



Characterization and chromatic evaluation of gypsum-based pastes for construction and heritage restoration

M. Paz Sáez-Pérez^{a,*}, Jorge A. Durán-Suárez^b, Amparo Verdú-Vázquez^c, Tomás Gil-López^d

^a Department of Architectural Constructions, Advanced Technical School of Building Engineering, University of Granada, c/ Severo Ochoa s/n, 18071 Granada, Spain

^b Department of Sculpture, Faculty of Fine Arts, University of Granada, Andalucía s/n. Edif. Aynadamar, 18071 Granada, Spain

^c Departamento de Tecnología de la Edificación, Escuela Técnica Superior de Edificación, Universidad Politécnica de Madrid, 28040 Madrid, Spain

^d Departamento de Tecnología de la Edificación, Escuela Técnica Superior de Edificación, Universidad Politécnica de Madrid, 28040 Madrid, Spain

ARTICLE INFO

Keywords:

Gypsum-based paste
Chromatic evaluation
Pigments
Reverse engineering
Construction
Heritage

ABSTRACT

This research evaluates the chromatic behavior of gypsum-based pastes containing added pigments which enable their use in both new construction projects as well as in restoration interventions for built heritage. Furthermore, the impact of adding pigments to the aforementioned material after twenty-eight and ninety days has also been studied. This was confirmed by carrying out compositional, mineralogical and physical studies of the raw materials and the pastes. The results indicate that all of the pastes studied have suitable mechanical strength values for the type of pastes studied, thereby confirming their suitability for on-site use based on their characteristics and behavior. Colorimetric analysis showed color variations that were clearly perceptible to the human eye, related to increases in luminosity which significantly exceeded 100%, and also to saturation losses featuring percentage variations of more than 100% on assessment after ninety days. This colorimetric analysis by means of quantitative spectrophotometry is of vital importance when determining the loss of color intensity of the pastes used, since subjective observation results in serious errors of interpretation. This type of study reflects the use of instrumental color measurements for this type of materials and mixtures.

1. Introduction

Currently, the study of pastes focuses upon the characterization of new mixes containing added artificial or natural fibers [1–7], with a view to increasing the mechanical properties of the resulting composites.

In the case of gypsum and gypsum-based pastes, the most common and most widespread method used in both the research and manufacturing fields, is to reinforce the gypsum matrix using glass fibers in order to improve impact resistance, achieving significant improvements in the end results [8,9].

In addition, using efficient materials with a low environmental impact is very important. However, the high cost of glass fibers compared to the low cost of gypsum, together with the weak interaction of natural fibers with binder matrices reduces their workability [10].

As a material, gypsum is plentiful and easy to extract, transform and distribute, which is what made it into a highly suitable construction material [11].

Focusing upon its origins, the gypsum-based paste is an artificial material, which is widely used, and which stands out due to its good preservation conditions, along with its ease of preparation, the availability of the raw materials and other characteristics such as its durability and versatility [12]. Where its use is concerned, it has unique advantages, including its low cost, good habitability, good performance as a thermal and acoustic insulator, good flame resistance and low energy consumption [10,13].

It is a material that can be easily and indefinitely recycled using suitable preparation processes which are based on the theory of hydration and dehydration [14].

Despite all of these advantages, it should be noted that gypsum-based pastes display a high level of fragility, low water resistance and low mechanical strength, thereby reducing their use in contexts which are subject to specific or shock loads [15].

Historically, gypsum has been used in many different ways in construction: for plastering walls and ceilings, interior stucco work, exterior cladding, interior partition walls, as a connecting element for ceramics

* Corresponding author.

E-mail addresses: mpsaez@ugr.es (M.P. Sáez-Pérez), giorgio@ugr.es (J.A. Durán-Suárez), amparo.verdu@upm.es (A. Verdú-Vázquez), tomas.gill@upm.es (T. Gil-López).

<https://doi.org/10.1016/j.conbuildmat.2021.124981>

Received 29 June 2021; Received in revised form 27 August 2021; Accepted 16 September 2021

Available online 25 September 2021

0950-0618/© 2021 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

and stone and as composite materials to extend the use of pastes to construction products such as blocks, porous bricks and sandwich panels, either with or without reinforcement [16,17] and also as a structural material in many ancient constructions [18].

The relevance and interest attached to gypsum-based pastes, originated in Greece in the sixth millennium BC [19] and they were widely used and developed by the Romans, who produced the oldest synthetic composites which are used as construction materials and found in all kinds of monuments. These are the focal points of numerous studies relating to preservation and restoration. Currently, these studies are focused on the knowledge of the behavior of synthetic composites through the effect of the different additions implemented in the manufacture of gypsum-based composites, favoring the improvement of the conditions and durability of the materials. [20] confirms that mixtures of gypsum and lime with metakaolin allow the use of these pastes in more humid environments, in the same way [21] shows how the use of silica fume as an additive improves the behavior against frost by reducing the softening of the pastes. And [22–24] confirm that the addition of blast furnace slag favors the durability of gypsum if the product is properly optimized, obtaining a low water absorption, high permeability, improved mechanical strength and a great behavior against stress states (cracking) without the presence of cracks or voids due to the dissolution of the dihydrate or the formation of ettringite [22].

The significant historical and architectural value acquired by these pastes means that knowledge and mastery of both their production and application form part of our cultural heritage [25] and as such, their state of deterioration and loss represent an issue that needs to be addressed when studying built heritage [26–28].

Despite its importance, it is acknowledged that for decades the study of gypsum and the definition of strategies aimed at its preservation have been totally neglected. Furthermore, the mid-twentieth century saw the rapid abandonment of traditional construction materials and techniques and the use of inappropriate materials, something that was true of all European countries and which led to an irreversible loss of data and fundamental information related to the knowledge of materials, which is difficult to recover in the present day.

Fortunately, in recent decades, terms such as authenticity and compatibility have become a priority in material characterization studies, compositional and microstructural characterization particularly standing out [29–34], leaving out aesthetic matters [25,35–37].

However, the building maintenance and preservation needed in the context of heritage requires more comprehensive action which also addresses aspects of an aesthetic nature. In this respect, colorimetry assessments and studies can be key in the fields of both preservation and restoration, and also to knowledge of the chromatic possibilities of pigments and techniques, the fundamental objective of which is to perform a respectful intervention and recovery of the said heritage and buildings.

As such, colorimetry is a highly useful tool bearing in mind that during the preservation process the aesthetic and chromatic characteristics of the object cannot be altered, and its original condition must be respected. In order to achieve this, a correct choice of the materials to be used during the different interventions must be made, taking into account the effectiveness of the treatments used and the chromatic modifications which the materials can withstand. It is, therefore, necessary to perform a colorimetric study before and during the preparation of the mixes at least.

Recent projects have applied the instrumental color study in the field of monumental heritage, analyzing the performance of the pigments treated with restoration products [38–44]. As such, the use of pigments in different applications within the field of Materials Engineering and in architectural heritage interventions is necessary in many cases in order to achieve a certain external appearance [45], as well as achieving consistent visual and aesthetic characteristics [46].

Technically, many studies and manufacturers have carried out

research into pigment characteristics, focusing mainly on production processes and their formulation, the most suitable application methods for protecting the environment, saving resources and product finish. However, their performance and effectiveness vary depending on the environment and the conditions of exposure.

The study of pastes and their application in construction requires knowledge of their characteristics and peculiarities. As such, the characterization of the pastes with the objective of ascertaining their suitability for the aforementioned purposes is essential so as to plan adequate measures for new construction work, maintenance, conservation and preservation of built heritage, as well as being able to establish and assess the causes of possible deterioration, an essential factor for necessary restorative interventions.

The characterization of the products allow to confirm mainly the suitability of pastes containing pigments for use in the most common applications of this type of paste, indicating specific performances which although not outstanding, are worth boosting.

The present article focuses upon the application of different pigments in gypsum-based pastes for use in new construction projects as well as in the field of restoration of cultural heritage and architectural interventions where it is recognized as a widely used material [47]. It can be highlighted the high durability conditions [48] and the improvement of the properties generated as confirmed by several researches, which expose its good behavior against other composites [48], together with the improvement of its mechanical resistance [49], fire resistance, load/weight reduction and even cost reduction [50].

In this respect, the intended use of the pigments studied, the suitability of their physical and chemical characteristics and the characteristics of the materials are examined, looking at the colorimetric implications at three different stages: twenty-four hours, twenty-eight days and ninety days.

The color difference values (total color ΔE , luminosity ΔL and chroma/saturation ΔC) between the mixes and the pure pigments for each of the mixes studied and for the established proportions, identify which of them offers the greatest effectiveness and stability and indicate their color specifications. Thereby highlighting the quantitative assessment of the influence of the manufacturing process, in relation to the final visual result, which is of great importance in any kind of intervention.

In this context, it is interesting to highlight that the analysis of pastes is crucial in what is known as the process of 'reverse engineering', making it possible to produce materials which are compatible both in new construction projects and in the context of restorative intervention and maintenance.

2. Materials and methods

2.1. Materials

In order to carry out the present research, three pigmented gypsum-based pastes were created, using different binders to produce them, which were gypsum, air lime and hydraulic lime, along with eight different inorganic pigments.

Where the gypsum used is concerned, this was supplied by CTS Spain and is white gypsum of the highest quality (containing at least 90% of hemihydrate) as shown by the XRD (Fig. 1). The limes were supplied by the same provider, CTS Spain. In the case of the air lime, following slaking in specific tanks, this is microfiltered and aged for a minimum period of six months subsequent dried, milled, packaged and sold. In the case of the hydraulic lime (NHL5), this is authentic pure natural lime resulting from the calcination of loamy limestone without additives.

With regard to the pigments used, these were acquired through Kremer Pigmente (online provider). In choosing them, in addition to the broad colorimetric range offered (yellows, greens, blues, reds and ochres), consideration was given to whether they were regularly used in manufacturing construction and restoration mortars. Their composition

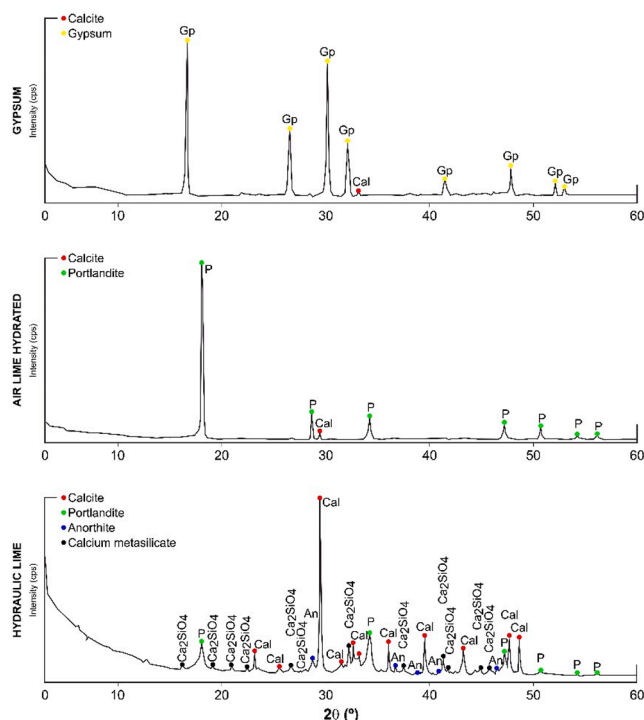


Fig. 1. XRD diffractogram of the gypsum, hydraulic lime and air lime. [55]

and names, including their color code [51] are shown in Table 1.

3. Characterization of raw materials

The chemical, mineralogical and colorimetric properties of the raw materials used to prepare the samples were studied via X-ray diffraction (XRD), X-ray fluorescence (XRF) and normalized colorimetric testing. The results are shown in Fig. 1 and Table 2 respectively.

For the XRD testing, the raw materials were analyzed using a Bruker D8 DISCOVER diffractometer featuring a DECTRIS PILATUS3R 100 K-A detector, from the Center for Scientific Instrumentation at the University of Granada (CIC). The Xpovder program [54] was used to determine its

Table 1

Acronyms and colour index name are based in the colours chart of The Society of Dyers and Colourists (SDC) [52] and American Association of Textile Chemists and Colorists (AATCC) [53]. Names of the commercial pigments/binders and manufacturers composition are given by suppliers.

Acronym	Colour index name	Commercial pigment/binders	Manufacturer's composition
PY34	77,600	Chromium yellow pigment	Lead chromate
PR104	77,629	Molybdenum orange pigment	Lead chromate, sulfate and molybdate
PY43	77,492	Ochre pigment	Iron hydroxide
PG23	77,009	Green earth pigment	Iron (II) silicoaluminates, Mg and K
PG15	77,288	Chromium green pigment	Chromium oxide
PBr7	77491-2	Natural sienna pigment	Calcined natural iron oxide
PY36	77,956	Zinc yellow pigment	Zinc chromate
PB29	77,007	Ultramarine blue pigment	Sodium polysulfide-aluminosilicate
PW25	77,231	Plaster of Paris	Calcium sulphate hemihydrate
PW18	77,220	Lime White	Calcium hydroxide-Portlandite
PW28	77,230	Natural hydraulic lime	Silica calcium aluminates and calcium hydroxide

composition.

Meanwhile, the X-ray fluorescence (XRF) testing was performed using a high-performance compact wavelength dispersive X-ray Fluorescence Spectrometer, of the brand PANalytical and model Zetium.

In order to perform the testing, the raw materials were ground in an agate mortar and subsequently passed through a test sieve with an ASTM N° 45 mesh size (diameter < 0.354 mm).

Where colorimetric characterization is concerned, the CIELAB-1976 [56] chromaticity coordinates were calculated for the different materials (see Fig. 2). In order to do this, diffuse spectral reflectance measures were used, producing a sample within the visible range of 360–740 nm, at 5 nm intervals, using a D65 illuminant.

In order to perform the testing, a Konica Minolta CM-2500c Spectrophotometer from the University of Granada was used.

The colorimetric distribution of the pigments and binders used is set out in Fig. 2, according to their CIELab 1976 values which are detailed in a part devoted to the chromaticity diagram (a* and b* ratio), as well as a luminosity component (L*). We can highlight that the pigments used in this study are distributed throughout three of the four quadrants of the a*-b* diagram: yellow-red quadrant, red-blue quadrant and green-yellow quadrant. As such, pigments PY43 (ochre pigment), PBr7 (natural sienna pigment) and PR104 (molybdenum orange pigment) contain mixtures of yellow and red tones (a*-b*) and medium luminosities (L*). Furthermore, pigments PY34 (chromium yellow pigment), PY36 (zinc yellow pigment), PG23 (green earth pigment) and PG15 (chromium green pigment) are mixes in different proportions of green and yellow tones, whilst their luminosities are diverse: high values (>=80%) for PY43 (ochre pigment) and PY36 (zinc yellow pigment), medium values for PG23 (green earth pigment, ≈ 63%) and low values (<50%) in the case of PG15 (chromium green pigment). Where the blue pigment PB29 is concerned (ultramarine blue pigment), it is noted that it contains a greater proportion of blue tone than of red tone, but in fact, this means that it displays a violet hue with a high level of saturation according to the relationship (C/S = √(a*² + b*²)), where C is chroma and S is saturation. Although, on the other hand, its luminosity is the lowest of all the materials used in this study (<34%).

Meanwhile, the binders are located in the red-blue quadrant, a factor which gives them a violet tone with very low saturation and values [C] of 8.18, 8.20 and 8.36. In fact, this is the lowest saturation of all of the materials used. These aspects, together with the high luminosity (L*) values displayed by the binders (from ≈ 85% to 94%), give them a visual appearance that is very similar in tone to white.

4. Design and preparation of the samples

Three different pastes were investigated; the first was composed exclusively of pure gypsum, the second of gypsum and air lime, and the third of gypsum with hydraulic lime. These mixtures being necessary to increase the mechanical properties and the durability of the pastes. All of them were combined with the pigments described in all cases. All binders and pigments were mixed in powder form.

A total of seventy-five samples were produced for testing (three of each type of paste and pigment, plus one sample for each paste without pigment). This meant a total of twenty-five test pieces for each paste, which were subjected to the different tests.

The components of each mix were measured out by volume, the final compositions being those shown in Table 3. When preparing the mixes, the different components (gypsum and lime/gypsum + pigment) were dry mixed, before finally adding drinking water in order to facilitate mixing and prepare the mixes which were left to set and harden in the following laboratory conditions: T = 22 degreesC and RH = 70%. The amount of mixing water (Table 3) was added to the total amount of dry mixes prepared.

The pastes were prepared in the proportions indicated and poured into molds, with dimensions of 16.5x4.5x4.5x4.5 cm for subsequent

Table 2
Chemical composition by XRF analysis (wt %) of raw materials. Data normalized to 100% (LOI-free).

SAMPLE	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	SO ₃	Cl	LOI
(wt %)													
Gypsum	0.51	0.40	0.21	0.11	0.60	32.20		0.05	0.20	0.02	45.5		20.11
Air lime	0.20		0.08		0.52	76.29	0.13	0.07		0.63	0.20	0.41	21.43
Hydraulic lime	12.91	4.05	1.90	0.03	0.94	58.65	0.10	0.92	0.25	0.05	0.09		19.92

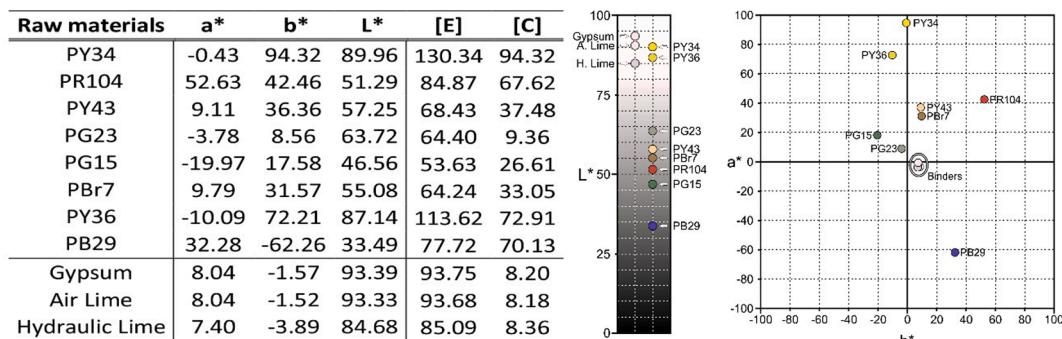


Fig. 2. Left. CIELAB 1976 [56] color coordinates of pigments and binders tested under illuminant D65. Where a*, means the amount of red (+) or green (-). b*, means the amount of yellow (+) or blue (-). L*, means the amount of light in one degree from black (0) to white (100), [E] means total color of the sample and [C] means the chroma of the sample. Right. Representation in the CIELAB-1976 system of pure pigments and binders used in the present study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3
Description of the formulations, components and dosages (by volume %) of the gypsum-based paste samples.

Denomination	Gypsum	Air lime	Hydraulic lime	pigment	Water added
	%	%	%	%	Volumen
P	80	0	0	20	0.5
PAL	65	15	0	20	0.5
PHL	65	0	15	20	0.5

setting and hardening, due to their optimum consistency and workability.

The average hardening time was twenty-eight days, (in laboratory conditions). In this case, in order to consider the setting time to be finished, during the final days, the samples were weighed regularly so as

to check that their weight remained constant, as an indication that the water had fully evaporated and the mix had hardened. After setting and hardening of the pastes in the molds, shrinkage of approximately 0,2% occurred.

Fig. 3 shows the gypsum test pieces with the eight pigments used, by way of example.

5. Methods

5.1. Scanning Electron Microscope (SEM)

The mineralogical, textural and microstructural characterization of the pastes was carried out by means of Scanning Electron Microscope (SEM) testing. This was performed using a GEMINI (FESEM) CARL ZEISS Scanning Electron Microscope (SEM), featuring a Röntec M Series EDX detector, belonging to the Center for Scientific Instrumentation at the

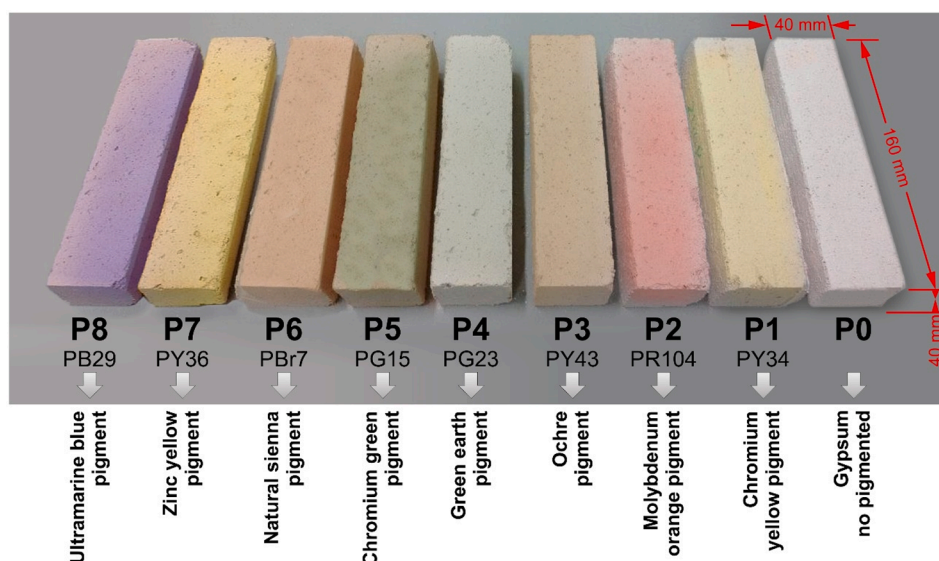


Fig. 3. Paste and gypsum samples (Type P), without pigment (P0) and with the different pigments used (P1 to P8) ninety days after their preparation.

University of Granada (CIC).

5.2. Mechanical tests

In order to calculate the flexural strength, sets of prismatic test pieces measuring 40 mm × 40 mm × 160 mm were used for each type of mix prepared, after twenty-eight days and at ambient temperature. In the case of compressive strength, cubic test pieces measuring 40 mm per side were used. In order to perform the tests the relevant standard was applied [57].

Breakage was achieved by using an IBERTEST EUROTEST MD2 universal testing machine. The testing speed was 1 mm/min for a sample interval of 64 mm, which breaks the sample by means of a central concentrated load, the load cell being fixed at 5kN. For the ultimate compressive strength test, an applied speed of 5 mm/min was used.

The mechanical strength results for the samples tested were obtained from the average of three test pieces for every dosage and pigment used.

5.3. Color tests

Once the samples were prepared, their diffuse spectral reflectance curve was measured using a Konica Minolta CM-2500c Spectrophotometer from the University of Granada (Spain), which has a wavelength of 360 nm to 740 nm and an observation system of 2/10 degrees (CIE 1931/2°, CIE 1964/10°). The measurement was taken after sampling every 5 nm within the visible range over a sampling area measuring some 8 mm in diameter and observing an illumination/observation geometry for each diffuse/2°10° simple sample, excluding the specular component of the reflection, as recommended in such cases by the CIE [58]. Furthermore, the Color Data Software SpectraMagic NX was used to present the simulations of the color variations for the samples affected.

The specular component of the reflection was excluded from all of the measurements, as recommended in these cases by the CIE [58]. Based on the said reflectance values, the CIELAB-1976 [56] chromaticity coordinates were calculated using a D65 illuminant, as were the total color difference (ΔE), luminosity (ΔL) and saturation (ΔC) values, in accordance with the CMC formulas (2:1) [59] for the different mixes. Five measurements were taken for each sample. The standard deviation for the values of each batch, obtained using Bessel's correction, did not exceed 3% of the associated average value in any case [60].

6. Results

6.1. Scanning Electron Microscope (SEM)

Fig. 4 shows the morphological analysis of the samples as well as the associated EDX analysis, for the central area of the samples.

The Scanning Electron Microscope studies highlight several aspects observed in the samples ninety days after their preparation. As such, recrystallization of gypsum minerals was detected visually in specific areas of the associated paste matrix samples measuring between \approx 25–45 μ m, and displaying an acicular habit (see areas with red edging which are yellow in color). These acicular recrystallizations could lead to the relative consolidation of microcracks due to shrinkage, identified in all of the pastes, also improving the associated mechanical strength values.

Meanwhile, the EDX analysis is highly consistent with each of the samples submitted, since in the case of the gypsum-pigment mix, the analysis mainly indicates the presence of calcium sulfate (S, Ca) along with markers for the natural sienna pigment which contains iron oxide (Fe) and some traces of Mg and Al. The analysis of the gypsum, air lime and pigment sample shows the presence of calcium sulfate (S, Ca) as expected, although in this case there is a larger proportion of Ca than S, and it includes traces of Mg and K, and of course the Fe markers from the pigment used. The final EDX elemental analysis clearly indicates the presence of calcium sulfate (S, Ca) with a higher proportion of Ca and the participation of the elements typically found in hydraulic lime: Si, Al, responsible for hydrolyzing the new composites, which give the pastes produced using this binder greater mechanical strength. In addition to observing traces of Mg, there are noticeable natural sienna pigment markers containing iron oxide (Fe).

6.2. Mechanical tests

Tables 4 and 5 show the results of the mechanical tests for the three types of mix at twenty-eight days.

In the case of compressive strength, it was established that the maximum strength for the 100% gypsum paste (type P samples) was 5.4 MPa \pm 0.02. In the case of the different pigmented samples, the results show full compatibility and the differences observed do not surpass the material without added pigment by more than 1.3%, this being the specific case of the mix containing green earth pigment (P + PG23).

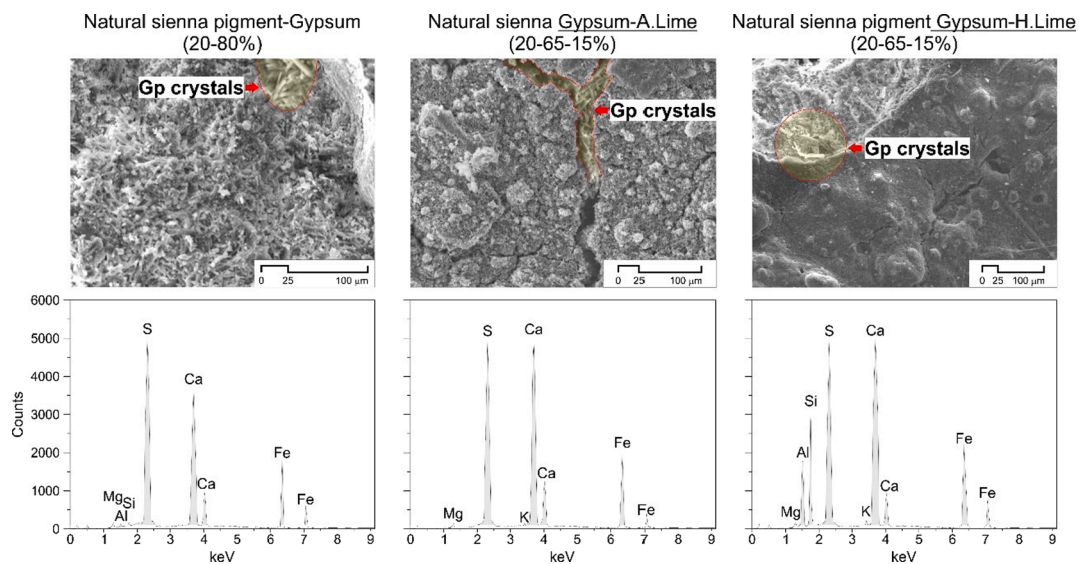


Fig. 4. Photomicrographs obtained using a Scanning Electron Microscope (SEM) of gypsum mixed with natural sienna pigment PBr7 (80–20%), gypsum mixed with air lime and natural sienna pigment PBr7 (65–15–20%) and gypsum mixed with hydraulic lime and natural sienna pigment PBr7 (65–15–20%). The lower section contains the associated EDX element analysis for the central area of the sample. In all cases, the scale represents 100 μ m.

Table 4

Average values for mechanical tests with the standard deviation for the groups of samples tested without pigment.

Binders	Flexural strength (MPa)		Compressive strength (MPa)	
	X	σ	X	σ
P	2.25	0.03	5.40	0.02
PAL	2.93	0.06	5.62	0.04
PHL	3.90	0.05	9.79	0.03

Table 5

Average values and standard deviation for the mechanical test results for each group of samples tested with the different pigments.

Binders	Flexural strength (MPa)		Compressive strength (MPa)	
	X	σ	X	σ
P				
P + PY34	2.25	0.03	5.41	0.04
P + PR104	2.26	0.05	5.43	0.06
P + PY43	2.25	0.04	5.42	0.01
P + PG23	2.27	0.03	5.47	0.01
P + PG15	2.27	0.01	5.43	0.03
P + PBr7	2.23	0.06	5.46	0.03
P + PY36	2.23	0.07	5.4	0.02
P + PB29	2.24	0.04	5.37	0.05
PAL	X	σ	X	σ
PAL + PY34	2.92	0.03	5.62	0.05
PAL + PR104	2.93	0.07	5.65	0.03
PAL + PY43	2.94	0.08	5.62	0.05
PAL + PG23	2.947	0.02	5.75	0.02
PAL + PG15	2.9189	0.05	5.55	0.07
PAL + PBr7	2.9419	0.04	5.61	0.06
PAL + PY36	2.929	0.06	5.59	0.04
PAL + PB29	2.92	0.03	5.64	0.01
PHL	X	σ	X	σ
PHL + PY34	3.91	0.04	9.81	0.03
PHL + PR104	3.9	0.05	9.77	0.05
PHL + PY43	3.92	0.03	9.75	0.02
PHL + PG23	3.93	0.02	9.95	0.03
PHL + PG15	3.93	0.02	9.81	0.06
PHL + PBr7	3.93	0.07	9.85	0.01
PHL + PY36	3.90	0.01	9.8	0.04
PHL + PB29	3.91	0.06	9.83	0.04

In the case of the gypsum-based pastes containing air lime (type PAL samples), the strength obtained was 5.62 MPa \pm 0.04. As such, it can be confirmed that the use of lime as a partial substitute by weight (15%) led to a 3.6% improvement in compressive strength. This slight gain in compressive strength is attributed to a small modification in the microstructure of the binder, in line with what is set out in [61 61].

As in the previous case, no notable differences are observed in the samples containing pigment, except in the mix containing green earth pigment (PAL + PG23), a difference of 2.3% being acknowledged.

For the PHL samples, the compressive strength of the white pastes was 9.79 MPa \pm 0.03. These results showed an increase in the compressive strength of 45% compared to the pure gypsum samples (type P) and of 43% compared to the gypsum samples with an air lime base (type PAL).

As confirmed in [62 62], this may be attributed to the chemical reaction of gypsum and hydraulic lime in the presence of water. The lime substitution affected the hydration process and caused rapid hydration due to the increased surface of the mix. The increased compressive strength may confirm that hydraulic lime is an active additive of gypsum for increasing the hydration rate and the hydration products, also showing that this behavior was due to the formation of carboaluminates.

This same improvement is observed throughout the pigmented sample series, one of the colored mixes being worth particular mention compared to the others, coinciding with what was observed in the previous mixes. A 1.6% increase is observed compared to the samples without pigment.

The results obtained when calculating the compressive strength of the three types of mix, enable improvements to be made to the resistance capacity. These results vary from the least resistant, P mixes, to the most resistant, PHL mixes, the increase being of 45%.

If we add each of the pigments to these same mixes, a slight increase in compressive strength is observed with pigment PG23 compared to the other pigments used in the three mixes studied. Focusing on the behavior of the aforementioned pigment, and in line with [64], [64] and [65], it is confirmed that the MgO found in this pigment, together with that contained in the binder (in P, in PAL and in PHL (almost twice the proportion) does not act exclusively as a binding material, but must be considered as part of the fraction of the aggregate material [64]. According to [65] Mg-limes have been reported to possess a certain amount of hydraulic set and develop a good ultimate strength. This fact could explain the improvement in the mechanical properties, particularly in terms of compressive strength that are checked in these pigmented mixes which include MgO.

The flexural strength results set out in Tables 4 and 5 reveal similar behavior to that described for compressive strength. An increased strength being observed as the established percentage of air lime and hydraulic lime respectively is incorporated in the mix. The minimum values are found in the pure gypsum samples (P samples), which achieve 2.25 MPa, the result obtained in the samples containing air lime (type PAL samples) being 23% higher at 2.93 MPa and in the case of the samples containing hydraulic lime (type PHL samples) a value of 3.90 MPa is reached, which is 25% higher than for air lime. A difference of 42% is recognized between the type P and type PHL samples.

Where the samples containing pigment are concerned, no significant differences are observed in any of the groups. The same can be said of the samples within the same group containing the different pigments. In the case of the 100% pure gypsum samples (type P), the flexural strength results are very similar to those of the white sample, a difference of < 1% being observed in all cases. The samples containing air lime (type PAL) show similar behavior, the differences being even smaller than for the previous group at < 0.5%. Finally, for the samples containing hydraulic lime (type PHL) the differences are also small, ranging between 0.5 and 0.7%.

6.3. Color tests

Table 6 (6.1, 6.2 and 6.3) and Fig. 5 shows the average values for the total color differences (ΔE), luminosity (ΔL) and saturation (ΔC) between the pure pigments and each of the binders tested in laboratory conditions, in the three phases of the study: after twenty-four hours, twenty-eight days and ninety days.

Table 6. List of average values for the total color differences (ΔE), luminosity (ΔL) and saturation (ΔC) between the pure pigments and each of the binders tested, in the three phases of the study: after twenty-four hours (Table 6.1), twenty-eight days (Table 6.2) and ninety days (Table 6.3).

Based on the data presented, and considering that visual perception (to the human eye) of total color variations occurs from $\Delta E \geq 3$ [59], the results pertaining to total color variation (ΔE) show for each pigment and interaction with the gypsum binder in a percentage of twenty-eight, that all of the mixes result in total color variations compared to the pure pigment in different proportions, the highest being those experienced in the gypsum-pigment PY34 (chromium yellow pigment) mix with values close to forty points ninety days after preparing the mix. The remaining mixes are clearly discernible to the human eye, particularly those ΔE variations with values of twenty to thirty points, in pigments PY43 (ochre pigment), PG23 (green earth pigment), PG15 (chromium green pigment), PBr7 (natural sienna pigment) and PY36 (zinc yellow pigment), with homogeneous results for the measurements taken after twenty-four hours, twenty-eight days and ninety days, in the case of pigment PY43, and displaying a gradual increase in the measurements taken after twenty-four hours, twenty-eight days and ninety

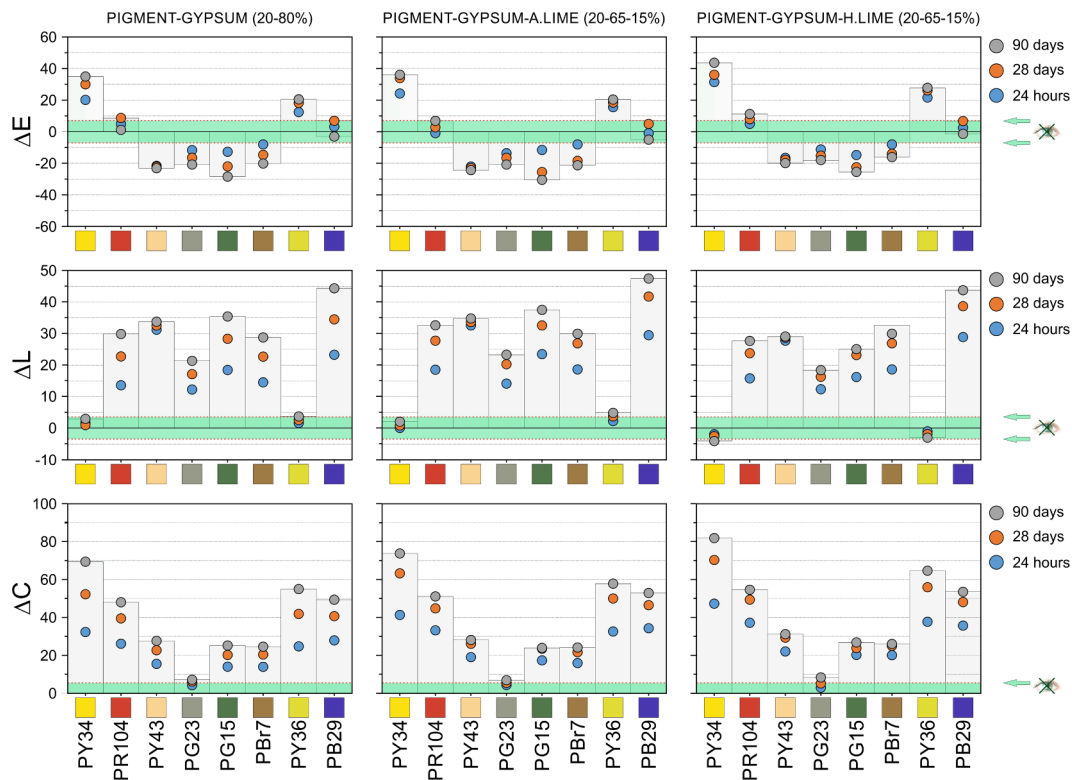


Fig. 5. Graphic representation of average values for the total color differences (ΔE), luminosity (ΔL) and saturation (ΔC) between the pure pigments and each of the binders tested in laboratory conditions, in the three phases of the study: after twenty-four hours, twenty-eight days and ninety days.

Table 6.1
Pigment-gypsum (20–80%).

	PIGMENT	24 Hours					
		ΔE	σ	ΔL	σ	ΔC	σ
24 h	PY34	20.14	2.16	1.06	0.32	-32.30	2.99
	PR104	1.49	0.07	13.58	0.91	-26.10	3.01
	PY43	-22.76	-2.74	31.24	2.10	-15.45	2.67
	PG23	-11.69	-1.89	12.31	1.55	-4.25	0.78
	PG15	-12.67	-0.55	18.53	1.38	-14.00	0.47
	PBr7	-8.09	-0.88	14.67	0.76	-13.91	2.77
	PY36	12.47	1.44	1.78	0.22	-24.69	2.01
	PB29	3.50	0.22	23.44	1.37	-28.06	1.92
28 days							
	PIGMENT	ΔE	σ	ΔL	σ	ΔC	σ
	PY34	30.05	3.06	1.13	0.17	-52.21	4.80
	PR104	5.69	0.34	22.72	1.07	-39.48	3.21
	PY43	-22.78	-2.17	32.75	1.57	-22.65	3.60
	PG23	-16.56	-1.89	17.18	0.83	-6.19	1.03
	PG15	-21.65	-1.87	28.44	1.34	-20.18	2.14
	PBr7	-14.68	-1.03	22.81	0.95	-20.36	2.11
	PY36	18.19	0.54	3.07	0.11	-41.78	1.82
PB29	6.93	1.08	34.60	2.67	-40.60	2.06	
90 days							
	PIGMENT	ΔE	σ	ΔL	σ	ΔC	σ
	PY34	34.93	3.01	2.13	0.11	-69.36	4.56
	PR104	7.85	0.97	29.75	2.18	-47.98	4.00
	PY43	-23.11	-2.17	33.75	1.93	-27.57	3.29
	PG23	-20.85	-2.19	21.38	1.77	-6.37	1.11
	PG15	-28.45	-0.05	35.50	2.49	-25.19	2.58
	PBr7	-20.18	-1.03	28.90	2.37	-24.51	2.73
	PY36	20.85	1.18	3.86	0.18	-54.88	3.92
PB29	-3.05	-0.89	44.55	2.30	-49.31	3.19	

Table 6.2
Pigment-gypsum-air lime (20–65-15%).

	PIGMENT	24 Hours					
		ΔE	σ	ΔL	σ	ΔC	σ
24 h	PY34	24.16	2.83	1.04	0.57	-41.31	3.36
	PR104	-0.62	1.01	18.70	1.31	-33.17	3.38
	PY43	-23.34	-2.07	32.81	2.50	-19.09	3.04
	PG23	-13.66	-1.22	14.28	1.95	-4.36	1.48
	PG15	-16.99	-0.88	23.44	1.78	-17.32	0.84
	PBr7	-11.60	-0.21	18.81	1.16	-15.97	3.14
	PY36	15.53	2.11	2.26	0.62	-32.54	2.38
	PB29	5.26	1.75	29.48	1.77	-34.29	2.29
28 Days							
	PIGMENT	ΔE	σ	ΔL	σ	ΔC	σ
	PY34	34.20	3.95	2.04	0.94	-63.29	5.29
	PR104	2.72	1.86	27.71	1.69	-45.08	3.70
	PY43	-23.49	-1.28	33.81	2.19	-26.07	4.09
	PG23	-19.70	-1.00	20.28	1.45	-5.24	1.27
	PG15	-25.56	-0.98	32.56	1.96	-23.50	2.63
	PBr7	-18.52	-0.14	26.89	1.57	-21.68	2.60
	PY36	19.71	1.43	3.94	0.73	-50.02	2.31
PB29	-0.98	1.11	41.56	3.29	-46.46	2.55	
90 Days							
	PIGMENT	ΔE	σ	ΔL	σ	ΔC	σ
	PY34	35.98	4.50	2.13	1.27	-73.72	5.01
	PR104	6.86	2.41	32.59	2.02	-51.11	3.42
	PY43	-24.04	-0.73	34.75	2.52	-28.16	3.81
	PG23	-22.71	-0.45	23.25	1.78	-6.16	0.99
	PG15	-30.46	-0.43	37.48	2.29	-23.92	2.35
	PBr7	-21.23	0.41	29.92	1.90	-24.11	2.32
	PY36	20.39	1.98	4.85	1.06	-57.78	2.03
PB29	-5.09	1.66	47.51	3.62	-52.91	2.27	

days for the rest of the pigments mentioned.

Finally, there are two pigments whose visual differences are less discernible to the human eye, due to the fact that their ΔE variations are close to the $\Delta E \geq 3$ limit. These are the mix of gypsum and red pigment PR104 (molybdenum orange pigment), whose values are low,

particularly in the case of the measurement after twenty-four hours and slightly higher after twenty-eight and ninety days respectively. Furthermore, the interaction between gypsum and pigment in the PB29 mix (ultramarine blue pigment) is on the limit of what is visually perceptible after twenty-four hours and ninety days and sufficiently

Table 6.3
Pigment-gypsum-hydraulic lime (20–65-15%).

	PIGMENT	24 Hours					
		ΔE	σ	ΔL	σ	ΔC	σ
24 h	PY34	31.42	3.33	-2.94	-0.81	-47.28	4.48
	PR104	4.92	0.33	15.71	2.05	-37.16	1.14
	PY43	-16.91	-1.93	27.85	2.59	-22.35	0.81
	PG23	-11.60	-2.39	12.28	1.32	-2.95	0.14
	PG15	-14.79	-2.94	21.56	2.49	-20.20	2.70
	PBr7	-7.94	-0.85	15.92	1.31	-20.08	1.92
	PY36	21.61	3.41	-2.14	-0.87	-37.69	0.92
	PB29	-1.06	0.19	28.57	0.63	-35.67	0.86
28 days	PIGMENT						
		ΔE	σ	ΔL	σ	ΔC	σ
	PY34	41.18	3.01	-4.06	-0.10	-70.30	4.69
	PR104	7.68	0.08	23.71	2.50	-49.34	1.35
	PY43	-17.03	-1.20	27.86	2.99	-29.65	1.02
	PG23	-15.62	-1.57	16.18	1.84	-4.90	0.07
	PG15	-22.45	-2.01	29.52	2.90	-23.78	2.91
	PBr7	-14.29	-1.02	23.03	1.83	-24.97	2.13
	PY36	26.57	3.07	-1.77	-0.15	-55.91	1.13
	PB29	2.47	0.19	38.47	1.21	-48.13	1.07
	90 days	PIGMENT					
		ΔE	σ	ΔL	σ	ΔC	σ
PY34		43.54	3.76	-4.09	-0.11	-81.86	5.26
PR104		11.27	0.10	27.60	2.75	-54.62	1.92
PY43		-18.93	-1.50	28.79	3.29	-31.19	1.59
PG23		-17.88	-1.96	18.31	2.02	-8.36	0.64
PG15		-25.43	-2.51	32.44	3.19	-26.54	3.48
PBr7		-16.07	-1.28	24.92	2.01	-26.00	2.70
PY36		27.79	3.84	-1.74	-0.17	-64.38	1.70
PB29		6.73	-0.24	43.51	1.33	-53.47	1.64

discernible to the human eye after twenty-eight days. All of the changes defined in the case of ΔE are the consequence of the sum and respective differences between the elements a^* , b^* and L^* .

Where the variations of luminosity ΔL are concerned, it is important to study and evaluate them. The mixes of pigments with gypsum in proportions of 20–80% show increases of disparate values which are close to 45% for the mixes containing blue pigment PB29 (ultramarine blue pigment), particularly for the measurement after ninety days. Pigments PR104 (molybdenum orange pigment), PY43 (ochre pigment), PG23 (green earth pigment), PG15 (chromium green pigment) and PBr7 (natural sienna pigment) experience medium-high variations, generally 5% lower than that of pigment PB29 (ultramarine blue pigment). Finally, there are two pigments which are the least affected due to their high initial luminosity (L^*) values: PY34 (chromium yellow pigment) and PY36 (zinc yellow pigment) with luminosity variations which are imperceptible to the human eye in all cases (after twenty-four hours, twenty-eight days and ninety days) for pigment PY34 and only after ninety days for PY36 (zinc yellow pigment).

Visually, in all cases, the increase in the L^* value involves an increase in clarity and a significant tendency for the samples to experience whitening.

Lastly, the changes due to ΔC imply changes in the saturation of the gypsum-pigment mixes. Looking at the graphs and the tables, the values which they represent are negative, which is a key factor enabling us to confirm that a visual effect called sub-saturation occurs in all of the samples, involving a proportional loss of purity of hue with a tendency to move towards the ‘neutral’ area of the chromaticity diagram, which following several cycles, results in a loss of density of the dominant hue in the sample. As such, in this respect, the variations in saturation (sub-saturation) may be classified as drastic in the case of pigments PY34 (chromium yellow pigment), PR104 (molybdenum orange pigment), PY36 (zinc yellow pigment) and PB29 (ultramarine blue pigment), as average variations in the case of pigments PY43 (ochre pigment), PG15 (chromium green pigment) and PBr7 (Natural sienna pigment), and as insignificant variations in the case of PG23 (green earth pigment), although they are detectable to the human eye after twenty-four hours, twenty-eight days and ninety days.

The values for the mixes composed of gypsum, air lime and pigment (65–15-20%) generally show increases of $\Delta E \approx 2-50\%$, $\Delta L^* \approx 2-40\%$ and $\Delta C \approx 3-30\%$, after twenty-four hours. After twenty-eight days, the increases vary in the case of $\Delta E \approx 6-70\%$, $\Delta L^* \approx 8-80\%$ and $\Delta C \approx 12-50\%$. The value after ninety days shows accumulated increases of $\Delta E \approx 9-105\%$, $\Delta L^* \approx 11-80\%$ and $\Delta C \approx 19-57\%$. These increases must be interpreted, in addition to the total color variation inherent in each of the new samples, greater whitening and sub-saturation of the samples, probably caused by the higher alkalinity in mixes containing 15% of air lime.

Finally, in the case of the paste-filler mix based on the formula using gypsum, hydraulic lime and pigment (65–15-20%) variations-increases are detected in $\Delta E \approx 30-330\%$, $\Delta L^* \approx 9-340\%$ and $\Delta C \approx 27-52\%$, after twenty-four hours. After twenty-eight days, the increases vary in the case of $\Delta E \approx 49-365\%$, $\Delta L^* \approx 30-800\%$ and $\Delta C \approx 50-87\%$. The value after ninety days shows accumulated increases of $\Delta E \approx 75-415\%$, $\Delta L^* \approx 40-1100\%$ and $\Delta C \approx 65-103\%$.

All of these changes have been represented in the form of a color chart in Fig. 6, taking into consideration the average values: a^* , b^* and L^* for each sample. The first row of the figure sets out the pure colors and the binders used in each type of paste, and the samples made from gypsum and pigment (80–20%), according to color coordinates (CIELab 1976) [56].

Where the gypsum and pigment paste is concerned, after the initial setting of twenty-four hours and subsequent hardening at twenty-eight and ninety days respectively, it can firstly be highlighted that due to the mere fact of mixing a gypsum binder, whose hue is very similar to white, with any of the pigments listed, the result obtained is a color with a predominantly clear whitish tone, fundamentally due to a loss of saturation and increase in luminosity. The remaining periods (twenty-eight and ninety days) boost the initial variation due to the complete

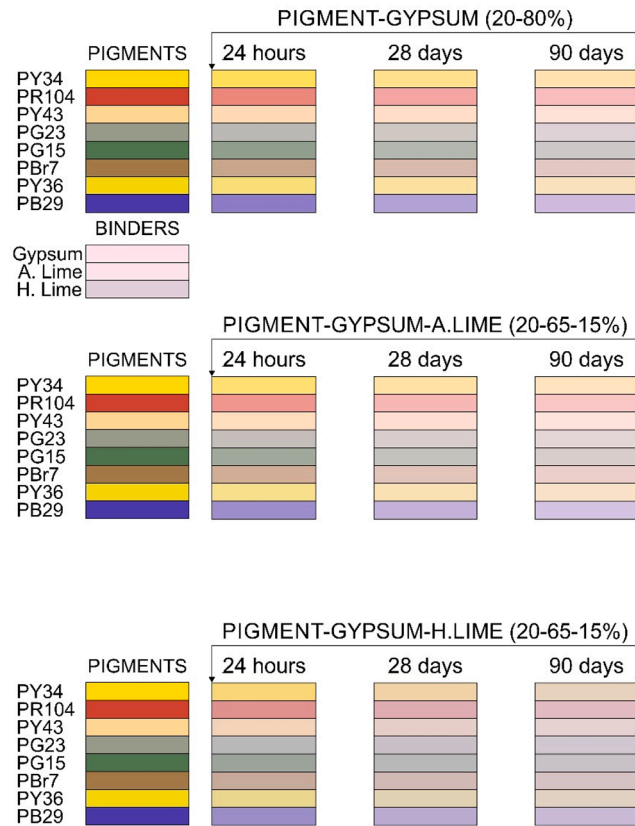


Fig. 6. Color chart for the different mixes and inorganic pigments used, indicating their color code and CIELab 1976 chromatic coordinates for the three stages of control (twenty-four hours, twenty-eight days and ninety days).

drying of the mixing water and hardening of the mix, together with a certain action of the pH of the gypsum paste, containing water, whose values range between ≥ 6.5 and ≤ 10.5 .

Fig. 6 also contains the representation of the mixes composed of gypsum, air lime and pigment (65–15–20%) where the color changes are more visible, particularly due to the progressive whitening of the samples after twenty-four hours, twenty-eight days and ninety days. This must be interpreted as being due to the higher alkalinity of the mix, especially of the air lime, with values of between ≥ 7 and ≤ 10.5 .

Finally, the mix of gypsum, hydraulic lime and pigment (65–15–20%), and its representation in the form of a color chart, incorporates a more visually significant blue hue in the hydraulic lime-based binder itself which certainly features less luminosity than the other binders. Consequently, in the resulting samples, a certain amount of contamination is observed which has a blue hue that comes from the binder, a lower increase in luminosity and, in general, a contrasting subsaturation of the samples which gradually progresses from twenty-four hours to the twenty-eight and ninety day stages. It is useful to note that the pH of the hydraulic lime with a high basicity of ≥ 12 , has the capacity to reduce the saturation of the samples in all of the time periods measured.

7. Conclusions

1. Focusing on the results obtained, it is possible to confirm the progress achieved by using air lime and hydraulic lime as additives to improve the qualities of gypsum pastes, this having been proven by the increase in the mechanical values of the final product.

2. The XRD and XRF results have made it possible to learn about the impact that composition has on the behavior of the mixes, and their importance in the dosage of binders and additives. The case of MgO and its impact on improving the compressive strength of final mixes was seen to be relevant, being more important in gypsum pastes containing hydraulic lime and, specifically, in the case where the sample is pigmented with green earth pigment (PG23), due to its high silicon aluminate and Mg content.

3. Based on the electron microscope study, it may be concluded that, due to the recrystallization of gypsum minerals, observed in all of the paste mixes, this fact may foster the consolidation of the cracks which appear as a product of contraction, improving their mechanical strength values.

4. All of the pastes studied have mechanical strength values in line with those accepted in other studies [67,68] or even higher [69], thereby confirming their suitability for on-site use based on their characteristics and behavior. All this confirms that the combination of gypsum with air lime and/or hydraulic lime improves mechanical strength of these mixes.

5. The colorimetric analysis showed total color differences for the pastes with added pigments, compared to the pure pigments, perceptible to the human eye in all cases, except for those featuring mixes of gypsum and pigment PR104 (80–20%) and gypsum, air lime and pigment PR104 (65–15–20%) after 24 h. At twenty-eight and ninety days, all of the total color variations were clearly perceptible to the human eye. In general, the causes of such significant color variations are due to the L^* component, with increases in luminosity which far exceed 100%, and also to a loss of saturation with percentage variations which exceed 100% following evaluation at ninety days. This colorimetric analysis by quantitative spectrophotometry is of vital importance to know the loss of intensity of the colors of the mortars used, since subjective observation gives rise to serious errors of interpretation, considering that these colored pastes have been designed for indoor use. Outdoor application of the pastes would require further tests of color development in which the climatic condition consequences would have to be analysed.

CRedit authorship contribution statement

M. Paz Sáez-Pérez: Conceptualization, Data curation, Formal

analysis, Investigation, Supervision, Validation, Methodology, Visualization, Writing - original draft, Writing - review & editing. **Jorge A. Durán-Suárez:** Conceptualization, Data curation, Formal analysis, Investigation, Supervision, Validation, Methodology, Visualization, Writing - original draft, Writing - review & editing. **Amparo Verdú-Vázquez:** . **Tomás Gil-López:** .

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to thank the reviewers for their thoughtful comments and efforts towards improving our manuscript. This work was supported by the REMINE Programme for Research and Innovation Horizon 2020 Marie Skłodowska-Curie Actions and RRRMAKER H2020-MSCA-RISE-2020 (Marie Skłodowska-Curie Research and Innovation Staff Exchange and was carried out under the auspices of Research Groups RNM 0179 and HUM 629 of the Junta de Andalucía. Funding for open access charge: Universidad de Granada / CBUA

References

- [1] M.N. Flores, M.M. Barbero-Barrera, Mechanical and physical enhancement of gypsum composites through a synergic work of polypropylene fiber and recycled isotactic graphite filler, *Constr Build Mater* 131 (2017) 165–177, <https://doi.org/10.1016/j.conbuildmat.2016.11.073>.
- [2] W. Wang, N. Chouh, The behaviour of coconut fibre reinforced concrete (CFRC) under impact loading, *Constr Build Mater* 134 (2017) 452–461, <https://doi.org/10.1016/j.conbuildmat.2016.12.092>.
- [3] J.P. Firmo, J.R. Correia, L.A. Bisby, Fire behaviour of FRP-strengthened reinforced concrete structural elements: a state-of-the-art review, *Compos B Eng* 80 (2015) 198–216, <https://doi.org/10.1016/j.compositesb.2015.05.045>.
- [4] D. Asprone, E. Cadoni, F. Iucolano, A. Prota, Analysis of the strain-rate behavior of a basalt fiber reinforced natural hydraulic mortar, *Cement Concr Compos* 53 (2014) 52–58, <https://doi.org/10.1016/j.cemconcomp.2014.06.009>.
- [5] R. Hamzaoui, S. Guessasma, B. Mecheri, A.M. Eshtiaghi, A. Bennabi, Microstructure and mechanical performance of modified mortar using hemp fibres and carbon nanotubes, *Mater Des* 56 (2014) 60–68, <https://doi.org/10.1016/j.matdes.2013.10.084>.
- [6] F. Iucolano, B. Liguori, C. Colella, Fibre-reinforced lime-based mortars: a possible resource for ancient masonry restoration, *Constr Build Mater* 38 (2013) 785–789, <https://doi.org/10.1016/j.conbuildmat.2012.09.050>.
- [7] S. Eve, M. Gomina, A. Gmouh, A. Samdi, R. Moussa, G. Orange, Microstructural and mechanical behaviour of polyamide fibre-reinforced plaster composites, *J Eur Ceram Soc* 22 (2002) 2269–2275, [https://doi.org/10.1016/S0955-2219\(02\)00014-6](https://doi.org/10.1016/S0955-2219(02)00014-6).
- [8] A.J. Majumdar, Glass fibre reinforced cement and gypsum products, *Proc R Soc A Math Phys Eng Sci* 319 (2006) 69–78, <https://doi.org/10.1098/rspa.1970.0166>.
- [9] Aizi, D.E., Kaid-Harche, M. Mechanical Behavior of Gypsum Composites Reinforced with Retama monosperma Fibers. *Proceedings* 2021, 63, 40.
- [10] F. Iucolano, L. Boccarusso, A. Langella, Hemp as eco-friendly substitute of glass fibres for gypsum reinforcement: impact and flexural behavior, *Compos Part B-Eng* 175 (2019), 107073, <https://doi.org/10.1016/j.compositesb.2019.107073>.
- [11] C. Mileto, F. Vegas, V. La Spinali, (2011) is gypsum external rendering possible? the use of gypsum mortar for rendering historic façades of Valencia's city centre, *Adv Mat Res* 250–253 (2011) 1301–1304, <https://doi.org/10.4028/www.scientific.net/AMR.250-253.1301>.
- [12] L. Rampazzi, C. Corti, R. Bugini, A. Sansonetti, M. Biraghi, L. Castelletti, I. Nobile, C. Orsenigo, Thermal analysis and archaeological chronology: the ancient mortars of the site of Baradello (Como, Italy), *Thermochim Acta* 572 (2013) 71–84, <https://doi.org/10.1016/j.tca.2013.08.015>.
- [13] C. Martias, Y. Joliff, C. Favotto, Effects of the addition of glass fibers, mica and vermiculite on the mechanical properties of a gypsum-based composite at room temperature and during a fire test, *Compos B Eng* 62 (2014) 37–53, <https://doi.org/10.1016/j.compositesb.2014.02.019>.
- [14] L.N. Henrik, Now: 100% wallboard recycling with gypsum recycling international, *Global Gypsum Mag* 98 (2017) 122–129.
- [15] M. Arikan, K. Sobolev, The optimization of a gypsum-based composite material, *Cement Concr Res* 32 (2002) 1725–1728, [https://doi.org/10.1016/S0008-8846\(02\)00858-X](https://doi.org/10.1016/S0008-8846(02)00858-X).
- [16] A.M. Rashad, Phosphogypsum as a construction material, *J Clean Prod* 166 (2017) 732–743, <https://doi.org/10.1016/j.jclepro.2017.08.049>.
- [17] O. Gencel, J.J. del Coz Diaz, M. Sutcu, F. Koksul, F.P. Álvarez Rabanal, G. Martínez-Barrera, A novel lightweight gypsum composite with diatomite and polypropylene

- fibers, *Construct Build Mater* 113 (2016) 732–740, <https://doi.org/10.1016/j.conbuildmat.2016.03.125>.
- [18] Bel-Anzué, P., Almagro, A., Sáez-Pérez, M.P., Rodríguez-Navarro, C. (2017). Influence of the calcination process in traditional gypsum with structural behavior. *Ge-conservación* n° 11, pp. 79–85. ISSN: 1989-8568.
- [19] J. Elsen, Microscopy of historic mortars - a review, *Cement Concrete Res* 36 (2006) 1416–1424, <https://doi.org/10.1016/j.cemconres.2005.12.006>.
- [20] M. Doleželová, L. Scheinherrová, A. Vimmrová, *Moisture resistance and durability of the ternary gypsum-based binders in 7th International Conference on Building Materials*, edited by E. Vejmelková et al. Trans Tech Publications, Uetikon-Zurich, 2015, pp. 81–87.
- [21] M.D. Butakova, S.P. Gorbunov, Study of the influence of complex additives on properties of the gypsum-cement-puzzolan binder and concretes on its basis, *Procedia Eng.* 150 (2016) 1461–1467, <https://doi.org/10.1016/j.proeng.2016.07.082>.
- [22] G. Camarini, J.A. De Milito, Gypsum hemihydrate-cement blends to improve renderings durability, *Constr. Build. Mater.* (2011), <https://doi.org/10.1016/j.conbuildmat.2011.04.048>.
- [23] T. Cerulli, C. Pistolesi, C. Maltese, D. Salvioni, *Durability of traditional plasters with respect to blast furnace slag-based plaster*, *Cem. Concr. Res.* 33 (2003) 1375–1383.
- [24] M. Pang, Z. Sun, H. Huang, Compressive strength and durability of FGD gypsum-based mortars blended with ground granulated blast furnace slag, *Materials* 2020 (13) (2020) 3383, <https://doi.org/10.3390/ma13153383>.
- [25] M.T. Freire, *Restoration of ancient Portuguese interior plaster coatings: Characterization and development of compatible gypsum-based products*, PhD Thesis, University of Lisbon, Instituto Superior Técnico, 2016.
- [26] F. Vasconcelos, in: *Considerations about decorative plasterwork*, (in Portuguese), 1966, pp. 34–43.
- [27] M. Conde, *Interview to vítor serrão*, *Pedra & Cal.* (2001) 14–16.
- [28] E. Vieira, *Stuccos in the context of decorative arts in Portugal*, Oporto, Portugal, In *I Encontro Sobre Estuques Port.*, 2008, pp. 19–26.
- [29] H.B. Fischer, B. Vtorov, *Characterization of historical gypsum mortars*, *ZKG Int.* 55 (2002) 92–99.
- [30] D. Sanz, *Analysis of gypsum used in external renders using geological techniques*, PhD Thesis, Polytechnic University of Madrid, Spain, 2009.
- [31] Franzoni, E., Sandrolini, F., Baldazzi, L. Characterization of gypsum-selenite plasters from historic buildings in the Emilia-Romagna region (Italy). In *Proceedings of the 2nd Hist. Mortars Conf. (HMC2010)*, RILEM TC 203-RHM Final Work, Prague, J. Válek, C. Groot, J.J. Hughes (Eds.). 2010, pp. 157–164.
- [32] Igea, J., Lapuente, P., Blanco-Varela, M.T., Martínez-Ramírez, S. Ancient gypsum mortars from Sta. María Magdalena church (Zaragoza, Spain): Advances in technological manufacture, In *Proceedings of the 2nd Hist. Mortars Conf. (HMC2010)*, RILEM TC 203-RHM Final Work, Prague, J. Válek, C. Groot, J.J. Hughes (Eds.). 2010, pp. 197–205.
- [33] J. Igea, P. Lapuente, S. Martínez-Ramírez, M.T. Blanco-Varela, *Characterization of mudejar mortars from san jil abbot church (Zaragoza, Spain): investigation of the manufacturing technology of ancient gypsum mortars*, *Mater. Construcc* 62 (2012) 515–529, <https://doi.org/10.3989/mc.2012.07311>.
- [34] J. Igea, J. Romera, S. Martínez-Ramírez, P. Lapuente, M.T. Blanco-Varela, *Assessment of the physico-mechanical behaviour of gypsum-lime repair mortars as a function of curing time*, *Environ. Earth Sci.* 70 (2013) 1605–1618, <https://doi.org/10.1007/s12665-013-2245-y>.
- [35] Theodoridou, M., Lofa, M., Ioannou, I. *Historic Gypsum Mortars from Cyprus: Characterization and Reinvention for Conservation Purposes*. In *Proceedings of the 3rd Hist. Mortars Conf. HMC2013*, Glasgow, 2013, pp. 1–8.
- [36] Middendorf, B., Knöfel, D. *Characterization of historic mortars from buildings in Germany and The Netherlands*, In *Conserv. Hist. Brick Struct.*, Donhead Publ. Ltd. Eds. N.S. Baer, S. Fitz, R.A. Livingston, 1998, pp. 178–196.
- [37] Tesch, V., Middendorf, B. *Optimised microstructure of calcium sulphate based mortars for the restoration of historic masonry*. In *Repair Mortars Hist. Mason.*, RILEM, Delft, Ed. C. Groot, 2005, pp. 345–353.
- [38] Vignola, M., Borgia, D., Pennacchio, R., Zerbinatti, M. (2020). *Mortars and plasters produced with earth-based sustainable mixes: a methodology proposal for recovery of vernacular architecture in Roero, Piedmont (Italy)*. In *proceedings of The International Archives of the Photogrammetry, Remote Sensing and Spatial Information Sciences*, Volume XLIV-M-1-2020, 2020. HERITAGE2020 (3DPast | RISK-Terra) International Conference, 9–12 September 2020, Valencia, Spain.
- [39] M. Melgosa, F.J. Collado-Montero, E. Fernández, V.J. Medina, *Estudio colorimétrico de los azulejos del Patio de las Doncellas del Real Alcázar de Sevilla (España)*, *Bol. Soc. Esp. Ceram. Vidrio.* 54 (2015) 109–118, <https://doi.org/10.1016/j.bsecv.2015.03.002>.
- [40] Rodríguez-Gordillo, J., Durán-Suárez, J.A., Sáez-Pérez, M.P. *Efecto de agentes ambientales en el cromatismo de pigmentos con aglutinantes pictóricos para su aplicación en conservación y restauración patrimonial*, ph investigación 2014, 3, 35–53. <http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/articulo/view/52>.
- [41] J. Rodríguez-Gordillo, M.P. Sáez-Pérez, J.A. Durán-Suárez, *Evaluación experimental del comportamiento cromático de pigmentos inorgánicos en diversos aglutinantes pictóricos*, ph investigación 1 (2013) 41–53, <http://www.iaph.es/phinvestigacion/index.php/phinvestigacion>.
- [42] R.W. Pridmore, 14th century example of the four unique hues, *Color Res. Appl.* 31 (2006) 364–365, <https://doi.org/10.1002/col.20229>.
- [43] V. Reillon, S. Berthier, *Modelization of the optical and colorimetric properties of lusted ceramics*, *Appl. Phys. A.* 83 (2006) 257–265, <https://doi.org/10.1007/s00339-006-3492-5>.
- [44] J.A. Durán-Suárez, J.A., García-Beltrán, A., Sáez-Pérez, M.P., Rodríguez-Gordillo, J. *Evaluation of the chromatic effectiveness of color pigments in restoration materials (lime and Portland cement)*, *Color Res. Appl.* 2000, 25, 286–291, [https://doi.org/10.1002/1520-6378\(200008\)25:4<286::AIDCOL9>3.0.CO;2-H](https://doi.org/10.1002/1520-6378(200008)25:4<286::AIDCOL9>3.0.CO;2-H).
- [45] E. Kirchner, G.-J. van den Kieboom, L. Njo, R. Supèr, R. Gottenbos, *Observation of visual texture of metallic and pearlescent materials*, *Color Res. Appl.* 32 (2007) 256–266, <https://doi.org/10.1002/col.20328>.
- [46] M.P. Sáez-Pérez, J. Rodríguez-Gordillo, J.A. Durán-Suárez, *Synthetic white pigments (white titanium and white zinc) in different binding media. Influence of environmental agents*, *Constr. Build. Mater.* 114 (2016) 151–161, <https://doi.org/10.1016/j.conbuildmat.2016.03.140>.
- [47] Sophia M., Sakhieswaran N., Ganesh Babu O. (2016). *Gypsum as a Construction Material- A Review of Recent Developments* IJRST. Int. J. Innov. Research Sci. Technol., Volume 2, Issue 12, May 2016. ISSN (online): 2349-6010, PP. 315-323.
- [48] N. Lushnikova, L. Dvorkin, in: *Sustainability of gypsum products as a construction Material. Sustainability of Construction Materials*, Elsevier, 2016, pp. 643–681, <https://doi.org/10.1016/B978-0-08-100370-1.00025-1>.
- [49] N. Naik, B. Bahadure, C. Jejurkar, *Strength and durability of fly ash, cement and gypsum bricks*, *Int. J. Comput. Eng. Sci.* 4 (5) (2014) 48–51.
- [50] Hashempour, M., Asaad Samani, A., Heidari, A. (2021). *Essential Improvements in Gypsum Mortar Characteristics*. IJE TRANSACTIONS B: Applications Vol. 34, No. 02, (February 2021) 319-325. 10.5829/ije.2021.34.02b.03.
- [51] AATCC (2002a) *Colour Index International*. Bradford: American Association of Textile Chemist and Colorist and Society of Dyers and Colourists, 2002 <<http://www.colour-index.com/>>].
- [52] <https://sdc.org.uk/>.
- [53] <https://www.aatcc.org/>.
- [54] Martín Ramos, J.D. (2004). *X Powder, a software package for poder X-ray diffraction analysis*, Legal Deposit, Spain, (GR1001/04).
- [55] D.L. Whitney, B.W. Evans, *Abbreviations for names of rock-forming minerals*, *Am. Mineralogist* 95 (2010) 185–187, <https://doi.org/10.2138/am.2010.3371.185> (0003-004X/10/0001-185\$05.00).
- [56] K. McLaren, *The development of the CIE 1976 (L*a*b*) uniform colour-space and colour-difference formula*, *Color. Technol.* 92 (9) (2008) 338–341, <https://doi.org/10.1111/j.1478-4408.1976.tb03301.x>.
- [57] UNE-EN 1015-11:2000/A1:2007 *Methods of test for mortar for masonry - Part 11: Determination of flexural and compressive strength of hardened mortar*.
- [58] D.B. Judd, G. Wysecki, *In Color in Business, Science, and Industry*, 3rd ed., Wiley-Interscience, New York, 1975.
- [59] AATCC (2005) *Test Method 173 CMC (TM-173-2005). Calculation of small differences for acceptability*. AATCC Technical manual. American Association of Textile Chemist and Colorist, 2006, pp. 311–315.
- [60] Fernández-Abascal, H.; Gujjarro, M.; Rojo, J. I. et al. *Cálculo de Probabilidades y Estadística*. Barcelona: Editorial Ariel, 1994, 282 pp., ISBN84-344-2094-5.
- [61] F. Pacheco-Torgal, J. Faria, S. Jalali, *Some considerations about the use of lime-cement mortars for building conservation purposes in Portugal: a reprehensible option or a lesser evil?* *Constr Build Mater.* 30 (2012) 488–494, <https://doi.org/10.1016/j.conbuildmat.2011.12.003>.
- [62] M.A.S.A.A. Hussein, *Enhancing the compressive strength property of gypsum used in walls plastering by adding lime*, *J. Univ. Babylon eng. sci.* 26 (2018) 3.
- [63] K.A. Prasanna, K.P. Sanjaya, *Effect of lime and ferrochrome ash (FA) as partial replacement of cement on strength, ultrasonic pulse velocity and permeability of concrete*, *Constr Build Mater.* 94 (2015) 448–457, <https://doi.org/10.1016/j.conbuildmat.2015.07.081>.
- [64] V. Brunello, D. Bersani, L. Rampazzi, A. Sansonetti, C. Tedeschi, *Gypsum based mixes for conservation purposes: evaluation of microstructural and mechanical features*, *Mater Construcc* 70 (337) (January–March 2020), e207, <https://doi.org/10.3989/mc.2020.05019>.
- [65] C. Atzeni, L. Massidda, U. Sanne, *Magnesian lime. Experimental contribution to interpreting historical data*, *Sci. Technol. Conserv. Cult. Herit.* 5 (2) (1996) 29–36.
- [66] R.M. Dheilley, A. Bouguerra, B. Beaudoin, J. Tudo, M. Queneudec, *Hydromagnesite development in magnesian lime mortars*, *Mater. Sci. Eng. A.* 268 (1–2) (1999) 127–131, [https://doi.org/10.1016/S0921-5093\(99\)00085-4](https://doi.org/10.1016/S0921-5093(99)00085-4).
- [67] Jara, L.M.S., Yepes, J.A.F. Pérez, J.J.P. *Analysis of the Resistance to Bending of Gypsum with Added Graphene*. *Coatings* 2021, 11, 650. 10.3390/.
- [68] Čárhová, M., Konáková, D., Vejmelková, E., Bartonková, E., Keppert, M. Cerný, R. *Properties of lime-cement plasters incorporating ceramic powder*. *Int. J. Comp. Meth. and Exp. Meas.* 2017, 5, 2, 144–153. 10.2495/CMEM-V5-N2-144-153.
- [69] J. Krejsová M. Doleželová *Resistance of mortars with gypsum, lime and composite binders against molds* *Acta Polytechnica CTU Proceedings* 21 2019 16 20 10.14311/APP.2019.21.0016.