Conservation of Cultural Heritage Building: Evaluation of $Ca[Zn(OH)_3]_2 \cdot 2H_2O$ Nanoparticles Coating Behavior Under Salt Crystallization Cycles

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Abstract. Calcareous stones are composed of a mixture of minerals and different cementing agents. Due to their heterogeneity, they are sensitive to the action of multiple environmental factors, including temperature, relative humidity, solar radiation, microorganisms, and salt crystallization processes that are the cause of degradation, inducing changes in their physical and chemical properties. Then it is desirable to account for specific studies on new nanomaterials that improve stone characteristics to extend its performance for long periods. In Yucatán, the calcareous stone is a traditional building material used since the prehispanic period, however, its susceptibility to deterioration has created a demand to elaborate protective treatments that improves its consolidation. This work shows the performance of new nanomaterials synthesized via sol-gel, based on calcium and zinc hydroxide dihydrate, with the formula $Ca[Zn(OH)_3]_2 \cdot 2H_2O$ (CZ) and applied on three Yucatán calcareous stones Calcehtok, Chichén Itzá and, Mayapán, and further evaluated under the sodium sulphate crystallization aging test. Results indicated that after applying CZ nanoparticles (NPs) to stones, physical and mechanical properties like capillarity, colour, propagation of ultrasonic velocity, and structure improved as they showed a decrease in stone cracks, cavities, and pores. The salt crystallization tests indicate significant changes in the control properties of untreated stones when compared to those specimens coated with CZ. In addition, a better performance was observed for the stones from Calcehtok, followed by Mayapán and Chichén Itzá, respectively.

Keywords: Stone · Salt crystallization · Conservation · Nanoparticles

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1 Introduction

The Yucatán Peninsula, formed by Campeche, Quintana Roo, and Yucatán, is geologically a platform with powerful strata of carbonate rocks [1]. From such strata, the Mayan civilization extracted and used these materials to construct its characteristic monumental buildings as temples, palaces, and other architectural elements that are currently found as vestiges in various archaeological sites [2]. Chichén Itzá and Mayapán are clear examples; since they were built entirely with limestone rock, they represent an essential economic element (tourism) and social identity in the Yucatán Peninsula [3].

Carbonate rocks, such as limestone, are easily disturbed; this process depends on intrinsic and extrinsic factors, leading to deterioration mechanisms, which produce changes in their properties, known as alteration indicators [4, 5]. An obvious example is the crystallization of salts in historical monuments built in stone [6] because they are generally exposed to very aggressive atmospheric conditions that are difficult to predict. Therefore, accelerated alteration tests are frequently used in a specialized laboratory to predict and understand these processes [7, 8]. Consequently, in this work, the effect of a saline environment on three limestone lithotypes was evaluated; two are from the archaeological sites of Chichén Itzá and Mayapán, and a commercial one, extracted from the town of Calcehtok. The test was evaluated recording the variation of weight and the visual deterioration observed; in addition, its physical-mechanical changes were analysed when coated with nanoparticles based on double zinc and calcium hydroxide dihydrate (CZ).

2 Materials and Methods

2.1 Materials and Stone Samples Characterization

The calcium zincate synthesized by the sol-gel method was characterized by X-ray diffraction and electron microscopy analyses, according to Soria Castro et al. [9]. The formation of CZ NPs can be described by the following reaction:

$$\mathrm{CaCl_2 \cdot 2H_2O + 2ZnO + 2H_2O + 2NaOH \rightarrow 2Zn(OH)_2Ca(OH)_2 \cdot 2H_2O} \\ \mathrm{+\ 2NaCl}$$

This study used three different types of limestone from the Yucatan Peninsula, which were provided by the Institute of Anthropology and History (INAH). The stones correspond to two decontextualized rock blocks found isolated in the vicinity of buildings from the archaeological sites of Chichén Itzá (CH) and Mayapán (CO). In addition, a stone of commercial origin was selected with contrasting visual characteristics, such as porosity and compaction to the previous two, named Calcehtok (CA).

Specimens consisting in stone cubes with dimensions of 3 × 3 × 3 cm, were analysed by propagation of ultrasonic velocity (Vp), spectrophotometry and the capillarity coefficient, before and after 20 days of applying CZ NPs on the surface of the coupons, to compare the differences in both and assess the protective treatment effectiveness. Only for the X-Ray diffraction (DRX) technique, a portion of the stone samples was powdered before analysis.

Propagation of ultrasonic velocity was measured to evaluate the mechanical properties and the distribution of the nanoparticles. In this study Vp was carried as specified in UNE EN 14579 [10], using a Proceq Pundit PL2 Pulser instrument. By means of this technique, the anisotropy index (dM %) can be determined, using the velocities (V) found for Vp, which are obtained measuring the three orthogonal directions in space of the stones evaluated. The anisotropy index is calculated as proposed by [11], as shown below in Eq. (1):

$$dM\% = [1 - (2Vpmin/(Vpmax + Vpmean))] \times 100 \tag{1}$$

where Vp_{max}, Vp_{min}, and Vp_{mean} are respectively the maximum, minimum, and mean values [11].

The chromatic parameters on the stones surface were measured with a spectrophotometer MINOLTA CM-700d using the Lab system or Lab colour space or CIELAB (Commission Internationale de l'Eclairage CIE 1976) [12]. The standard illuminant was D50 and observer 10°; measured parameters were L*, which accounts for luminosity, a*, and b* for coordinates chromatic parameters defined in the ASTM 313-76 system (ASTM 2000) [13]. The total colour difference ΔE* [14] is obtained by the Eq. (2):

$$\Delta E* = \left[(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2\right]^{1/2} \tag{2}$$

The capillarity coefficient was determined to analyse the hydric behaviour through the stone. This technique shows the amount of water absorbed, expressed by the mass increase of the stone per unit area for the square root of time ($kg/m^2\ s^{1/2}$), and the time interval of the amount of water absorbed by the sample, was automatically monitored (every 1, 3, 5, 10, 15, 30 min and 1, 3, 5, 8, 24 h), when its lower surface is in contact with the water reservoir, following the norm AENOR, UNE-EN 1925:1999 [15].

The resistance to salt crystallization test was carried out following the UNE-EN 12370 [16] standard to evaluate the effect of the salt crystallization mechanism in rocks, the influence and behaviour of CZ NPs as a protective coating. The procedure consists of immersing the specimens with and without the treatment of the CZ NPs in a saturated solution of sodium sulphate decahydrate for 2 h. Once the time has elapsed, the stone samples are placed in the oven for 16 h at 105 °C (±5 °C) to leave only the salt crystals in the samples. Subsequently, they are removed from the oven and stored in a desiccator for 2 h before repeating the cycle. Thus, a total of 15 repetitions were performed.

3 Results

The X-ray diffraction for the untreated (natural) stones with contrasting characteristics showed that CA contains only 100% calcite ($CaCO_3$), CH is formed by two minerals, 90% calcite and dolomite ($CaMg(CO_3)_2$) at 10% and CO has only 100% dolomite (see Fig. 1). The petrophysical characterization tests that were carried out for the three lithotypes are ultrasound speed transmission, anisotropy index, colorimetry, and the capillary coefficient.

Table 1 shows the average data of the three types of limestone evaluated without and with the nanomaterial treatment, using the techniques of propagation of ultrasonic velocity (Vp) and the anisotropy index (dM%).

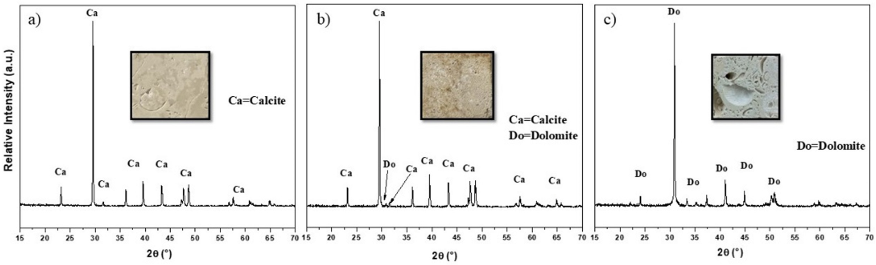

Fig. 1. X-ray diffraction patterns of the stones: **a** Calcehtok, **b** Chichén Itzá and **c** Mayapán

Table 1. Propagation of ultrasonic velocity values and anisotropy index for the three types of limestone

Stone		Vp (m/s)	dM (%)
CA	Untreated	995 ± 27	2.7
	Treated	1045 ± 137	1.1
CH	Untreated	879 ± 27	17.2
	Treated	815 ± 122	3.2
CO	Untreated	832 ± 73	24.3
	Treated	883 ± 81	21

Calcehtok (CA) without the treatment shows an ultrasound transmission speed of 995 m/s; after applying the CZ NPs, the transmission speed was 1045 m/s; the same trend was observed for Mayapán, as the speed increased from 832 to 883 m/s. In the Chichén Itzá sample, the wave transmission speed decreased from 879 to 815 m/s. The anisotropy index decreased in the three cases after treated with CZ NPs. This observation could be due to the transformation of calcium hydroxide to calcium carbonate phase, which causes a consolidating action [17]. This result is relevant, considering that CZ in its chemical formula is composed of $Ca(OH)_2$, and the stones evaluated in this investigation are limestones in nature.

The spectrophotometry results for Calcehtok, Chichén Itzá, and Mayapán without and with CZ NPs are presented in Table 2, where L* = Luminosity, a* = Red tone, b* = Yellow tone, ΔE* = Global change of color. Calcehtok showed that the luminosity increases from 82.04 to 85.64, and Chichén Itzá and Mayapán decreased. The parameter a* represents the red hue, which decreases for CH from 2.09 to 2.01 as it is a reddish stone. Previous studies by X-ray diffraction of González et al. [18] showed that the red coloration for the Ticul stone from the State of Yucatán is due to iron minerals in the form of iron hydroxide-oxide, such as goethite ($FeO(OH)$) and hematite (Fe_2O_3). In the case of CA, such parameter decreases from 2.12 to 1.94 since it is a stone with a cream hue; and the compound has a white coloration, which could cause this decrease. For this reason, the parameter b* increases for CH from 10.686 to 11.91 and Mayapán from 10.71 to 11.21.

Table 2. Color parameters values for three types of limestone

Stone		L*	a*	b*	ΔE
CA	Untreated	82.04 ± 2	2.12 ± 0.3	12.34 ± 2	4.60
	Treated	85.64 ± 1	1.94 ± 0.3	9.44 ± 0.8	
CH	Untreated	85.05 ± 2	2.09 ± 0.4	10.686 ± 2	2.17
	Treated	83.25 ± 1	2.01 ± 0.2	11.91 ± 1.6	
CO	Untreated	85.53 ± 0.8	1.25 ± 0.2	10.71 ± 0.7	1.96
	Treated	83.64 ± 2	1.49 ± 0.2	11.21 ± 0.7	

Figure 2 shows the trend for a* and b* coordinates of the untreated and treated stones with CZ NPs, and it is seen with the help of the chromatic circle, also we can see the parameter L* representing the luminosity from 0 to 100. However, the concentration of the nanomaterial used (5 mg/mL), is not perceptible to the human eye (ΔE $<$ 5), and therefore it could be used in cultural heritage conservation.

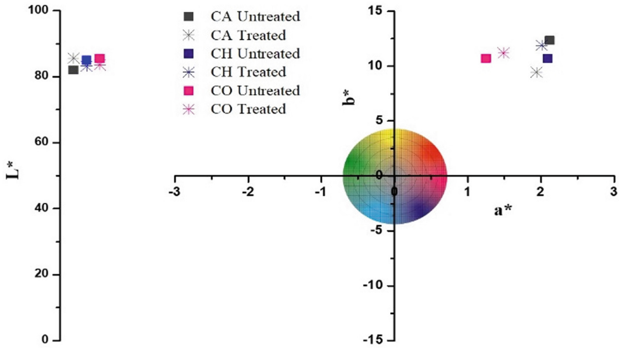

Fig. 2. Parameters of a*, b* (graph right), and L* (graph left) of limestone samples comparing with the chromatic circle, as a reference.

The mass loss at the end of the 15 salt crystallization cycles is presented in Table 3. Values for initial mass (IM), final mass (FM), and the difference (ΔM) were assigned.

The effect of CZ NPs the stones was satisfactory when compared for those that do not contain nanoparticles, since there is a more significant degradation and consequently greater loss of mass in the untreated stones. This behaviour indicates that the test specimens coated with $Ca[Zn(OH)_3]_2 \cdot 2H_2O$ delay crystallization of salts; this comparison shows the behaviour of weights values as the test progresses (see Fig. 3).

In the case of Calcehtok, the stones showed changes in their behaviour from cycle 5. These stones with and without treatment obtained a significant increase in their mass because the test tubes reached their maximum saturation, since, from that cycle, the specimen tends to have a gradual loss in its weight. Chichén Itzá behaved differently, in the case of stones without nanoparticles, there was a loss in mass at cycle 6, shedding

Table 3. Mass loss ratio of untreated and treated samples with CZ NPs

Stone		IM (g)	FM (g)	ΔM (g)
CA	Untreated	110.20 ± 4	109.83 ± 2	−0.37
	Treated	105.39 ± 3	105.42 ± 2	0.03
CH	Untreated	104.61 ± 2	97.01 ± 0.9	−7.6
	Treated	99.63 ± 1	99.26 ± 0.8	−0.37
CO	Untreated	63.03 ± 1	61.82 ± 0.8	−1.21
	Treated	60.95 ± 0.9	61.16 ± 0.7	0.24

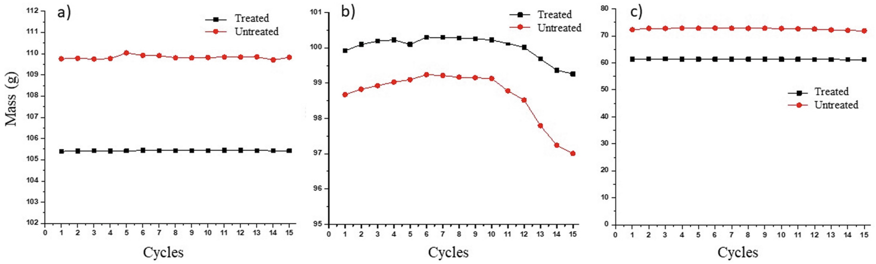

Fig. 3. Cycles of resistance to salt crystallization: **a** Calcehtok, **b** Chichén Itzá, and **c** Mayapán.

visible part of its material due to degradation, and recovering the weight loss for the absorption of the salt solution, tended to be constant until cycle 10, and after that, it lost more matter abruptly. With the CZ NPs, it was observed that the change in weights between cycles 6 and 10 remained more stable and then slightly decreased, even losing rocky material. The stone from Mayapán was the one that maintained almost imperceptible stability in its weights throughout the test. However, the detachment of the control stone was observed higher compared to the stone with $\mathrm{Ca[Zn(OH)_3]_2{\cdot}2H_2O}$.

Table 4 shows the comparative results of the capillarity coefficient test of the limestone lithotypes with and without the CZ NPs and after the tests of resistance to salt crystallization. The average capillarity coefficient was compared before and after treatment with the CZ NPs for Calcehtok was 0.0014 and 0.00049 $\mathrm{kg/m^2\ s^{1/2}}$, and for Chichén Itzá, 0.015 and 0.015 $\mathrm{kg/m^2\ s^{1/2}}$, finally for Mayapán was 0.008 and 0.006 $\mathrm{kg/m^2\ s^{1/2}}$, respectively. These results are similar to those obtained by López-Arce et al. [19].

In the case of untreated CA, which is a more compact stone with lower porosity according to its anisotropy index (Table 1), being under the accelerated effect of salts, an increase in weight is observed, and for stones with greater porosity is observed to decrease or maintain their weight, this is due to the loss of rocky material. Some authors [8] attribute this behaviour to the growth of saline crystals inside the stone pores. In some cases, the increase in capillarity coefficient values is due to their weight; in others, the crystals lead to greater internal tension. The stone gives rise to exceed the threshold of the resistance to traction of the stone, causing its sandblasting.

Table 4. Capillary coefficient results of limestone specimens

Stone	CA kg/m^2 s$^{1/2}$	CH kg/m^2 s$^{1/2}$	CO kg/m^2 s$^{1/2}$
Untreated	0.0014	0.015	0.008
Treated	0.00049	0.015	0.006
Salt/untreated	0.0016	0.012	0.003
Salt/treated	0.0011	0.012	0.002

When applying the CZ NPs in the limestone coupons, the results show greater resistance to hydric tests and resistance to salt crystallization; these can be observed in the capillarity curves (Fig. 4).

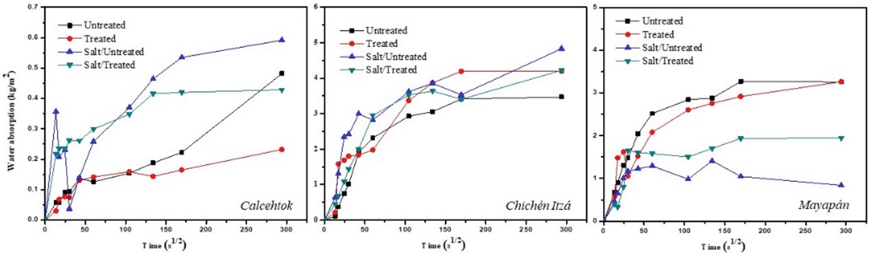

Fig. 4. Capillarity curves obtained during water absorption of limestone specimens

The results of the water absorption by capillarity of the specimens without and with CZ NPs, and after the exposure of accelerated crystallization cycles, show an improvement in the water properties of the treated stone. For Calcehtok, the values decreased when CZ NPs were applied, compared to the untreated stone, therefore the amount of water absorption is less. After the salt cycles the mass increases as a result of the presence of mineral thenardite, that corresponds to sodium sulphate (salts) found by XRD, which can be observed on the outer surface of the sample (see Fig. 5). The Chichén Itzá stone presents its maximum water absorption when the specimens were analysed after the salt test, which caused its fragility, producing erosion in the upper face in addition to its fragmentation and multiple cracks, thus, the results showed a decrease in the values of the capillary coefficient. Mayapán showed similar behaviour to that of Chichén Itzá. In both cases, initially, the water tests affected its original mass after the accelerated salt test, the maximum deterioration was observed. However, the deterioration was less for nanoparticles treated stones.

Table 4 shows the values of visual deterioration for the three limestone specimens without treatment and treated with CZ NPs after the salt test. The treated stones showed a more compact appearance, and greater resistance compared to the untreated stones, which showed a more significant loss of mass volume in the vertices and edges of the

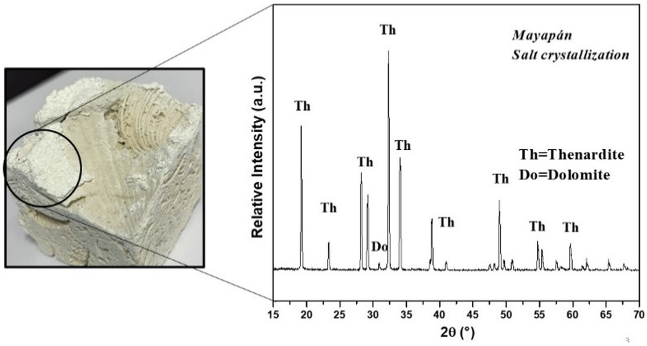

Fig. 5. X-ray diffraction pattern of the Mayapán after salt crystallization.

coupon (Fig. 6) similar to the work reported by Fort et al. [8], since the orientation of the stones for the test was according to the anisotropy measurements.

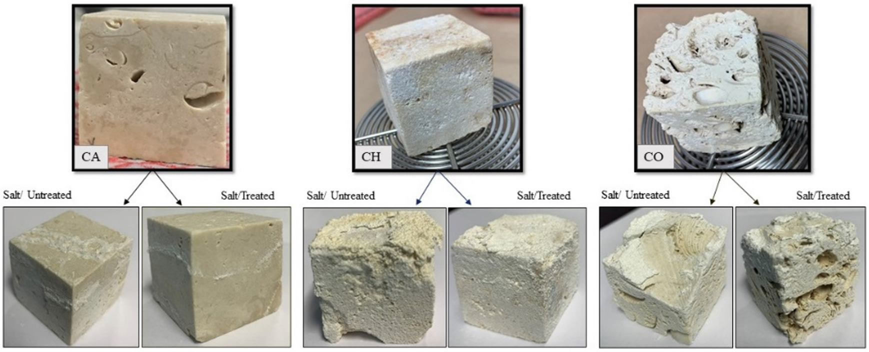

Fig. 6. Limestone specimens after the salt crystallization test (cube dimension ~ 3 cm^3)

4 Conclusions

The CZ nanoparticles used for the protection of the carbonaceous nature control stones have shown to be effective in improving the petrophysical properties of Calcehtok and Mayapán, by achieving an increase in the degree of cohesion of the stone, also an increase in the ultrasound propagation speed and a decrease in the anisotropy index. In addition, there is a decrease in the capillarity coefficient, which gives rise to an improvement against the water deterioration factors except for Chichén Itzá, which could be affected in the coefficient test of capillarity creating more cracks or micro-fissures in its interior. Therefore, the measurement values are affected. The concentration of nanomaterial used is imperceptible to the human eye, and no presence of by-products that could damage the material could be detected. Furthermore, the test of resistance to salt crystallization shows maximum values of visual erosion in limestone specimens without the treatment of CZ NPs than those in which the nanomaterial was applied, so they showed greater resistance and a more compact structure. Therefore, it is concluded that the calcium-zinc hydroxide dihydrate compound could be considered as an innovative nanomaterial to preserve and conserve historical monuments.

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