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REMOVING CALCIUM CARBONATE DEPOSITS FROM ARCHAEOLOGICAL CERAMICS. TRADITIONAL METHODS UNDER REVIEW

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ABSTRACT

Although insoluble salts are one of the most common alteration forms that archaeological ceramics can present, the methods for their removal have not really changed within the past forty years. Furthermore, not many studies on the topic have been recently published. In this paper, a methodology to study the suitability of different traditional treatments for the removal of these salts, has been established. For this aim, ceramic mock-ups made out of a marketed red clay were fired up to 700ºC in an electric kiln. Their composition and physical properties were studied. Several tests were conducted in laboratory for the growth of calcium carbonate deposits similar to the ones that can appear naturally on archaeological ceramics. The method that provided the more alike deposits, was followed and applied onto the ceramic mock-ups. Different cleaning treatments based on three chemical products and three application methods were put into practice for the removal of such deposits. The products included two acids and a chelating agent and the application methods were direct and indirect, by immersion and using pulps and gels. The specimens' characteristics were studied again to determine their changes due to the cleaning treatments. The analytical techniques of XRD and SEM, for mineralogical and elemental composition, microroughness, colour measurements, stereoscopic microscopy were used, and results showed efficacy differences linked to the product and application method. In general, the products applied by immersion and cellulose pulp poultice were more effective than gel treatments, which were less effective with any of the three products tested.

KEYWORDS: Cleaning treatments, pulp poultice, rigid gel, insoluble salts, calcium carbonate deposits, chemical methods, archaeological ceramics, and conservation of cultural heritage, SEM, XRD, microroughness, microscopy.

1. INTRODUCTION

In archaeological sites, ceramics are the most abundant materials recovered due to their high physical and chemical resistance. These materials provide valuable information from an historical point of view. They contribute to the dating of the archaeological sites, also to increase knowledge about their function, the interactions among communities and the materials and processes for their production (Orton et al, 1997, pp.38, 47). However, they do not remain unalterable over time as they can present abrasions, breakings, material loss, stains and salts. Both soluble and insoluble salts are the most common and challenging alterations, as they appear both in the external and internal surface of many pieces and can cause severe conservation problems. Their presence can imply a pressure increase inside the pores, which can lead to cracking, deformation, material loss and surface cover, and result into the decline of the artistic, social and historical values of these pieces. Among insoluble salts, calcium carbonate deposits are one of the most common ones, which solubility product constants ($CaCO_3$ $k_{sp}= 2.8\times10^{-9}$), makes it very difficult to remove.

The cleaning treatments applied for the removal of soluble salts are traditionally based on water baths. However, insoluble salts –or salts with a low solubility in water (Berducou, 1990)– deposits present more hardness and adherence to the ceramic surfaces, which complicates their removal. Indeed, one of the most common solutions is to apply mixed treatments; combining chemical and mechanical methods. In this way, once the chemical one has soften the deposits, they are removed by mechanical means using scalpels, gravers and micro drillers, among others. Nevertheless, it is very difficult to control them and avoid any surface damage because chemical methods are based on products, such as acids, complex agents and ion exchange resins that react chemically with the insoluble deposits.

The use of hydrochloric, acetic, citric and nitric acids at 10-20% vol. has been the most traditional treatment, especially for calcium carbonate deposits. Some authors proved that ceramics might be damaged because of these treatments in terms of chemical and mineralogical composition, as well as physical properties, such as colour or roughness (Buys and Oakley, 1993; Fernández, 2003; Johnson and Iceland, 1995; Johnson, 1999). Nevertheless, they are still in use (Casaletto et al, 2008; Crisci et al, 2010). Alternatively, other products such as chelating agents are applied instead of acid ones. They are able to form bounds with metallic ions to result in soluble salts, and their pH values tend to be more basic. The most common ones derive from the ethylene-diamine-tetra-acetic acid (EDTA) used at 5%-10% m/v (Pearson, 1987; Abd-Allah et al, 2010). More recently, other products known as ion exchange resins have been applied with success (Casaletto et al., 2008; Crisci et al, 2010). Although they are not yet widely used and their suitability for the conservation of archaeological ceramics has not been studied either.

With respect to application methods, immersion for direct and poultices for indirect ones are the most common (Berducou, 1990). Nevertheless, since the 1980s, gels and thickening agents have been explored as an alternative application method (Wolbers, 2000; Carretti et al, 2008; Giorgi et al, 2010; Bonelli et al, 2016). Even though, they are not yet very common in archaeological conservation. Despite the removal of soluble and insoluble salts can imply serious risks for the conservation of ceramics, few specialized researchers have carried out the evaluation of cleaning methods (Casaletto et al., 2008; Johnson et al, 2011, Coladonato et al, 2013).

In order to know more about the products and application methods in use at present time in Spain, a survey among national and provincial archaeological museums, as well as conservation research centres and freelance employees, was conducted (Unpublished report). The results showed that more than half of the respondents (51.8%) established that insoluble salts deposits appear in some of the interventions that they perform. Other interesting result was that the application of mixed treatments for the removal of these salts is the most common removal technique (87.1%). More specifically, chelating agents and acid solutions are the most usual chemical products (72.7% and 54.5%, respectively), followed by ion exchange resins (23.6%). When talking about the application methods, immersion (59%), poultices (36%) and gels (20%), resulted to be the preferred ones. Finally, only 9.3% of the survey-respondents carry out studies after the treatments in order to determine whether the ceramic objects have been damaged or not. Therefore, at present time traditional products and application methods are still widely used without being aware of their consequences on the conservation state of the ceramic objects.

All the commented above led us to study the suitability and efficacy of several treatments applied to remove insoluble salts from archaeological ceramics by following a methodology specifically designed, and employing several analytical techniques: Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), micro-roughness measurements, colour assessment, stereoscopic microscopy.

2. MATERIALS AND METHODS

Ceramic specimens' elaboration.

As original ceramics cannot be used before having validated the designed methodology, thirty-six ceramic specimens of 5x5x1cm were manufactured in laboratory conditions with a red-marketed clay (Sio-2® ARGILA). Another twelve ceramic specimens of smaller dimensions 2.5x5x1cm were manufactured at the same conditions for the growth of the calcium carbonate deposits tests. All the specimens were dried in a climatic chamber (Vötsch Indusrietechnik VCL 4010) for 72 hours at controlled conditions of temperature and relative humidity (25ºC; 50% RH). Afterwards, they were fired up to 120ºC in an electric kiln (SNOL 30/1300 L) to evaporate the water inside the pores. Finally, they were fired up to 700ºC, reproducing archaeological ceramics' low firing temperatures (Shepard, 1980, pp.414) and open apparent porosity values around 28% (Rye, 1981). In both cases, the heating rate was set at 2ºC per minute and 5 minute soak. They were all labelled as N, followed by their corresponding digit.

Density and porosity test by volumetric method.

A density test following UNE-EN 1936:2007 was performed to determine the porosity (open porosity or porosity accessible to water), bulk and real densities, and water saturation of the ceramic specimens; compactness index was calculated as the quotient between both densities.

Mineralogical and elemental composition.

Mineralogical composition of ceramic specimens was studied by X- ray Powder Diffraction (XRPD) with a Panalytical X´Pert MPD equipment in Bragg-Bretano θ-θ configuration (Cu Kα radiation, 45kV, 40mA, angular range 5-70º with a step of 0.02º and 1s counting time). For this purpose, fragments of the ceramics were finely grinded with an agate mortar. Mineralogical composition of soil and calcium carbonate deposits was analysed by XRD equipment PHILIPS ANALITICAL PW 1752, 40KV and 30 mÅ operating conditions, Cu anode, graphite monocromator and PC-ADP DIFFRACTION software. Samples were grinded by means of an agate mortar and soil 125 µm grit size was sieved. Elemental composition was studied by Energy Dispersive Spectroscopy (EDS) with an X-Max spectrometer of Oxford Instruments, with a resolution of 127 eV - 5.9 KeV, coupled to a Scanning electron microscope (SEM) JEOL JSM 6335F. Fragments of 5x3x2mm were metalized with gold. Microphotographs of ceramic surfaces were taken at 100x, 400x, 750x and 1500x magnification on one face of each ceramic specimen.

Stereoscopic microscopy observation.

Leica MZ125 stereoscopic microscope with a digital camera Leica DC150 was used to study ceramic surfaces. Five areas were examined in one of the faces of the selected ceramic specimens, one in each corner and one more in the centre of the face, with 1x and 5x magnification.

Micro roughness measurements.

Roughness was measured with a TRACEit (by Innowep) optical surface roughness tester. Five measurements were conducted, in the same areas examined with the stereoscopy microscope. The measuring field was 5×5 mm and the resolution 500×500 lines. Among some of the UNE-EN ISO 4287:1999 roughness parameters (Ra, Rq and Rz), Ra (the arithmetic average of roughness' absolute values of the profile) was selected as the most suitable to compare the results before the growth of salts deposits and after the cleaning tests performed. Data were processed with Gwyddion® version 2.54 to elaborate 3D maps.

Colour measurements.

Colour measurements were performed with a Konika Minolta CM-2600d spectrophotometer with a spot size of 3 mm in SCI mode, CIELAB space from 360-740 nm, step size of 10 nm, standard observer 10º, under D65 light source (UNE-EN 15886:2011). Five measurements were conducted in the same areas as roughness measurements were taken. Lightness (L*), red/ green coordinates (a*) and yellow/ blue coordinates (b*) were studied (ISO/CIE 11664-4:2019). Total colour difference was also established by the formula CIEDE2000, which is based on the CIELAB colour space. Given a pair of colour values, in this case, before the growth of salts deposits and after their removal, in CIELAB space L^*_1, a^*_1, b^*_1 and L^*_2, a^*_2, b^*_2, the CIEDE2000 colour difference between them is calculated as follows:

$$\Delta E_{00}^{12} = \Delta E_{00}(L_1^*, a_1^*, b_1^*; L_2^*, a_2^*, b_2^*) = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T\left(\frac{\Delta C'}{k_C S_C}\right)\left(\frac{\Delta H'}{k_H S_H}\right)}$$

(Sharma et al, 2005).

Growth of insoluble salt deposits.

Lime putty of four years maturation time (PROEISCON) and limewater obtained from it, were used for the growth of calcium carbonate deposits, together with soil from the archaeological site of Guarrazar (Toledo, Spain), used as aggregate, in order to favour the carbonation process and to reproduce original deposits' characteristics. All the pieces were placed into a carbonation chamber Dycometal CCK -25/81, simulating soil conditions at 20ºC and 60% RH; and at an atmosphere of 1600 ppm CO_2, boosting carbonation process.

Cleaning treatments.

Regarding the cleaning tests, three chemical products were selected. Two acids, one weak as the acetic acid (Panreac) and one strong, as the nitric acid (Panreac). Also a chelating agent, the EDTA tetrasodium salt (Panreac). For the indirect application methods, cellulose pulp BC 1000 (ARBOCEL® JRS) and a rigid gel, Vanzan® NF-C (CTS) were chosen, as they both can be used with the three chemical products selected. Japanese paper of 20 g was used as the barrier element for both indirect methods.

Conductivity measurements.

Conductivity measurements during the neutralisation process after the cleaning treatments were carried out with a conductivity meter and pH meter Delta-Ohm, HD2156.2.

2.1. *Material Preparation - Methodology*

2.1.1. Growth of calcium carbonate deposits

In order to simulate the calcium carbonate deposits that appear on archaeological ceramics surfaces, several tests for the growth of the deposits were conducted.

i) Three tests based on limewater were applied onto nine ceramic specimens of 2.5x5x1cm. The tests consisted on (1) limewater bath for 24 hours, (2) limewater bath for 24 hours and later covered with plastic film for 72 hours, and (3) soil with limewater (1:3) applied by brush and covered for 72 hours. During the baths, the specimens were completely covered by the limewater. The specimens were put into a carbonation chamber, for 3, 7 and 10 days. From these tests, efflorescence of different colour and thickness were obtained (Fig.1). As they did not meet the required characteristics, because only a light veil was created in the best case, other tests with lime putty were carried out.

ii) In order to obtain thicker deposits, a mixture of soil and lime putty (1:3 vol) (4) was directly applied onto three specimens of 5x5x1cm. The ceramic pieces were placed in the carbonation chamber at the same conditions for 1, 4 and 7 days (Fig.1).

The test performed with soil and lime putty directly applied and carbonated for 7 days allowed the growth of 1-2 mm thick deposits with enough hardness and adherence to the ceramic surfaces, similar to the ones that appear on original archaeological ceramics. Therefore, this test was implemented to the ceramic specimens selected for the cleaning tests.

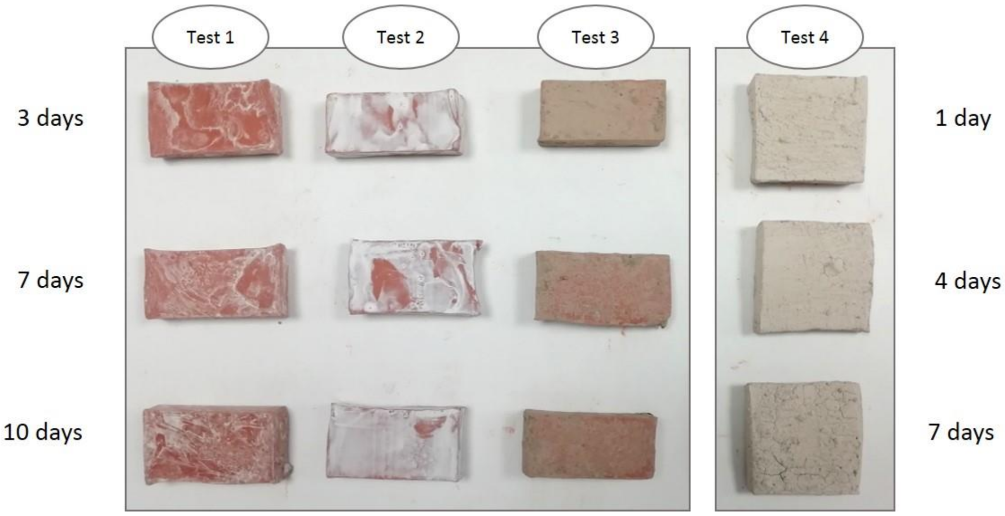

Figure 1. Tests (1, 2 and 3) conducted with limewater, carbonated for 3, 7 and 10 days, from top to bottom. Tests conducted with lime putty and soil (4), carbonated for 1, 4 and 7 days, from top to bottom.

2.1.2. Cleaning tests

Once all the pieces were covered with the calcium carbonate deposits by the selected procedure, nine cleaning tests were carried out (Table 1). According to the literature reviewed, a weak acid (acetic acid), a strong acid (nitric acid) and a chelating agent (EDTA tetrasodium salt) were chosen as the chemical products to be tested. For the application, immersion was selected as the direct method, and cellulose pulp poultice and a rigid gel (Vanzan® NF-C) as the indirect ones. In the case of the immersion method, before placing the pieces into the solutions, they were immersed in a deionised water bath. Therefore, the pores were filled in so the solution cannot flow that deep and damage the clay core. In order to remove the remains of the deposits after the chemical treatments, it was decided to do it mechanically with wood swabs for being the least harmful. Finally, the neutralisation process to remove any products' remains, consisted in static baths of deionised water, changed every 24 hours until conductivity measurements reached balance. After neutralisation process, specimens were dried in a drying chamber.

The criteria followed for the cleaning tests were minimum and constant product concentration, minimum chemical treatment time and constant pH, as indicated in UNE 41806-5-1:2009 IN and UNE 41806-5-2:2009 IN. These criteria were respected as long as it was possible, being constant pH the predominant one as it characterised the cleaning treatment. One example for this is the case of the Vanzan® NF-C gel (VG), as when added to the acetic acid solution, the pH increased. As constant pH was a requirement, it was necessary to add more acetic acid to the solution so the pH remained 2.70. With the other chemical products tested, the changes in pH were considered as not significant so their concentration remained at the minimum point: 1%.

Table 1. Chemical cleaning tests.

App. method	Immersion (I)				Cellulose pulp poultice (CPP)				Vanzan NF-C gel (VG)			
Product	N	%	pH	Time (min)	N	%	pH	Time (min)	N	%	pH	Time (min)
Acetic acid (AA)	9	1	2.70	2	23	1	2.70	10	29	10	2.70	10
Nitric acid (NA)	30	1	1.00	2	28	1	1.00	10	31	1	1.16	15
EDTA tetrasodium salt (E)	21	1	10.88	4	13	1	10.88	10	27	1	9.90	30

3. RESULTS

In table 2 are gathered the results from the density and porosity test. Data show a high homogeneity, so average values are taken into consideration.

In the following figure the appearance of the ceramic specimens before de growth of the salt deposits, with them and after their removal can be examined. Differences among the cleaning treatments tested are even noticeable at first sight (Fig. 2).

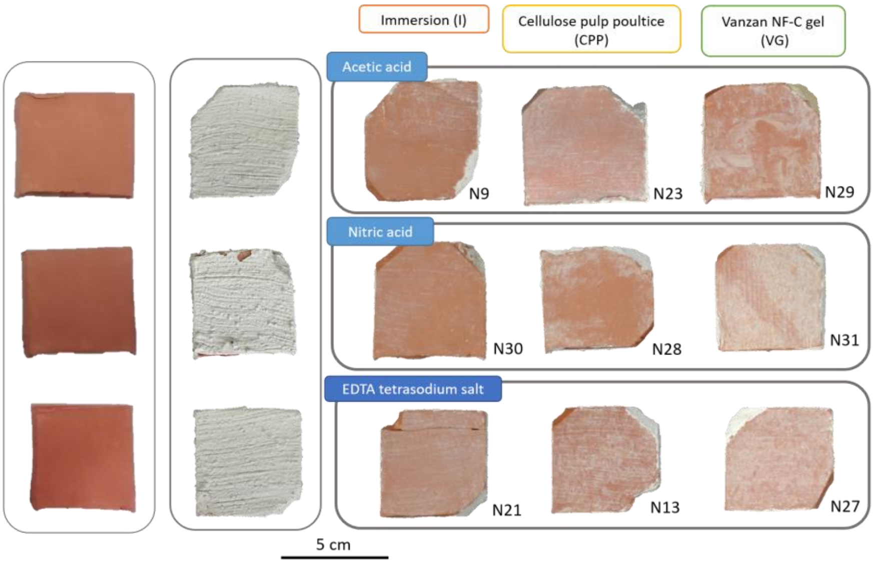

Figure 2. From left to right, specimens before the growth of calcium carbonate deposits, with the deposits and after their removal.

Table 2. Values of some physical properties of the ceramic specimens.

	Open porosity %	Real density gr/cm^3	Bulk density gr/cm^3	Water saturation %	Compactness index %
N9	32.93	2.73	1.83	17.99	0.67
N23	32.90	2.73	1.83	17.96	0.67
N29	33.15	2.73	1.82	18.16	0.67
N30	32.95	2.73	1.83	17.99	0.67
N28	32.97	2.73	1.83	18.01	0.67
N31	32.87	2.73	1.83	17.92	0.67
N21	33.18	2.74	1.83	18.14	0.67
N13	32.90	2.73	1.83	17.98	0.67
N27	32.96	2.73	1.83	18.02	0.67
Average values	32.98±0.11	2.73±0.00	1.83±0.00	18.02±0.08	0.67±0.00

The mineralogical composition of the red-marketed clay was established both in dried conditions and once fired up at 700ºC. XRD analysis determined that the clay in dried conditions is composed by a great amount of quartz (SiO_2) [JCPDS 01-089-1628], and the main phyllosilicates are muscovite [JCPDS 01-080-0743] and chlorite-serpentine [JCPDS 00-052-1044]. Hematite (Fe_2O_3) [JCPDS 01-085-0599], calcite ($CaCO_3$) [JCPDS 01-072-1652], dolomite [$CaMg(CO_3)_2$] [JCPDS 01-073-2361] and microcline [JCPDS 01-076-0918] were also found. However, when fired up at 700ºC, the chlorite-serpentine and dolomite are not detected, whereas montmorillonite appears [JCPDS 00-013-0259].

The soil, used as aggregate, and the insoluble salt deposit are analysed. The soil is composed by quartz (SiO_2), calcite ($CaCO_3$), muscovite and anorthite [JCPDS 00-041-1486]. In addition to that, the deposit also present portlandite [$Ca(OH)_2$] [JCPDS 01-078-0315], from the lime putty.

After the removal of the deposits, the composition of the residues on specimens was studied again (Fig. 3). In XRD diffractograms small differences on calcite peak intensity (height) are noticeable when comparing results obtained after gel cleaning treatments (N27), that present more salt residues (in calcite and quartz peaks) than specimens treated with cellulose pulp poultice (N28), with less residues.

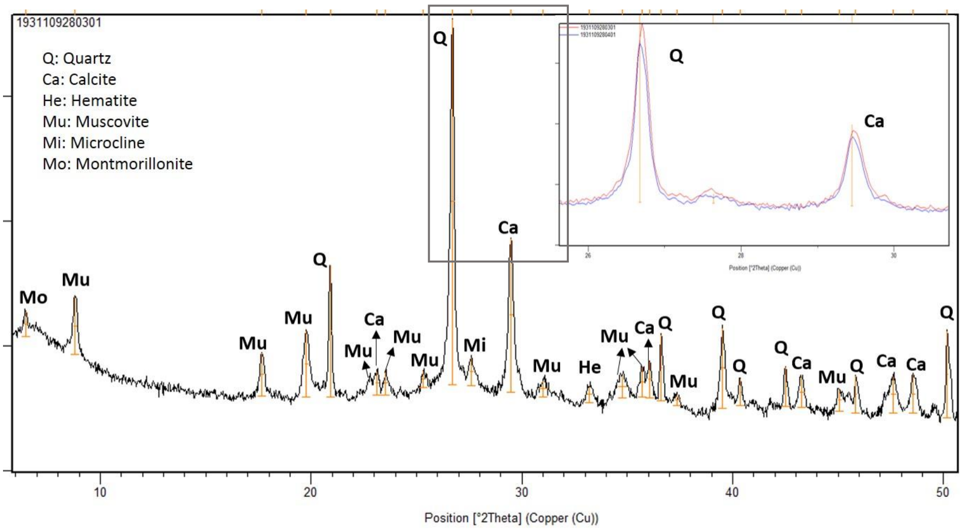

Figure 3. XRD diffractograms of the residues of the deposits in specimen N27. In the enlarged image, a slight increase in peaks intensities is noticeable.

On the other hand, elemental analysis carried out on the ceramic specimens before the growth of salt deposits, detected Al and Si as main elements and Ca, Fe, K and Mg as minors.

After the cleaning treatments, it was possible to establish an increase in Ca concentration (atomic %), in all the tests performed. Although EDS analysis is a non-absolute and semi-quantitative method, the tendency of the results is clear on data (Table 3). The higher Ca values (atomic %) are found in gel applications (N29, N31 and N27), and reached the highest level with the chelating agent (N27). These results are even noticeable at first sight, as commented above (Fig. 4).

In addition, the images taken with stereoscopic macroscopy after the treatments, noted incisions caused by the mechanical action of the wood swabs in all cases. Besides, residues of carbonate deposits were detected, more abundantly in the ceramic specimens treated by indirect methods: N23, N29, N28, N31, N13 and N27 (Fig. 4).

Table 3. Elements detected in the clay before the growth of the deposits and after the cleaning treatments.

[1]Product and app. method	AA I	AA CPP	AA VG	NA I	NA CPP	NA VG	E I	E CPP	E VG
Specimens Ca (Atomic %)	N9	N23	N29	N30	N28	N31	N21	N13	N27
Original state	8.1	7.9	6.4	8.8	7.4	5.2	27.1	8.3	6.3
After cleaning treatments	8.2	30.7	36.1	23.5	27.1	33.0	39.9	19.2	64.1

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[1] AA: Acetic Acid NA: Nitric Acid E: EDTA tetrasodium salt I: Immersion CPP: Cellulose Pulp Poultice VG: Vanzan N-FC Gel

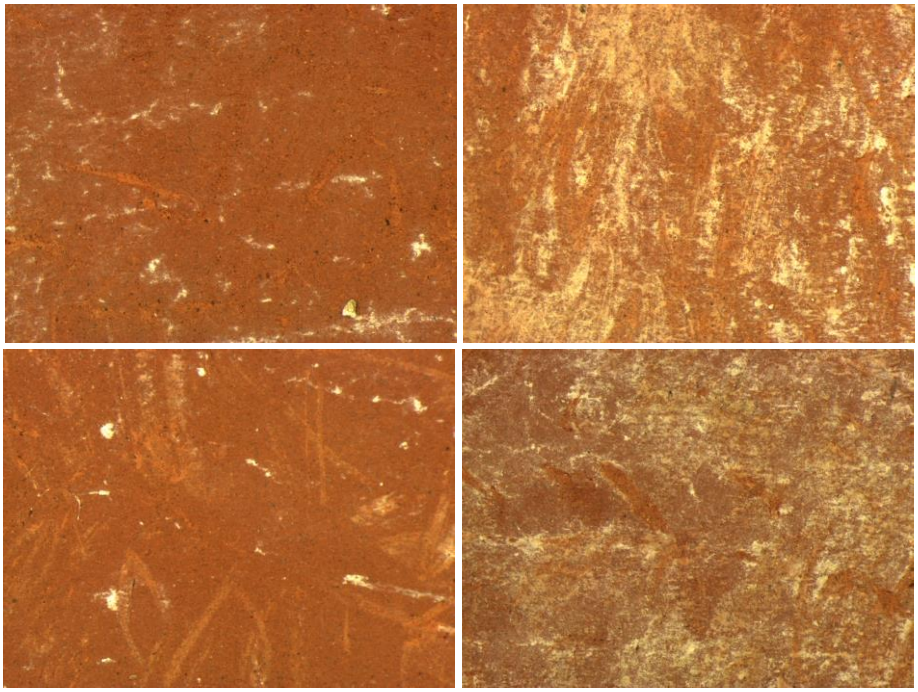

Figure 4. Incisions and residues of calcium carbonate deposits after the cleaning treatments detected in specimens N23 1x, N29 1x, N30 1x and N27 1x, from left to right and from top to bottom.

Furthermore, in SEM images it is possible to identify carbonate particles as granular and round shape aggregates of small size in all the specimens (<100nm, Fig. 5, spectrum 1), they can be easily distinguished from clay particles (Fig. 5, spectrum 2).

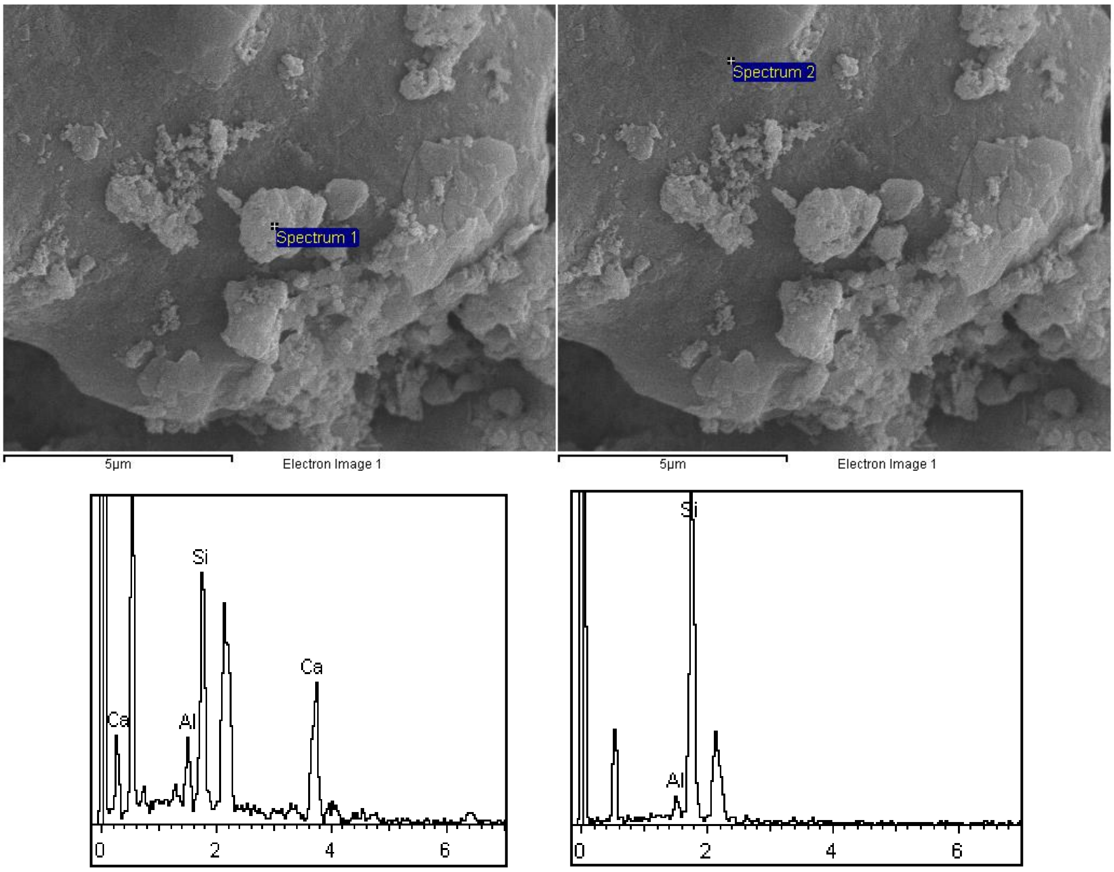

Figure 5. Calcium carbonate and clay particles detected and analysed (Spectrums 1 and 2, respectively), in specimen N9. Other elements' peaks are also detected.

Likewise, it is possible to perceive that surfaces are smoother, as carbonates have created a thin coating on them (Fig. 6).

These results are linked with micro-roughness ones. Ra average values of the nine ceramic specimens were determined before and after the growth of the deposits and the cleaning treatments (Table 5). Data show a general slight reduction in Ra values in all the specimens; which is positive as an increase in roughness would mean a higher exposure of the ceramics to the environment. Besides, changes are connected with the product used and the application method. In acid treatments, a higher decrease is determined in gel applications, meaning a higher carbonate content. However, in case of the chelating agent EDTA tetrasodium salt, Ra decreased more, although there are not significant differences among application methods, as Ra values are more similar.

The most remarkable decrease is suffered by the specimen N27, treated with the chelating agent and applied by the rigid gel. It is possible to appreciate this variation on 3D maps (Fig. 7).

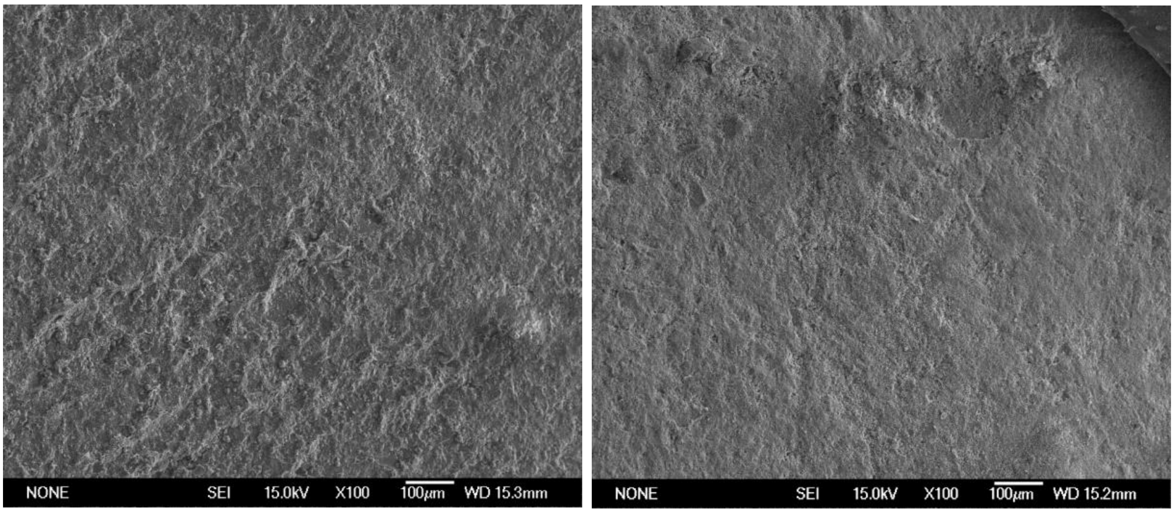

Figure 6. Ceramic surface of specimen N28 before the growth of the deposits (left), and after their removal (right), with nitric acid applied by cellulose pulp poultice.

Table 5. Ra (µm) average values before the growth of the calcium carbonate deposits and after their removal.

[2]Product and app. method	AA I	AA CPP	AA VG	NA I	NA CPP	NA VG	E I	E CPP	E VG
Ceramic specimen	N9	N23	N29	N30	N28	N31	N21	N13	N27
Average Ra (µm) BEFORE	2.43±0.57	3.28±0.52	3.11±0.37	3.07±0.30	3.16±0.55	3.00±0.57	3.16±0.64	3.28±0.49	3.31±0.52
Average Ra (µm) AFTER	2.11±0.53	2.49±0.40	1.91±0.17	2.49±0.30	2.73±0.28	1.66±0.37	1.75±0.39	1.91±0.23	1.78±0.31

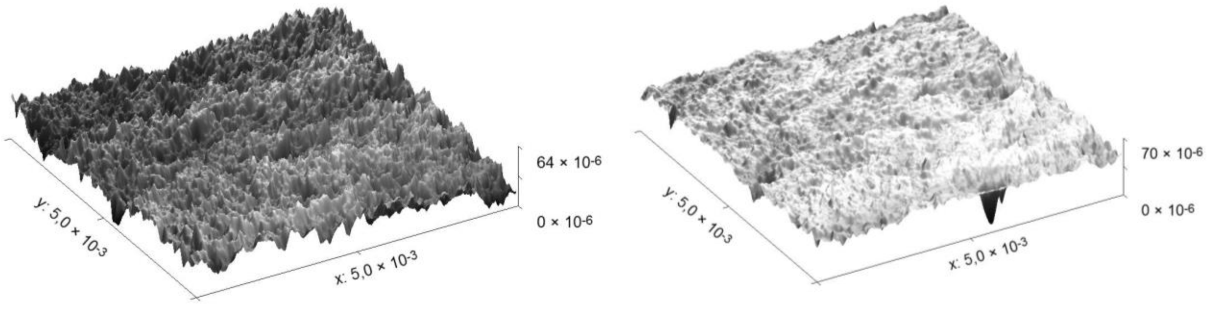

Figure 7. 3D map of Ra values before the growth of salts deposits (left) and after their removal (right), on specimen N27. Axes units in meters.

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[2] AA: Acetic Acid NA: Nitric Acid E: EDTA tetrasodium salt I: Immersion CPP: Cellulose Pulp Poultice VG: Vanzan N-FC Gel

Colour measurements also support the previous results mentioned. Average measurements for L*, a* and b* parameters before the growth of the deposits, and their corresponding RGB values (Bratitsi et al, 2018), are gathered in Table 6. In this case, the values obtained were very similar among them, so an average value was determined for all the ceramic pieces studied. The correspondence between CIELAB and RGB spaces has been obtained with Adobe Photoshop© CS4 software. On the other side, Tables 7 and 8 gather the values after the removal of the deposits, as well as the total colour difference.

In general, lightness values increase, as this parameter is directly linked to the light colour residues left on ceramics surfaces; whereas ab* values decrease (linked to the original colour of the ceramic surface). Total colour differences were established, finding greater changes within gel application methods, ΔE_{00}= (8.7 – 2.6), and among chelating agent tests, ΔE_{00}= (6.1– 10.6); accordingly to the results previously commented.

ΔE_{00} values under 0.73-1 (Melgosa et al, 2001; Mokrzyckl and Tatol, 2011) are not noticeable to human eye, which, in this research, it would mean that the treatments have been effective as they have removed the carbonate deposits to the point that the ceramic specimens' colour is similar to the original state. In this case, all the treatments are noticeable to human eye. In spite of which, nitric acid applied by cellulose pulp poultice (N28) and immersion (N30), and acetic acid applied by immersion (N9) showed the best results, according to ΔE_{00} values.

Table 6. Average values of CIELAB and RGB parameters before the growth of the calcium carbonate deposits.

		L*(D65)	a*(D65)	b*(D65)	R	G	B
Average values	SCI	54.43±0.73	18.81±0.35	21.98±0.26	168	116	92

Table 7. Average values of CIELAB parameters and total colour difference after the removal of salt deposits.

[3]Product and app. method	AA I	AA CPP	AA VG	NA I	NA CPP	NA VG	E I	E CPP	E VG
Ceramic specimen / CIELAB values	N9	N23	N29	N30	N28	N31	N21	N13	N27
L*(D65)	54.27±1.05	56.69±1.72	59.50±1.97	55.08±0.53	55.16±1.19	65.23±2.10	60.98±1.15	63.28±2.34	63.45±0.82
a*(D65)	17.06±1.10	16.55±1.46	14.36±1.58	17.53±0.46	18.07±1.09	9.35±1.36	12.94±0.55	11.81±1.36	11.12±0.87
b*(D65)	17.79±2.42	16.97±2.59	15.76±1.37	18.86±0.78	20.10±1.88	10.23±0.83	11.78±0.66	11.62±1.33	11.64±1.01
ΔE_{00}	2.6±1.5	3.8±2.1	6.1±1.4	2.0±0.6	1.6±1.4	12.7±2.2	8.7±1.0	9.8±2,6	10.6±1.2

Table 8. Average values of RGB parameters after the removal of salt deposits.

[4]Product and app. method	AA I	AA CPP	AA VG	NA I	NA CPP	NA VG	E I	E CPP	E VG
Ceramic specimen / RGB values	N9	N23	N29	N30	N28	N31	N21	N13	N27
R	164	171	176	169	169	65	61	63	63
G	118	126	135	120	120	9	13	12	11
B	99	108	117	98	98	10	12	12	13

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[3] [4] AA: Acetic Acid NA: Nitric Acid E: EDTA tetrasodium salt I: Immersion CPP: Cellulose Pulp Poultice VG: Vanzan N-FC Gel

4. CONCLUSIONS

According to the results, all the techniques applied allowed to study the influence of products, application methods and treatment times on the efficacy of calcium carbonate deposits removal.

Within products, acetic and nitric acid solutions show better results than the EDTA tetrasodium salt. Besides, immersion and cellulose pulp poultice application methods, were more effective than the rigid gel. The reason for this is probably the lack of time for the products to react with the deposits, as the gel releases the products in a very slow and controlled way. In further research, application times will be extended to check whether the results change or not.

Finally, according to compositional analysis obtained, the treatments applied did not damage ceramic surfaces, as differences caused by them have not been detected.

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