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Influence of inorganic and organic additives on spectrophotometry of lime mortars

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Abstract: Variation in colors in lime base mortars by adding materials like clay, manufacturing brick ash, quarry powder, and maize starch have been analyzed in this research. Such additions were compared with a sample mortar made only of sand and clay. In order to quantify the color, Chromatic coordinates, expressed in coordinates C.I.E. (L*, a* and b*) were measured. These analyses determine the median chromatic coordinates which are between red and yellow, maybe as orange. To design a mortar in that original color the measured values L*, a* and b* were taken into account. The present work shows the results of color of lime mortars which provides acceptable aesthetic results according to the original colors of the monuments that is intended to be restored but without diminishing the mechanical resistance of them.

Key words: Spectrophotometry, lime, mineral additions, mortars, restoration.

Influencia de aditivos orgánicos e inorgánicos en la espectrofotometría en morteros de cal

Resumen: En el presente trabajo se analizaron las variaciones de color de mezclas de mortero base cal con adiciones de materiales como: arcilla, ceniza de ladrillo, polvo de ignimbrita y fécula de maíz; comparando dichas adiciones con un mortero testigo de cal-arena. Para cuantificar el color, se midieron las coordenadas colorimétricas, expresadas en función de las coordenadas C.I.E. (L*, a* y b*). Estos estudios determinan las coordenadas cromáticas medias, que están en la gama de rojo-amarillo como es el naranja. En el diseño de un mortero con ese color original se tendrían que tener en cuenta los valores medidos de L*a*b*. El presente trabajo muestra los resultados de color del mortero base cal que proporciona resultados estéticos aceptables según los colores originales de los monumentos que se pretenden restaurar pero sin demérito de la resistencia mecánica de los mismos.

Palabras clave: Espectofotometría, cal, aditivos minerales, mortero, restauración.

Introduction

Gradual deterioration of the stone in historic monuments caused by physical, chemical, structural or anthropogenic agents, requires restoration procedures which part of them can consist on the application of binders or lime mortars not only for aesthetic purposes, but for protecting the exposed facades of the colonial architectural monuments built with ignimbrites stones from quarries of the surroundings. The first approach to conserve these monuments was to replace the damaged blocks but as the city grew and all the quarries around it were covered, it was not possible to find the same rock quality and worse, the active quarries were not enough appropriate to replace the blocks, so the best way in the meantime of finding new quarry stones for restoration works in monuments was to protect (cover) the non-sculpted facades. However, as the historic center of Morelia city – Mexico - is listed as UNESCO World Heritage Centre, there are rules according with restoration, specifically with color, than the mortars must comply. Morelia is also called the Pink City.

As it is widely known, lime mortars are not real hard building materials (Pozo, 2015; Grilo et al, 2014; Ventol à et al, 2011), therefore additions are considered to modify the mechanical, physical and aesthetic properties. Additions can be included as powder: the ones mentioned in this article, powder of the unaltered quarry stones, ash dust from the ovens in which bricks are fired, montmorillonite clays, and corn starch. Other additions can be incorporated in a liquid/semi-liquid state as milk, blood, oil, egg yolk and white, lard, cactus sap; and fibbers for increasing flexural strength like cotton, wool, goat hair, chicken feathers. The powder additions can modify the color of mortars, and simultaneously they can also modify their mechanical properties, although this research only will refer to color as an aesthetical characteristic of its appearance.

The liquid additions modify the color of the lime mortars, but unfortunately towards a greenish tonality, and we were looking for pink color located between yellow and red axes, as indicated for the exposed ignimbrites taken from the colonial buildings (house of culture, Colegio San Nicolas). Then we decided to characterize the mortar color tending to pink, and fortunately the powder additions result in this aesthetic property. Of course the mortar color is not identical to the architectural patrimonial ignimbrites, the new restoration works must be noted (Stefanidou et al 2015).

The necessity to avoid or to minimize the visual impact of the protecting material during restoration requires the development of quantitative methods of color determination in this kind of material. The methods based on the visual comparison of colors (Esbert et al 1989:5-26; Tabasso 1992: 45-57) have been replaced by other methods based on spectrophotometry (Tabasso 1992: 45-57).

In the past it has been demonstrated the benefit that supposed the application of preventive measures that curb the deterioration of cultural inheritance; its preservation must be set as a main objective and search the measures necessary for the most suitable environmental conditions (Concha et al 2009), such as SO2 and particulate matter (PM), both mostly generated by fossil fuel combustion are the main causes of aesthetic and material deterioration on patrimony construction, particularly on carbonate materials (Bonazza et al 2005: 2607-2618; Grossi et al 2008: 143-160; Sablier and Garrigues 2014). In contaminated urban areas, the facades use to present black crusts on them, specially containing carbon and sulphur, gypsum, from the fossil fuels combustion by mobile vehicles (Bonazza et al 2005: 2607-2618; Grossi et al 2007: 117-130; Fronteau et al 2010: 25-34; Perez et al 2016). To preserve cultural inheritance it is a must trying to preserve the architectural monuments, but of course it could be a risk for the originality of the monument, as there is not a complete safe way to do conservation or restoration in Human Inheritance (Concha et al 2009).

The criteria to replace stones in a historic building should be based on geological, geotechnical and aesthetic parameters instead of visual methods, qualitative-subjective aspects or economical consideration (Taboada et al 1998:203-210; Dreesen and Dusar 2004: 273-287). When the original quarry stones are not in use any more it can commonly derive in an inadequate substitution, where a mosaic of original and substituted elements come together. This, not only provokes an unpleasant effect related to the change of color, but also, it does not comply international criteria for restoration and in force legislation, recommendations and guidelines related to national patrimony monuments (ICOMOS 1975; Llamas 2002; Prieto et al 2011).

Spectrophotometry measures the spectral reflectance of a material using certain directions and detection of fixed and unique lightness. Having such spectral reflectance and supposing a determined illuminant and observer colorimeter pattern, the color specification of the sample is eventually obtained. The International Commission of Illumination (CIE) recommends, that such color specification is tridimensional, being nowadays the space of color CIE 1976 (L*a*b*), usually designed as CIELAB (CIE 2014).

The purpose of spectrophotometry applied to works of art or to cultural patrimony, through spectrophotometric measurement, is to register, very precisely, the magnitudes that identify color attributes such as tone, clarity and saturation (Manlio 2005, 2015).

The chromatic reintegration materials have been very varied for some decades, but some novel materials have been used lately because of their workability, which carries an aesthetic function while integrating them in the original work (Lastras-Pérez et al 2011-2012). Some researches performed in Mexico have characterized mechanically and physically materials with varied organic and inorganic additives (Martínez-Molina et al 2010; Velazquez-Pérez 2015) with which prehistoric and colonial monuments were built (Sickels 1981-829; Magaloni 2008, Martinez et al 2008). It is necessary to determine the color variations which each additive confers to the mix because when using any mix for the restoration of monuments, we have to take into account the color of the restoration materials because they should not affect the historical monument aesthetically in a global set, such in a way to avoid a color loss. Therefore, the material used in chromatic reintegration should not loose its colorimetric properties showing a clear difference from the original material as a result of a wrong intervention (Lastras-Pérez et al 2011-2012).

In this study the result of a color analysis of lime mortars is shown. The study was done by adding organic or inorganic materials applied to walls as coatings, searching for a color that gives acceptable aesthetic results according to the original colors of architectural monuments to be restored, but preserving at the same time the mechanical resistance of mortars.

Methodology

This research started with previous studies on additives in different percentages [Velazquez-Perez 2015]. The additives were chosen according to their workability, adhesion, and the presence of cracks due to drying; as a result we study different additions - related to lime percentages weight: clay, 25%; quarry stone powder, 50%; brick ash, 50%; and corn starch, 2%. With the elaborated mixtures, brick walls were built and covered with these different mortars to evaluate their behavior and to measure the color of the dry mortars, comparing them through spectrophotometry, adhesion and carbonation depth tests, performed for both the control mixture and the modified mixtures.

—Mix Design

The materials used for this research were: Lerma River Sand: quality tests were carried out in accordance with current regulations. The sand material used was between sieves 4 to sieve 30, ASTM, the one that passes through sieve number 4, trying to reproduce the mix that is prepared to restore buildings in the State of Michoacán, Mexico. It is a silica sand. Water: tap water was used. Cementing material: Industrial lime from the Piedras de Lumbre stone quarry, in Jungapeo, Mexico, was used. Materials added as pigments: As said before, the powder additions came from ash of burnt wood in the manufacturing of handmade bricks, ignimbrite powder from the stone quarries surrounding Morelia, Mexico called Cointzio and "Jamaica", corn starch, and clay, the montmorillonite clay was classified as CL according to the Unified Soil Classification System (USCS). It also comes from the surroundings of Morelia, Mexico, sifting and adding them dry.

There is no a standardized method to design mortar mixes. For this work we used the weight ratio 1:2.5 for lime mortar, one portion of lime and two point five portions of sand. This proportion was suggested in previous works and widely used in restoration works (Arreola-Sanchez 2009, in press, Bedolla Arroyo 2010).

The amount of water used for the sample tests was selected according to fluidity tests of the cementing paste and the ones recommended in previous works [Martinez et al 2002, Bedolla et al 2008, 2010, Camacho 2001, Cortes 2002]. The amount of water fixed for the control mortar was 1:2. Besides, we did the fluidity test to learn about its workability.

The flow of mortars was determined by a table of flow, which is a circular metal plate that serves to expand a mortar cone through a number of falls given on the table frame according to ASTM-C- 311-04, which specifies that, for the design of mixtures, a fluidity of 110 ± 5% must be reached. This method is used to regulate the amount of water in the pastes and mortars that allows us to compare which additives demand more water compared to the control.

—Spectrophotometry

Spectrophotometry was performed on in situ dry mortars with a spectrophotometer (BLUE-NH300) with the BLUE-NH300 software. To quantify the color, we measured the chromatic C.I.E. parameters L*, a* and b*:) where L* represents the sample lightness, and a* and b* are the chromatic parameters, and they represent the chromatic scale from red to green and the chromatic scale from blue to yellow respectively, and the total color variation (dE*) with formula 1:

$$dE^*=\sqrt{(dL^2+da^2+db^2)}$$

Results and Discussion

— Workability of the Mixtures

In this study, proper physical appearance, color, texture, flexibility and also adequate workability were pursued, not being possible to fix a water proportion for all the mixtures. Therefore, the quantity of water was determined based on how easy to handle the mixture was according to restorers and masons' experience. We registered the fluidity of the mixture and the need of water for each mortar. The resultant fluidity was 99%. Based on this, we began to elaborate the mixes with different additives [table 1].

Table1.- Features fresh state and results of fluency.

Mix	Adding Percentage (%)	Nomen-clature	Physical behavior of fresh mortar	Relation A/C	Fluency
Control	0	Control	Mix presented good workability, no color, no odor, without bleeding and without contractions.	1.2	99%
Clay	25	ACA	Mixing very workable, is very adherent, manageable to flattened and specimens, presented Brown clear and odorless. No delays setting and presented the minimum bleeding.	1.2	86%
Quarry dust	50	PC	Mixing very workable, cohesive and manageable to flatten and specimens, presented pink clear and odorless. No delays setting and presented the minimum bleeding.	1.3	87%
Corn starch	2	ALM	Workable, manageable to make flattened mixture and specimens, presented white clean and odor-free. No delays setting and I present the minimum bleeding.	1.2	90%
Ash brick	50	CEL	Mixing very workable, adherent, manageable to flatten and specimens, presented grey clear and odorless. No delays setting and presented the minimum bleeding.	1.4	86%

From table 1 , we realize how all the additives used, were less workable than the sample mixture (sand and clay only) and two of them, quarry stone powder and ash from brick manufacturing, needed even more water than the control mixture (quarry stone dust and clay only). This may be due to the fineness of such materials with (sieved through a 0.0737 mm mesh), which would increase the superficial area and its need of water in the mixture. This fact favors the lime base mortars because when hardened are more porous than the control mortar and it favors the CO_2 flow through the mortar matrix which helps the mechanical work.

—*Spectrophotometry Test*

The color measurements were recorded on the covering mixes. The results are shown in figure 1 and table 2, where it is possible to observe that regarding the total color variation with respect to the control mortar, there was a great variation between the mixture with corn starch, being the closest to the control mixture (sand and clay only), outstanding with the highest value the mixture with ash from brick manufacturing. As for the results da* and db* we can observe that the values of the three mixtures are positive, which emphasizes that color is on the range of red-yellow. We can also observe this in the graphic that represents the Cartesian plane where all the values of the mixtures are on the first quadrant. On other hand, on the vertical axis to the right of the Cartesian plane of figure 2, we can see the change of lightness (dL*) because the farther it is from the control mixture (sand and clay only) (center of the vertical axis) the closer to black it is, as in the case of the ash from brick manufacturing.

Table 2.- Variation of chromatic parameters.

Sample name	Nomen-clature	L*	a*	b*	dL*	da*	db*	dE*
Clay	ACA	71.56	5.84	15.04	-8.46	3.86	8.56	12.64
Quarry dust	PC	67.96	9.48	9.29	-12.06	7.5	2.81	14.48
Corn starch	ALM	74.59	2.41	7.41	-5.43	0.43	0.93	5.53
Ash brick	CEL	62.09	3.61	9.94	-17.93	1.63	3.46	18.33
Contro (Only Lime mortar)	CON-TROL	80.02	1.98	6.48	0			
House of culture Almena	HCA	48.66	9.3	13.31	-31.36	7.32	6.83	32.92
House of culture Canaleta	HCC	47.94	7.17	9.48	-32.08	5.19	3	32.64
House of culture Canaleta	CNC	62.92	5.51	9.99	-17.1	3.53	3.51	17.81
Colegio San Nicolas Base of the column	CNB	53.67	3.89	9.09	-26.35	1.91	2.61	26.55

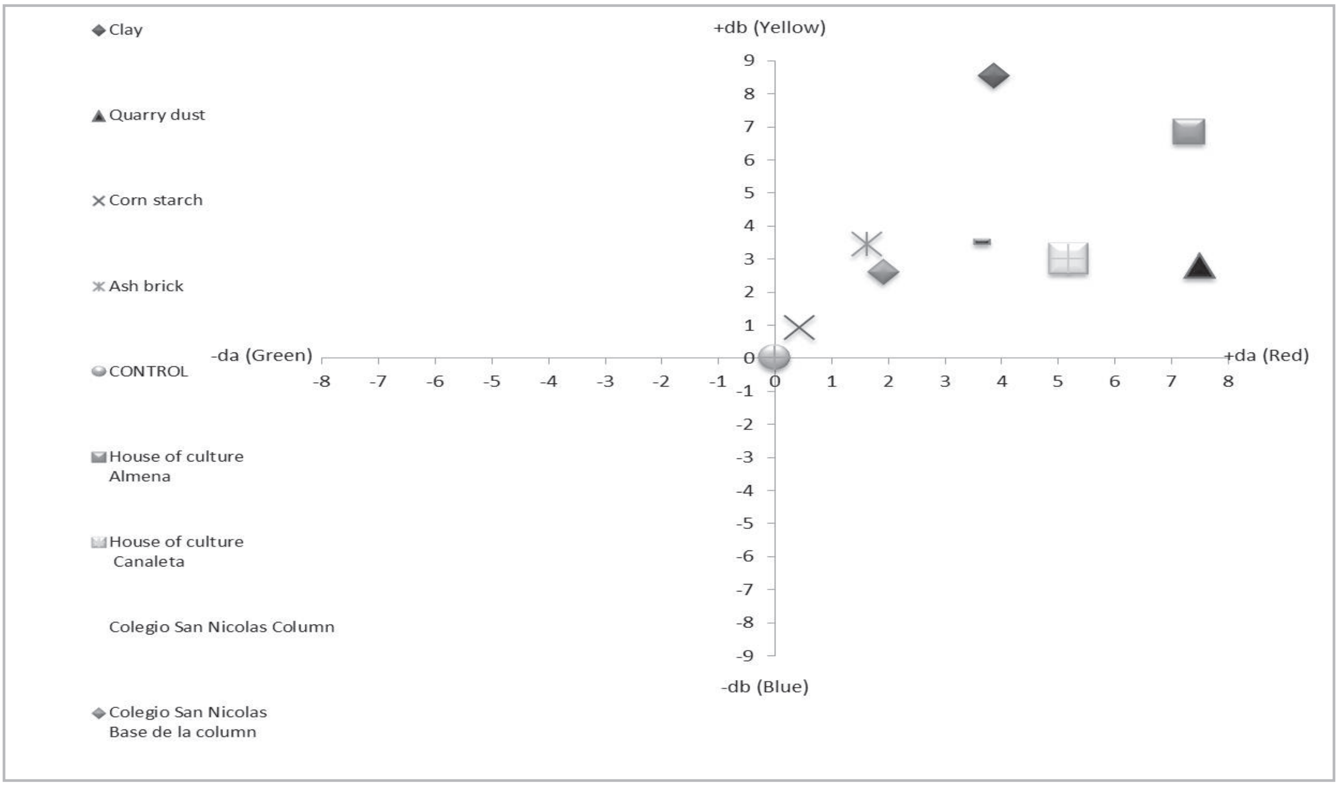

Figure1.- Color results of the studied mixtures.

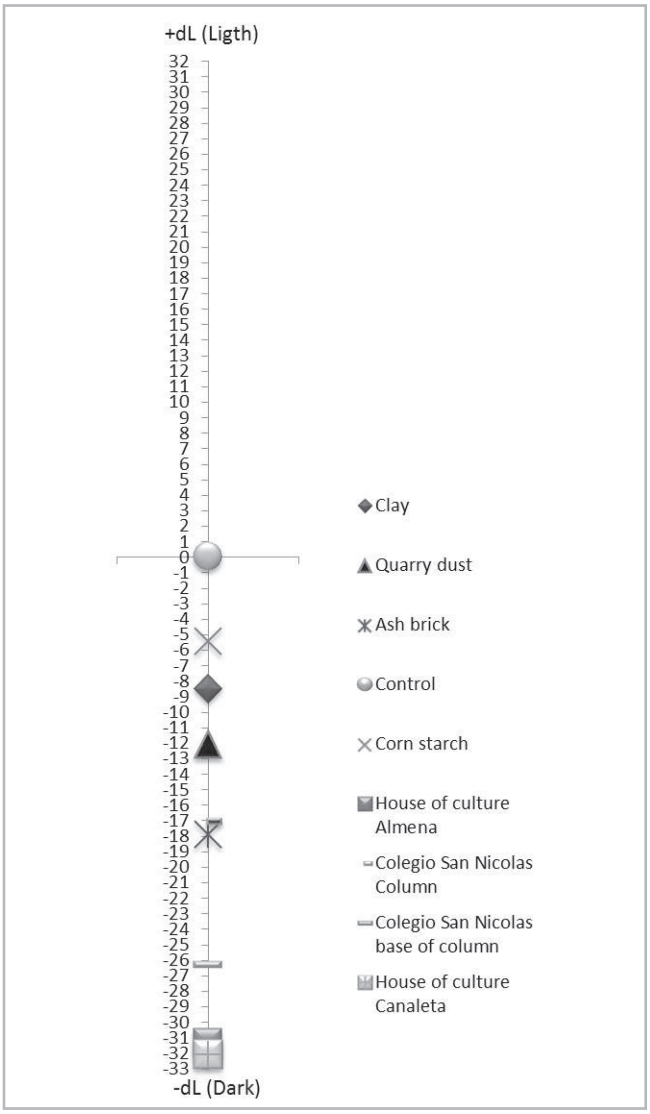

Figure 2.- Lightness variability.

Conclusion

According to the results of this research we may conclude that all the mixtures darken with respect to the control mixture, which is interesting because it offers a variety of colors that may be used in different zones of Mexico, such as Morelia, Puebla, Querétaro and Zacatecas. Being the colors very similar, it is relevant to mention that this is only part of a larger research. We continue looking for materials which compatible in color with the stones in historical monuments, carefully trying to find the most similar color and also similar to the materials employed with good mechanical characteristics and long durability.

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