EVALUATION OF THE EFFICIENCY OF RESIN BOUND MORTARS IN THE AMBIT OF STONE RESTORATION

Stephan Kröner, Xavier Mas i Baberà y María Teresa Doménceh-Carbó
Instituto Universitario de Restauración del Patrimonio de la Universidad Politécnica de Valencia.
Laboratorio de análisis físico-químico y medioambiental de obras de arte

AUTOR DE CONTACTO: Stephan Kröner, ustephan@upvnet.upv.es

ABSTRACT: *This study presents the results of the applicability of resin bound mortars in the ambit of stone conservation and restoration. Historical buildings, as well as sculptures or ornamental artworks exposed to environmental influences, composed by natural stone materials suffer severe alteration/degradation in the course of time. Due to this account, the physiochemical-chemical properties of epoxy and polyester resin bound mortars have been compared with those of two massive, mostly recrystallised Campanian limestone samples (Buixcarró rosa and Barxeta crema¸ Valencia - Spain).*
After the first petrological characterisation of the natural stones, the mortar aggregate used was obtained by extracting the stone material from the quarry; then by crushing it and incorporating the adjusted proportion dosage in order to obtain an artificial rock with the closed match to the natural stone concerning aspect, colour, texture and porosity. The test specimens were subjected to accelerated physiochemical ageing tests as recommended by the International Standards 25 PEM RILEM, Normal and UNE. The morphological changes have been controlled by the Optical Microscope (OM) and the Scanning Electron Microscope (SEM).

KEYWORDS: resin bound mortar, physiochemical properties, Scanning electron microscopy, Barxeta crema, Buixcarró rosa

1 INTRODUCTION

The appropriate selection of the chosen mortar in the ambit of stone restoration and conservation of historical monuments is essential at the time of intervention. The physiochemical properties of mortar should match as close as possible to those of the unaltered original stone material (masonry, sculpture, ornament etc.). This could be considered as a fundamental requirement in order to avoid incompatibilities of the "host rock" with the repair/ replacement mortar. Resin bound mortars, e.g., show excellent results for mechanical behaviour and also satisfactory resistance to different alteration agents [1], but when used within construction material that has a completely different physiochemical behaviour a converse effect might occur and deterioration can be accelerated [2].

In the cultural heritage of Valencia, as well as throughout Spain, limestone is largely employed and accessory minerals (clay minerals, iron oxides, quartz content, etc.) as well as porosity (intracrystalline, interparticle, open, etc.) and degree of compaction determine the resistance against alteration processes. In this context the use of ordinary limestone samples and sandstones for construction, should be mentioned, while rocks like marble or compact limestone with few pores, which can be polished, are mainly used for decoration and sculpture purposes. Thus, this investigation focuses on rocks of special interest within the Valencian Community and also seeks to establish methods in the ambit of conservation, restoration of monuments, sculptures and ornaments.

Resin bound mortars can normally be obtained by mixing a synthetic polymer (e.g. in this case Epoxy and Polyester), the corresponding catalyst and crushed stone powder with the adequate particle size distribution. While the binder mainly determines the cohesive properties of the mortar, the particle size distribution of the filler, being the major component of the mortar, influences the mechanical properties of the mortar [1,3]. In this investigation the commercial resins SeciFix-20 and Serifix have been used as binder and crushed *Barxeta crema*, respectively *Buixacrró rosa* stone has been added as a filler.

In this study, these two limestone samples, and the corresponding resin bound mortars have been subjected to standard acceleration tests in order to determine whether the latter ones could be used for restoration purposes.

2 EXPERIMENTAL

2.1 Mortar Preparation

The special mounting resins from the Strues Company *SpeciFix-20* (Epoxy) and *SeriFix* (Polyester) have been used to prepare the mortar specimens. The elaborated binder/aggregate ratios for both repair mortars and resins, the *Bateig crema* and the *Buixcarró rosa*, was 1:3.6. The mortar pastes were obtained using the amount of resin required to achieve normal consistency and a good workability. In the case of the *Barxeta crema* mortars, three different pigments (white, ochre and brown) have been added to simulate the natural stone colour to the most successful effect. Table 1 and 2, presents these results together with the amount of catalyst added. Three prisms of 50x50x50 mm for salt crystallisation, freezing-thawing and absorption/de-absorption tests and three samples (160x40x40 mm) for flexural and compressive strength tests were prepared using moulded casts and remoulded 48h later.

Table 1: Composition of resin bound mortars in [%]. Aggregate/ binder =3.6:1.

	Aggregate <0,25 mm	SpeciFix-40 (Epoxy)	Catalyst	White Pigment Gluspol Composite concentrated	Ochre Pigment Bayer 910	Brown Pigment Calcinated 25
Barxeta crema	78,170	18,393	3,065	0,324	0,0310	0,0154
Buixcarró rosa	78,462	18,462	3,077			

Table 2: Composition of resin bound mortars in [g]. Aggregate/ binder =3.6:1.

	Aggregate <0,25 mm	SpeciFix-40 (Epoxy)	Catalyst	White Pigment Gluspol Composite concentrated	Ochre Pigment Bayer 910	Brown Pigment Calcinated 25
Barxeta crema	78,170	18,393	3,065	0,324	0,0310	0,0154
Buixcarró rosa	78,462	18,462	3,077			

Table 3: Properties of the natural stones and resin bound mortars

	Real Density [g/cm^3]	Standard deviation	Open porosity %	Standard Deviation
Barxeta crema	2,71	<0,01	0,68	0,12
Barxeta crema Polyester	2,08	<0,01	<0,01	<0,01
Barxeta crema Epoxy	2,01	<0,01	<0,01	<0,01
Buixcarró rosa	2,72	<0,01	0,60	0,06
Buixcarró rosa Polyester	2,08	<0,01	<0,01	<0,01
Buixcarró rosa Epoxy	2,01	<0,01	<0,01	<0,01

2.2 Instrumentation

2.2.1 Physical Property Determination

A detailed petrological characterisation of the two limestone samples has been described previously by Kröner et al. [4]. Complementary analyses have been performed for a physical characterisation, like hydrostatic weight and water saturation in order to determine real density and open porosity. Results for natural stones and resin bound mortars are presented in Table 3.

A water absorption/de-absorption test was carried out following the NORMAL [5] recommendation on the test specimens. The natural stones as well as the resin bound mortars show low porosity values clustering around 0.06% and 0.14% (*Barxeta crema*). Results of the absorption (de-absorption) are represented in Figure 1.

2.2.2 Mechanical Evaluation

The three-point flexural test after the EN-196-1/996 norm [6] was performed on the mortar specimens using a loading rate of 4 mm/min. A compression strength test was carried out on the two fragments of each specimen, showing that the previous flexural test and the rate of loading was 10 mm/min. Results are shown in Table 4, and an example of the natural *Buixcarró rosa* stone after flexural failure is given in Figure 2. Concerning the resin bound mortar; no value for the compression strength could be obtained, because the test was stopped without rupture of the samples when a load of 100 MPa was reached.

2.2.3 Salt crystallisation test

Standard Salt crystallisation ageing [7]: this consisted of 15 cycles in which the test specimens were immersed for 4 h in a saturated sodium sulphate solution (14% $Na_2SO_4 \cdot 10H_2O$). They were then dried for 19 h at 60°C and finally cooled for 3 h at 20 °C. After 15 cycles they were subjected to immersion for one week in tap water and once again dried at 60°C. Due to low porosity values the natural stones as well as the resin bound mortars have been not affected by the test. No visual aspect change nor weight loss/ gain (weight loss/ gain within error <0,01) could be measured.

2.2.4 SO_2 Pollutant Chamber

This test was performed in a SO_2 saturated pollutant chamber after Kesternich (DIN 50.018). It consisted of drying the test specimens at 60°C until obtaining a non-varying weight. Then 7 cycles (168h) of accelerated ageing were carried out: 8h at 40°C with 0,2-2 1/g SO_2 concentration and 100% RH followed by 16h drying at room temperature (Table 5). After the test, the specimens were weighted and analysed by the electron microscope (SEM/EDX). The Figures 4-7 show the results from SEM element analyses line scans in order to determine sulphur penetration depth (gypsum formation).

2.2.5 Freezing and Thawing Cycle Ageing

In this test, the alternate freezing and thawing cycles were applied to the sample specimens following the RILEM recommendations [8]. 48 cycles were applied, and one cycle consisted of immersing the samples for 18 h in water at 8 °C followed by 6 h of freezing at -15°C. The water accessible porosity was very low in the natural stones as well as in the resin bound mortars (Table 3) and test specimens were not affected after 48 cycles. No visual aspect change nor weight loss (weight loss within error <0,01) could be measured. Figure 3 shows *Barxeta crema* test specimens before and after the test.

Table 4: Mechanical properties of the natural stones and resin bound mortars

	Flexure [MPa]	Standard dev.	Compression [MPa]	Standard dev.
Barxeta crema	12,38	1,35	58,46	22,88
Barxeta crema Polyester	38,06	0,84	>100 MPa	-
Barxeta crema Epoxy	46,52	0,85	>100 MPa	-
Buixcarró rosa	9,65	3,78	62,70	27,73
Buixcarró rosa Polyester	37,24	0,41	>100 MPa	-
Buixcarró rosa Epoxy	46,07	0,31	>100 MPa	-

Table 5: SO_2 saturated pollutant chamber test after Kesternich (DIN 50.018).

	Cycle O [g]	Cycle 7 [g]	Weight gain [%]
Barxeta crema	1,5970	1,6215	1,53
Barxeta crema Polyester	1,0623	1,0795	1,62
Barxeta crema Epoxy	0,9813	0,9960	1,50
Buixcarró rosa	1,2162	1,2393	1,90
Buixcarró rosa Polyester	0,7602	0,7730	1,68
Buixcarró rosa Epoxy	0,6770	0,6925	2,29

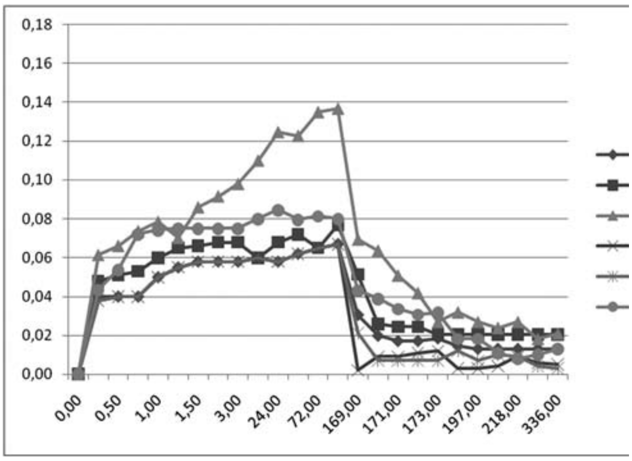

Figure 1: Weight [%] versus time diagram.
Absorption (0-168 h) – De-absorption (168-336h) lines for the different test specimens.

2.2.6 SEM/EDX

Morphological examination and chemical composition of the mortars and limestone were obtained by using a *Jeol JSM 5410* scanning Electron Microscope, operating with a Link–Oxford–Isis microanalysis system. The analytical conditions were: 20 kV accelerating voltage, 2×10^{-9}A beam current and 15 mm working distance. The polished samples were carbon-coated to eliminate charging effects.

3 RESULTS AND DISCUSSION

Low porosity values could be determined for both, natural stones as well as the resin bound mortars. Nevertheless for the mortars, almost zero water accessible porosity was measured, with a density of about 2,71 g/cm^3 as compact limestone is quite normal and similar to marble. The resin bound mortars significantly lower the density down to 2,01 g/cm^3 for the Epoxy resin and 2,08 g/cm^3 for the Polyester resin, respectively. This fact might be important for a structural engineer while calculating maximum stress loads for buildings. Scattering results for mechanical flexural and compression tests for the natural stones have been obtained (Table 4, observes standard deviation). This is due to the clay-filled flattened veins without any preferred orientation, which are crosscutting the host rock [4]. These veins present preferred failure surfaces (Figure 2) and depending of their orientation regarding the stress field, the rupture occurs at high (maximum strength σ_1 perpendicular to veins) or at very low values ($\sigma_1 \parallel$ veins). While using these materials someone has to be conscious of the isotropic behaviour of these limestone samples. On the other hand the resin bound mortars show very high values of compressive strength (outside the measuring range, above 100MPa), and higher values of flexure strength of 46 MPa for Epoxy and 38 MPa for Polyester resin.

The physical properties, low porosity and water accessibility have a strong influence on the behaviour of the mortar and natural stone when subjected to accelerated alteration tests. Even after 48 freezing-thawing cycles, following RILEM recommendations, no deterioration effect on the test specimens could be observed (Figure 3). No alteration effect was shown post the salt crystallisation test, after 15 cycles of immersion in sodium sulphate, being also due to low porosity values of both natural stones and mortars.

Completion accelerated ageing due to atmospheric pollution was simulated in a SO_2 pollutant chamber (Kesternich DIN 50.018) and later analysed by SEM/EDX. After 7 cycles the outer part of the limestone samples were partly transformed to gypsum, as it can be observed in SEM images (formation of gypsum needles) and in the sulphur penetration profile lines. Penetration depth is in the range of 0,1-0,3mm. On the other hand sulphur precipitation on the surface of the resin bound mortars could be observed clearly (Figures 6 and 7). Penetration of sulphur inside the mortars is more or less none existing, as it can be seen at a magnification of 300x in Figure 7 (only surface precipitation).

Figure 2. Buixcarró rosa after flexural failure. Note: failure follows clay vein/surface (red).

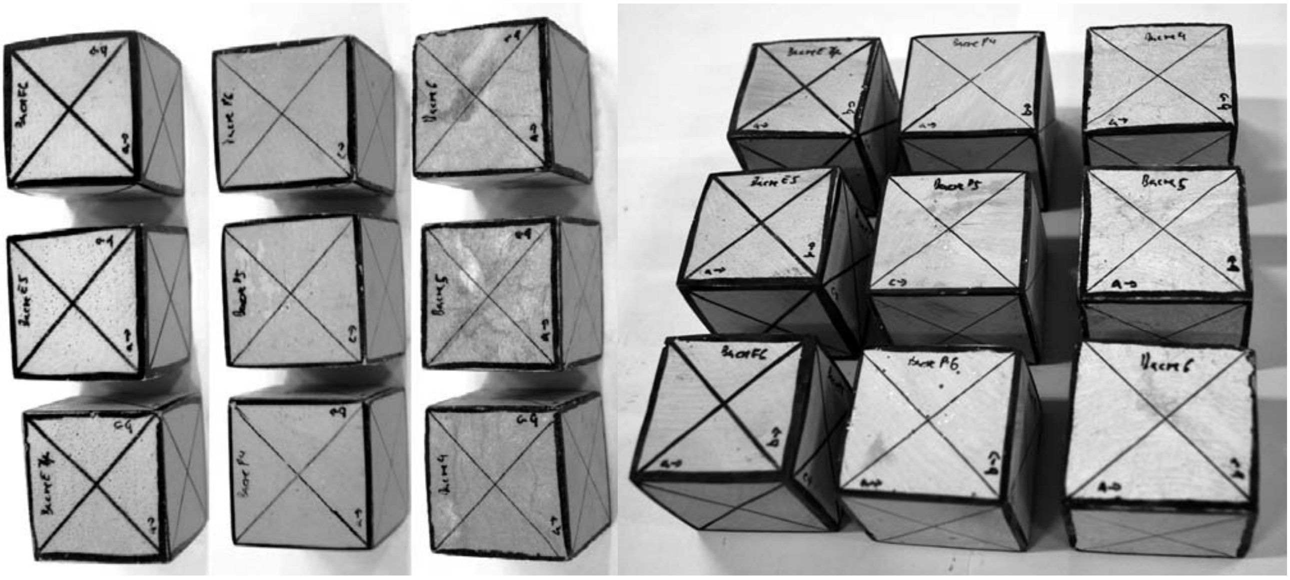

Figure 3: Barxeta crema test specimens before (left) and after (right) the freezing-thawing test. First row: Barxtea crema mortar with Epoxy resin (BacreE); second row: Barxeta crema mortar with Polyester resin (BarcreP); third row: natural stone Barxeta crema (Bacre).

4 CONCLUSIONS

The tested resin bound mortars offered satisfactory results by exceeding the mechanical behaviour in comparison to the natural limestone samples. For static considerations low density values favour their application.

Good resistance against different alteration agents, which may cause the deterioration of the mortars, could be confirmed by the accelerated ageing tests. The growing importance of alteration due to environmental pollution was simulated in a SO_2 pollutant chamber and element profile line scans confirmed good resistance of the resin bound mortars.

It can be concluded, that the properties of the applied resin bound mortars, *SpeciFix-20* (Epoxy) and *SeriFix* (Polyester), fulfil satisfactorily the desired requirements in the ambit of stone restoration of the two limestone samples *Barxeta crema* and *Buixcarró rosa*.

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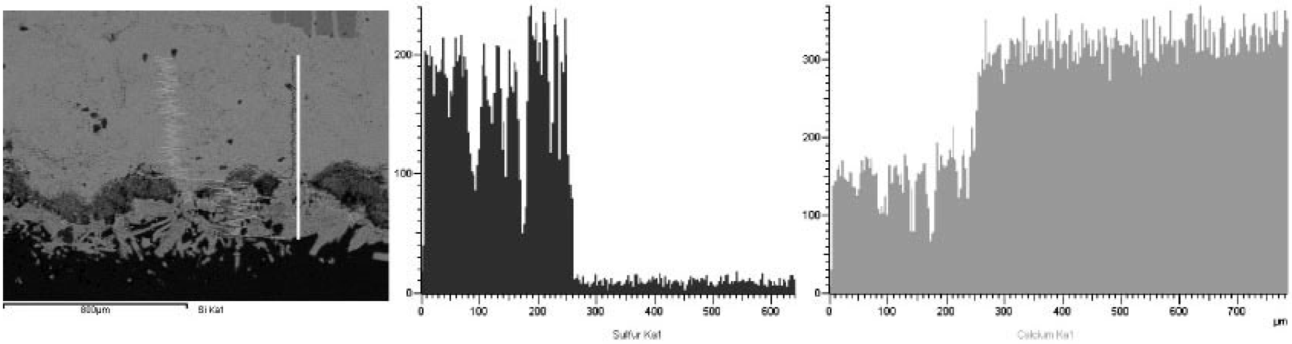

Figure 4. SEM image and profiles after SO2 saturated pollutant chamber test of the natural Barxtea crema stone. Penetration depth of sulphur (gypsum formation) 0,25-0,30 mm. Element profiles indicated by a white line. Width of images: 1,8mm. Profiles: left: Sulphur; Right; calcium.

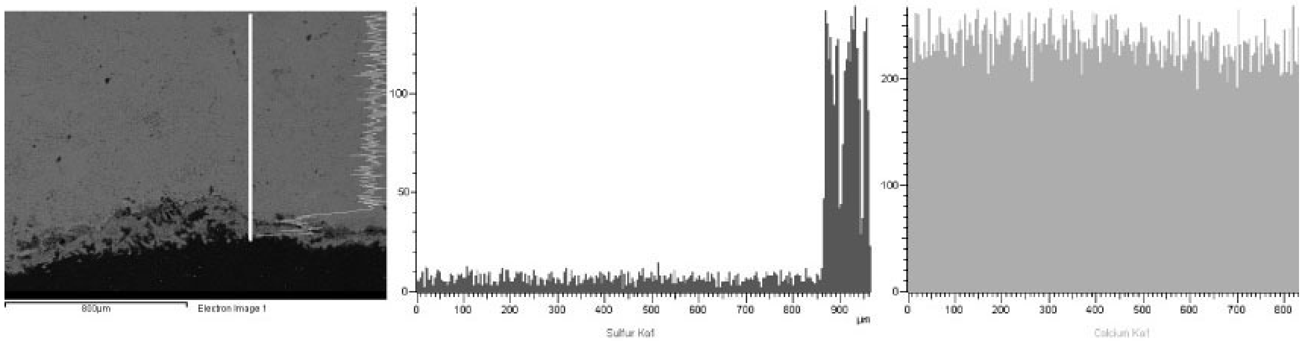

Figure 5: SEM image and profiles after SO2 saturated pollutant chamber test of the natural Buixcarró rosa stone. Penetration depth of sulphur ca. 0,1 mm. Element profiles indicated by a white line. Width of images: 1,8mm. Profiles: left: Sulphur; right; Calcium.

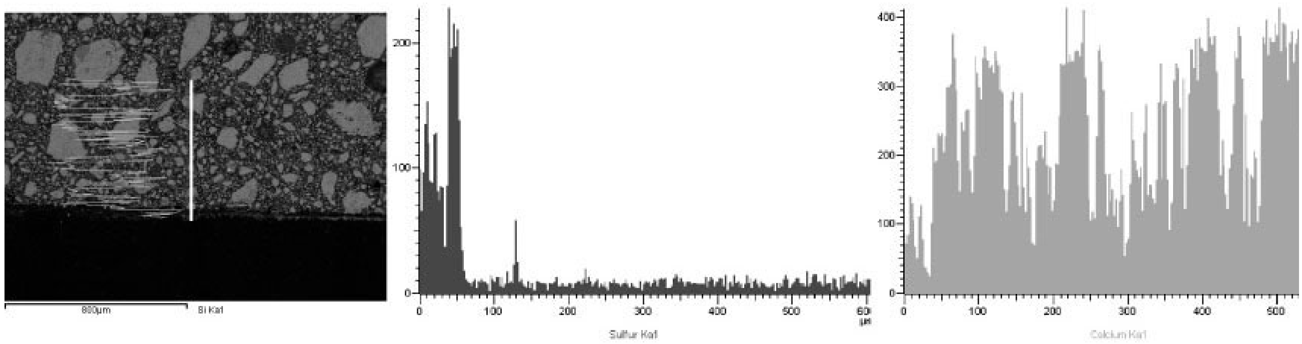

Figure 6: SEM image and profiles after SO2 saturated pollutant chamber test of the Barxtea crema epoxy mortar. Penetration depth of sulphur <0,02 mm. Element profiles indicated by a white line. Width of images: 1,8mm. Profiles: left: Sulphur; right; Calcium.

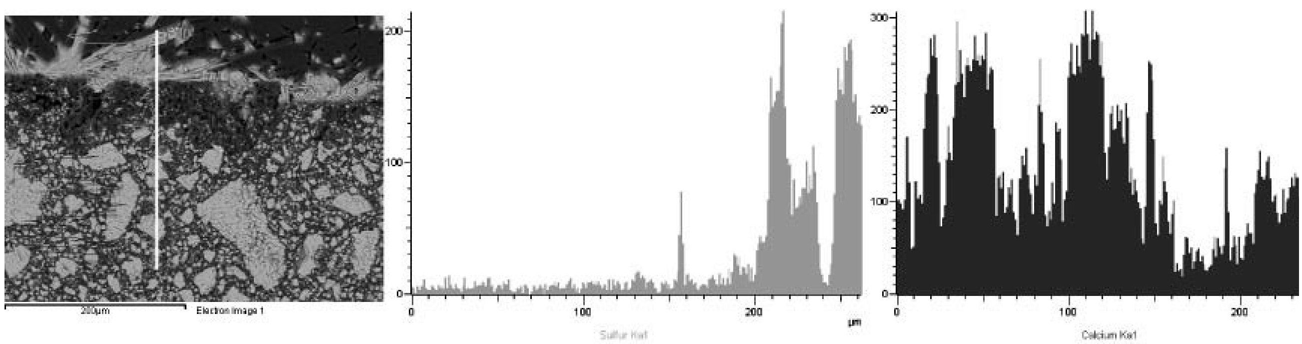

Figure 6: SEM image and profiles after SO2 saturated pollutant chamber test of the Barxtea crema epoxy mortar. Penetration depth of sulphur <0,02 mm. Element profiles indicated by a white line. Width of images: 1,8mm. Profiles: left: Sulphur; right; Calcium.

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Versión española

TITULO: ***Evaluación de la aplicabilidad de morteros compuestos en el ámbito de la conservación y restauración pétrea.***

RESUMEN: *Este estudio presenta los resultados de la aplicabilidad de morteros compuestos en el ámbito de la conservación y restauración pétrea. Edificios históricos compuestos por materiales de piedra natural, así como esculturas ornamentales u obras de arte expuestas a diferentes agentes ambientales, sufren una grave alteración/degradación con el paso del tiempo. Por esta razón, las propiedades físico-químicas de morteros de poliéster y resina epoxi han sido comparadas con las de dos calizas masivas ambas del Campaniano (Cretácico Superior), en gran parte recristalizadas (Buixcarró rosa y crema¸ Barxeta Valencia - España).*
Para la preparación del árido usado en los morteros de ensayo, se hizo necesario un proceso de triturado de la piedra extraída de la cantera, junto con una primera caracterización petrológica de las piedras naturales. A continuación se hizo la incorporación de la proporción de dosis ajustada para obtener una roca artificial, con un aspecto similar a la piedra natural en cuanto al color, textura y porosidad. Las muestras fueron sometidas a ensayos de envejecimiento físico-químicos acelerados siguiendo las recomendaciones de las Normas Internacionales de PEM 25 RILEM, Normal y UNE. Los cambios morfológicos han sido contrastados mediante el microscopio óptico (OM) y el microscopio electrónico de barrido (SEM).

PALABRAS CLAVES: *mortero compuesto, propiedades físico-químicas, microscopía electrónica de barrido, Barxeta crema, rosa Buixcarró*