



Chelating agents for the removal of calcareous deposits from archaeological ceramic materials. Compositional evaluation after immersion and physical gel application methods

Águeda Sáenz-Martínez^{1,a} , Marta Pérez-Estébanez¹ , Mónica Alvarez de Buergo² , Margarita San Andrés¹ 

¹ Departamento de Pintura y Conservación-Restauración, Facultad de Bellas Artes, Universidad Complutense de Madrid (UCM), C/ Pintor el Greco 2, 28040 Madrid, Spain

² Instituto de Geociencias IGEO (Consejo Superior de Investigaciones Científicas y Universidad Complutense de Madrid), C/ Doctor Severo Ochoa 7, 28040 Madrid, Spain

Received: 7 October 2022 / Accepted: 26 March 2023

© The Author(s) 2023

Abstract The removal of calcareous deposits from archaeological ceramics is a very normal conservation-restoration treatment. Among the products used, chelating agents are quite common, including ethylenediaminetetraacetic acid salts (EDTA) (Berducou in *La Conservation en archéologie: méthodes et pratique de la conservation-restauration des vestiges archéologiques*, Masson, Paris, 1990; Buys and Oakley *The conservation and restoration of ceramics*, Butterworth-Heinemann, Oxford, 1993; Crisci et al. in *Appl Phys A Mater Sci Process*, 2010. <https://doi.org/10.1155/2009/893528>). Nevertheless, some studies have proved that they can cause damages on the ceramic pieces, regarding changes in their composition, such as dissolution of calcareous components and metallic oxides leaching (Gibson in *Stud Conserv*, 1971. <https://doi.org/10.1155/2009/893528>; Fernández and Seva Sautuola in *Rev del Inst Prehist y Arqueol* 9:471–982, 2003). As a consequence, their artistic values might also change. In spite of that, these products are nowadays still in use, meaning that the treatments might be changing the information that archaeological ceramics carry. However, from the 80 s onwards a more secure alternative to direct application methods based on thickening agents was developed. With the aim of analysing the degradation mechanisms that may take place after the cleaning treatments' application, ceramic specimens with artificial calcareous deposits (Sáenz-Martínez et al. in *Eur Phys J Plus* 136:798, 2021) were treated with a low-concentrated solution of EDTA tetrasodium salt applied by immersion and thickened with xanthan gum powder (Vanzan® NF-C). Finally, the products from the cleaning treatments were neutralised, respectively, by immersion and by rinsing with deionized water. The composition of the ceramic samples was established before the growth of calcareous deposits and after the treatments, in order to determine their effectiveness and safety. According to the results, EDTA salt treatments, both by immersion and thickened, were effective regarding the removal of the calcareous deposits and did not modify the elemental and mineralogical original composition of the specimens (XRF, XRPD, TG-DSC). In addition, no gel residues were detected by FTIR-ATR.

1 Introduction

Insoluble salts deposits commonly appear on archaeological ceramics' surfaces during their burial in terrestrial contexts, coming from diluted salts. Depending on ceramics porosity, the recrystallization of these salts may occur inside their matrix or on their surface. However, this process is slower than for soluble salts, so in this case is less likely that they provoke physical damages in the ceramics. Nevertheless, these surface deposits might hide decoration, stamps, impressions and even fingerprints that might help archaeologists and historians to determine their raw materials, elaboration processes, chronology and uses [1]. For this reason, their removal becomes an essential treatment in order to study ceramic surfaces, in spite of the irreversibility of the cleaning process [2]. Due to the low solubility of the deposits, usually composed by calcium carbonate ($K_{PS} \text{CaCO}_3 = 3.36 \times 10^{-9}$)¹ [4], conservators–restorers have been using a wide variety of chemical products to accomplish their removal, including acids, chelating agents and, more recently, ion exchange resins [5–7], as well as solutions rich in carbon dioxide [8, 9]. Chemical cleaning is based on the capacity of some products to transform insoluble salts into soluble complexes [10, 11]. In this way, chemical products soften the deposits, being therefore easily removed by scalpels and micro-motors. However, over the years, some researchers pointed out the inconvenience of using these products [12–15], as they cannot distinguish between the components of the deposits and the ones that

¹ The solubility product or equilibrium constant is the ionic product of the molar concentrations of the ions present in a saturated solution of the compound [3].

Focus Point on Scientific Research in Cultural Heritage 2022 Guest editors: L. Bellot-Gurlet, D. Bersani, A.-S. Le Hô, D. Neff, L. Robinet, A. Tournié.

^a e-mail: agsaenz@ucm.es (corresponding author)

constitute the ceramics. In this way, acids may dissolve original carbonates such as calcite (CaCO_3) and dolomite [$\text{CaMg}(\text{CO}_3)_2$], and chelating agents may form stable compounds with metallic ions (Ca^{+2} , Fe^{+2} , Mg^{+2} , etc.), changing the original composition of the ceramic pieces, along with their properties. Besides, the effervescence resulting from the reaction between the acids and the calcium carbonate might also imply physical damages on ceramic surfaces, more pronounced in low-firing temperature ceramics, ceramics with low cohesion and specially in calcareous ceramics ($\text{CaO} > 6\%$) [12, 16, 17]. Apart from the eventual differences in the aesthetic values of these pieces (colour, brightness, roughness, etc.), the changes caused by the cleaning treatments might make a relevant modification in the composition, physical and chemical properties of the ceramics. Along with these effects, their archaeological interpretation might differ, changing the understanding of History.

Being aware of the disadvantages of using solutions of chemical products, safer alternative application methods were developed within the painting field [18–20], improving the benefits of the already-known poultices, mainly composed by cellulose or clays. Physical gels obtained by thickening the chemical solutions with diverse polymers (agar, xanthan and gellan gum, polyacrylic acids, etc.) were developed for reducing the evaporation rate of the cleaning products, decreasing their diffusion and focusing the treatment action [18, 21–25]. Due to the success gained, these gels were widespread among the conservation of other materials [26–29], although they are not yet very common within archaeological ones [30]. However, they would provide an alternative to the direct application by immersion of most of the solutions used to remove calcareous deposits, by increasing the control of the reactions that take place and, as a result, their consequences.

Low-concentrated solutions of acids were proven to be safe, in terms of elemental and mineralogical composition of ceramic specimens, regardless of their firing temperature (650–1100 °C) [31]. Thus, this research aimed to study the efficacy and safety of a chelating agent applied by immersion and physical gel for the removal of artificial calcareous deposits, by determining the composition of several ceramic specimens before and after the cleaning treatments developed. With this purpose, complementary techniques such as X-ray fluorescence (XRF), X-ray powder diffraction (XRPD) and thermogravimetric analysis with differential scanning calorimetry (TG-DSC) were used, along with Fourier transform infrared-attenuated total reflectance analysis (FTIR-ATR), also selected to identify the eventual residues of salts and gel. The results from the treatments based on both application methods would throw light on the actual and future conservation-restoration procedures.

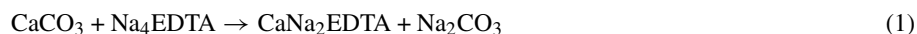
2 Materials and methods

2.1 Ceramic specimens

Eight ceramic specimens ($5 \times 5 \times 1 \text{ cm}^3$) fired from a temperature of 650 up to 1100 °C, with one of their faces covered with artificial calcareous deposits were used, by following the methodology already published [31]. The artificial deposits generated were only superficial, according to microprobe analysis (Fig. 1). The images resulted from the analysis of a polished cross section of specimens fired at 650 and 800 °C before (PRE) and after the carbonation process (CAR), showed no differences regarding their Ca content. Besides, the artificial deposits cannot be observed in the surface (upper area) of the images, as they separated themselves during the cross section samples preparation. Four samples were used for the immersion cleaning treatments (E) and the rest for the gel application method (EE). Throughout the research, four specimens of each firing temperature were analysed and the small differences detected were ascribed to the variability of the ceramic material, as the methodology followed was alike.

2.2 Cleaning treatments

The product selected for the cleaning treatments was the chelating agent EDTA tetrasodium salt ($[\text{CH}_2\text{N}(\text{CH}_2\text{COONa})_2]_2 \cdot 4\text{H}_2\text{O}$; Na_4EDTA to short), as its molecules form stable chemical bonds with calcium metallic ions (Ca^{+2}). As a result of the reaction, soluble salts of sodium carbonate are formed:



Equation 1 shows chemical reaction between the calcium carbonate from the artificial deposits and the EDTA chelating agent.

A solution of the product was prepared at 1% w/v in deionised water, following the criteria of minimum product concentration from the Spanish standard UNE 41,806–2 IN: 2009 [32]. The pH value was set at 10.79 ± 0.01 (measured with a Seven Compact pH meter S220 METTLER TOLEDO, sounding line InLab® Expert Pro-ISM). Being pH value $\cong 11$ the optimum for the complexation of Ca^{+2} [33]. The gel was prepared at room temperature (20–25 °C) by adding 2 g of the Vanzan® NF-C powder to 100 mL of the Na_4EDTA solution (2% m/v) with constant stirring. The pH values of the gel were checked and did not change in relation to the Na_4EDTA solution. Japanese paper (60 g/m^2) was used as barrier element between the ceramics' surfaces covered by the deposits and the gel. The gel was directly applied with a palette knife with 2–3 mm thickness. Besides, the pieces treated with the gel were covered with a plastic film in order to reduce the evaporation rate of the solution added and the drying of the gel. In Fig. 2, the immersion procedure (Fig. 2a and b) and the physical gel application method (Fig. 2c and d) are shown. Both treatments were pursued several times in order to remove entirely and safely the deposits by the mechanical cleaning (MC) as described below. For each application, in both immersion and gel form, a fresh solution and mixture, respectively, were used.

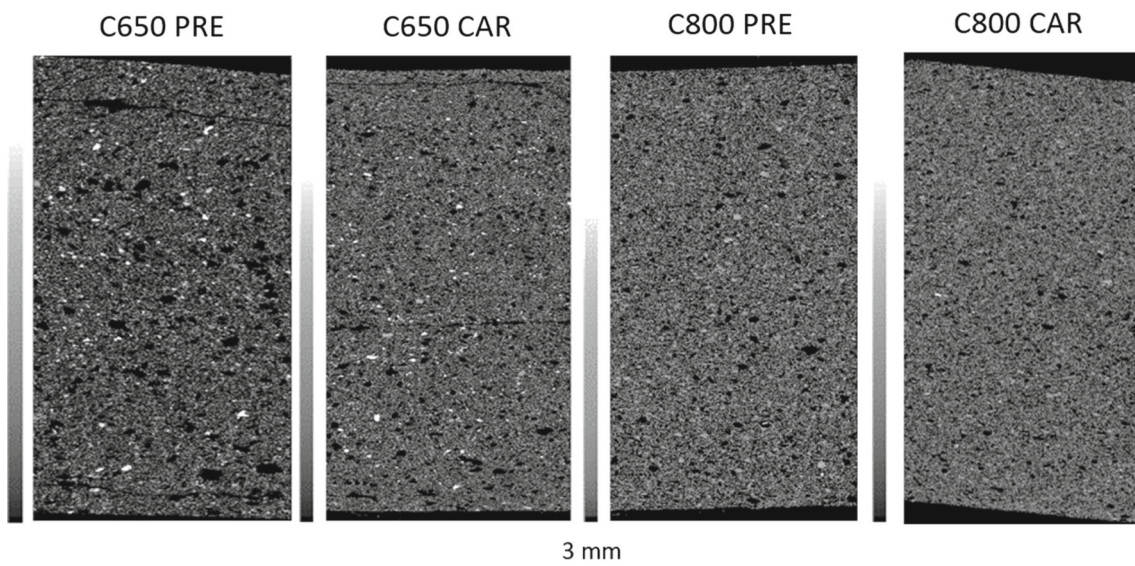
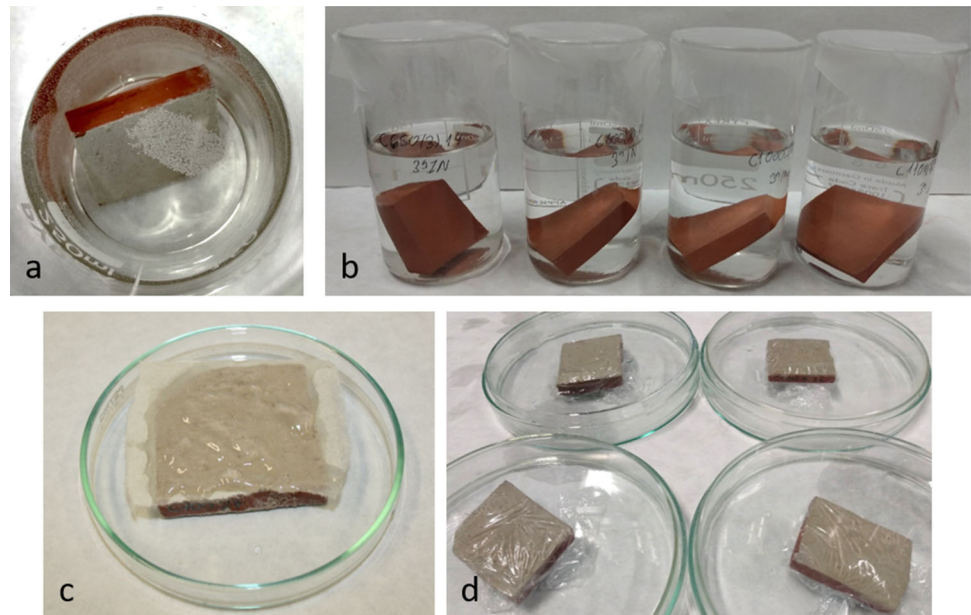


Fig. 1 Comparison of the calcium content in the electron microprobe images of the cross section samples of ceramic specimens fired at 650 and 800 °C, before (PRE) and after (CAR) the carbonation process. The vertical bars indicate the calcium content, being higher in lighter areas and lower in darker ones

Fig. 2 Cleaning treatments pursued by immersion with the Na_4EDTA solution (a, the first immersion and b, the third one), and in gel form (c, ceramic specimen covered with the Japanese paper and the gel and d, ceramics also covered with the plastic film)



The minimum time for the reaction to be effective, included as an important parameter in Spanish standard UNE 41,806–2 IN: 2009 [32], was experimentally established in 30 min, regardless of the application method. After both the immersion and the gel application, a mechanical cleaning with wooden sticks was pursued (MC) in order to remove the calcareous deposits partially transformed into Na_2CO_3 , which allows their mechanical removal. This process was repeated as many times as necessary until the deposits were completely removed, except for the last applications, as the ceramic surfaces were quite exposed after the previous removal of most of the calcareous deposits generated (Table 1). In general, longer times were needed for the ceramic specimens fired at lower temperature, which presented wider deposits than the specimens elaborated at 1100 °C, accordingly to the thermogravimetric analysis already published [31]. After the treatments, the deposits do not longer interfere in the visual appreciation of the specimens' surfaces, as it is shown in Fig. 3, so it can be concluded that they have been effective, no matter the application method of the Na_4EDTA solution: immersion (E) and gel (EE).

Besides, two cleaning tests by immersion and with the Na_4EDTA gel were pursued on two ceramic specimens fired at 650 °C (C650 EL and EEL), which did not have the artificial calcareous deposits on them. These trials were done in order to establish the differences between the ceramic patterns and the specimens treated, in the most adverse case, as the solution entered in direct contact with the ceramics.

Table 1 Characteristics and conditions of the cleaning treatments pursued with the chelating agent Na_4EDTA at 1% w/v, applied by immersion and Vanzan® NF-C gel onto the ceramic specimens. The acronyms include the firing temperature of each specimen treated (650–1100), followed by the letters regarding the cleaning treatments: E, for the immersion in the chelating agent's solution and EE, for the solution thickened. MC: mechanical cleaning

Acronym	Application method	Cleaning agent (pH)	Treatment time	Procedure
C650 E	Immersion	Na_4EDTA (10.79)	180'	30' + MC + 30' + MC + 60' + 30' + 30'
C800 E				
C1000 E				
C1100 E				
C650 EE	Vanzan® NF-C gel	Na_4EDTA (10.79)	180'	30' + MC + 30' + MC + 30' + 30' + 30' + 30'
C800 EE				
C1000 EE				
C1100 EE				

Fig. 3 The appearance of the ceramic specimens before and after the carbonation process (PRE and CAR, respectively), and the treated specimens with the solution of Na_4EDTA by immersion (E) and thickened with Vanzan® NF-C (EE)



In all cases, soluble salts resulted from the reaction, as well as the remains of the products used were removed with deionised water ($\text{pH} \approx 6\text{--}7$) by immersion and rinsing in an approximated ratio of 1:15 g/ mL [34]. The process was monitored with conductivity measures (K) (Delta-Ohm HD2156.2) at 0, 5, 10, 15, 30, 60, 120, and 180 min after the first immersion or the first rinsing with water. The endpoint was established by reaching twice the value 2, or lower, in the variable K_{norm} [35], after renewing the water, following the methodology from previous research [31]. For most of the treated ceramic specimens, five immersions or rinsing were necessary. After that, the ceramic specimens were introduced in a climatic chamber (Vötsch Industrietechnik VCL 4010) for 24 h (20°C and 50 % RH).

2.3 Chemical and mineralogical analysis

The electron microprobe analysis of a cross section of ceramic samples before (PRE) and after the carbonation process (CAR) was carried out with a JEOL Superprobe JXA-8900 M at a potential of 20.0 kV, a beam intensity of 50 nA, measurements of 25 ms/point with a total of 900×450 measurement points. Backscattered electron images were obtained of the elemental composition of the surfaces studied ($3.5 \times 7 \text{ cm}^2$ approx.), and the distribution of four representative elements (Ca, Fe, Si and Mg) was established.

Table 2 XRF results of the major and minor elements of the ceramic specimens' patterns C650 and C800 PRE, before the carbonation process, and the specimens C650 and C800 E treated by immersion in the Na₄EDTA solution, expressed in oxides

Specimen	Major and minor elements (oxides %)									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	MgO	TiO ₂	Na ₂ O	P ₂ O ₅	MnO
C650 PRE	60.28	19.21	6.62	5.63	3.82	3.08	0.83	0.24	0.16	0.12
C650 E	53.19	19.65	8.57	7.44	5.05	4.29	1.07	0.36	0.18	0.15
C800 PRE	60.29	19.28	6.61	5.55	3.83	3.01	0.84	0.31	0.15	0.11
C800 E	53.23	19.30	8.71	7.54	5.05	4.33	1.09	0.35	0.19	0.15

Table 3 Absolute variation (%) of the content in major and minor elements detected by XRF of the ceramics treated by immersion with Na₄EDTA (C650 and C800 PRE), in comparison with the patterns of the same firing temperature (C650 and C800 PRE). The increase in the metallic components denoted the absence of an aggressive effect of the chelating agent

Specimen	Absolute variation (%)									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	MgO	TiO ₂	Na ₂ O	P ₂ O ₅	MnO
C650 E	- 7.09	0.45	1.95	1.81	1.23	1.21	0.24	0.12	0.02	0.03
C800 E	- 7.06	0.02	2.11	1.99	1.22	1.32	0.26	0.04	0.04	0.04

The elemental composition of the ceramic specimens was determined by X-ray fluorescence (XRF) under vacuum with a Panalytical Axios equipment, before (PRE) and after the cleaning treatments pursued with the Na₄EDTA chelating agent (E: by immersion, EE: with physical gel Vanzan® NF-C, EL: by immersion in non-carbonated specimens and EEL: by physical gel Vanzan® NF-C in non-carbonated specimens). Fragments of the specimens were finely grinded with an agate mortar.

On the other hand, the mineralogical phases were established by X-ray powder diffraction (XRPD) with a Panalytical X Pert MPD equipment in Bragg–Brentano θ - θ configuration (Cu K α radiation, 45 kV, 40 mA, angular range 5–70° (2 θ) with a step of 0.02° and 1 s counting time). The phase identification was conducted with the HighScore Plus® 3.0e (3.0.5) PANalytical software, using the PDF-2 2002 ICDD database. The samples were also grinded to powder.

Analysis by Fourier transform infrared spectroscopy coupled with attenuated total reflectance (FTIR-ATR) was performed on powder samples (10 mg) of the ceramic specimens before and after the treatments, as well as the gel itself. The equipment used was a FTIR Alpha II spectrometer with attenuated total reflectance (ATR) module, by Bruker, together with Opus® software for the analysis of the spectra. Analyses were performed in a range of 400–4000 cm⁻¹, with a resolution of 4 cm⁻¹ and scanning time of 24 measurements. The spectra obtained were scaled to the near 1000 cm⁻¹ band with the OMNIC® 8.2.387 software (Thermo Fisher Scientific).

Besides, thermogravimetric analyses with differential scanning calorimetry (TG-DSC) were also carried out. A simultaneous thermal analysis equipment SDT Q600 (TA® Instruments) was used and 10 mg of powder samples were analysed in a platinum capsule at a heating rate of 10 °C/min, from room temperature to 1000 °C in nitrogen atmosphere with a 100 mL/min flow. The results obtained were examined with TA Universal Analysis® software.

3 Results and discussion

3.1 X-ray fluorescence analysis (XRF)

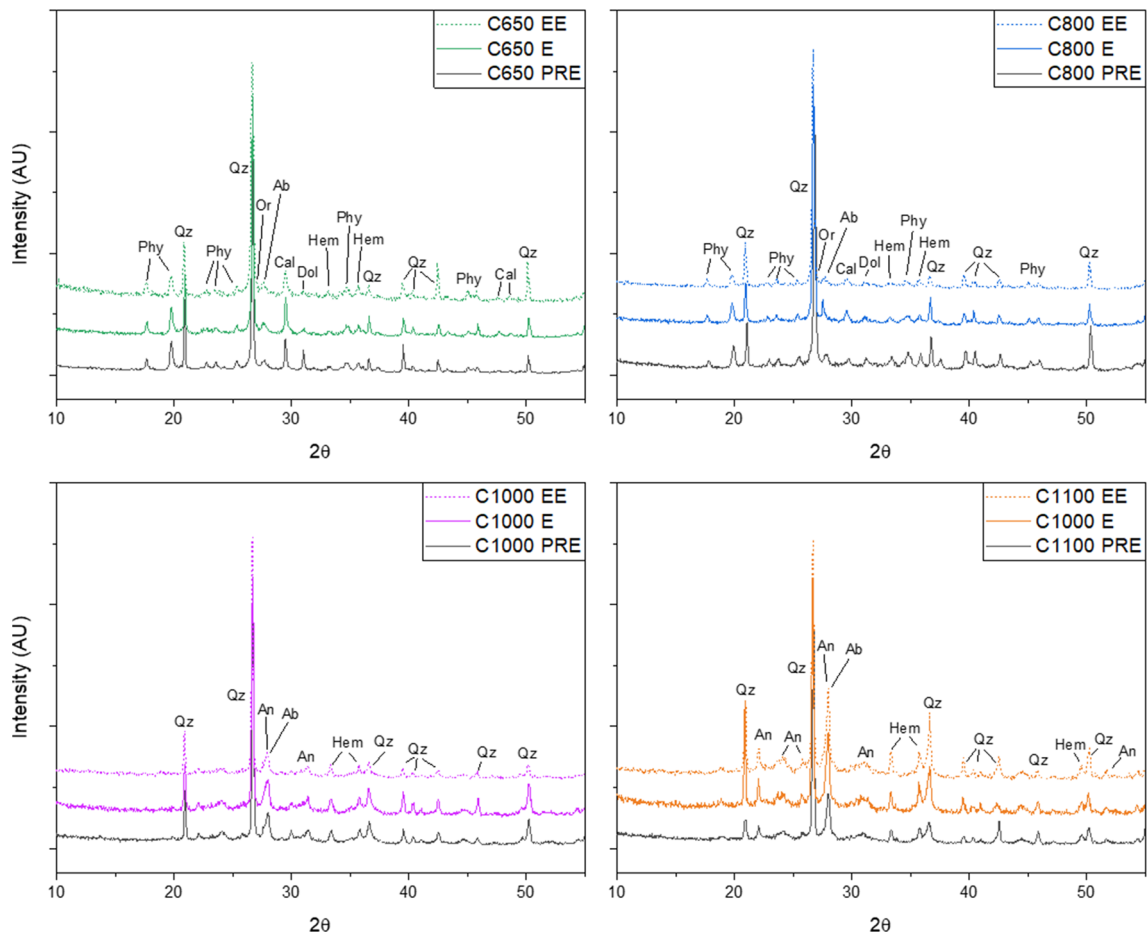
The XRF analysis was pursued on the ceramic specimens' patterns C650 and C800 before the carbonation (PRE), and on the carbonated specimens treated by immersion in the Na₄EDTA solution of the same firing temperatures for being the most vulnerable ones (C650 E and C800 E) amongst all the firing temperatures reproduced, due to their mineralogical composition (Table 2).

The data obtained and gathered in Table 3 show a low increase in Fe and Ca content (% oxides), near the error margin of 2%, established for the equipment and technique used. However, there was a decrease in Si content, although it was not linked to the cleaning treatment, as the chelating agent does not form compounds with Si, but it does with metals as Fe and Ca, which did not happen. For this reason, the decrease in Si content was linked to the adjustment after the increase detected in Fe and Ca. Due to these results, the specimens treated with Na₄EDTA in gel form were not analysed, considering it a gentler procedure.

In the same way, data from the non-carbonated specimens treated by immersion and with Na₄EDTA gel, named as C650 EL and EEL, respectively, showed no changes on the elemental composition (Table 4), taking into account the error margin.

Table 4 Absolute variation (%) of the content in major and minor elements detected by XRF of the non-carbonated ceramics treated by immersion and with Na₄EDTA gel (C650 EL and EEL), in comparison with the pattern of the same firing temperature (C650 PRE)

Absolute variation (%)									
Specimen	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	TiO ₂	MgO	P ₂ O ₅	MnO
C650 EL	0.02	0.10	- 0.01	- 0.18	0.05	0.03	- 0.13	0.01	0.01
C650 EEL	0.19	- 0.12	0.19	0.07	0.09	0.01	- 0.41	- 0.01	0.01

**Fig. 4** Diffraction patterns of the ceramic specimens before the carbonation process (PRE) and after the cleaning treatments with Na₄EDTA by immersion (E) and gel (EE), in pieces fired at 650, 800, 1000 and 1100 °C. Ab: albite; An: anorthite; Cal: calcite; Dol: dolomite; Hem: hematite; Phy: phyllosilicates (muscovite and/or illite); Or: orthoclase; Qz: quartz. Results analysed with HighScore Plus® 3.0e (3.0.5) PANalytical software and figures created with Origin® 2019 (9.60) software

3.2 X-ray powder diffraction analysis (XRPD)

The mineralogical changes of the ceramic specimens were studied by XRPD. Figure 3 includes the diffraction patterns of the carbonated specimens, fired at 650 to 1100 °C, and treated by immersion and the gel form of the Na₄EDTA solution (E and EE, respectively) compared to the ceramic specimens' patterns before the carbonation (PRE). The mineralogical phases detected changed depending on the firing temperature, due to the mineral transformations that take place [36–41], which was already commented in the case of the clay used within this research [31]. In this way, all the non-treated specimens (PRE) were mainly composed by quartz (SiO₂) [JCPDS 01-086-1629] and phyllosilicates (muscovite KAl₃Si₃O₁₀(OH)₂ [JCPDS 01-076-0929] and/or illite KAl₂(Si₃Al)O₁₀(OH)₂ [JCPDS 00-043-0685]), also feldspars (albite Na(AlSi₃O₈) [JCPDS 01-071-1150] and orthoclase (K(AlSi₃O₈) [JCPDS 01-076-0749]), as well as oxides such as hematite, (Fe₂O₃) [JCPDS 01-085-0599]. The specimens fired at low temperatures (650 and 800 °C) also contain calcite (CaCO₃) [JCPDS 01-072-1651] and dolomite (CaMg(CO₃)₂) [JCPDS 01-073-2361], which decomposed and combined with the also decomposed orthoclase, changed into anorthite (CaAl₂Si₂O₈) [JCPDS

Fig. 5 Diffraction patterns of the non-carbonated ceramic specimens before the carbonation process (PRE) and after the cleaning treatments with Na_4EDTA by immersion (EL) and gel (EEL), in pieces fired at $650\text{ }^\circ\text{C}$. Ab: albite; Cal: calcite; Dol: dolomite; Hem: hematite; Phy: phyllosilicates (muscovite and/or illite); Or: orthoclase; Qz: quartz. Results analysed with HighScore® Plus 3.0e (3.0.5) PANalytical software and figures created with Origin® 2019 (9.60) software

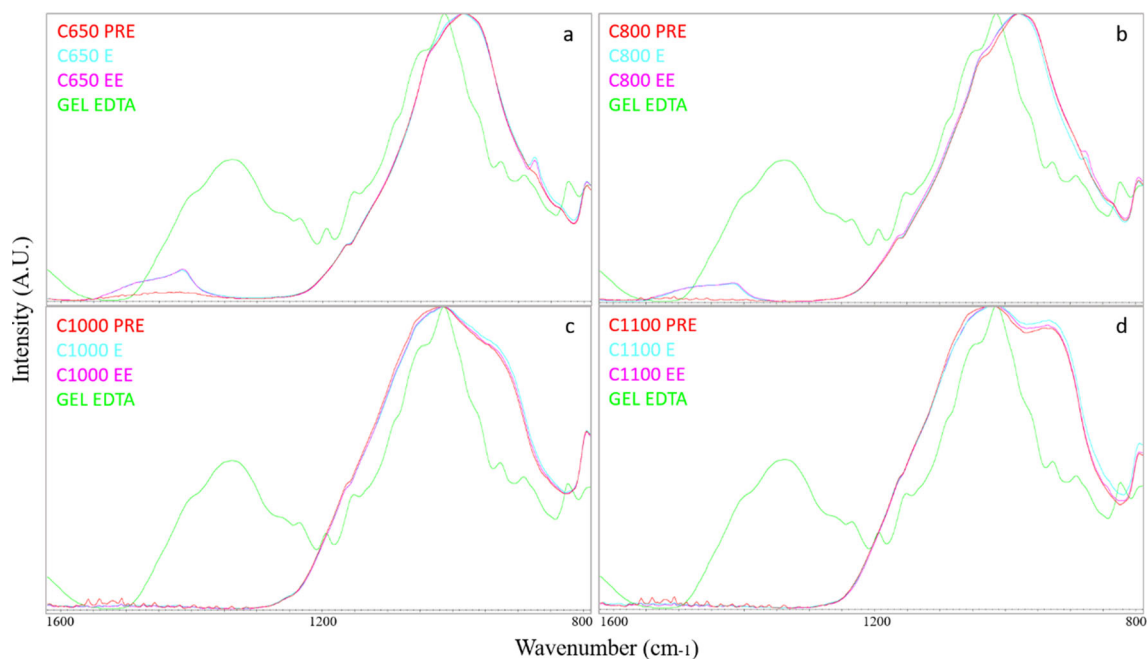
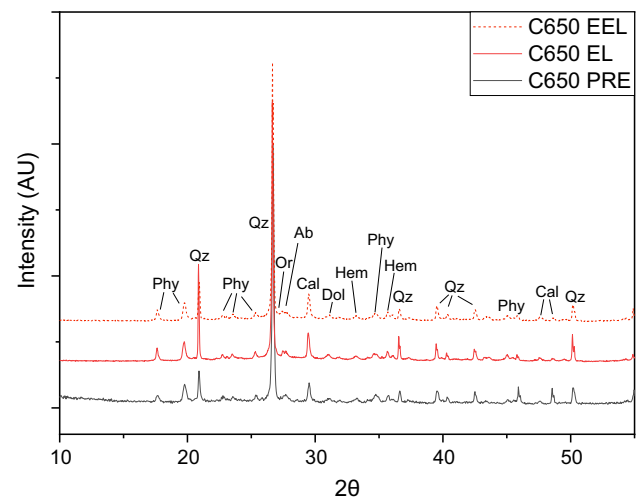


Fig. 6 Detailed of the FTIR-ATR spectra between 1600 and 800 cm^{-1} wavenumber, scaled to band at 1000 cm^{-1} of the ceramic specimens before the carbonation process (PRE) and after the cleaning treatments by immersion (E) and gel (EE). As well as the spectra of the Na_4EDTA gel alone, to identify the eventual gel residues left during the treatments: **a** $650\text{ }^\circ\text{C}$, **b** $800\text{ }^\circ\text{C}$, **c** $1000\text{ }^\circ\text{C}$ y **d** $1100\text{ }^\circ\text{C}$. An increase in the intensity of the band near 1450 cm^{-1} , assigned to the CaCO_3 , was detected in specimens C650 and C800 E and EE. Created with OMNIC® 8.2.387 software (Thermo Fisher Scientific)

01-089-1459] above $950\text{ }^\circ\text{C}$ [42]. On the other hand, qualitative differences in the mineralogical composition were not detected in the ceramics after the treatments, as the phases identified did not change (Fig. 4).

Besides, the XRPD analysis of the non-carbonated ceramic specimens fired at $650\text{ }^\circ\text{C}$, and treated with Na_4EDTA by immersion and gel (EL and EEL), went along with the results previously commented. No differences have been detected on the mineralogical phases identified, paying special attention to calcite and hematite (Fig. 5). Again, these results go in the same direction as the ones obtained by XRF, meaning that there have not been either significant mineralogical changes or compositional ones due to the cleaning treatments.

3.3 Fourier transform infrared-attenuated total reflectance analysis (FTIR-ATR)

FTIR-ATR analysis showed an intensity rise of the band assigned to carbonate ($\sim 1450\text{ cm}^{-1}$) [43–47] in low-firing specimens C650 and C800 treated both by immersion (E) and gel (EE) compared with the samples before the treatments (PRE) (Fig. 6a and b). Taking into account the solubility of Na_2CO_3 , this increase has been linked to calcium carbonate remains from the artificial calcareous deposits. These results would imply that there were still remains of the deposits artificially grown, although they cannot be detected

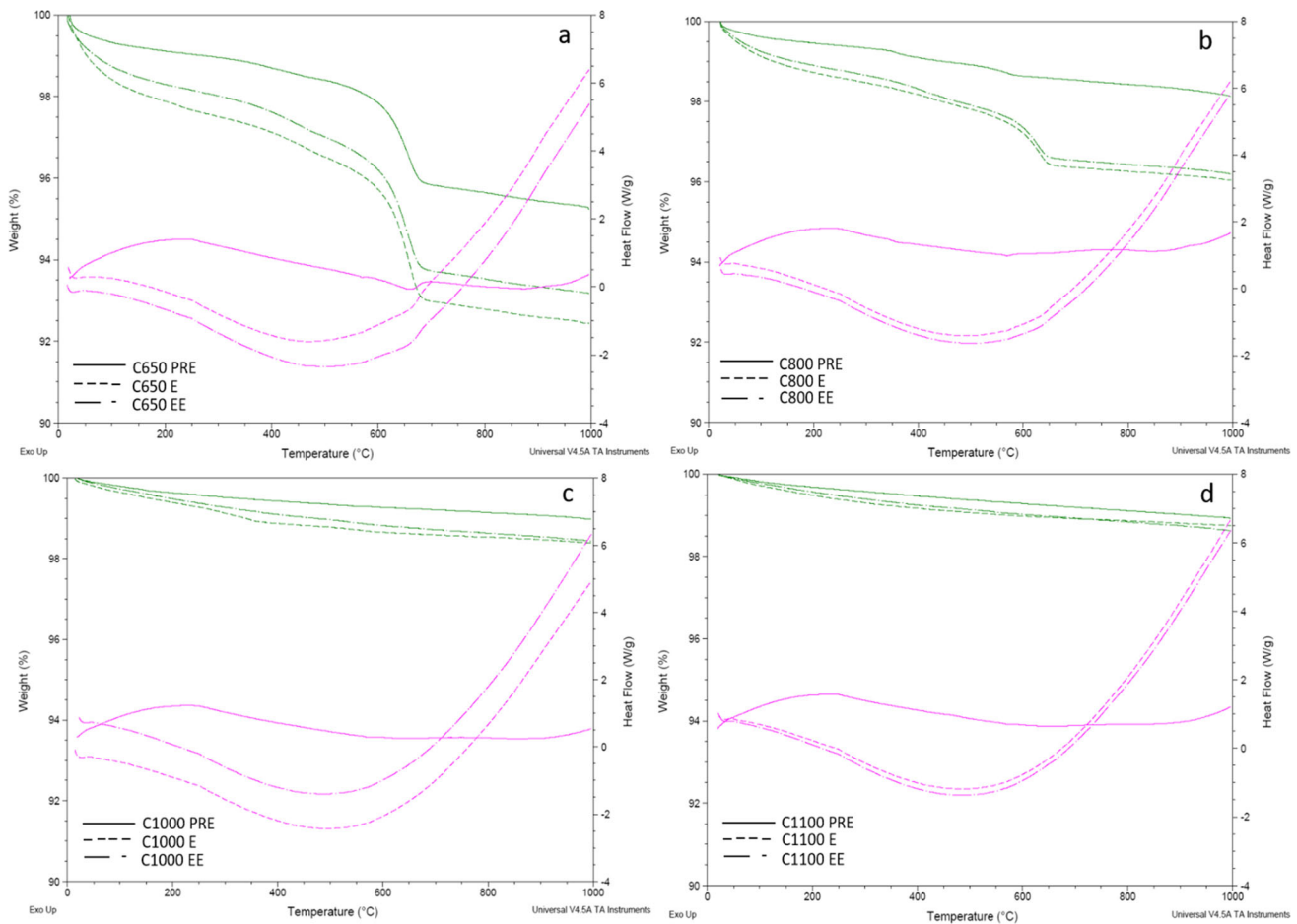


Fig. 7 Thermograms of the ceramic specimens before (PRE) and after the cleaning treatments with the chelating agent by immersion (E) and by gel (EE), being **a** 650 °C, **b** 800 °C, **c** 1000 °C and **d** 1100 °C. In pink colour the heat flow (w/g) curve and in green the weight (%). The decarbonation process can be clearly identified in C650 and C800 specimens both before and after the cleaning treatments and in C1000 and C1100 after the treatments, due to the endothermic peaks and the weight losses linked to them. Created with TA Universal Analysis® software

at naked eye, either by XRF, or XRPD. However, in ceramic specimens fired at higher temperatures (C1000 and C1100), no remains were identified (Fig. 6c and d). Furthermore, changes in the region assigned to the gel prepared with the chelating agent solution ($1400\text{--}1300\text{ cm}^{-1}$) were not detected in the specimens treated by this method (EE) (Fig. 5), which means that there were not gel residues left. Taking this into account, the removal of gel residues was effective for all the specimens.

3.4 Thermogravimetric analysis–differential scanning calorimetry (TG–DSC)

Thermogravimetric analysis complemented the information provided by XRPD. TG–DSC curves were evaluated taking into account the mass loss expressed as percentage (in green), and the heat flow of samples as a function of temperature (in pink) (Figs. 7 and 8).

In the thermograms of the specimens before the cleaning treatments (PRE) fired at low temperatures (650 and 800 °C) were detected endothermic peaks linked to an important mass loss between 470 and 710 °C (Fig. 7 and Table 5). These losses were related to the decomposition of the calcium carbonate from the ceramic [48–52]. Though, in the thermograms of specimens fired at higher temperatures (1000 and 1100 °C), these mass losses were not detected, according to the absence of carbonate as it was seen with XRPD. On the other hand, an increase on the weight loss in this region was observed in all the specimens after the cleaning treatments with the chelating agent (E and EE). Meaning that, although at naked eye the treatments were considered effective, there were still calcareous remains from the artificial deposits, also detected by FTIR-ATR analysis, as previously commented. However, according to the estimated amount of calcium carbonate calculated by Eq. 2, the CaCO_3 content after the treatments was in all cases lower than after the carbonation process (CAR), with the exception of the specimen C1000 EE, although it implied a small difference (Table 5). In this aspect, it is important to bear in mind that the artificial calcareous deposits generated were composed of both calcium carbonate and calcium hydroxide, which was not totally transformed during the carbonation process [31]. However, calcium hydroxide was neither identified in treated samples. This means that the treatments were effective, both by immersion and gel, as they removed enough quantity of the calcareous deposits so they could not be seen. Taking into account the estimated amount

Fig. 8 Thermograms of the non-carbonated treated ceramic specimens with the chelating agent by immersion (EL) and gel (EEL), in comparison with an untreated sample (PRE), all of them fired at 650 °C, for being the most vulnerable of all the ceramic specimens elaborated. In pink the heat flow (w/g) curve and in green the weight (%). The endothermic peak linked to the decomposition of the calcium carbonate is detected in the three specimens, and connected with a similar weight loss. Created with TA Universal Analysis® software

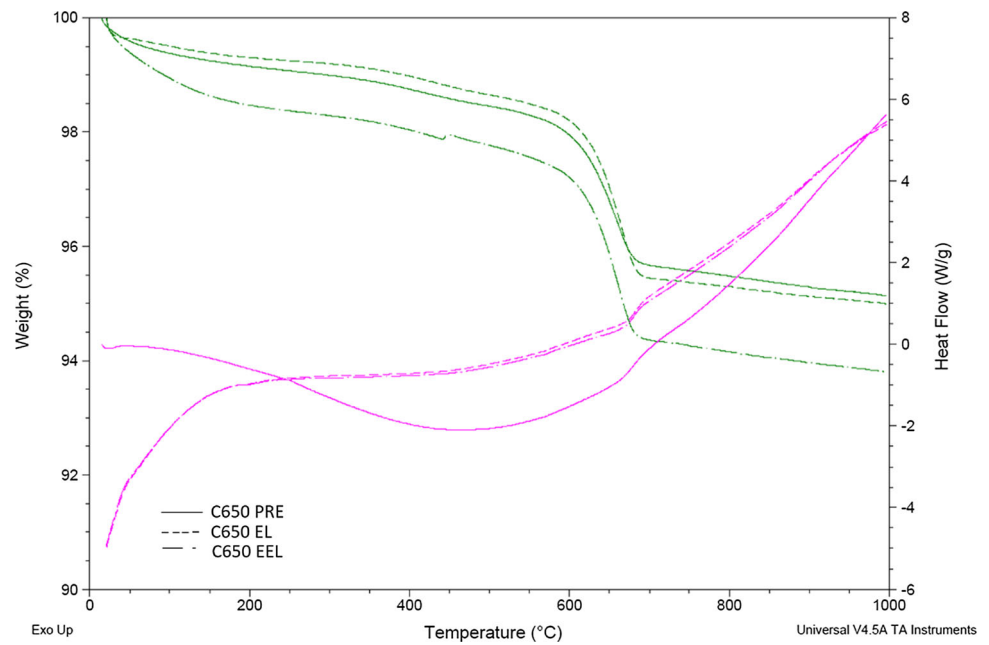
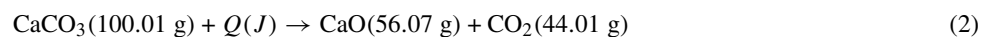


Table 5 Range of temperatures, weight loss and content of calcium carbonate in specimens at the four firing temperatures, before and after the carbonation process (PRE and CAR, respectively), and after the treatments with the chelating agent (E, immersion and EE, gel)

Specimen	Initial temperature °C	Final temperature °C	Weight loss %	% CaCO ₃
C650 PRE	500	712	2.6	5.9
C650 CAR	513	696	4.1	9.3
C650 E	549	703	3.3	7.5
C650 EE	538	701	3.1	7.1
C800 PRE	482	595	0.3	0.7
C800 CAR	519	667	1.1	2.5
C800 E	538	668	1.3	3.0
C800 EE	523	664	1.2	2.7
C1000 PRE	—	—	—	—
C1000 CAR	537	642	0.7	1.6
C1000 E	469	606	0.2	0.5
C1000 EE	485	601	0.2	0.5
C1100 PRE	—	—	—	—
C1100 CAR	519	633	0.4	0.9
C1100 E	—	—	—	—
C1100 EE	—	—	—	—

of calcium carbonate, no significant differences were detected between the two application methods (Table 5), so their effectiveness regarding the removal of the deposits was quite similar.

On the other hand, the thermograms of the non-carbonated specimens fired at 650 °C and treated by immersion (EL) and gel (EEL) showed high similarity with the untreated ceramic specimen (C650 PRE) (Fig. 8). In fact, the weight losses linked to the thermal decomposition of the calcium carbonate, as well as its estimated content indicated a slight increase of this compound after the cleaning treatments (Tables 5 and 6). These results can only be explained by the variability of the ceramic specimens, as no artificial deposits have been produced on them. Therefore, even in this exceptional case with an extreme cleaning action, the treatments did not imply a reduction of the original calcium carbonate content, proving the safety of the solution and the application methods used.



Equation 2 shows thermal decomposition of calcium carbonate into calcium oxide and carbon dioxide, including the molecular weight of each component in grams.

Table 6 Range temperatures, weight loss and calcium carbonate and calcium content (%) identified by TG-DSC analysis in an untreated sample (PRE) and two non-carbonated samples treated with the chelating agent by immersion and gel (EL and Eel, respectively)

Specimen	Initial temperature °C	Final temperature °C	Weight loss %	% CaCO ₃	% Ca
C650 PRE	510	708	2.8	6.4	2.6
C650 EL	490	711	3.2	7.3	2.9
C650 EEL	484	715	3.5	8.0	3.2

4 Conclusions

In the first place, the treatments designed for the removal of the artificial calcareous deposits based on Na₄EDTA chelating agent applied by immersion and in gel form were effective, as the concretions do not longer impede a correct appreciation of the ceramic specimens' surfaces. Indeed, the results obtained from TG-DSC analysis demonstrated a reduction of the calcium carbonate content after the cleaning procedures, in comparison with the carbonated ceramic specimens. Nevertheless, FTIR-ATR and TG-DSC results indicated the presence of deposits remains on low-fired ceramic specimens (C650 and C800 E and EE), probably due to differences in the deposits thickness and adherence. On the other hand, differences in the content of calcium and iron oxides identified by XRF were within the error margin of the equipment used.

Besides, the treatments pursued on the non-carbonated ceramics did not imply a decrease of the calcium carbonate content, indeed a slight increase was detected, linked to the variability amongst the specimens. In this way, none of the techniques used, including XRF, XRPD and TG-DSC, detected a decrease of the amount of metallic compounds (Fe and Ca) as a result of the chelating agent action on the ceramics, proving the safety of the cleaning treatments even in the most extreme situation when the cleaning agents are directly in contact with the ceramic surface.

Besides, after both treatments (immersion and gel), neither remains of the products that resulted of the reaction, nor eventual gel residues were identified, according to FTIR-ATR data.

In addition, no significant differences were detected between the two application methods employed (immersion and gel), regarding the application times, effectiveness and safety of the treatments. From a restoration point of view, the immersion would be more recommended for its simplicity, although the gel application would be useful for punctual interventions and in situ treatments, when archaeological ceramic objects cannot be moved to the laboratory.

Acknowledgements The authors gratefully acknowledge the research programme Top Heritage-CM (S2018/NMT-4372), Interdisciplinary Thematic Platform PTI-PAIS (CSIC), the Research Assistance Centres (CAI) of Geological Techniques and X-ray Diffraction (UCM) and X-Ray Fluorescence (UGR), Palarq Foundation (PR2004_19/02) and the research group Cultural Heritage Documentation, Conservation and Restoration Techniques (UCM-930420). They also thank Complutense University of Madrid and Banco Santander for the postdoctoral position of Marta Pérez-Estébanez (CT39/17) and Águeda Sáenz-Martínez's PhD scholarship (CT17/17-CT18/17), and the Spanish Ministry of Science and Innovation for the Postgraduate Student's Scholarship at *La Residencia de Estudiantes* (2020–2021). They are also grateful to the Laboratory of Materials (LabMat, Faculty of Fine Arts, UCM) and the Petrophysics Laboratory of the Institute of Geosciences (IGEO, CSIC-UCM).

Funding Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature. Partial financial support was received from the research programme Top Heritage-CM (S2018/NMT-4372) and Palarq Foundation (PR2004_19/02). This research was also supported by Complutense University of Madrid and Banco Santander with Águeda Sáenz-Martínez's PhD scholarship (CT17/17-CT18/17), and the Spanish Ministry of Science and Innovation with the Postgraduate Student's Scholarship at *La Residencia de Estudiantes* (2020–2021). Complutense University of Madrid also funded the postdoctoral position of Marta Pérez-Estébanez (CT39/17). Ministerio de Ciencia e Innovación under Grant Number by Beca para estudiantes de Postgrado en la Residencia de Estudiantes (2020–2021).

Data Availability Statement The datasets generated during and/or analysed during the current study are not publicly available. [Authors' comment: All data included in this manuscript are available upon reasonable request by contacting the corresponding author.]

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. S. Buys and V. Oakley, in *The conservation and restoration of ceramics*, (Butterworth-Heinemann, Oxford, 1993), pp. 25–27
2. C. Caple, *Conservation Skills: Judgement, Method and Decision Making* (Routledge, London, 2000)
3. D. A. Skoog, D. M. West, F. J. Holler and S. R. Crouch, in *Fundamentos de Química Analítica* (McGraw Hill, México D.F., 2015)
4. W.M. Haynes, *CRC Handbook of Chemistry and Physics* (CRC Press, London, 2014)

5. B. Carrascos Maoliner, *La Conservación y Restauración de Objetos Cerámicos Arqueológicos* (Tecnos, Barcelona, 2009), p.92
6. M.P. Casaletto, G.M. Ingo, C. Riccucci, T. de Caro, G. Bultrini, I. Fragalà, M. Leoni, *Appl. Phys. A* (2008). <https://doi.org/10.1016/J.CULHER.2012.03.010>
7. J.O. Pons, *Restauración Rehabil.* **75**, 46–51 (2003)
8. M. Coladonato, B. di Odoardo, E. Prunas, *Proc. Chem.* (2013). <https://doi.org/10.1016/j.proche.2013.03.009>
9. C.F. Ibáñez, *Monte Buciero* **9**, 303–325 (2003)
10. M. C. Berducou, in *La Conservation en archéologie: méthodes et pratique de la conservation-restauration des vestiges archéologiques* (Masson, Paris, 1990), pp. 101–103
11. J.M. Cronyn, W.S. Robinson, *The Elements of Archaeological Conservation* (Routledge, London, 1990)
12. J.S. Johnson, H.M. Erickson, H. Iceland, *MRS Proc.* (1995). <https://doi.org/10.1557/PROC-352-831>
13. A. Harrison, *Anatol. Archaeol. Stud.* **18**, 271–280 (2008)
14. N. H. Aprilita, E. Tri Wahyuni, Mahirta, F. Yulita Putri Yuani and R. Deborah, *Am. J. Appl. Chem.* (2014) Doi: <https://doi.org/10.11648/j.ajac.20140205.14>
15. J. Olive, C. Pearson, *Stud. Conserv.* (1975). <https://doi.org/10.1179/sic.1975.s1.011>
16. P. O'Brien, *J. Archaeol. Sci.* (1990). [https://doi.org/10.1016/0305-4403\(90\)90004-O](https://doi.org/10.1016/0305-4403(90)90004-O)
17. J.M. Skibo, M.B. Schiffer, *J. Archaeol. Sci.* (1987). [https://doi.org/10.1016/S0305-4403\(87\)80008-0](https://doi.org/10.1016/S0305-4403(87)80008-0)
18. P. Cremonesi, in *Proceedings from the Cleaning 2010 International Conference*. Universidad Politécnica de Valencia (Smithsonian Institution, 2003) pp 179–183
19. R. Wolbers, in *Cleaning Painted Surfaces: Aqueous Methods* (Archetype Publications, London, 2000)
20. D. Stulik and V. Dorge, in *Solvent Gels for the Cleaning of Works of Art: The Residue Question* (Getty Conservation Institute, Los Angeles, 2004)
21. M. Anzani, M. Berzioli, M. Cagna, E. Campani, A. Casoli, P. Cremonesi, M. Fratelli, A. Rabbolini and D. Riggiardi, in *Il prato: Quaderni Cesmar 7* vol 6 (Il Prato, Padua, 2008)
22. P. Baglioni, L. Dei, E. Carretti, R. Giorgi, Langmuir (2009). <https://doi.org/10.1021/la900961k>
23. Campani E, Casoli A, Cremonesi P, Saccani I and Signorini E, in *Quaderni del Cesmar* vol 7 (Il Prato, Padua, 2007) pp 31–51
24. E. Carretti, L. Dei, R.G. Weiss, P. Baglioni, *J. Cult. Herit.* (2008). <https://doi.org/10.1016/j.culher.2007.10.009>
25. S. A. Varghese, S. M. Rangappa, S. Siengchin and J. Parameswaranpillai, in *Hydrogels Based on Natural Polymers* (Elsevier, 2019) pp 17–47
26. D. Chelazzi, E. Fratini, R. Giorgi, R. Mastrangelo, M. Rossi and P. Baglioni, in *Gels and Other Soft Amorphous Solids* (ACS Publications, 2018) pp 291–314
27. S. Iannuccelli, S.B. Sotgio, *Pap. Annu.* **29**, 25–39 (2010)
28. E. Carretti, L. Dei, *Molecular Gels* (Springer, Berlin/Heidelberg, 2004), pp.929–938
29. A. Passaretti, L. Cuvillier, G. Sciutto, E. Guilminot, E. Joseph, *Appl. Sci.* (2021). <https://doi.org/10.3390/app11083405>
30. T. Giraud, A. Gomez, S. Lemoine, C. Pelé-Meziani, A. Raimon, E. Guilminot, *J. Cult. Herit.* (2021). <https://doi.org/10.1016/j.culher.2021.08.014>
31. Á. Sáenz-Martínez, M. Pérez-Estébanez, M.S. Andrés, M.A. de Buergo, R. Fort, *Eur. Phys. J. Plus* **136**, 798 (2021). <https://doi.org/10.1140/epjp/s13360-021-01784-3>
32. AENOR, Conservación de edificios. Limpieza de elementos constructivos. Parte 5–2: Técnicas de limpieza con agua. UNE 41806-2: 2009 IN (AENOR, Madrid, 2009)
33. P. Sánchez Batanero and A. Sanz, in *Medel Química analítica básica* (Ediciones Simancas S.A., Valladolid, 1985)
34. J. Unruh, *Stud. Conserv.* (2001). <https://doi.org/10.2307/1506839>
35. C. White, M. Pool, N. Carroll, *J. Am. Inst. Conserv.* (2010). <https://doi.org/10.1179/019713610804500564>
36. L. Maritan, L. Nodari, C. Mazzoli, A. Milano, U. Russo, *Appl. Clay Sci.* (2006). <https://doi.org/10.1016/j.clay.2005.08.007>
37. T. Kazakou, T. Zorba, G. Vourlias, E. Pavlidou, K. Chrissafis, *Thermochim. Acta* (2019). <https://doi.org/10.1016/j.tca.2019.178412>
38. L. Nodari, E. Marcuz, L. Maritan, C. Mazzoli, U. Russo, *J. Eur. Ceram. Soc.* (2007). <https://doi.org/10.1016/j.jeurceramsoc.2007.03.031>
39. J.S. Reed, *Principles of ceramic processing* (Wiley, New York, 1995)
40. A. Gibson, A. Woods, *Prehistoric Pottery for the Archaeologist* (Leicester University Press, London, 1997)
41. A. O. Shepard, in *Ceramics for the Archaeologist*. Publication 609 (Carnegie Institute of Washington, Washington D.C., 1956)
42. G. Cultrone, C. Rodríguez-Navarro, E. Sebastian, O. Cazalla, M. De La Torre, *J. Eur. J. Mineral.* (2001). <https://doi.org/10.1127/0935-1221/2001/0013-0621>
43. M.P. Andersson, C.P. Hem, L.N. Schultz, J.W. Nielsen, C.S. Pedersen, K.K. Sand, D.V. Okhrimenko, A. Johnsson, S.L.S. Stipp, *J. Phys. Chem. A* (2014). <https://doi.org/10.1021/jp5053858>
44. I. Arrizabalaga, O. Gómez-Laserna, J.A. Carrero, J. Bustamante, A. Rodríguez, G. Arana, J.M. Madariaga, *Anal. Methods* (2015). <https://doi.org/10.1039/C4AY02189D>
45. L. Ellis, M. Derrick, R. Newman, *Glas. Ceram. Conserv.* (2007). <https://doi.org/10.5334/jcms.156>
46. C.E. Weir, E.R. Lippincott, *J. Res. Natl. Bur. Stand. Phys. Chem.* **65A**, 3 (1961)
47. R. Ylmén, U. Jäglid, *Int. J. Concr. Struct. Mater.* (2013). <https://doi.org/10.1007/s40069-013-0039-y>
48. A. Arizzi, G. Cultrone, *Constr. Build. Mater.* (2012). <https://doi.org/10.1016/j.conbuildmat.2011.12.069>
49. C. Genestar, C. Pons, A. Más, *Anal. Chim. Acta* (2006). <https://doi.org/10.1016/j.aca.2005.10.058>
50. A. Moropoulou, A. Bakolas, P. Moundoulas, E. Aggelakopoulou, S. Anagnostopoulou, *Cem. Concr. Compos.* (2005). <https://doi.org/10.1016/j.cemconcomp.2004.02.017>
51. A. Bonazza, C. Ciantelli, A. Sardella, E. Pecchioni, O. Favoni, I. Natali, C. Sabbioni, *Period di Mineral.* (2013). <https://doi.org/10.2451/2013PM0027>
52. J.I. Alvarez, I. Navarro, P.J.G. Casado, J.I. Alvarez-Galindo, *Thermochim. Acta* (2000). [https://doi.org/10.1016/S0040-6031\(00\)00624-9](https://doi.org/10.1016/S0040-6031(00)00624-9)