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Testing acid products thickened with xanthan gum for the removal of calcium carbonate deposits on ceramics



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ABSTRACT

One of the most frequent alterations to archaeological objects is the presence of calcium carbonate deposits, which usually appear on stone and pottery. Their existence makes analysing these historical artefacts more difficult, so their removal becomes necessary. Nonetheless, the most popular methods for their elimination include applying a combination of chemicals followed by a mechanical action, both of which have the potential to harm the artefacts. Since the 1980s, thickened products have been widely employed as safer substitutes for conservation treatment procedures. They are not yet widespread in the archaeological community, though.

This research arose from the need of determining the possible changes that pottery objects might suffer due to the use of thickened acid products to remove surface calcium carbonate deposits. Acetic and nitric solutions thickened with xanthan gum were used to remove the artificial deposits generated over ceramic mock-ups fired up to different temperatures. The results were satisfactory based on visual and colorimetric evaluation. Nevertheless, the confined acetic acid on mock-ups fired below 1100 °C showed surface stains or colour changes, that were connected to calcium acetate residues by TG-DSC and ATR-FTIR techniques. However, mock-ups treated with the confined nitric acid showed no signs of soluble salts remaining.

Besides, no mineralogical changes were detected on the ceramic mock-ups treated, regardless of the acid used. Furthermore, tests were performed on low fired mock-ups without calcium carbonate deposits as a worst-case scenario to establish the safety of the designed treatments. The findings indicated that there were no compositional changes caused by the removal procedures.

As a result, it may be inferred that the thickening acid-based treatments were safe and effective on the ceramic mock-ups and could be applied to other similar pottery findings.

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1. Introduction

Gels and thickened products have been used in conservation treatments from the 1980s onwards as alternative and safer application methods than traditional ones. Since then, diverse researches have studied their properties, benefits and possible applications to the conservation of cultural heritage (CH) objects

[1–4]. However, they remain little-used in archaeological conservation [5].

A gel is defined as a colloidal dispersion able to capture a large fraction of solvent [6]. Recently, gels elaborated with natural thickeners, such as chitosan, xanthan gum, agarose, etc., have been promoted in line with current European and international regulations [7–9]. Thickened products allow a more controlled action of the conservation treatments, as the interaction with the object surface occurs in a slowly way, depending on features like its porosity and roughness. Besides, the higher specificity of the action, the lower product concentration is needed, which would also contribute to a reduced toxicity of the treatment.

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Gel and thickened-based treatments have been proved to prevent or reduce the alteration risk during cleaning of original pieces [8,10–12]. However, it becomes essential to consider the possibility of any left residues on the intervened surface, which would carry on with the chemical action [2], especially possible polymer residues from the confining matrix. Chemical or physical gels with great mechanical properties offer advantageous alternatives to viscous polymer dispersions and weaker physical gels. However, fluids confined in retentive matrices may exhibit slower surface contact kinetics than unconfined ones, which would reduce the effectiveness of treatments.

In archaeological conservation, one of the main interventions involves the removal of surface deposits on several materials, including: stone, pottery, glass and metals. Modern theories stand up for leaving these deposits if they remain stable and using non-invasive techniques for the study of the objects [2]. Due to a lack of funding, this approach might occasionally be challenging. Thus, removing these accretions becomes essential to enable a proper study of the objects' surfaces. Consequently, traditional mix cleaning methods are still used, consisting of a combination of mechanical and chemical actions to successfully clear up both the more external deposits and the ones in direct contact with the object surfaces [13]. Nevertheless, the mechanical action may end up harming the objects' surfaces. Besides, numerous studies have also demonstrated that pottery items can suffer both compositional changes and surface damage after acid-based cleaning procedures [14–19].

2. Research aim

The purpose of this study was to evaluate the efficacy of the indirect application of acid products to remove calcium carbonate deposits (CCD) from ceramic surfaces, considering their concentrations, application method, treatment time and consequences for pottery objects.

After studying the effect of acid cleaning agents applied by immersion, the present research focuses on assessing acetic and nitric acid solutions at low concentrations thickened with xanthan gum. Cleaning tests were conducted on ceramic mock-ups fired at different temperatures from 650 to 1100 °C and covered by artificially generated CCD.

Using multiple analytical techniques, including colour spectrophotometry, powder X-ray diffraction (PXRD), Fourier transform infrared-attenuated total reflectance (ATR-FTIR) spectroscopy, Thermogravimetry and Differential Scanning Calorimetry (TG-DSC) analyses, the efficacy, safety and the possible adverse side effects of these treatments were assessed.

3. Materials and methods

3.1. Ceramic mock-ups

With the aim of determining the efficacy of the treatments on ceramic substrates, but without harming original archaeological pottery pieces, eight ceramic mock-ups of 5 × 5 × 1 cm were manually modelled out of a commercial red clay (Sio-2® ARGILA; Ceramica Collet S.A.), and fired in a kiln at 650, 800, 1000 and 1100 °C (SNOL 30/1300 L) [20]. Afterwards, CCD were artificially grown on their surfaces to simulate the concretions that appear during their burial [21–24]. The chemical composition of the clay used was provided by the supplier company. The main chemical components identified by XRF included: SiO₂, Al₂O₃, and other components in minor concentration (Fe₂O₃; CaO; K₂O; MgO). These data were complemented by PXRD and oriented aggregates pat-

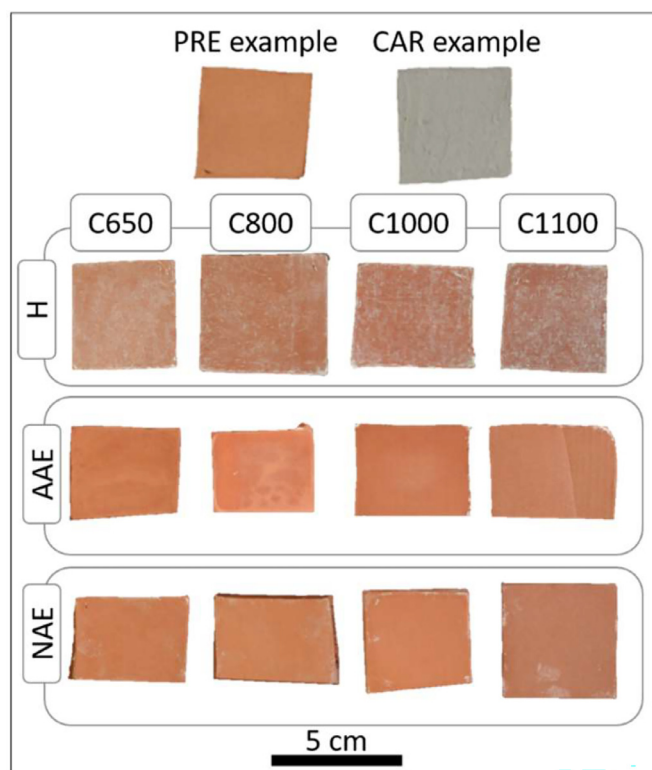


Fig. 1. Images of the cleaning treatments tests pursued with water (H), acetic acid (AAE) and nitric acid (NAE), all of them thickened with xanthan gum. PRE: before carbonation, CAR: carbonated.

terns (OA), which concluded the presence of calcite and dolomite in mock-ups fired under 1000 °C [22].

3.2. Cleaning tests

For the removal of the artificial deposits, diverse cleaning methods were designed following the guidelines found in the applicable standards [25,26], in addition to the previously indicated bibliography. Several basic criteria were established: **1)** minimum product concentration; **2)** minimal treatment time; **3)** minimal mechanical intervention; and **4)** simplicity of the treatments.

These principles are focused on maximising resources and minimising risks, both for the interventions themselves and for professionals involved. .

Following these criteria, the selected products included a weak acid, acetic acid (CH₃COOH), and a strong acid, nitric acid (HNO₃), as they are some of the most frequently used in archaeology conservation [27]. Solutions of both were prepared: acetic acid 96% (Panreac®) (10% v/v); and nitric acid 65% (Panreac®) (1% v/v) [22].

Regarding the thickening agent, the natural polymer xanthan gum extracted from the bacterium *Xanthomonas Campestris* was selected. Its structure is very similar to that of cellulose, with the presence of acidic side chains. Its main feature is the change from an ordered to an “irregularly coiled” chain formation, which gives the gel its thixotropic properties. Furthermore, it shows a high-water retention capacity and quickly hydrates into a gel at ambient temperature, allowing aqueous solutions to be applied to water-sensitive surfaces. Xanthan gum gels also allow warm applications, up to 60 °C. Besides, they can be used for basic and acid solutions, due to their stability in a wide pH range (2–12).

Subsequently, both solutions were thickened with xanthan gum (Vanzan® NF-C, CTS®) at 2% w/v (Table 1), until a transparent, viscous polymer dispersion was obtained. Then, the mixtures were

Table 1

Cleaning treatments pursued onto the ceramic mock-ups, both with and without deposits. **H**: deionised water thickened with xanthan gum; **AAE** and **AAEL**: acetic acid thickened with xanthan gum, on mock-ups with and without CCD, respectively; **NAE** and **NAEL**: nitric acid thickened with xanthan gum, on mock-ups with and without CCD, respectively.

	Mock-up	Acronym	pH	Concentration	Treatment time
Deionised water cleaning treatment	C650	H	6.5 ± 0.1	2%	14 days
	C800				
	C1000				
	C1100				
Acetic acid cleaning treatments	C650	AAE	2.88 ± 0.1	10%	40 min
	C800				
	C1000				
	C1100				
Nitric acid cleaning treatments	C650*	AAEL	2.77 ± 0.1	1%	30 min
	C650	NAE	1.57 ± 0.1		40 min
	C800				
	C1000				
	C1100				
	C650*	NAEL	0.73 ± 0.1		30 min

* Ceramic mock-ups without CCD.

directly applied with a palette knife, 2–3 mm thick onto the deposits covering the ceramic surfaces, with Japanese paper as barrier element (60 g/m²) moistened with deionised water to ensure its adherence to the deposits. Besides, a plastic film was used to wrap the mock-ups with the removal products, to further slow-down the evaporation and drying of the mixture, prolonging the removal action [23]. The stability of xanthan gum gels should theoretically decrease below pH values of 2, yet at pH values of nitric acid, its consistency was adequate to be used as a physical gel. The reactions between both acid solutions with the calcium carbonate from the deposits allowed the following mechanical cleaning (MC), pursued with blunt wooden sticks. For each application a fresh mixture was used.

Prior to cleaning, it was necessary to moist the ceramic surfaces so that their pores became clogged to reduce the penetration of the cleaning agents [25]. Pre-wetting was performed by immersing the surface (with the deposits) in deionised water for 5 min prior to the intervention.

Besides the cleaning tests performed onto ceramic mock-ups with the artificial CCD on their surfaces, two tests –one with each acid – were applied onto low temperature fired mock-ups (650 °C), without the artificial CCD. These trials were done to determine the consequences of the treatments in the most adverse case, as the cleaning products entered in direct contact with the ceramics.

Additionally, an experiment with thickened deionised water xanthan gum (H) was conducted on ceramic mock-ups covered with the deposits [28]. This was done to assess its removal efficacy, and to confirm the need of using diverse cleaning solutions to increase it. The test was considered useful because water is less harmful to ceramic specimens than acid-basic solutions, but it is also less effective. Table 1 shows that, after checks every 24 h, a longer treatment period was necessary since shorter applications failed to eliminate the CCD.

3.3. Residues' removal

All soluble salts produced by the reactions and the residues of the products utilised were cleared away using deionised water (pH 6–7) at a ratio of approximately 1:15 g/mL [29]. Conductivity measurements (K) (Delta-Ohm HD2156.2) were used to track the process. Following the methods from earlier studies [23–25], the endpoint was established by reaching twice the value 2, or lower, in the variable K_{norm} [30], after renewing the water. The ceramic mock-ups were later introduced in a climate chamber (Vötsch Indusrietechnik VCL 4010) for 24 h (20 °C and 50% RH).

3.4. Techniques and equipment

3.4.1. Colour spectrophotometry

The CIE L*a*b* system [31] was used to determine colour parameters before (PRE) and after the cleaning treatments (AAE & NAE), to establish their efficacy. Specifically, the total colour variation parameter (ΔE_{00}) [32] was the factor used to quantify differences, based on two of the five thresholds stipulated by Mokrzycki & Tatol (2011) [33] which relate the total colour difference and its perceptibility by an observer. In this research the first and the third thresholds have been considered:

- When $0 \leq \Delta E_{00} \leq 1$, the difference is imperceptible.
- When $2 \leq \Delta E_{00} \leq 3.5$, the difference is perceptible also by an inexperienced observer.

A Konika Minolta CM-2600d spectrophotometer was used with the following measurement conditions: area of 3 mm diameter in SCI mode, spectral range 360–740 nm, data acquisition every 10 nm, CIE 10° standard observer, D65 standard illuminant [26]. Five measurements were performed on each ceramic mock-up. The mean values were calculated for each coordinate of the CIE L*a*b* space.

3.4.2. Powder X-ray diffraction (PXRD)

The ceramic mock-ups were analysed by PXRD before carbonation (PRE) and after the cleaning treatments, to identify possible changes in the mineralogical composition. About 0.2 g of ground samples were analysed with a Bruker D8 ADVANCE A25 diffractometer in Bragg-Bretano θ - θ configuration, using a Ni filter and LynxEye SSD160-2 position sensitive detector. Measurements were performed with Cu K α radiation, 45 kV, 40 mA, angular range 5° and 70° (2θ), with a step size of 0.02° and a counting time of 1 s/step. Phase identification was performed with the High-Score Plus® 3.0 PANalytical software, using the PDF-2 2002 ICDD database.

3.4.3. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)

This technique was employed to detect possible variations in the bands associated with calcite, as well as the presence of soluble salts and residues after the acid cleaning treatment. Powder samples of 10 mg were analysed before the carbonation (PRE) and after the cleaning treatments. In addition, samples of the used gels were studied.

The FTIR Alpha II spectrometer with attenuated total reflectance (ATR) module, from Bruker, was used together with the Opus®

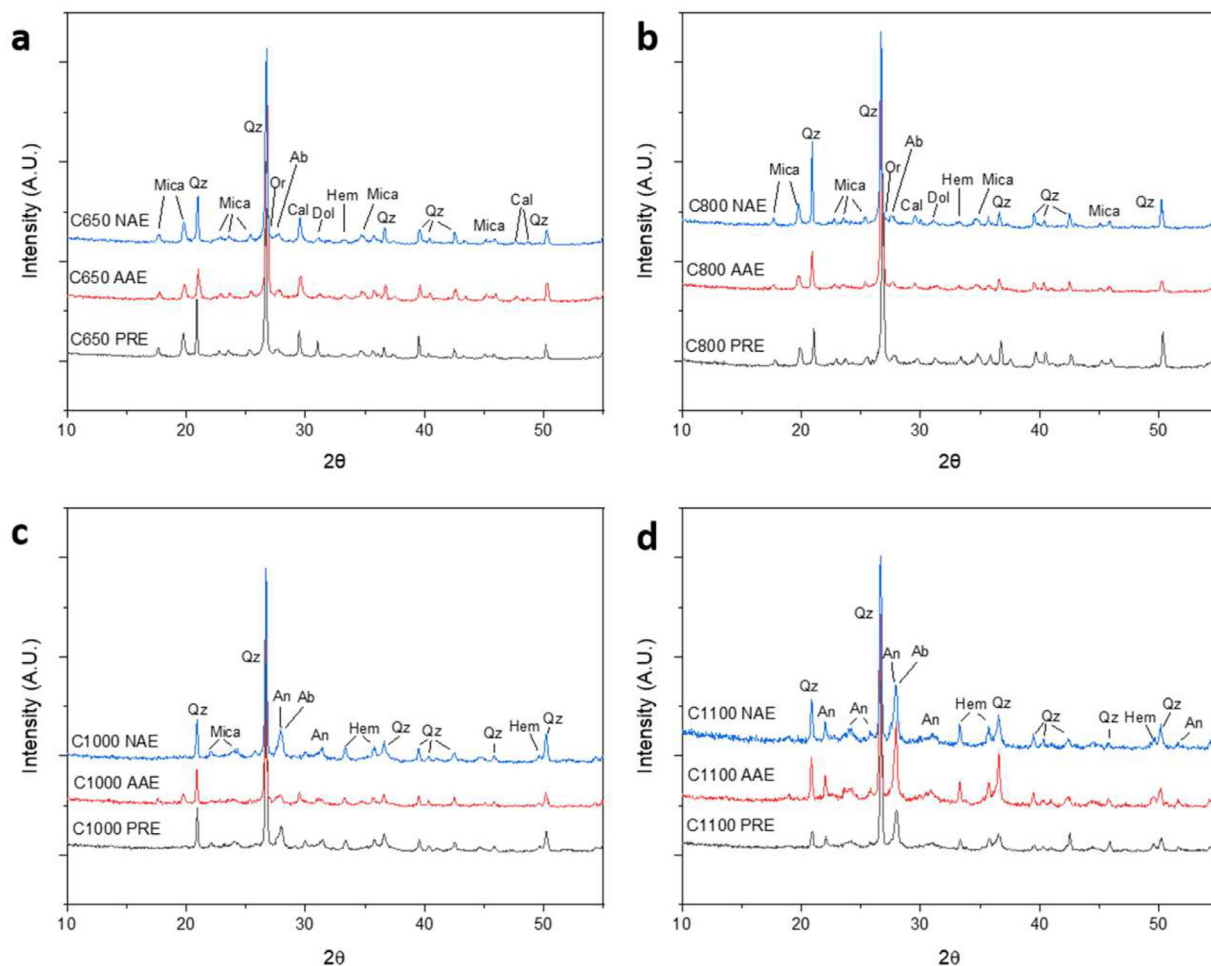


Fig. 2. PXRD patterns of the ceramic mock-ups before (PRE) and after the cleaning treatments with thickened acetic acid (AAE) and nitric acid (NAE): **a** 650 °C, **b** 800 °C, **c** 1000 °C and **d** 1100 °C. Ab: albite; An: anorthite; Cal: calcite; Dol: dolomite; Hem: hematite; Mica: muscovite and/or illite; Or: orthoclase; Qz: quartz.

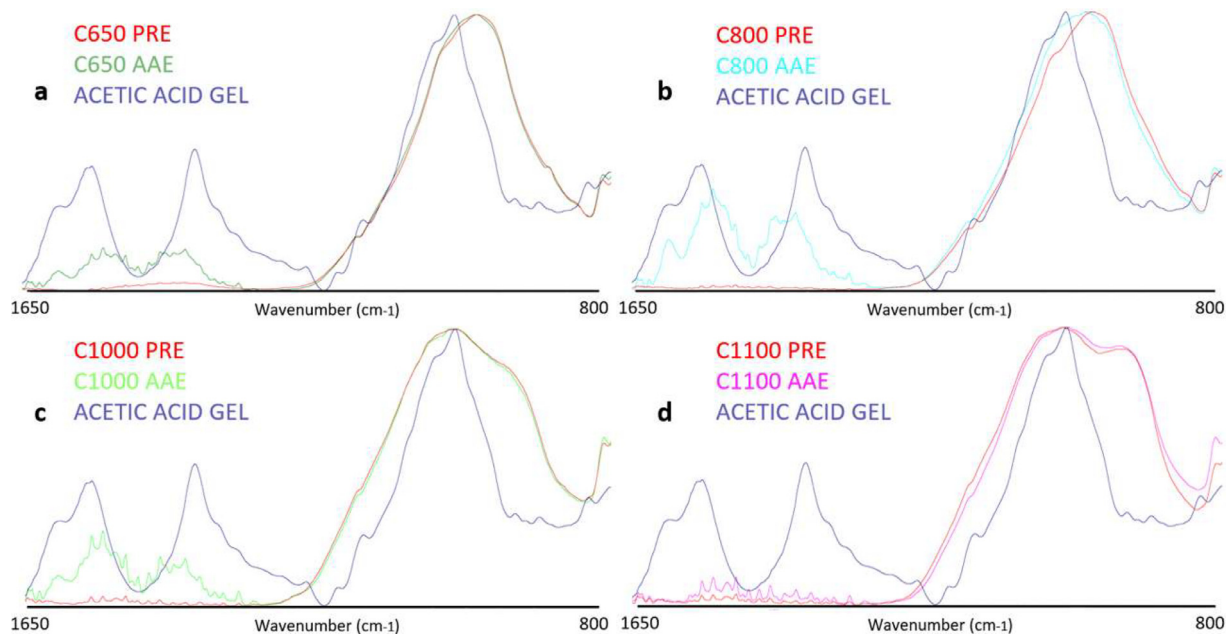


Fig. 3. Detail of the scaled ATR-FTIR spectra of the ceramic mock-ups before (PRE) and after treatment with thickened acetic acid solution (AAE): **a** 650 °C, **b** 800 °C, **c** 1000 °C and **d** 1100 °C, besides the spectra obtained from the confined acetic acid itself. Bands linked to calcium acetate were identified between 1250 and 1650 cm^{-1} .

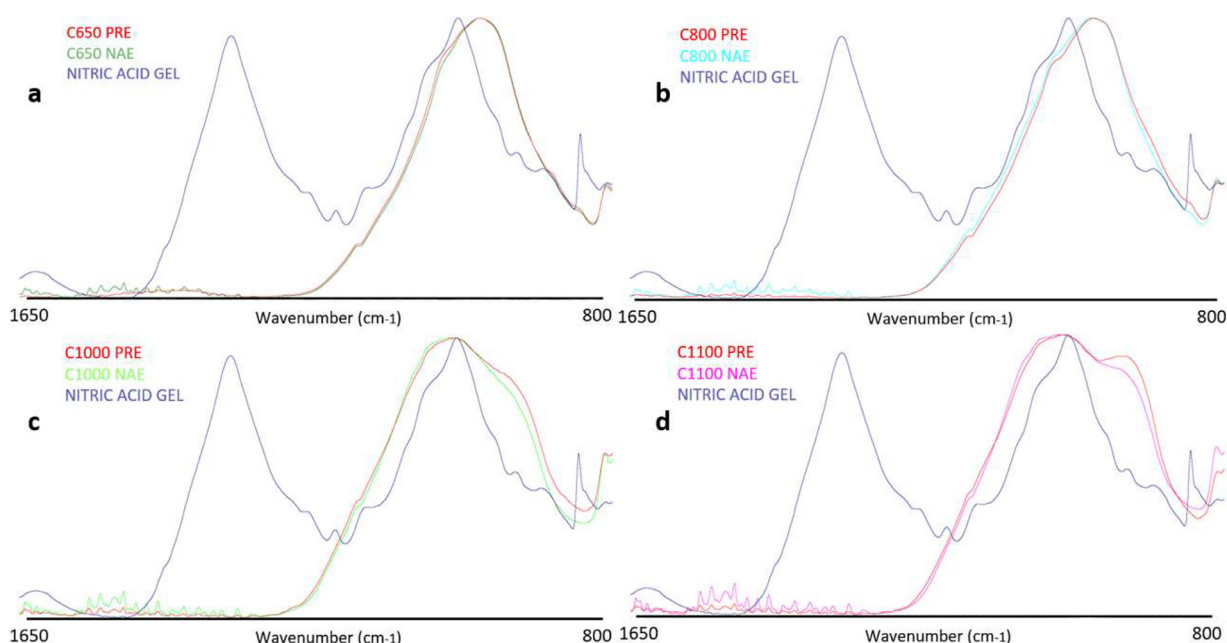


Fig. 4. Detail of the scaled ATR-FTIR spectra of the ceramic mock-ups before (PRE) and after treatment with thickened nitric acid solution (NAE): **a** 650 °C, **b** 800 °C, **c** 1000 °C and **d** 1100 °C, besides the spectra obtained from the confined nitric acid itself. No differences were detected.

software for the analysis of the spectra, in a range of 400–4000 cm^{-1} , a resolution of 4 cm^{-1} , and scanning time of 24 measurements. The spectra were plotted using Origin® 2019 and scaled to the near 1000 cm^{-1} band with OMNIC® 8.2.387 software.

3.4.4. Thermogravimetry – differential scanning calorimetry (TG-DSC)

In order to quantify the calcium carbonate before and after the cleaning treatments and to determine the possible non-crystalline phases associated, powder samples of 10 mg were studied before and after the cleaning treatments. Thermal analysis equipment SDT Q600 (TA® Instruments) was used, with a platinum capsule, a heating rate of 10 °C/min, from room temperature to 1000 °C, in a nitrogen atmosphere with a 100 ml/min flow. The results obtained were evaluated with TA Universal Analysis® software.

4. Results and discussion

4.1. Ceramic mock-ups with calcium carbonate deposits

4.1.1. Macroscopic observation and colour spectrophotometry

In ceramic mock-ups treated with the xanthan gum thickened deionised water (H), the removal was not effective. The gel only softened the calcium carbonate concretions, which could be then removed by mechanical means (wooden sticks), but surface residues remained, being impossible to remove them mechanically without damaging the ceramics' surfaces (Fig. 1). The colour measurements corroborated these observations, with a total colour variation above the perception limit of an inexperienced observer ($\Delta E_{00} \geq 2$) (in C650 and C800 H: $\Delta E_{00} > 3$; in C1000 and C1100 H: $\Delta E_{00} > 10$) [33].

In the ceramic pieces treated with thickened acetic acid (AAE), at first sight the cleaning efficacy is good, given that the CCD, even the most superficial ones, were removed. However, heterogeneously distributed stains or differences in colour were identified on pieces C650, C800 and C1000 AAE (Fig. 1). These differences in surface colouration were reflected in the ΔE_{00} with values above the perception limit of an inexperienced observer in C800 ($\Delta E_{00} > 6$) and C1000 AAE ($\Delta E_{00} > 3$). The causes for the appearance of

these stains were related to possible traces of soluble salts resulting from the reaction between acetic acid and calcium carbonate (CaCO_3) from the deposits. This theory was later confirmed by the ATR-FTIR analyses (see Section 4.1.3).

Finally, the cleaning tests carried out with thickened nitric acid (NAE) were effective from macroscopic observation, having removed even the superficial calcium carbonate remains (Fig. 1). The total colour variation values corroborated this effectiveness, as the results indicated that the differences would not be perceptible by an inexperienced observer ($\Delta E_{00} \leq 2$) and, in C800 and C1100 NAE, the differences would be imperceptible ($\Delta E_{00} \leq 1$).

4.1.2. Powder X-ray diffraction (PXRD)

In order to identify possible mineralogical variations, samples were taken from the mock-ups before the carbonation process (PRE) and after the cleaning treatments (AAE & NAE).

Regarding the ceramics treated with thickened acetic acid (AAE) in which surface stains were identified, the PXRD patterns showed no differences in the mineral composition of the different areas visible to the naked eye (Fig. 2). No calcium acetate was detected. Furthermore, the peak corresponding to calcite ($2\theta = 29.5^\circ$) identified in the low temperature specimens (C650 and C800), remained constant after the cleaning treatment [25], although it could be either the calcite from the ceramic matrix or from the CCD (Fig. 2).

In the same way, in the PXRD patterns of the specimens intervened with the thickened nitric acid (NAE), no variations in the mineral phases identified for each firing temperature were detected, which would indicate that their mineralogical composition was not altered. Likewise, the peak assigned to calcite ($2\theta = 29.5^\circ$) could also be distinguished in the low firing temperature ceramic specimens (Fig. 2). No calcium nitrate was identified, meaning no soluble salt residues were left.

4.1.3. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)

In line with the analyses carried out by PXRD on the specimens treated with thickened acetic acid (AAE), the stains identified with the naked eye were studied individually by ATR-FTIR and,

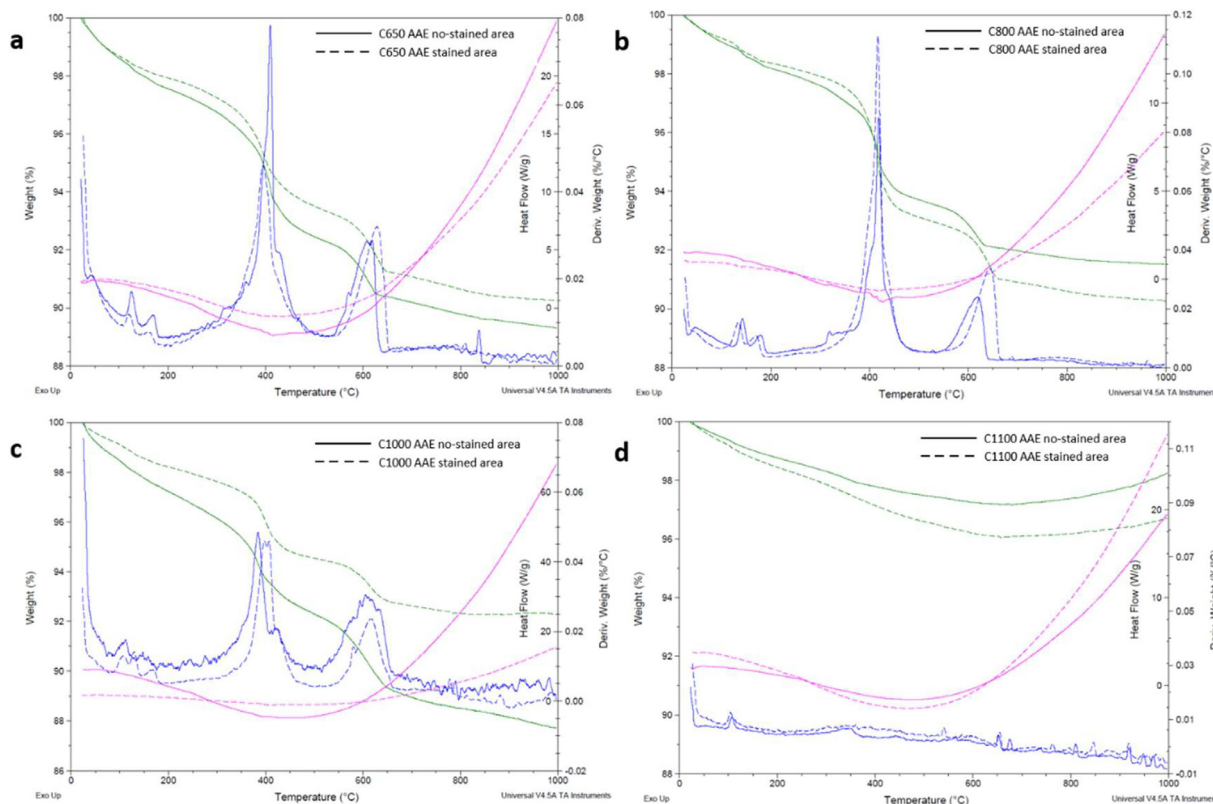


Fig. 5. Thermograms of the stained and non-stained areas identified on the ceramic mock-ups after treatment with thickened acetic acid (AAE): **a** 650 °C, **b** 800 °C, **c** 1000 °C and **d** 1100 °C. In pink, the heat flow (W/g) curve; in green, the weight (%), and in blue, the derived of the weight (%/ °C).

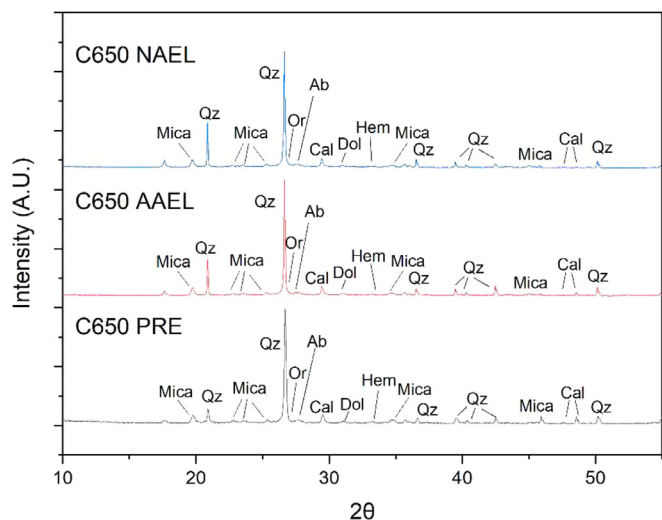


Fig. 6. PXRD patterns of the ceramic mock-ups without CCD (650 °C), before (PRE) and after the cleaning treatments with thickened acetic acid (AAE) and nitric acid (NAEL). Ab: albite; An: anorthite; Cal: calcite; Dol: dolomite; Hem: hematite; Mica: muscovite and/or illite; Or: orthoclase; Qz: quartz.

as no differences were found in the detected bands, regarding non-stained areas, the spectrum that best represented each specimen (AAE) was selected for comparison with the spectra of the specimens before the treatment (PRE).

The spectra of the mock-ups treated with the confined acetic acid (C650, C800, and C1000 AAE) contained differences in the region ranging 1200 and 1600 cm^{-1} , where two bands were visible (1430 cm^{-1} and 1540 cm^{-1}) (Fig. 3) assigned to calcium

acetate's $[\text{Ca}(\text{CH}_3\text{COO})_2]$ C–O bond vibrations. On the one hand, the bands between 1528 and 1604 cm^{-1} (including the vibration at 1540 cm^{-1}), accounts for the antisymmetric strain $\nu_{\text{as}}(\text{C}-\text{O})$, whereas the symmetric strain vibration $\nu_{\text{s}}(\text{C}-\text{O})$ was found about at 1450 cm^{-1} . In addition, in the region between 3500 and 4000 cm^{-1} , bond stress vibrations, possibly due to the presence of water $\nu(\text{O}-\text{H})$ were identified in all the spectra [34].

The spectra of the ceramic mock-ups (before the carbonation process, PRE and after the cleaning tests with the thickened acetic acid, AAE), were also compared with the spectra obtained from the confined acetic acid itself, which allowed to determine their similarity in the bands previously identified (Fig. 3). These findings suggested that desalting performed after cleaning was ineffective because it left soluble salt remains in the mock-ups. However, such bands were not found in specimen C1100 AAE, indicating that the desalination in this case was successful. This could be due to a smaller deposit, resulting in less calcium acetate $[\text{Ca}(\text{CH}_3\text{COO})_2]$ being produced.

On the other hand, the spectra of the mock-ups treated with the thickened nitric acid solution (NAE) showed low intensity bands in comparison with the samples before the carbonation process (PRE): in the regions 3800–3000 cm^{-1} and 1800–1500 cm^{-1} , linked to water vibration; and 1500–1300 cm^{-1} , [35,36]. Detailed analysis of the latter range, with the bands scaled to the band near 1000 cm^{-1} (Fig. 4), including the spectrum of the confined nitric acid itself, showed no bands associated with the nitrate ion and, therefore, no traces of the calcium nitrate $[\text{Ca}(\text{NO}_3)_2]$ generated during the cleaning treatments, nor of the gel used. Therefore, the desalination would have been effective, as well as the Japanese paper as a barrier element. This coincides with the absence of surface staining on the mock-ups treated with the thickened nitric solution (NAE), compared to those treated with the acetic acid (AAE).

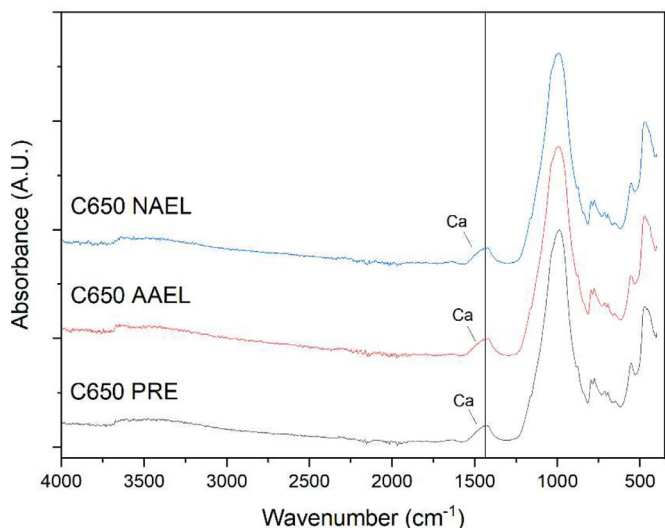
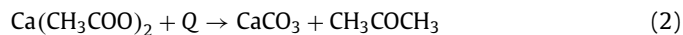
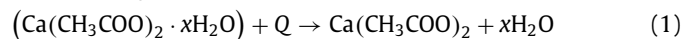


Fig. 7. ATR-FTIR spectra of the ceramic mock-ups without CCD (650 °C), before (PRE) and after treatments with thickened acetic (AAEL) and nitric acid (NAEL). No differences were detected in the band linked to calcium carbonate (~1450 cm⁻¹).

4.1.4. Thermogravimetry – differential scanning calorimetry (TG-DSC)

In the thermograms of the stains identified in the ceramic mock-ups treated with the thickened acetic acid (AAE), the presence of calcium acetate was corroborated, in line with the ATR-FTIR results, based on the mass losses associated with its thermal transformations [36]: **1)** between 150 and 200 °C and, **2)** between approximately 200–240 °C (Eq. (1)). Besides, the mass loss around 400 °C (between 260 and 500 °C), is associated, according to Bilton et al. (2012) [37], with acetone decomposition from the transformed acetate (Eq. (2)) (Fig. 5). Although the mass losses in the same temperature range can also be associated with calcium hydroxide and muscovite, given the low amount of ceramic matrix on the sample, data would indicate that this is a compound foreign to

the mock-ups and the generated deposits, also bearing in mind the identification of the calcium acetate by ATR-FTIR. Other two mass losses between 100 and 200 °C were identified and linked to the presence of hygroscopic water and hydrated salts [37–40]. Finally, the mass loss between 530 and 670 °C indicated the decomposition of CaCO₃ into CaO (Eq. (3)).



Since the thermograms of both the stained and no-stained areas were very similar (Fig. 5), in order to compare the mock-ups after the treatments (AAE) with respect to the pre-carbonation phase (PRE), a sample was taken, including both areas. In these samples, the results previously discussed, related to the decomposition of the hydrated calcium acetate, were partially blurred, as the acetate salts were only superficial and, when analysing an overall sample, the intensity of the mass variations decreased.

The thermograms obtained from the ceramic specimens treated with thickened nitric acid solution (NAE) showed similarities to those of the specimens treated with acetic acid (AAE). In this line, a slight decrease in mass up to 200 °C, associated with the elimination of hygroscopic water and hydrated salts, was identified in the low-temperature specimens (C650 and C800 NAE). In addition, two other losses were identified, between 400 and 500 °C and 500–750 °C, which were also observed in the C1000 NAE mock-up, but with much lower intensity. These losses were linked to the dehydroxylation of the chemical water from the muscovite and calcium hydroxide in the deposits generated, and to the decomposition of the calcium carbonate, respectively. On the other hand, in the C1100 NAE specimen, no variations were identified between the thermograms of the NAE specimen and the specimen before carbonation (PRE).

Nevertheless, no relevant differences were identified with respect to the concentration of calcium carbonate after the cleaning treatments, regardless the product used.

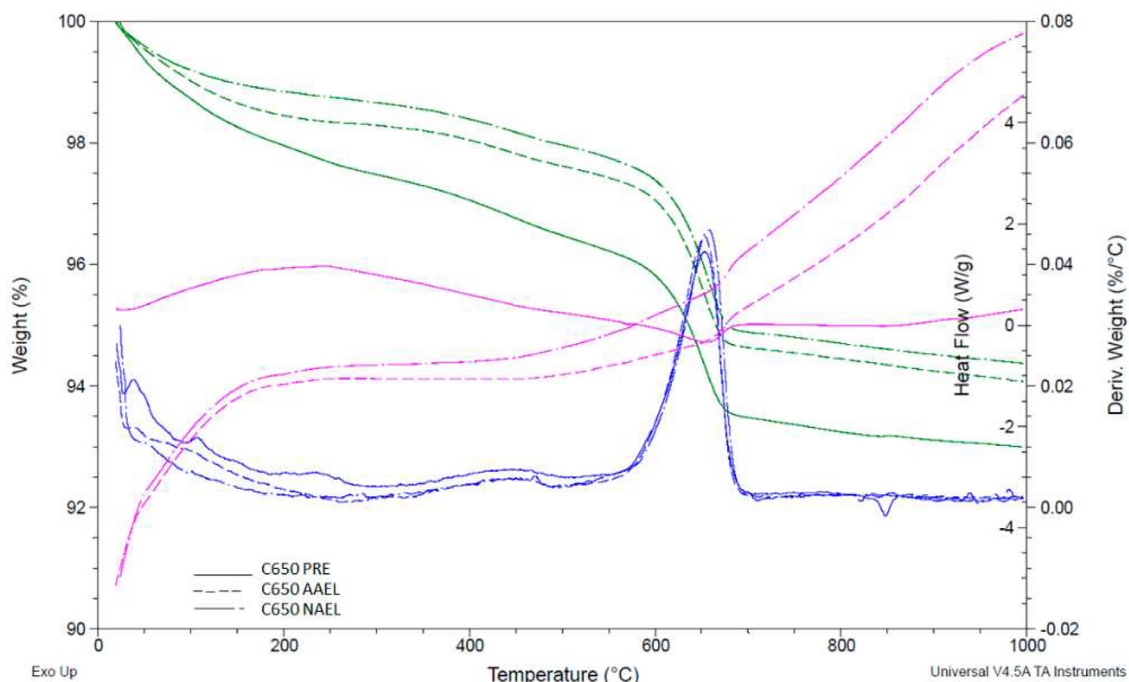


Fig. 8. Thermograms of the ceramic mock-ups without CCD (650 °C), before (PRE) and treated with thickened acetic acid (AAEL) and nitric acid (NAEL). In pink, the heat flow (W/g) curve; in green, the weight (%), and in blue, the derived of the weight (%/ °C).

4.2. Ceramic mock-ups without calcium carbonate deposits

4.2.1. Powder X-ray diffraction (PXRD)

For both cleaning treatments (AAEL & NAEL), mineral phases detected remained constant after the tests performed onto the ceramic surfaces (Fig. 6), including calcite ($2\theta = 29.5^\circ$). Diffraction peaks related to calcium acetate or nitrate were not identified, in line with previous results (see Section 4.1.2).

4.2.2. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectra obtained followed the same line as those obtained by PXRD, as no differences were observed after the cleaning treatments carried out on the specimens (Fig. 7). The $\sim 1400\text{ cm}^{-1}$ band (calcite) was identified in the two ceramic mock-ups treated, with very similar intensities before (PRE) and after the cleaning treatments (AAEL & NAEL). Moreover, no new bands linked to soluble salts were observed, as a product of the cleaning agents used: calcium acetate (1450 cm^{-1} and $1604\text{--}1528\text{ cm}^{-1}$); nitrate ($1200\text{--}1500\text{ cm}^{-1}$), and sodium bicarbonate (NaHCO_3) ($1000\text{--}1093\text{ cm}^{-1}$). Although it might be assumed that their formation would not have occurred in the absence of CCD, the agents may have interacted with the ceramic matrix's original CaCO_3 .

4.2.3. Thermogravimetry – differential scanning calorimetry (TG-DSC)

According to the thermograms of the treated mock-ups, the mass losses associated with the thermal decomposition of calcium carbonate ($530\text{--}670\text{ }^\circ\text{C}$) did not show relevant differences with respect to the untreated mock-ups (Fig. 8). In fact, the detected mass losses were slightly higher in the treated specimens, which would indicate a higher concentration of calcium carbonate. Since no CCD were generated on these specimens, these variations may be due to the heterogeneity of the specimens, and/or the limitations of the technique, even though they were made with the same commercial clay and methodology. In no case can they be linked to the removal of the original CaCO_3 from the matrix ceramics. This would indicate that treatments based on acid solutions thickened with xanthan were safe for the mock-ups, even for those fired at low temperature.

5. Conclusions

Based on colorimetric evaluation, the removal of the artificial CCD using acetic and nitric acid solutions thickened with xanthan gum (AAE & NAE) was effective. However, three of the four ceramic mock-ups treated with the confined acetic acid (AAE) showed superficial stains, confirmed by colour spectrophotometry.

The residue's removal was not effective enough with the acetic acid treatments (AAE), as calcium acetate remains were identified by ATR-FTIR on the ceramic mock-ups' surfaces. However, the presence of these salts cannot be directly linked to the stains, as they were found on both lighter and darker areas. Deeper research should be done to determine whether these stains can be derived from soluble salts and their movement within the ceramic matrix. On the other hand, no soluble salts due to the nitric acid treatments (NAE) were detected on the respective mock-ups. TG-DSC analysis also supported these findings. They can also be explained by different solubility in water for both calcium and nitrate acetate salts. However, a diverse desalination methodology should be explored, specifically for salts with lower solubility rates, as the rinsing procedure, by determining the endpoint with the selected variable (K_{norm}), was not effective enough in this case.

With respect to the safety of the tested treatments, TG-DSC results showed that the original concentration of calcium carbonate

did not vary because of the cleaning treatments (AAEL & NAEL), indicating that even in the worst-case scenario, their original composition did not change. In this approach, it may be expected that no differences will occur at higher firing temperatures since these experiments were conducted on low fired ceramic mock-ups ($650\text{ }^\circ\text{C}$). The developed treatments are therefore safe for the samples used.

Regarding the firing temperatures, no significant variations were found associated with the cleaning treatments, despite the fact that mock-ups fired at higher temperatures ($>1000\text{ }^\circ\text{C}$) showed lower amount of soluble salts residues, most likely as a result of smaller CCD.

With respect to any potential residues from the xanthan gum-thickened acid solutions, none were found by the techniques employed. Nonetheless, tests with chemical gels will be conducted in the future.

These results can help the professionals from the CH field to select more adequate products and application methods depending on the conservation case-studies. In this way, they could also be extrapolated to other similar materials (e.g., stone). Throughout the research, the importance of testing first with mock-ups rather than with original pieces has become clear.

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