DEVELOPMENT OF CERAMIC FORMULATIONS WITH HUMIDITY-REGULATING CAPABILITY FOR ENVIRONMENTAL COMFORT

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ABSTRACT

This paper presents the results of the experiments conducted in the development of ceramic compositions with a humidity-regulating capability for improving air quality in controlled environments, using raw materials that were able to adsorb humidity. The targeted composition needed to enable fabrication of a ceramic tile with a humidity-regulating capability exceeding 140 g/m^2 in 24-hour cycles.

The raw materials analysed for this purpose were natural aluminosilicates, such as attapulgites, bentonites, sepiolites, and diatomaceous earths, as well as semi-processed raw materials such as gibbsite (aluminium hydroxide). Tests were also performed with synthetic raw materials such as precipitated silica and an aluminosilicate designed to adsorb humidity.

Characterisation tests were performed on the starting materials and formulated compositions to obtain information on their microstructure, in particular specific surface area and pore size distribution. Functional information was also obtained by determining the water adsorption isotherms and performing climatic chamber and bending strength tests.

Of the studied raw materials, the sepiolite and the synthetic aluminosilicate provided the best characteristics for use in ceramic compositions; 900ºC was found to be the optimum firing temperature for obtaining the highest humidity regulation with appropriate mechanical strength. A composition was obtained that was able to provide the sought-after characteristics.

1. INTRODUCTION

Nowadays in developed society we live with a great number of ‘technological conveniences’. These conveniences have their advantages (wellness), but also their disadvantages (high energy consumption). Aware of the need to protect the environment, society is demanding that companies should develop sustainable products that do not jeopardise the achieved level of well-being. In this sense, the European Union is committed to reducing energy consumption by 20% (in comparison with the projected levels) by the year 2020 [1].

The development of thermally isolated housing, aimed at reducing energy consumption, has given rise to a new problem, namely the regulation of the internal climate and in particular of ambient humidity and air quality. The market offers air-conditioners, humidifiers, dehumidifiers, ionisers, deodorisers, etc., which have caused housing energy consumption to shoot up. It thus becomes necessary to reconsider the current situation and to commit to the development of safe and sustainable processes.

In Europe, a total of 1500 Mm^2 was cooled in 2005 [2] and this is expected to rise to 2300 Mm^2 by 2015. In this figure, Italy (25%) and Spain (24%) were the countries with the largest percentage of cooled m^2 in buildings. According to the Spanish National Institute for Statistics, 35.5% of Spanish homes had air-conditioning in 2008 [3], the Regions of Murcia, Extremadura, Andalusia, and Valencia having the most air-conditioning units, all above 50% of the homes. With regard to heating, 73.3% of Spanish homes has a heating system, and more than 90% of homes has such a system in Regions like La Rioja, Aragón, Navarre, and Castile and Leon.

The use of apparatuses for regulating humidity, such as air conditioners or humidifiers, has not reduced the percentage of damage to housing caused by humidity or the number of people with allergic diseases (sick building syndrome). However, energy costs in Spain have risen enormously, despite the development of units with low energy consumption.

The humidity range in which a person feels comfortable is considered to lie between 40 and 70%. Studies have shown that, when the humidity remains within this range, the reproduction of allergy sources such as mites and bacteria decreases. In addition, this humidity range is effective for controlling the reproduction of viruses and static electricity build-up [4,5].

From a sustainable development viewpoint, the optimum solution to the above problem is self-regulation of the internal climate (in particular of humidity) by the building materials themselves.

The humidity-regulating capability of a material is defined by the Kelvin equation. This equation relates the pore size of a material to the relative humidity at which capillary condensation occurs [6]. Therefore, this makes it desirable to obtain materials with high porosity and small pore sizes.

At present, there are numerous ways of synthesising porous materials [7]. However, these synthesis methods are unsustainable, since they use oil as raw material. For this reason, in this study, clay minerals were selected as a starting material. Clay minerals contain micropores, which can be effective in producing construction materials with a humidity-regulating capability [8]. Selection of the appropriate clay minerals would allow specific microstructures with the required ambient humidity adsorption/desorption properties to be designed, features that are difficult to attain with other construction materials like timber, plastics, or gypsum.

There are certain products that display such capabilities [9], which use natural raw materials of volcanic origin in Japan. These products exhibit the following characteristics: a humidity-regulating capability of 80 g/m^2 (in 8-hour cycles) between 50 and 90% relative humidity or 140 g/m^2 (in 24-hour cycles) [9]. In the patent that describes these materials, the firing temperature for this product is stated to be 800ºC, but it does not specify the product's mechanical strength though it does indicate that the porosity is high.

Other authors describe the use of materials such as aluminium hydroxide or silica gel, which exhibit good adsorption properties, though compositions with low bending strength are obtained (50 kg/cm^2) [10].

An intelligent natural resources approach would involve using clay or natural materials that are available in Europe for the production of humidity-regulating materials that are able to provide comfort in domestic and occupational environments. This was the main aim of this study, though for comparative purposes, synthesis raw materials were also used in the experiments.

2. Experimental

2.1. Materials characterisation

The materials at issue in this study needed to have a high reversible humidity adsorption capability and, if possible, to display maximum values in the environmental comfort zones. This humidity adsorption property is related to the specific surface area of the sample and the structural nature of the material, i.e. its mineralogical composition and pore size, which make that specific surface area useful. The tests selected for the assessment of the suitability of the raw materials in regulating humidity were as follows: determination of the water adsorption isotherm and specific surface area. The evolution of these properties with thermal treatment temperature was evaluated.

2.1.1. Materials

Different natural and synthetic materials were selected in order to determine their suitability for the formulation of ceramic compositions that would be able to regulate ambient humidity. The test materials were divided into different groups, based on their structure: aluminosilicates, silicates, and oxides and hydroxides. In the aluminosilicates, a distinction was made between those of a clayey and those of a non-clayey nature. A material obtained by hydrothermal synthesis at ITC (synthetic aluminosilicate of an amorphous nature, hereafter $SiAl_{am}$), which exhibited excellent adsorbent properties, was also included.

Of a clayey nature				**Non-clayey**		**Synthetic**
Bentonite	Attapulgite	Sepiolite	Nano-clay	Diatomaceous earth	Natural zeolite	Synthetic $SiAl_{am}$

Oxides		**Hydroxides**
Precipitated silica	Gamma-alumina	Gibbsite (aluminium hydroxide)

Table 1 Test materials: aluminosilicates (of a clayey, non-clayey, and synthetic nature), natural silicates (diatomaceous earth), and oxides and hydroxides.

2.1.2. Adsorption–desorption water isotherms

An adsorption isotherm (also known as a sorption isotherm) describes the adsorption equilibrium of a material at a surface (in a more general form, on a bounding surface) at constant temperature. The water adsorption tests were conducted with a Quantachrome (Aquadyne) automated gravimetric system, in which the adsorbed quantity of water is analysed by weighing at different temperatures.

Sample weight is constantly monitored and recorded as relative humidity varies automatically by the mixture of dry carrier gas with a saturated gas stream.

Figure 1 Aquadyne

2.1.3. Specific surface area (BET)

The adsorption/desorption curves to determine the specific surface area were obtained, using nitrogen gas as adsorbent, with a Micromeritics TriStar 3000 instrument in accordance with standard ISO 9277:1995.

Before the test, the samples were dried in an oven at 110ºC for 2 hours and then outgassed using a nitrogen stream at 300ºC.

2.2. Composition preparation and characterisation

2.2.1. Composition preparation

The raw materials used for each composition were homogenised in a planetary mill, using a 310 ml capacity jar, acetone as fluid, and alumina balls. Milling time was 20 minutes at 230 rpm. After mill discharge, the composition was dried under infrared lamps and then sieved on 400 µm mesh.

The base composition (percentage by weight), to which raw materials with humidity adsorption properties were added, is shown in Table 2.

Quartz	Kaolinite	Potassium feldspar	Calcite	Illite/ Mica	Albite	Haematites	Others
38	20	10	14	14	3	<1	1

Table 2 Percentage by weight of the mineralogical components of the base composition.

The preparation route differed, depending on the type of adsorbent material.

- Natural raw materials:

For each composition, the material was moistened to a moisture content of about 0.055 kg water/kg dry solid, and test pieces measuring 2x8 cm were pressed at a specific pressure of 250 kg/cm^2. After pressing, the pieces were dried in a laboratory oven for at least two hours and then fired at the chosen peak temperatures. The firing cycle used involved a fast rise to 500ºC, a heating rate of 25ºC/min from 500ºC to the peak working temperature, and a 6-minute hold at peak temperature; fast cooling then followed down to quartz transformation, the cooling rate being 5ºC/min from 590 to 540ºC, with subsequent fast cooling to room temperature.

The various tests were then performed on the fired test pieces.

- Synthetic raw materials:

With a view to minimising the quantity of adsorbent material, this was dry mixed with spray-dried powder. Pressing and firing were analogous to those of the foregoing case.

2.2.2. Pore size distribution of the thermally treated pieces

The pore size distribution of each thermally treated sample was determined with a Micromeritics model AutoPore IV (9500) mercury porosimeter. The variation of the mercury intrusion volume of the tested sample was recorded as a function of the pressure applied on the sample by means of this technique. The instrument transforms the applied pressures into pore diameter values in accordance with equation 1, which yields a plot of the cumulative intrusion volume as a function of the average analysed pore diameter.

$$D = -\frac{4\gamma \cos\theta}{P}$$

Equation 1

where D is the characteristic pore diameter; P, applied pressure; γ, mercury surface tension, and θ, its contact angle.

Before the test, the samples were dried in an oven at 110ºC for two hours.

2.2.3. Bending strength

The tests were performed in a mechanical testing machine at a constant deformation rate of 5 mm/min.

The three-point bending device consists of two bottom edge supports, which are usually cylindrical, on which the test piece is placed and a support, also cylindrical, set on top of the test piece, through which the load is applied. The tensile strength of a piece subjected to a three-point bending test is given by the following expression:

$$\sigma = \frac{3 \cdot F_{max} \cdot L}{2 \cdot b \cdot e^2}$$

Equation 2.

where: σ is fired mechanical strength (kg/cm^2);

F_{max}, maximum force before rupture or breaking load (kgf);

L, span between supports (cm);

b, test piece width (cm), and

e, test piece thickness (cm).

2.2.4. Determination of the humidity-regulating capability (HRC)

Tests were conducted on the selected compositions to assess their humidity-regulating capability in internal environments.

This was done by preparing test pieces measuring 10x10 cm by uniaxial pressing from powder conditioned in the same way as above. Their humidity-regulating capability was evaluated in a climatic chamber by the method described below.

In order to measure its adsorption capability, the ceramic test piece was placed in a chamber, setting the relevant ambient temperature conditions and relative humidity of 50%. Once equilibrium had been reached, i.e. the ceramic piece exhibited a constant weight, P1, a relative humidity of 90% was set. After a given period of time (8 or 12 hours) the piece was weighed, yielding a value, P2 (Figure 2). The quantity of water adsorbed after this period of time was the difference P2–P1.

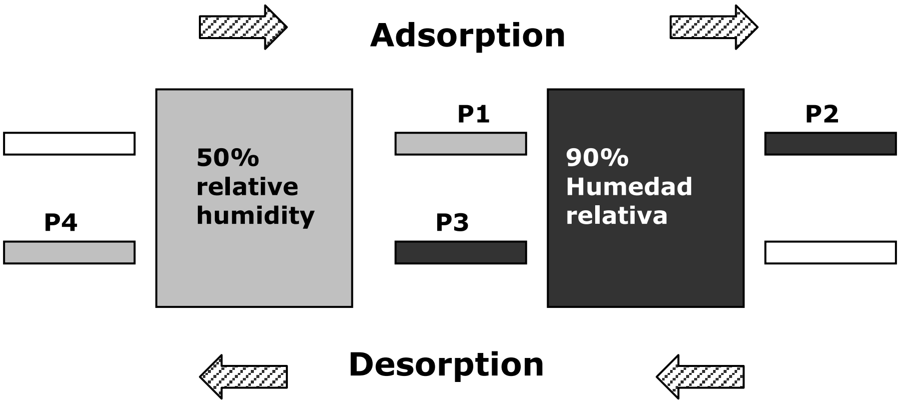

Figure 2 Graphic illustration of the method of measuring the adsorption capability (a) and desorption capability (b) of a ceramic wall tile.

The ability to release water vapour into the ambient is measured in reverse form. The ceramic piece is introduced into the measurement apparatus and a relative humidity of 90% is set. Once equilibrium is reached, i.e. the ceramic piece attains a constant weight, P3, a relative humidity of 50% is set. After a given period of time (8 or 12 hours) the piece is weighed, yielding a value, P4 (Figure 2). The quantity of water vapour released after this period of time is the difference P3–P4.

The humidity-regulating capability (HRC) of a ceramic wall tile is quantified by means of the following equation:

$$\boxed{\text{Humidity-regulating capability (HRC)} = \{(P2-P1)+(P3-P4)\}/2}$$

3. RESULTS

3.1. Materials characterisation

3.1.1. Specific surface area

To perform the study, natural and synthetic materials were selected that had a high specific surface area and could serve as bases for the formulation of ceramic compositions with a humidity-regulating capability. Since these materials were to be incorporated into ceramic compositions and subjected to a firing process, the variation of specific surface area with temperature was also studied.

The results obtained, detailed in Tables 3 and 4, show that the greatest unfired specific surface area was displayed by the aluminosilicates such as attapulgite and sepiolite, and the synthetic aluminosilicate. However, though materials such as the precipitated silica or aluminium hydroxide exhibited a lower specific surface area, this specific surface area was better preserved when temperature increased. This is because when aluminosilicates of a clayey nature are thermally treated, they lose their layered structure, which provides them with the necessary conditions to have humidity adsorbent properties.

However, in the humidity adsorption process, not only does the specific surface area of a sample play a role, but so do other factors such as the porous structure of the materials. The water adsorption/desorption isotherms of the materials were, therefore, also characterised.

		Of a clayey nature				**Non-clayey**		**Synthetic**
		Bentonite	Attapulgite	Sepiolite	Nanoclay	Diatomaceous earth	Natural zeolite	Synthetic $SiAl_{am}$
BET (m^2/g)	Unfired	65	291	340	73	14	37	303
	800ºC	12	100	110	26	5	20	180
	900ºC	7	85	72	0.2	3	5	130
	1000ºC	3	31	20	0.2	1	2	62

Table 3 Results of the variation of the specific surface area with temperature of the test aluminosilicates and natural silicate.

		Oxides		**Hydroxides**
		Precipitated silica	Y-alumina	Gibbsite
BET (m^2/g)	Unfired	199	37	115
	800ºC	196	20	113
	900ºC	191	5	106
	1000ºC	188	2	91

Table 4 Results of the variation of specific surface area with temperature of the test oxides and hydroxides.

3.1.2. Water adsorption–desorption isotherms

The water adsorption/desorption isotherms of the unfired materials and of the materials after thermal treatment at 900ºC are shown in Figures 3 and 4, respectively.

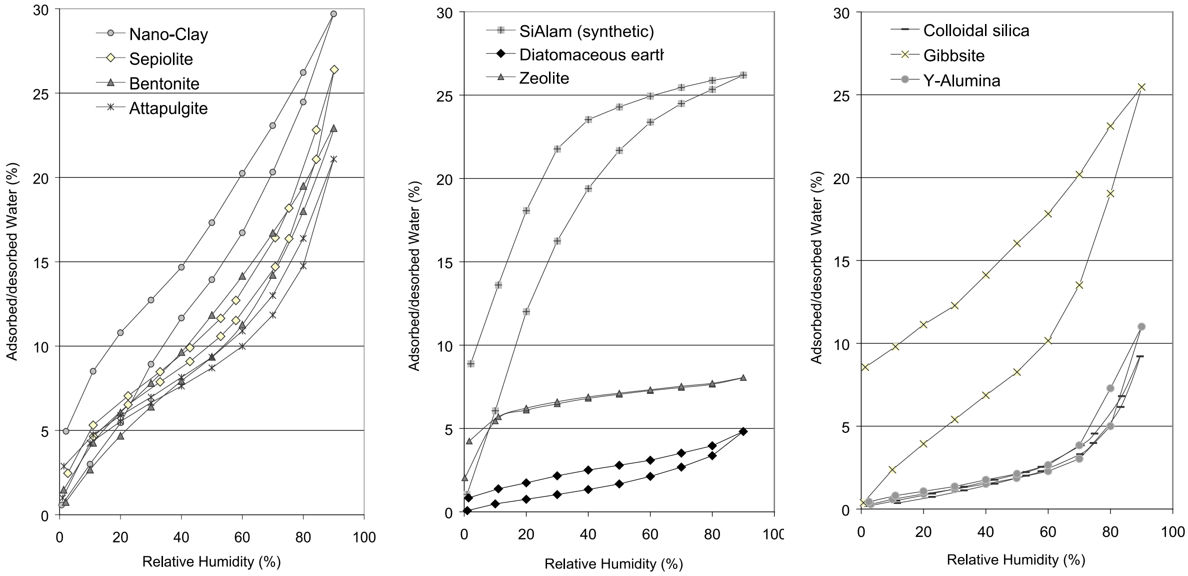

Figure 3 Water adsorption–desorption isotherms of the unfired test materials.

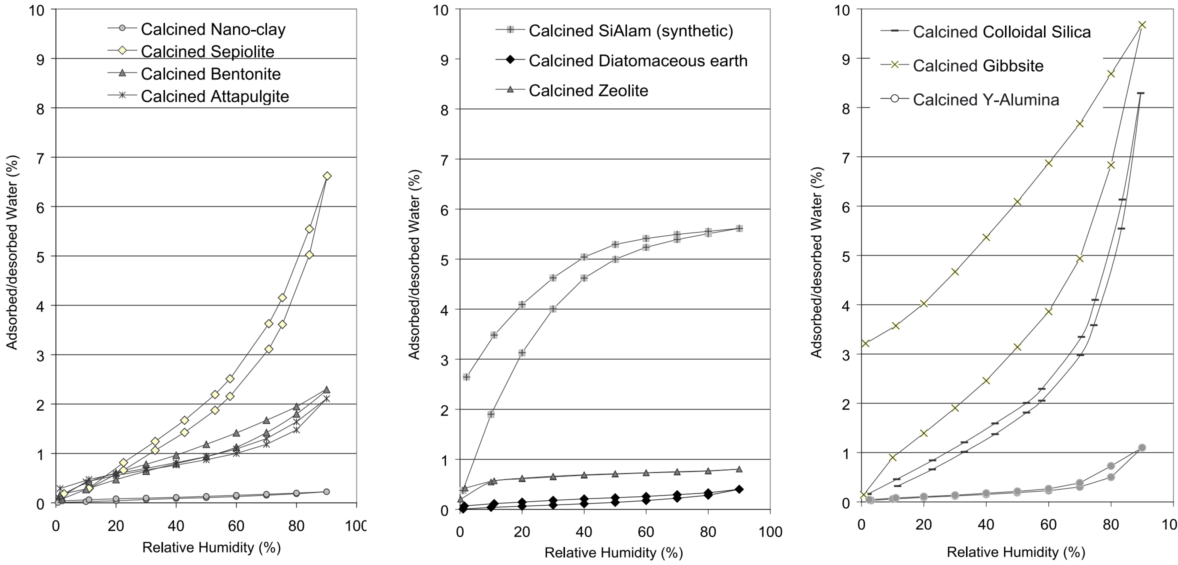

Figure 4 Water adsorption–desorption isotherms of the test materials calcined at 900ºC.

The results show that there were different adsorption curve shapes: the zeolite and, in particular, the synthetic amorphous aluminosilicate had different adsorption curves from the rest. The difference consisted in their being able to adsorb water and to reach their maximum water adsorption capability at low relative humidity percentages. This is very interesting from a technological viewpoint, since the typical average humidity values in buildings lie between 40 and 70% humidity.

In the test materials of a clayey nature, sepiolite was the material that had the greatest water adsorption capability, even at thermal treatment temperatures of 900ºC, and it was able to adsorb a maximum of 7% of its weight in water. Although materials such as the nano-clays, with unfired maximum adsorptions of 30%, had an enormous potential since they were the most reactive, they lost their structure more quickly and hence their adsorbent properties more readily than the other studied materials.

Of the materials included in the section on oxides and hydroxides, the precipitated silica (synthetic material) and the aluminium hydroxide (gibbsite) both exhibited good performances. However, the gibbsite, despite its excellent performance in preserving its specific surface area as well as in its water adsorption maximum, displayed a high hysteresis in the desorption curve. This entailed a limitation since, though it readily adsorbed humidity, it was unable to release it with the same ease. In addition, in spite of not displaying a significant reduction in its specific surface area with thermal treatment, its humidity adsorption properties were affected, which could be due to the aluminium hydroxide conversion into amorphous aluminium oxide at about 400ºC. This material maintains its specific surface area up to about 900ºC, since at higher temperatures it is transformed into corundum.

For composition preparation, three materials were chosen, one being of natural origin while the other two were synthetic, with good adsorption–desorption properties. In particular, sepiolite was chosen as natural raw material, and the aluminosilicate and the precipitated silica as synthetic raw materials.

3.2. Composition formulation and characterisation

3.2.1. Base composition

The characteristics of the fired test pieces made from the base composition used in conducting the tests are detailed below.

Bulk density (g/cm³)	Average pore diameter (μm)	Total pore volume (cm³/g)	Apparent porosity (%)	Bending strength (kg/cm²)	HRC (g/m²) 24h
1.745	1.20	0.190	33	175	<5

Table 5 Characteristics of the fired test pieces made from the base composition. Firing temperature 1100ºC.

3.2.2. Compositions with natural raw material: Sepiolite

The test compositions using sepiolite as raw material are given in Table 6.

	Composition 1	Composition 2	Composition 3	Composition 4
Base composition	95	90	80	75
Sepiolite	5	10	20	25

Table 6 Percentage by weight of the components of the different test compositions using sepiolite.

Different firing temperatures were used with a view to determining the variation with temperature of the parameters of interest: humidity-regulating capability, bending strength, average pore size, and porosity.

These parameters are plotted as a function of firing temperature in Figure 5.

The results of the different figures show that at every sepiolite percentage, when firing temperature was raised, the humidity-regulating capability and porosity decreased while mechanical strength and average pore size increased. In addition, at every firing temperature, when the sepiolite percentage was increased, the humidity-regulating capability rose while mechanical strength and average pore size decreased. The foregoing suggests that there was a close relationship between the humidity-regulating capability and average pore size.

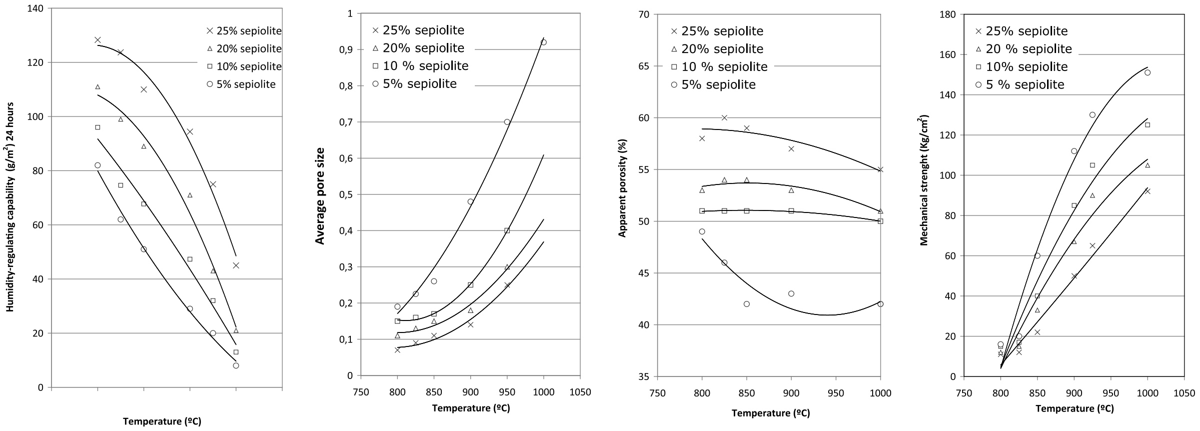

Figure 5 Plot of the variation of the humidity-regulating capability, average pore size, apparent porosity, and mechanical strength of different sepiolite compositions with peak firing temperature.

It was further observed, as was to be expected, that with the increase in porosity, either owing to decreased temperature or to sepiolite addition, the mechanical strength of the piece decreased, though this is not the only factor of influence because mechanical strength also depends on the crystalline/amorphous phases that form in thermal treatment.

A composition with 20% sepiolite, thermally treated at 900ºC, was able to provide a humidity-regulating capability of 95 g/m^2, an average pore size of 0.13 microns, a density of 1.19 g cm^{-3}, and a porosity of 57%. However, the bending strength was low, namely 71 kg cm^{-2}. In order to try to remediate this drawback, a low-temperature flux was added to the composition, in proportions not exceeding 1%, which raised its mechanical strength to 100 kg cm^{-2}, while hardly altering its humidity-regulating capability.

3.2.3. Compositions obtained from synthetic raw materials: aluminosilicate and precipitated silica

The compositions of the studied mixtures using the synthetic raw materials, i.e. aluminosilicate and precipitated silica, are detailed in Table 7. For economic reasons, the tested limit in this type of raw materials did not exceed 5% by weight of the total formula. The results obtained with these compositions are listed in Table 8.

Table 8 shows that mechanical strength increased in composition 5 in detriment to its humidity-regulating capability, whereas composition 6 developed precisely the opposite effect: that is, a good humidity-regulating capability and low mechanical strength.

	Composition 5	**Composition 6**
Base composition (%)	99	95
Adsorbent (%)	Synthetic $SiAl_{am}$: 1	Precipitated silica: 5

Table 7 Percentage by weight of the components of the different test compositions using the synthetic raw materials.

	Composition 5	**Composition 6**
Bending strength (kg/cm^2)	124	59
HRC (g/m^2) 24 h	32	119

Table 8 Bending strength and humidity-regulating capability of test pieces obtained from compositions that contained synthetic raw materials fired at 900ºC.

Research is currently on-going with a view to improving both compositions by optimising process conditions or the composition and adding some additive, in order to obtain maximum humidity adsorption with acceptable mechanical strength.

4. CONCLUSIONS

The possibility of obtaining ceramic compositions for fabricating tiles with a humidity-regulating capability was studied.

For this purpose, different natural and synthetic raw materials were studied that, a priori, might exhibit good humidity-regulating capabilities. It was verified that, though the specific surface area of the material influenced the quantity of adsorbed water, no clear relationship was found between specific surface area and the humidity adsorption capability of the material. Materials with similar specific surface areas displayed very different adsorption–desorption curves, indicating that the humidity-regulating capability phenomenon was intimately related to the porous structure of the material. Of the studied raw materials, the materials that displayed the best characteristics were the sepiolite (among the studied natural raw materials) and the precipitated silica (among the studied synthetic raw materials).

With relation to the composition formulations, a composition incorporating sepiolite (20%) was obtained with a good humidity-regulating capability (95 g/m^2) and acceptable mechanical strength (100 kg/cm^2). The use of synthetic compounds in humidity-regulating compositions needs to be optimised.

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