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CARBONATION PROCESS AND PROPERTIES OF A NEW LIME MORTAR WITH ADDED SEPIOLITE

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ABSTRACT

Sepiolite is a clay mineral ($Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4$) which due to its fibrous structure has considerable absorbent and adsorbent properties making of it an ideal material for supporting different products, such as toxines, oil, biocides, etc.
In this work, the influence of the sepiolite on the carbonation process of lime mortars with sand/lime 3/1 ratio, and also on the physical, chemical, mechanical and rheological properties as well as the microstructural characteristics of the same mortars has been studied.
It has been proved that sepiolite slows down the rate of carbonation process in these lime mortars due to its capacity for water adsorption without affecting the mechanical behaviour of the mortars. However, it has been observed that sepiolite affects the microstructural development of the composite.
The influence of the sepiolite on the rheological behaviour of these lime mortars has also been established by a mathematical equation which correlates the viscosity and the content of sepiolite in the mortar. This equation can also determine, for different water/(lime + sand) ratios, the optimum amount of sepiolite which could be added to the mortar for achieving the best plasticity.

INTRODUCTION

By definition, a mortar is an agglomerate composed of grains of sand joined together by a binder (lime, cement, etc.). It has a plastic consistency and is traditionally used as a building material.
Lime mortars were developed and used by the Roman civilization throughout its Empire, and calcium hydroxyde or slaked lime has been a typical binder in mortars since ancient times. Then, during the mid-18th century, hydraulic binders were discovered. This lime was then gradually replaced by hydraulic limes and finally by cement (second half of the 19th century). However, slaked lime continued to be used until the beginning of the 20th century (1).

Recently, some Roman mortars used to support mosaics in the Roman city of Italica, Spain, have been studied and characterized (2,3). This city was founded by the Romans in the second century A.D., and more than 133 mosaics and pavements have been catalogued. From this characterization study has been deduced that the main cause of deterioration in these lime mortars is a biological attack, with the colonization and development of organisms such as lichens, mosses, vascular plants, etc.

Reparation and restoration of historic monuments requires considerable knowledge of lime mortars. The first recommendation (4) when carrying out an intervention on any monument, is to use materials with physical and chemical characteristics, and similar properties to those of the original material to be replaced.

The main objective in this investigation is to develop a new repair mortar to support the mosaics, based on lime and with biocide characteristics capable of preventing the development of microorganisms.

Sepiolite ($Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4$) (5) has been chosen as a support material for the biocide. Besides, sepiolite is a very common mineral in Spain. This mineral has some properties and characteristics which make it an ideal material for this purpose. Among these are its high volume stability (it does not swell), its considerable chemical and structural stability in strongly basic media (6), and its considerable adsorbent and absorbent properties.

The properties of the sepiolite are closely related to its structure (see figure 1), which is made up of layers of tetrahedrons of silicon linked by oxygen atoms to a central octahedric plane of magnesium atoms. The silicon tetrahedrons are inverted every six units, which causes formation of longitudinal channels with dimensions of 3.6 x 10.6 Å (5). These channels are called zeolitic and give the sepiolite a high specific surface area

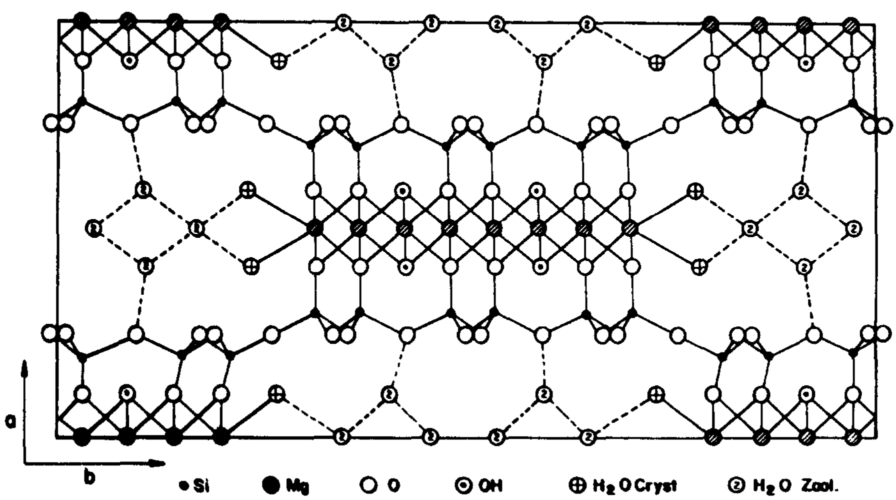

FIGURE 1
Structure of the sepiolite

which increases its adsorbent and absorbent properties. On the other hand, the weak surface load of sepiolite, together with the absence of swelling and the needle shape of its particles, confers a singular rheological behaviour on this material.

The objective of this work is to determine the influence of the sepiolite on the carbonation process of lime mortars, as well as the physical, chemical, mechanical properties and the rheological behaviour of this composite.

EXPERIMENTAL

The materials used to prepare the mortars were: sepiolite from Vallecas (Madrid, Spain) provided by TOLSA, sand and lime. Table I shows the chemical analyses of these materials.

TABLE I

Chemical Analyses of the Lime, Sand and Sepiolite

	SiO_2	MgO	Al_2O_3	CaO	Fe_2O_3	SO_3	PF*	IR**
Sand	98.92	0.28	0.18	0.00	0.06	0.00	0.05	0.40
Lime	0.39	0.00	1.10	73.82	0.20	0.00	24.45	0.02
Sepiol	55.10	19.43	5.91	5.13	1.96	0.00	12.02	0.10

* Loss of ignition at 1000ºC ** Insoluble residue in HCl 1:5

In Table II the different compositions of prepared lime mortars are shown. The samples containing 1 and 5% weight of sepiolite have a water/(lime+sepiolite) ratio of 0.9, while the samples with 10% of sepiolite were prepared with a water/(lime+sepiolite) ratio of 1.1, as a lower amount of water did not permit an adequate mixture.

Mortar test cubes with sides measuring 35 mm were prepared. Initial curing in all cubes was identical and carried out as follows: for the first 3 days the samples were maintained in the moulds and subjected to carbonation by CO_2 flow in a chamber having a relative humidity of 50%. After this time, all cubes were demoulded and their subsequent curing processes were different according to the objectives previously established by this work:

a) In order to determine the influence of sepiolite on the rate of the carbonation process of the lime mortars. The samples were maintained in the carbonation chamber for three days more, then dried for one hour in an oven at 105ºC. They were subsequently weighed and returned to the carbonation chamber. This cycle was repeated until the test cubes achieved a constant weight, considered as total carbonation of the mortars. This was confirmed by analysis of $Ca(OH)_2$ content through the ethylene-glycol method (7).

b) In order to evaluate the influence of sepiolite on the physical, chemical and mechanical properties and characteristics. The test cubes were maintained during 28 days in the carbonation chamber, and then the following tests were carried out:

TABLE II

Lime Mortar Compositions

sand/lime	% sepiolite add	water/(lime+sand)
3/1	0	0.9
3/1	1	0.9
3/1	5	0.9
3/1	10	1.1

TABLE III

Compositions of the Mortars Used in the Rheological Study.

sand/lime	water/(lime+sand)	% sepiolite
3/1	0.23	0 0.5 1 3
3/1	0.30	0 3 5
3/1	0.40	0 3 7 10 15
3/1	0.52	0 3 15 20

1. Compressive strength.
2. Porosity accessible to water.
3. Free $Ca(OH)_2$ content.
4. Microstructural analysis through SEM/EDX.

The influence of sepiolite on the rheological behaviour of the lime mortars was studied by preparing samples with sand/lime ratio 3/1, according to Spanish standard (8), and adding different amounts of sepiolite. Several water/(lime+sepiolite) ratios were studied. The compositions prepared are shown in Table III. The rate of flow of these mortars in a plastic state was measured with a maniabilimeter. This test was carried out in accordance with a French standard (9).

RESULTS AND DISCUSSION

1. Influence of sepiolite on the carbonation process in lime mortars (sand/lime ratio ≈ 3/1)

Figure 2 shows the weight evolution of lime mortars (3/1) (with and without sepiolite) with time.

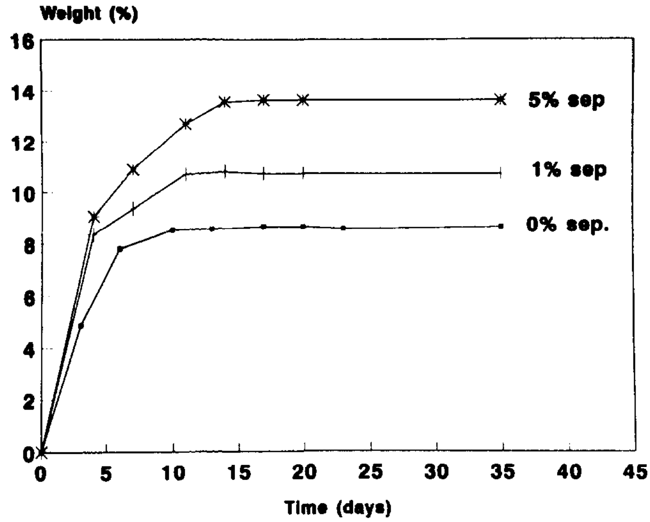

FIGURE 2
Weight versus time relationship for the different mortars

The following observations can be done when analyzing Figure 2:

(i) Mortars containing sepiolite are slightly heavier than mortars not containning the additive.
This is justified on the basis of the structure of the sepiolite. The adsorbent properties of the sepiolite are due both to the internal zeolitic channels and to the external silanol groups (Si-OH). Sepiolite is consequently capable of retaining a considerable amount of water.

(ii) The time at which mortars reach constant weight increases with the amount of sepiolite. So, in the mortar without sepiolite and with the drying process applied in this test, total carbonation is achieved in 10 days, while in the mortar with 10% sepiolite, the total carbonation is not achieved until 18 days. Therefore, sepiolite delays the carbonation process in 3/1 lime mortars.

As known, the variation in the rate of the carbonation process of portland cement concrete at room temperature depends on the relative humidity (RH) (10). So, when relative humidity reaches values above 85% or lower than 40%, the degree of this reaction decreases sharply. In the first case, the controlling step from the kinetic point of view is the diffusion of the CO_2 dissolved in the superficial water towards the interior of the material, whose porous system is almost saturated with water. In the second case, the CO_2 easily diffuses towards the interior of the material and the controlling step of the reaction is the dissolution of the CO_2. The rate of the carbonation process is maximum when the relative humidity is between 50 and 70%.

The decrease in the velocity of the carbonation process in the mortars containing sepiolite is thought to be fundamentally due to the fixing of water molecules on the surface of the sepiolite through the silanol groups by hydrogen bridges. Therefore, more sepiolite in the mortar produces more water adsorption capacity. The test was carried out at a relative humidity of 50%, and in this situation, while the free water decreases, the CO_2 dissolution also decreases, so the rate of carbonation is slower.

2. Influence of sepiolite on the physical, chemical and mechanical properties of lime mortars (sand/lime = 3/1)

All the samples analyzed in this section have been constantly cured in the carbonation chamber during 28 days.

Table IV shows the values of compressive strength for the whole of the studied lime mortars, together with free $Ca(OH)_2$ content. Porosity accessible to water and density of the samples are also given.

TABLE IV

Physical, Chemical and Mechanical Properties

Sample	**Strength (MPA)**	**Porosity (%)**	**Density (g/cm^3)**	**% wt free lime**
0%	5.4	29.77	1.804	0.46
1%	4.8	30.84	1.794	0.57
5%	5.2	30.53	1.726	0.15
10%	4.1	39.42	1.574	0.07

Figure 3 shows the evolution of compressive strengths and free $Ca(OH)_2$ content versus amount of sepiolite in the mortar.

The results obtained show that sepiolite, up to 5% wt, slightly modifies the mechanical behaviour of the mortars. The slight decrease of strengths observed in these mortars is due to the fact that the sepiolite is replacing lime, and therefore the final materials have a smaller quantity of the $CaCO_3$ binding component. The small differences in the porosity values of the mortars with and without sepiolite are due to the experimental method.

The mortar having 10% sepiolite behaves different to the others. Its compressive strenght and density are slightly lower, while its porosity is notably higher. The higher water/(lime + sepiolite) ratio necessary for these mortars to be formed explains the different characteristics described.

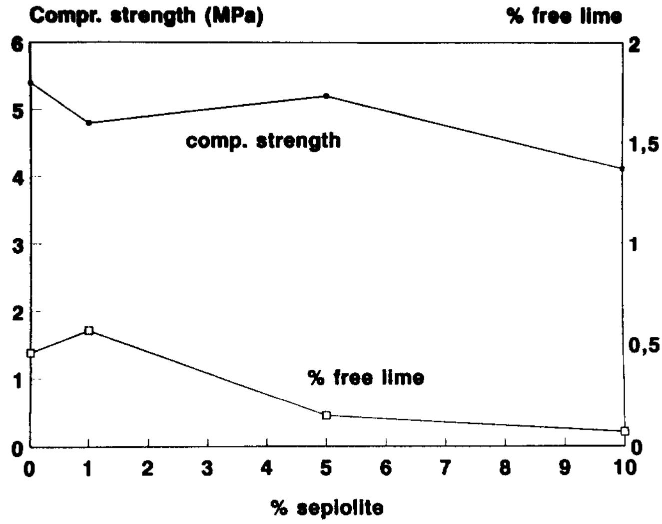

FIGURE 3
Compressive strenght and free lime versus amount of sepiolite in the mortar

Micrograph nº 1
General aspect of the mortar without of sepiolite

Micrograph nº 2
General aspect of the mortar with 1 % of sepiolite

The microstructural analysis carried out by SEM/EDX on these mortars has shown that sepiolite fundamentally modifies the nature and size of the $CaCO_3$ crystals. Micrographs 1-4 show general aspects of the mortars having 0, 1, 5 and 10% respectively. It can be deduced from these micrographs that sepiolite causes the $CaCO_3$ to be present in larger and more coherent particles, creating larger spaces or hollows. In micrograph 4, corresponding to the mortar with 10% sepiolite, small needles can be seen in the bulk of the mortar, which are the needle shaped particles of sepiolite. Micrograph 5 shows the details of a particle of sepiolite in the mortar.

Micrograph nº 3
General aspect of the mortar
with 5% of sepiolite

Micrograph nº 4
General aspect of the mortar
with 5 % of (sep+bioc)

Micrograph nº 5
Particle of sepiolite in the mortar

The addition of sepiolite to lime mortars modifies the texture not only by introducing a new microstructural element, of needle morphology, but also by its adsorbent capacity which modifies the velocity of carbonation and the quantity of free water in the porous system, causing the previously mentioned microstructural modification.

3. Influence of sepiolite on the rheological properties of lime mortars.

Figure 4 shows the flow time in mortars depending on the amount of sepiolite added. Maximum flow time was 20 minutes. It can be observed that for the same percentage of sepiolite, on increasing the water/(lime+sand) ratio, the flow time decreases.

For a fixed water/(lime+sand) ratio, when the percentage of sepiolite is increased, the flow time increases, which way indicates that the viscosity of the mortar also increases. This increase reaches a viscosity that even prevents workability.

The curves in Figure 4 show a similar tendency, with a line almost parallel to the x axis (except for the water/(lime + sand) ratio 0.23), from which a sudden rise in the flow time is produced; so, for each water/(lime + sand) ratio there is a critical amount of sepiolite associated to a marked increase in the viscosity of the mortar.

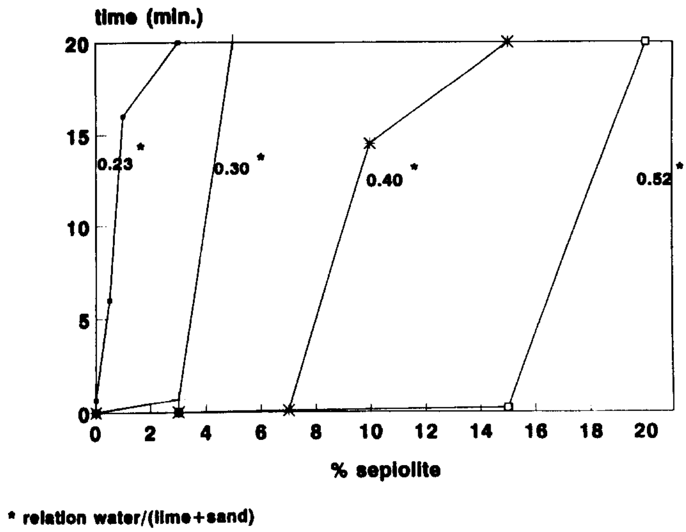

FIGURE 4
Flow time versus amount of sepiolite added for different mortars.

The four curves were fitted to the same mathematical equation:

$$y=0.5a_0[1+erf[(x-a_1)/a_2\sqrt{2}]] \quad (1)$$

where y is the flow time; x is the percentage of sepiolite added to mortar; a_0, a_1, a_2 are curve-fit coefficients and erf (x) is an error function:

$$erf(x)=\frac{2}{(\sqrt{\pi})}*\int_0^x \frac{1}{e^{u^2}}du$$

and a_0, a_1 and a_2 are constants for each water/(lime+sand) ratio. In Table V the values of these constants are presented.

By increasing the water/(lime+sand) ratio, for a constant content of sepiolite in the mortar (x), the values of a_1 and a_2 increase.

Figure 5 shows the fitted curves corresponding to the four water/(lime+sand) ratios studied.

Function (1) has a minimum and a maximum. The minimum corresponds to the critical value of sepiolite (P_{min}) from which the viscosity of the mortar abruptly increases, and the maximun point (P_{max}), corresponds to the other critical value of sepiolite from which the paste is so viscous that it is not workable at all. Both points are determined from the fitted curves and correspond to the inflextion points in the curves. The values of these points for each one of the water/(lime+sand) ratios studied are presented in Table VI.

TABLE V

Values of the Constants a_i for the Differents Water/(Lime+Sand) Relationship

H_2O/(lime+sand)	a_o	a_1	a_2
0.23	20.01	0.69	0.37
0.30	25.11	4.39	0.73
0.40	20.00	9.46	9.46
0.52	17.19	17.19	17.19

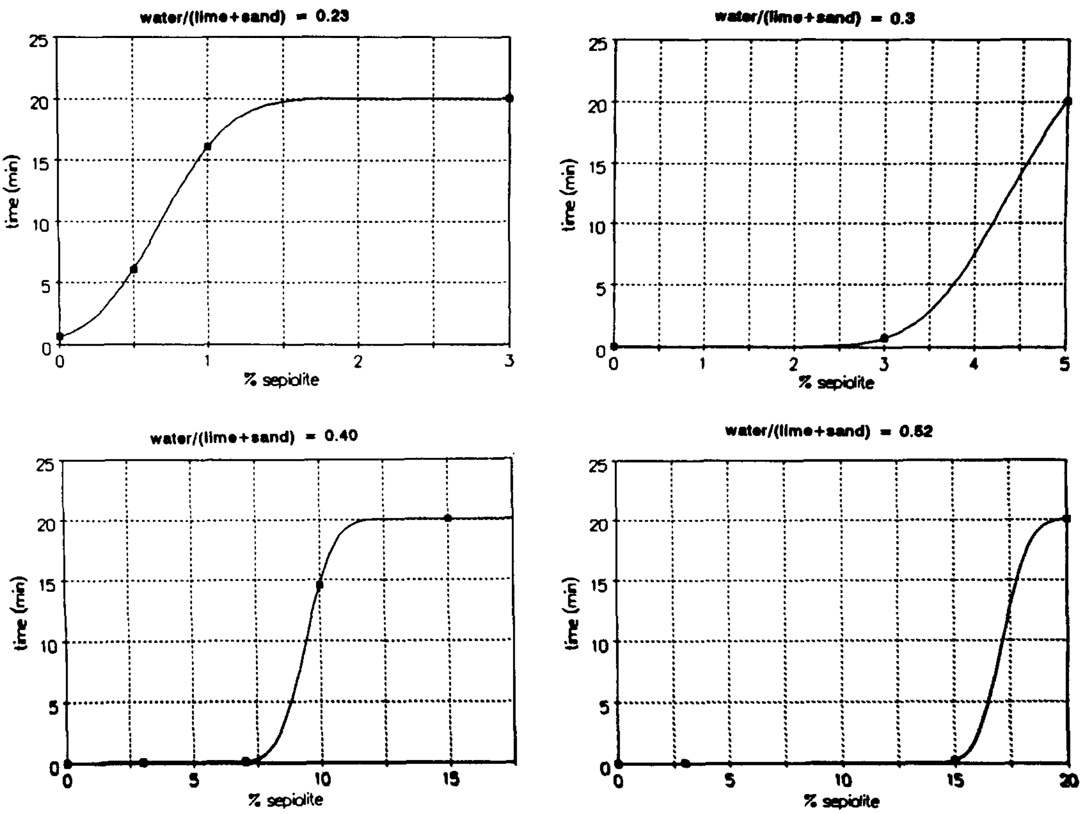

FIGURE 5
Fitted curves corresponding to the four water/(lime+sand) ratios

Figure 6 presents the existing correlation between the critical value of sepiolite (P_{min}) and the water/(lime+sand) ratio of the mortar. As it is shown in this figure, this ratio is lineal in type, meaning that from here it is possible to calculate, for a given water/(lime+sand) ratio in 3/1 mortars, the minimum quantity of sepiolite which should be added to the mortar to improve workability.

TABLE VI

Maximun and Minimum Points, Amount of Water Relationship

H_2O/(lime+sand)	P_{min}	P_{max}	Pto inflexion
0.23	0.15	1.23	0.69
0.30	3.36	5.43	4.39
0.40	8.17	10.75	9.46
0.52	15.83	18.55	17.19

For a constant addition of sepiolite, the increase of the water/(lime + sand) ratio leads to a decrease in viscosity of the mortar. The indirect measurement of viscosity, as indicated in the experimental section, is carried out by vibration, which is why suspensions of high viscosity are produced.

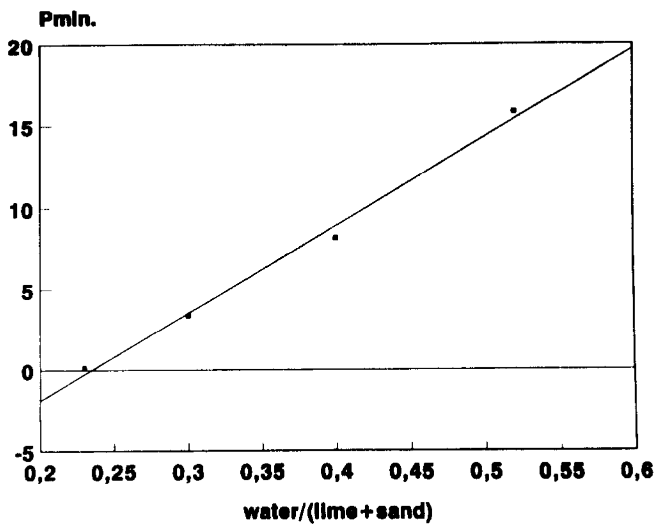

FIGURE 6
Amount of minimun sepiolite versus water/(lime+sand) ratio.

At the begining the viscosity of the mortar is low due to the high content of free H_2O. However, since the experiment is carried out by vibration so that the sepiolite fibers disperse, forming a network of high viscosity, and although the content of free H_2O is high, the effect of the orientation of the sepiolite particles prevails. The greater is the water/(lime+sand) ratio, and hence the water content, the longer the time necessary for forming the network of particles of sepiolite.

CONCLUSIONS

Sepiolite decreases the rate of carbonation process of lime mortars due to its capacity for water adsorption, which provokes a decrease in the content of free water in the porous system of the mortar. This decrease impedes or makes CO_2 dissolution difficult, a step which, from the kinetic point of view, controls the carbonation process.

Incorporation into the mortar less than 5% sepiolite by weight does not affect the mechanical behaviour of the mortar. However, it appears to affect the microstructural development of the paste with high $CaCO_3$ packing and crystal size.

The presence of sepiolite in the mortar significantly alters its rheological behaviour. The following mathematical equation correlates the viscosity of the mortar and the content of sepiolite:

$$y=0.5a_0[1+erf[(x-a_1)/a_2\sqrt{2}]]$$

From this equation a method has been proposed to determine the optimum content of sepiolite to add to the 3/1 mortars, so that its plasticity is suitably adequate when the water/(lime+sand) ratio is modified.

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