STUDY OF THE PHYSICAL PROPERTIES OF HYDRAULIC AND RESIN BOUND MORTARS USED FOR MAKING SCULPTURE REPLICAS FROM *TOSCA DE ROCAFORT* AND *BATEIG* STONES

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ABSTRACT: *This work presents the results obtained from the evaluation of mortars applied in the elaboration of replicas in the conservation and restoration of artistic and monumental heritage (sculptures and ornamental pieces). Two types of mortars have been studied, using Tosca de Rocafort (a variety of Godella stone) and Bateig (a variety of Novelda stone) stones as fillers: a) mortars using inorganic hydraulic binders and b) resin bound mortars using polymeric binders.*
These lithic materials, present in the Valencian Region, can be found in outstanding monuments in the city of Valencia (La Lonja, Cathedral, Serranos Gate, among others) where they exhibit considerable physical, chemical and biological deterioration.
In contrast to the case of hydraulic mortars, scientific studies aimed at the optimisation of resin bound mortar preparation are rarely found in literature despite the fact that their use is widely extended all over Europe. Similarly, little information concerning these two types of stone materials was found (Roig Salom, 1995; Mas i Barberà, 2006).
In this research, values of porosity accessible to water, water absorption, bulk densities and real densities, saturation coefficient and compression and flexion strength have been determined on a series of test specimens prepared with polyester and acrylic resin, as well as lime-gypsum, as binders of the mortars. The experiments performed have led the authors to establish that the studied resin bound mortars have higher stability and resistance properties in comparison to those made of hydraulic mortars and natural stone.

KEYWORDS: replica, resin bound mortars, hydraulic mortar, composite, Bateig stone, Tosca de Rocafort stone, SEM/EDX, mechanical tests

INTRODUCTION

Most stone materials used for monuments suffer degradation when they are exposed to the elements, and therefore, the study of their physical/chemical properties, as well as the alteration mechanisms taking place, is essential as a prior step to an intervention process on stone monuments. In addition, Davis and Sims (1983) have shown the importance of knowing the properties of the materials to be used alongside the original natural stone in the intervention process on the monument since a minimum resemblance between the original material and the intervention mortar in appearance, texture and colour is essential in conservation. This issue is of interest in extreme environments where the materials present a rapid loss of their physical and chemical properties. In more recent works (Rosier, 1990, Roig Salom, 1995, Cavallini and Chimenti, 2000, Mas i Barberà, 2006), replacement of the whole or a missing part of the original sculpture or ornamental piece has been proposed as an alternative to *in situ* conservation of the monument. In such instances, the original pieces are reinstalled in museums or indoor locations where environmental conditions can be controlled.

This paper presents an approach to the study of hydraulic and resin bound mortars applied to the conservation of stone monuments, especially in treatments such as sealing, replacement of missing parts or elaboration of a replica of the altered sculpture or the ornamental piece, as an alternative to natural stone. The mortars have been prepared from hydraulic and organic polymeric binders using *Tosca de Rocafort* and *Bateig* stone as fillers. The binder mainly determines the cohesive properties of the mortar, whereas the particle size distribution of the filler, the major component of the mortar, influences the its mechanical properties. Nevertheless, the physical and chemical properties of the mortar depend simultaneously on both the filler and the binder selected, as well as on their content and morphology (Roig Salom, 2003).

Values of porosity accessible to water, water absorption, bulk densities and real densities, saturation coefficient and compression and flexion strength have been determined on a series of test specimens prepared with polyester and acrylic resin, as well as lime-gypsum, as binders of the mortars.

EXPERIMENT PROCEDURE

Instrumentation

- The morphological examination and chemical composition of the test specimens were obtained using a Jeol JSM 6300 Scanning Electron Microscope operating with a Link-Oxford-Isis microanalysis system. The analytical conditions were: 20 kV accelerating voltage, 2x10-9A beam current and 15 mm working distance. Samples were carbon coated to eliminate charging effects.

-Analytical balance from precise instruments model BJ410 C, ISO 9001.
-Leica GZ6 stereoscopic microscope equipped with a Leica CLS100 cold light source with ring lamp.

Specimen preparation

A series of hydraulic and resin bound mortar test specimens have been prepared in which finely ground *Tosca de Rocafort* and *Bateig* stone powder, with particle size ranging between 0-1000 µm, has been bound with a hydraulic or synthetic resin binder. In parallel, a series of test specimens prepared with original stones have been prepared for use as reference materials. The composition of the obtained test specimens is summarized in Table 1 and Figure 1.

Series A: Test specimens were prepared using Estratil AL-100 (Rhone Poulenc), a polyester prepolymer dissolved in styrene, acting as a reactive monomer (33%). The copolymerisation reaction was catalysed by cobalt octoate incorporated into the initial prepolymer solution (0.2%). The reaction was initiated by adding ethylmethylketone peroxide (2%). The polymerisation reaction was produced at room temperature and the curing time was 25 min (see Table 1).

Series B: Test specimens were prepared using Plasticrete P-Cast A0-2 bi-compound acrylic resin (Camattini SPA) (Table 1).

Series C: Test specimens using aerial lime (Lafarge) and Alamo 70 gypsum (MSW Corporation) have been prepared in which two different additives, Mowilith SDM5 (Rohm and Haas) or Boric acid (Panreac) are added, for reinforcing the structure (Table 1).

RESULTS AND DISCUSSION

Water absorption

The water absorption test was carried out following the Normal 7/81 (1981) recommendation on (50x50x50) mm test specimens. Three replicas were used in order to assess the repeatability of the method.

Figure 2 shows a higher water absorption value in the specimens elaborated with lime/gypsum mortars, while acrylic mortars exhibit a lower value, close to that of natural stone. In contrast, the polyester mortars show the lowest values, denoting an almost complete absence of water absorption.

On the other hand, lime/gypsum mortars show rapid water absorption during the first hour, after which time water absorption values gently

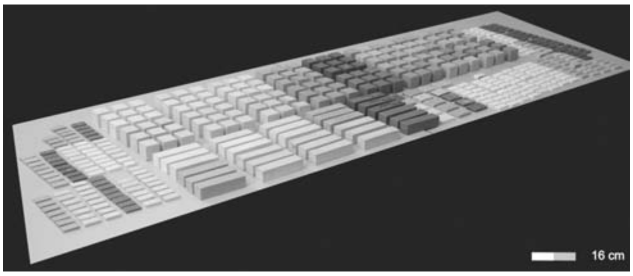

Figure 1. Test specimens used in the different laboratory tests were prepared in the laboratory from Silastic 3483 silicone elastomer moulds. Test specimens were prepared to attend to procedure rules from DIN, UNE, ASTM and RILEM

POLYESTER RESIN BOUND MORTAR (MP-BC)		
Reference		BATEIG STONE **(BC)** **COMPOSITION (WEIGHT %)**
MP- BC	Powdered Bateig stone Particle size distribution: (0.80-1.00) mm	64.0
	Powdered Bateig stone Particle size distribution: (0.06-0.25) mm	19.5
	Polyester resin ESTRATIL AL 100	16.5
POLYESTER RESIN BOUND MORTAR (MP-TR)		
		TOSCA DE ROCAFORT **(TR)** **COMPOSITION (WEIGHT %)**
MP-TR	Powdered Tosca de Rocafort stone Particle size distribution: (0.25-0.42) mm	66.6
	Powdered Tosca de Rocafort stone Particle size distribution: (0.06-0.25) mm	16.7
	Polyester resin ESTRATIL AL 100	16.7

Table 1. Composition of the different test specimens:
Serie A) polyester resin bound mortars

ACRYLIC RESIN BOUND MORTAR (MA-BC)		
		BATEIG STONE **(BC)** **COMPOSITION (WEIGHT %)**
MA-BC	Particle size distribution: (0.80-1.00) mm	56.9
	Bayer shade natural pigment	0.40
	Acrylic resin PLASTICRETE P-CAST A 02	42.7
ACRYLIC RESIN BOUND MORTAR (MA-TR)		
		TOSCA DE ROCAFORT **(TR)** **COMPOSITION (WEIGHT %)**
MA-TR	Particle size distribution: (0.25-0.42) mm	39.7
	Particle size distribution: (0.06-0.25) mm	9.9
	Acrylic resin PLASTICRETE P-CAST A 02	49.6
	Bayer ochre natural pigment	0.3
	Bayer shade calcine natural pigment	0.5

Table 1. Serie B) acrylic resin bound mortars

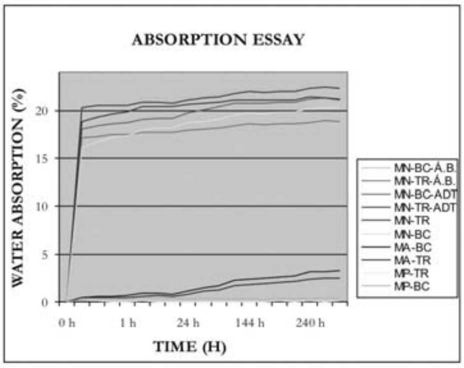

Figure 2. Water absorption values of the mortars elaborated

Figure 3. Porosity values of the mortars elaborated

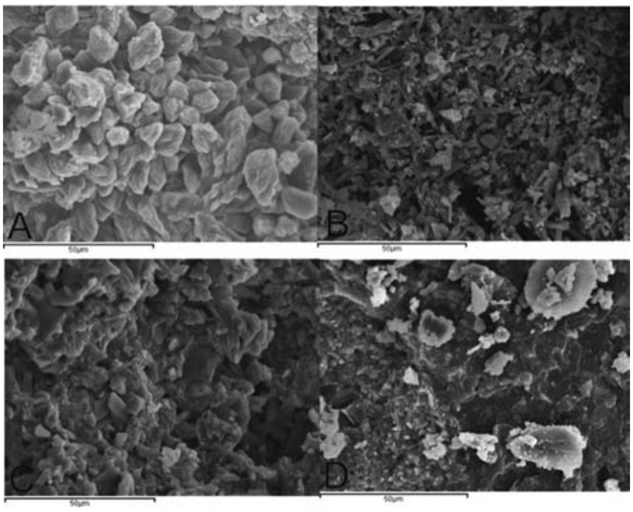

Figure 4 (a-d). Internal structures of the mortars studied compared with the Tosca de Rocafort natural stone: a) Tosca de Rocafort-natural stone; b) Tosca de Rocafort-lime and gypsum mortar with Mowilith SDM5; c) Tosca de Rocafort-acrylic mortar.; d) Tosca de Rocafort-polyester mortar

<table>
<tr><th colspan="3">HYDRAULIC MORTAR (MN-BC-ADT)</th></tr>
<tr><td></td><td></td><td>BATEIG STONE (BC)
COMPOSITION (WEIGHT %)</td></tr>
<tr><td rowspan="5">MN-BC-ADT</td><td>Particle size distribution: (0.42-0.80) mm</td><td>46.6</td></tr>
<tr><td>Gypsum ALAMO 70</td><td>23.3</td></tr>
<tr><td>Aerial lime</td><td>11.7</td></tr>
<tr><td>Water + Mowilith SDM5</td><td>17.5</td></tr>
<tr><td>Bayer shade calcine natural pigment</td><td>0.9</td></tr>
<tr><th colspan="3">HYDRAULIC MORTAR (MN-TR-ADT)</th></tr>
<tr><td></td><td></td><td>TOSCA DE ROCAFORT (TR)
COMPOSITION (WEIGHT %)</td></tr>
<tr><td rowspan="6">MN-TR-ADT</td><td>Particle size distribution: (0.42-0.80) mm</td><td>46.2</td></tr>
<tr><td>Gypsum ALAMO 70</td><td>23.1</td></tr>
<tr><td>Aerial lime</td><td>11.5</td></tr>
<tr><td>Water + Mowilith SDM5</td><td>17.3</td></tr>
<tr><td>Bayer ochre 920 natural pigment</td><td>0.6</td></tr>
<tr><td>Bayer shade calcine natural pigment</td><td>1.3</td></tr>
<tr><th colspan="3">HYDRAULIC MORTAR (MN-BC-AC.BOR)</th></tr>
<tr><td></td><td></td><td>BATEIG STONE (BC)
COMPOSITION (WEIGHT %)</td></tr>
<tr><td rowspan="5">MN-BC-AC.BOR</td><td>Particle size distribution: (0.42-0.80) mm</td><td>46.6</td></tr>
<tr><td>Gypsum ALAMO 70</td><td>23.3</td></tr>
<tr><td>Aerial lime</td><td>11.7</td></tr>
<tr><td>Water + Boric acid</td><td>17.5</td></tr>
<tr><td>Bayer shade natural pigment</td><td>0.9</td></tr>
<tr><th colspan="3">HYDRAULIC MORTAR (MN-TR-AC.BOR)</th></tr>
<tr><td></td><td></td><td>TOSCA DE ROCAFORT (TR)
COMPOSITION (WEIGHT %)</td></tr>
<tr><td rowspan="6">MN-TR-AC.BOR</td><td>Particle size distribution: (0.42-0.80) mm</td><td>46.2</td></tr>
<tr><td>Gypsum ALAMO 70</td><td>23.1</td></tr>
<tr><td>Aerial lime</td><td>11.5</td></tr>
<tr><td>Water + Boric acid</td><td>17.3</td></tr>
<tr><td>Bayer ochre 920 natural pigment</td><td>0.6</td></tr>
<tr><td>Bayer shade calcine natural pigment</td><td>1.3</td></tr>
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Table 1. Serie C) lime/gypsum mortars.

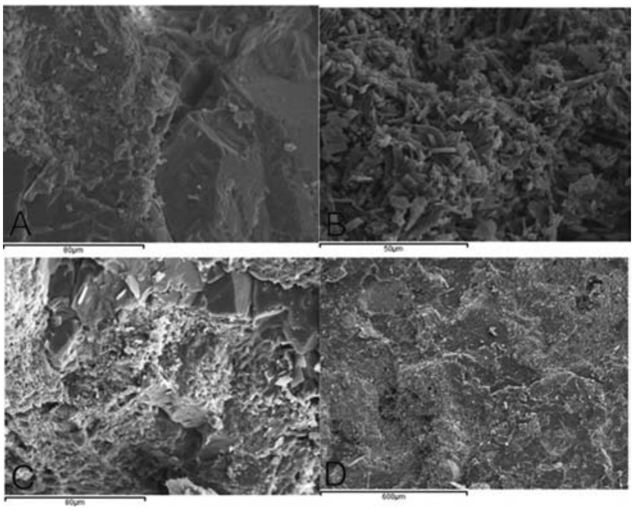

Figure 5 (a-d). Internal structures of the mortars studied compared with the Bateig natural stone: a) Bateig-natural stone; b) Bateig-lime and gypsum mortar with Mowilith SDM5; c) Bateig-acrylic mortar; d) Bateig-polyester mortar

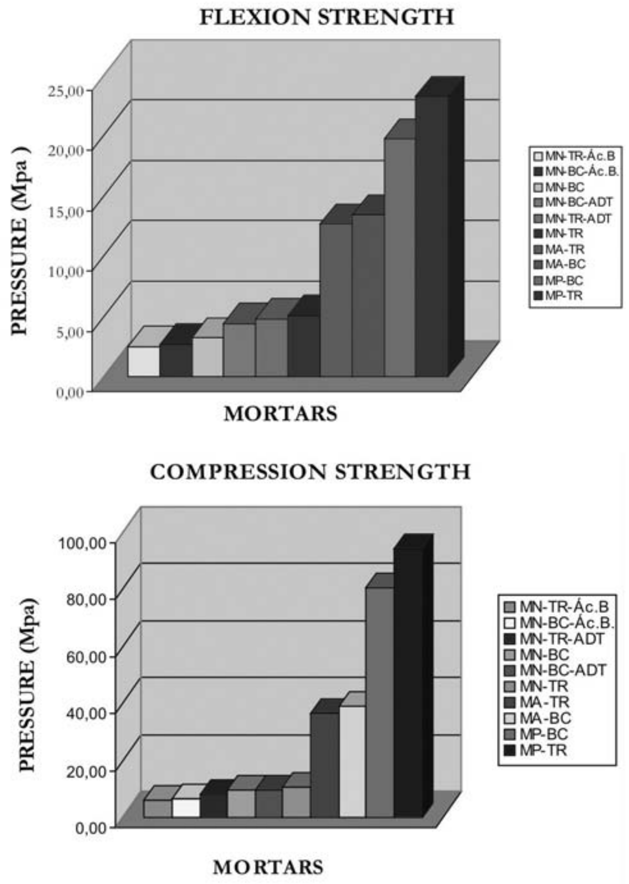

Figure 6. Comparison of the compression and flexion strength values of the different mortars versus natural stones.

increase until the saturation value, which is achieved at 244 hours. In contrast, appreciable changes in the water absorption values of resin bound mortars are not observed before 144 hours and the saturation values are achieved at 258 hours. The differing behaviour between the two types of mortars studied concurs with the higher porosity exhibited by the lime/gypsum mortars in comparison to the acrylic and polyester mortars.

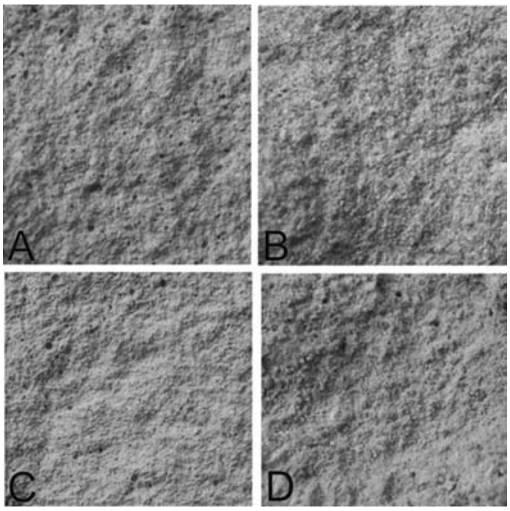

Figure 7. Comparison of the surface of the different mortars versus natural stones after the compression and flexion strength

Porosity accessible to water

The porosity accessible to water test was carried out using the RILEM I.1 recommendation. In this case, three specimens with a size of (50x50x50) mm were used.

The synthetic mortars show very low porosity values (Figure 3), manifesting good binding properties as regards the powder in the mixture (Figure 4.d; 5.d). Only lime/gypsum mortar with the acrylic resin additive showed lower porosity values (Figure 4.c; 5.c).

Bulk and real densities

This test was carried out following the RILEM I.2 recommendation on (50x50x50) mm test specimens. Three replicates were used in order to assess the repeatability of the method.

Table 2 summarizes the values of density for the set of test specimens studied. The largest values of real densities were obtained from natural stone specimens (*Tosca de Rocafort*: 2.46 g/cm^3 and *Bateig*: 2.62 g/cm^3). Hydraulic mortars exhibited values slightly lower than those obtained from the natural stones, and resin bound mortars exhibited the lowest values (1.95 g/cm^3 for *Tosca de Rocafort* and 1.92 g/cm^3 for *Bateig* mortars). On the other hand, the bulk density values found in resin bound mortars were close to those of real density. In contrast, natural stones exhibited a slight decrease in the bulk density value, and a significant decrease in the bulk density values for hydraulic mortars was found. These results concur with the previous experiments, as differences in density values can be associated with the degree of porosity exhibited by the material. Thus, the larger the difference between real and bulk density, the larger the network of interconnected pores in the stone.

Saturation coefficient

This test was carried out following the RILEM II.1 recommendation on (50x50x50) mm test specimens. Three replicates were used in order to assess the repeatability of the method.

Table 3 summarizes the density values for the set of test specimens studied. The results obtained from original stone are similar to those found in hydraulic lime/gypsum mortars and notably higher than those from resin bound mortars. The significantly lower saturation coefficient values exhibited by polyester mortars (2.21% and 3.8%, respectively) should be noted, which denote the notably low porosity present in these mortars.

Mortar	Real density (g/cm^3)	Standard deviation (S)	Bulk density (g/cm^3)	Standard deviation (S)
Stone TR	2.46	0.01	1.99	0.03
Stone BC	2.62	0.01	2.28	0.01
MN-TR	2.30	0.02	1.64	0.01
MN-BC	2.35	0.01	1.64	0.01
MN-TR-ADT	2.02	0.01	1.33	0.00
MN-BC-ADT	2.08	0.02	1.54	0.01
MN-TR-AC. BOR	2.28	0.02	1.62	0.01
MN-BC-AC. BOR	2.24	0.00	1.63	0.00
MA-TR	1.84	0.01	1.82	0.01
MA-BC	1.94	0.00	1.90	0.00
MP-TR	1.95	0.00	1.94	0.00
MP-BC	1.92	0.01	1.91	0.01

Table 2. Real densities and bulk densities. Values obtained for the mortars studied.

Mortars	Saturation coefficient (%)	Standard deviation (S)
Stone TR	75.6	0.4
Stone BC	71.9	0.2
MN-TR	78.41	0.1
MN-BC	74.14	0.02
MN-TR-ADT	74.1	0.1
MN-BC-ADT	73.46	0.03
MN-TR-AC.BOR	78.76	0.02
MN-BC-AC.BOR	79.89	0.03
MA-TR	27.9	0.9
MA-BC	35.6	0.7
MP-TR	2.21	0.09
MP-BC	3.8	0.8

Table 3. Saturation coefficient values obtained for the studied mortars.

Compression and flexion strength

The compression and flexion strength essay was carried out under the UNE-EN-196-1 recommendation for test methods on cements. In this case, three specimens with a size of (160x40x40) mm were used.

If we observe Figure 6.a. corresponding to the flexion strength essay, we can see significant differences between the series of mortars. The results obtained from the synthetic mortars are higher than the lime/gypsum mortar values. In the same way, the acrylic mortars show similar values to the quarry stone. Regarding the compression strength essay (Figure 6.b.), the synthetic mortars continue to be more durable than the lime/gypsum mortars and the quarry stone, especially the polyester mortars, which evidence excellent properties of adhesion as well as conglomerate. Figure 7 shows the fracture surface obtained from the lime/gypsum mortars, acrylic mortars and quarry stone after the flexion strength. In these cases, a likeness in colour and structure was obtained.

CONCLUSIONS

-The water absorption values obtained from acrylic bound mortars are similar to natural stone. In the lime/gypsum mortars, they are higher, whereas those of the polyester mortars are practically null.

-The hydraulic bound mortar test specimens (MN) possessed a similar porous internal structure to the natural stone. However, the synthetic mortars (MA and MP) exhibited a shortage of porous characteristics.

-The synthetic mortars possess much lower bulk densities and real densities than the hydraulic bound mortars, which evidence major porosity that is higher than that of quarry stone.

-In the saturation coefficient essay, the acrylic and polyester mortars exhibited low values while those of the hydraulic mortars are similar to quarry stone.

-The hydraulic bound mortar test specimens (MN) submitted to compression and flexion strength tests showed values slightly below those of natural stone. However, synthetic mortar test specimens surpassed the forecasted expectations .

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Versión española

TITULO: Estudio de las propiedades físicas de los morteros de aglutinantes hidráulicos y de resina aglutinada usados para hacer réplicas de esculturas de las piedras Tosca de Rocafort y Bateig

RESUMEN: *Este trabajo presenta los resultados obtenidos en la evaluación de morteros aplicados a la elaboración de replicas en conservación y restauración del patrimonio artístico y monumental (esculturas y piezas ornamentales). Se han estudiado dos tipos de morteros usando como relleno las piedras tosca de Rocafort (una variedad de la piedra Godella) y Bateig (variedad de la piedra Novelda): a) morteros que usan aglutinantes hidráulicos inorgánicos y b) morteros de resina aglutinada con aglutinantes poliméricos.*

Estos materiales líticos, que se encuentran en la región valenciana, pueden encontrarse en los más destacados monumentos de Valencia (La lonja, Catedral, Puerta de Serrano, entre otros) donde muestran un considerable deterioro físico, químico y biológico.

A diferencia de los referentes a morteros hidráulicos, se encuentran raramente estudios científicos centrados en la optimización de la preparación de morteros de resina aglutinada a pesar de que su uso está ampliamente extendido en toda Europa. Del mismo modo, escasamente se encontró información sobre estos dos tipos de materiales pétreos. (Roig Salom, 1995, Mas i Barberà, 2006).

En este estudio los valores de porosidad accesible al agua, absorción de agua, densidad aparente y real, coeficiente de saturación y compresión y resistencia a la flexión han sido determinados con series de tests-muestra preparadas con poliéster y resina acrílica, así como también cal-yeso como aglutinante de los morteros. Los experimentos realizados han llevado a establecer las propiedades de estabilidad y resistencia más altas de los morteros de resina aglutinada por comparación con las de morteros hidráulicos y piedra natural.

PALABRAS CLAVES: *replica, morteros de resina aglutinada, compuesto, piedra Bateig, piedra Tosca de Rocafort, SEM/EDX, pruebas mecánicas)*