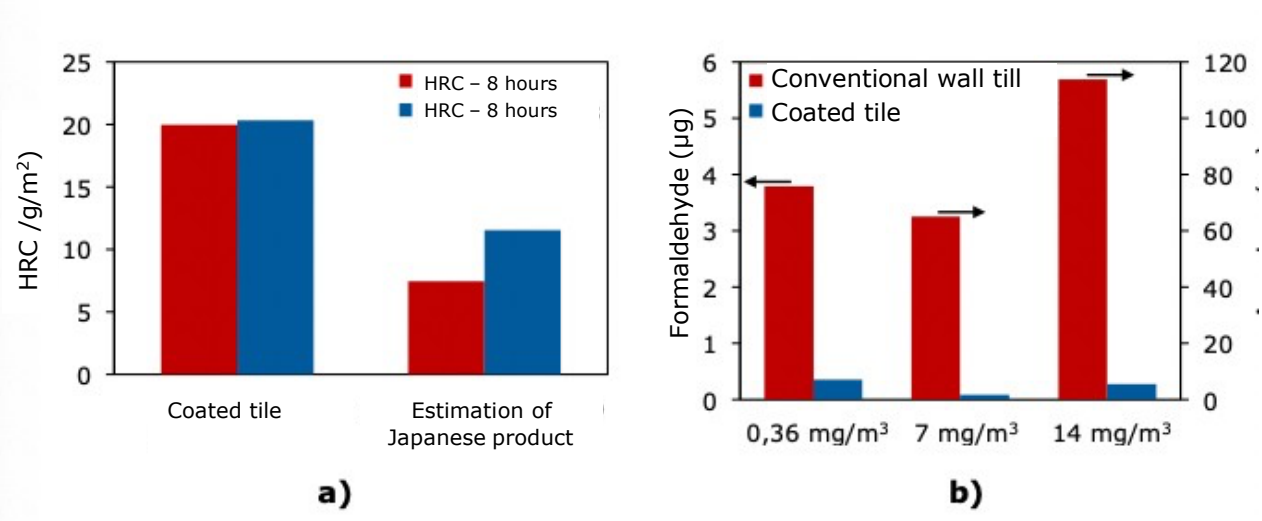

Figure 6. *a) Humidity-regulating capability (HRC), b) Formaldehyde and ammonia adsorption at two concentrations*

4 CONCLUSIONS

Four compositions used in the ceramic tile industry were analysed to assess their properties for use in tiles with a humidity regulation functionality, as well as a composition designed from one of these. The tiles made with the compositions that contained gibbsite provided the best humidity regulation.

Humidity regulation depended on pore microstructure, mainly on the presence of mesopores (2–50 nm). The adsorption and desorption phenomena were related to the filling and emptying of the mesopores by capillary condensation. The quantity and size of the mesopores defined the humidity regulation capability of the material. Without mesopores, even though the existing porosity was very high, the porosity had little effect on the humidity regulation capability.

Using the composition with the greatest humidity-regulating capability, a ceramic tile was designed in which this composition was incorporated as a coating. Subsequent decoration layers were applied on the coating, avoiding complete surface sealing by discontinuous applications using inkjet technology. These tiles were manufactured according to the same scheme used in industrial practice. The humidity-regulating capability and VOC adsorption was verified to be held in the tiles made, much higher humidity regulation and VOC adsorption values being obtained than those of commercial products.

5 ACKNOWLEDGEMENTS

The authors thank the Spanish Ministry of Science and Innovation and the European Regional Development Fund (ERDF) for the funding received in the CONFORTMA RTC-2017-5904-5 project. The collaboration of the company Vicar in developing the compositions is also gratefully acknowledged.

6 REFERENCES

[1] Burge, P.S. "Sick building syndrome". Occupational and Environmental Medicine, 61 (2004) 185-190.

[2] Ishida, E.H. "Canalización de las fuerzas de la naturaleza – Los materiales conscientes del ser humano y de la tierra pueden crear nuevas olas". VIII World Congress on Ceramic Tile Quality, QUALICER 2004, Castellón (Spain).

[3] Fukumizu, H.; Yokoyama, S. "Study on a new humidity controlling material porous soil "allophane" – Evaluation of humidity controlling performance in practical houses". Resources Processing, 52 (2005) 59-64.

[4] Watanabe, O.; Fukumizu, H.; Ishida, E.H. "Desarrollo de un material de construcción con control autónomo de la humedad mediante mesoporos". X World Congress on Ceramic Tile Quality, QUALICER 2008, Castellón (Spain).

[5] Gómez-Tena, M.P.; Bengochea, M.A.; Sánchez, E.; Guaita, L.; Machí, C. "Desarrollo de formulaciones cerámicas con capacidad reguladora de humedad para el confort ambiental". XII World Congress on Ceramic Tile Quality, QUALICER 2012, Castellón (Spain).

[6] Vu, D.H.; Wang, K.S.; Bac, B.H.; Nam, B.X. "Humidity control materials prepared from diatomite and volcanic ash". Construction and Building Materials, 38 (2013) 1066-1072.

[7] Barba, A.; Beltrán, V.; Felíu, C.; García, J.; Ginés, F.; Sánchez, E.; Sanz, V. "Materias primas para la fabricación de soportes de baldosas cerámicas". Instituto de Tecnología Cerámica, 2nd ed. (2002).

[8] Sing, K.S.W.; Williams, R.T. "Historical aspects of capillarity and capillary condensation". Microporous and Mesoporous Materials, 154 (2012) 16-18.