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...
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 boasting.

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 dryed, milled, packaged and sold. In the case of the hydraulic lime (NHLS), 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
Table 1

| Acronym | Colour index name | Commercial pigment/binder | 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) silicoaluminate, Mg and K |
| PG15    | 77,288           | Chromium green pigment    | Chromium oxide             |
| PR7     | 77,491-2         | Natural sienna pigment    | Calcined natural iron oxide |
| PY36    | 77,956           | Zinc yellow pigment       | Zinc chromate              |
| PR29    | 77,007           | Ultramarine blue pigment  | Sodium polysulphate- aluminoisolate |
| 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 |

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.

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 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), PR7 (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 PG36 (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 red tone, but in fact, this means that it displays a violet hue with a high level of saturation according to the relationship ($C/S = \sqrt{a^* + b^*}$), 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.

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
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, textual 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

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

| SAMPLE       | SiO₂   | Al₂O₃  | Fe₂O₃  | MnO   | MgO   | CaO   | Na₂O  | K₂O   | TiO₂  | P₂O₅  | SO₃   | Cl    | LOI   |
|--------------|--------|--------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 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 |

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 |
|--------------|--------|----------|----------------|---------|-------------|
| P            | 80     | 0        | 0              | 20      | 0.5         |
| PAL          | 65     | 15       | 0              | 20      | 0.5         |
| PHL          | 65     | 0        | 15             | 20      | 0.5         |

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.
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 ≈ 25–45 μm, 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 ± 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).
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 + 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     | 0.03 |
| P + PG23  | 2.27     | 0.03 | 5.47     | 0.01 |
| P + PG15  | 2.27     | 0.01 | 5.43     | 0.03 |
| P + PB7   | 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       |          |      |          |      |
| 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| 2.948    | 0.05 | 5.55     | 0.07 |
| PAL + PB7 | 2.9419   | 0.04 | 5.61     | 0.06 |
| PAL + PY36| 2.929    | 0.06 | 5.59     | 0.04 |
| PHL       |          |      |          |      |
| 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 + PB7 | 3.93     | 0.07 | 9.85     | 0.01 |
| PHL + PY36| 3.9       | 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 ± 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].

As in the previous case, no notable differences are observed in the samples containing pigment, except in the mix containing green earth pigment (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.

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 c0.5%. 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 ΔE ≥ 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-eighty, 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), PB7 (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
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 values are perceptive after twenty-four hours 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 6.1 Pigment-gypsum (20–80%).

| PIGMENT | 24 Hours | | | | |
|---------|----------|---|---|---|---|
| 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 |

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

| PIGMENT | 24 Hours | | | | |
|---------|----------|---|---|---|---|
| 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 |

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.

[38x64]close to the discernible to the human eye, due to the fact that their days for the rest of the pigments mentioned.

Pigment-gypsum (20

The values are low, particularly in the case of the measurement after twenty-four hours and slightly higher after twenty-eight and ninety days respectively.
discernible to the human eye after twenty-eight days. All of the changes defined in the case of $\Delta E$ are the consequence of the sum and respective differences between the elements $a^*$, $b^*$ and $L^*$.

Where the variations of luminosity $\Delta L$ 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 PB7 (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 low initial luminosity (L*) values: PY34 and PB29, particularly for the measurement after ninety days. After twenty-eight days, the increases vary in the case of $\Delta E \approx 30–330\%$, $\Delta L^* \approx 9–340\%$ and $\Delta C \approx 27–52\%$, after twenty-four hours. After twenty-eight days, the changes vary in the case of $\Delta E \approx 49–365\%$, $\Delta L^* \approx 9–800\%$ 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 whithish 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 variation in $L^*$ value.

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

| PIGMENT | $\Delta E$ | $\sigma$ | $\Delta L$ | $\sigma$ | $\Delta C$ | $\sigma$ |
|---------|-----------|---------|-----------|---------|-----------|---------|
| 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    |
| PB7     | -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    |

Where the variations of luminosity $\Delta L$ 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 PB7 (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 low initial luminosity (L*) values: PY34 and PB29, particularly for the measurement after ninety days. After twenty-eight days, the increases vary in the case of $\Delta E \approx 30–330\%$, $\Delta L^* \approx 9–340\%$ and $\Delta C \approx 27–52\%$, after twenty-four hours. After twenty-eight days, the changes vary in the case of $\Delta E \approx 49–365\%$, $\Delta L^* \approx 9–800\%$ 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 whithish 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 variation in $L^*$ value.

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 changes vary in the case of $\Delta E \approx 49–365\%$, $\Delta L^* \approx 9–800\%$ 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 whithish 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 variation in $L^*$ value.

Lastly, the changes due to $\Delta C$ 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 PB7 (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.

![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).](image-url)
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 $\geq 6.5$ and $\leq 10.5$.  

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 $\geq 7$ and $\leq 10.5$.

Finally, the mix of gypsum, hydraulic lime and pigment (65–20%), 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 $\geq 12$, 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 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 RRMAKER 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 isostatic graphite filler, Constr Build Mater 131 (2017) 165–177, https://doi.org/10.1016/j.conbuildmat.2016.11.073.

[2] W. Wang, N. Chouw, 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. Bishy, 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.2015.05.046.

[4] D. Asprone, E. Cadoni, F. Lucano, A. Prota, Analysis of the strain-rate behavior of a basalt fibre reinforced natural hydraulic mortar, Cement Concr Compos 53 (2014) 52–58, https://doi.org/10.1016/j.cemconcomp.2014.06.009.

[5] R. Hamzouzi, S. Guesssama, B. Mecheri, A.M. Estghiab, A. Benabhi, 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. Luciano, 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 polylamide fibre-reinforced plaster composites, J Eur Ceram Soc 22 (2002) 2269–2275, https://doi.org/10.1016/S0955-2219(02)00145-6.

[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 Behaviour of Gypsum Composites Reinforced with Retama monosperma Fibers. Proceedings 2021, 63, 65, 40.

[10] F. Luciano, L. Boccarossa, 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 Spinalis, (2011) is gypsum external rendering possible? the use of gypsum mortar for rendering historic façades of valenca’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. Sansonnetti, M. Biraghi, L. Castelletti, I. Nobile, C. Orsengo, 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. Hendrik, Now: 100% wallboard recycling with gypsum recycling international, Global Gypsum Mag 98 (2017) 122–129.

[15] M. Arikian, K. Sobolev, The optimization of a gypsum-based composite material, Cement Concr Res 32 (2002) 1725–1728, https://doi.org/10.1016/S0001-6975(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 Cox Diaz, M. Sutcu, F. Koksal, F.P. Alvarez Rabanus, G. Martinez-Barrera, A novel lightweight gypsum composite with diatomite and polypropylene
G. Maranini, J.A. De Milito, Gypsum hemihydrate-cement blends to improve renderings durability, Constr. Build. Mater. (2011), https://doi.org/10.1016/j.conbuildmat.2011.04.012.

G. T. Ceraldi, C. Pistolesi, C. Mutalese, D. Salvioni. Durability of traditional plasters with respect to blast furnace slag-based plaster, Cem. Conc. Res. 33 (2003) 1375-1382.

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/ma13123383.

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.

F. Vasconcelos, in: Considerations about decorative plasterwork, (in Portuguese), Publicações do Instituto Português de Artes Decorativas, 2012.

M. D. Butakova, S. P. Gorbunov, Study of the influence of complex additives on properties of the gypsum-cement-pozzolan binder and concretes on its basis, Procedia Eng. 150 (2016) 1461-1467, https://doi.org/10.1016/j.proeng.2016.07.082.

D. B. Judd, G. Wyszecki. In Color in Business, Science, and Industry, 3rd ed., Wiley-Interscience, New York, 1975.

A. Atascue-Pérez, J. A. Durández, Evaluación de los pigmentos halloysiticos, ph investigación 2014, 3, 35-53. http://www.ihapx.ph/finphivignification/index.php/finphivignificacion/article/ view/82.

J. Rodríguez-Gordillo, J. Sáez-Pérez, J.A. Durán-Suárez, Evaluación experimental del comportamiento cromático de pigmentos inorgánicos en diversos aglutinantes pictóricos, ph investigacion 1 (2013) 41-53, es/phinvignification/index.php/finphivignificacion, http://www.ihapx.ph.