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Chemical cleaning of encrustations on archaeological ceramic artefacts found in different Italian sites

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ABSTRACT The micro-chemical and micro-structural nature of inorganic thick encrustations, deposited during long-term archaeological burial on Roman, Greek and medieval ceramic artefacts and obscuring significant decoration details, were investigated by means of scanning electron microscopy combined with energy-dispersive spectrometry, optical microscopy, X-ray photoelectron spectroscopy, X-ray diffraction and differential thermal analysis and thermogravimetry. Analytical results showed the presence of carbonates mixed with low amounts of silicate, chlorides, sulphates and phosphates containing Ca, Fe, Na, K, Al and Ti. Extensive preliminary comparative trials and different chemical cleaning methods and materials were used to remove the thick carbonatic encrustations without altering the underlying coloured decoration layers. The micro-chemical and micro-morphological characterisation of the cleaned ceramic surfaces showed that a styrene-divinylbenzene copolymer cationic resin with fine particle size represents a reliable and effective cleaning material when applied under controlled conditions (temperature = 30 °C, relative humidity = 100%, application time = 24 h) by using a simple, low-cost and safe procedure.

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1 Introduction

A complex problem faced in the conservation of ancient artefacts is represented by the cleaning of thick encrustations from the surfaces of historical and artistic artefacts (ceramics, glasses, frescoes, stone monuments and statues, metals and wood). The removal of encrustations and hard-soiled deposits is an essential intervention, but yet controversial because the encrustations hinder significant decoration details and obscure the historical, social and artistic values of an ancient object but their removal could be harmful to the object itself. The commonly adopted procedure is mainly based on a mechanical cleaning that must be carried out in a very gentle and careful way, avoiding any surface damage that may produce material and/or information loss.

In the case of archaeological ceramic artefacts the widespread conservation and restoration treatments consist of dif-

ferent steps, such as a preliminary consolidation (if required), the cleaning of each single shard, the assemblage and finally a possible integration of the object [1–3].

The choice of the cleaning procedure is crucial, since it is an irreversible process and it could induce irrecoverable damage. Essential for the conservator is the knowledge of the chemical nature and structure of the encrustations to be removed. They can be composed by insoluble salts, such as calcareous concretions, sulphated encrustations, alumino-silicate crusts also containing soluble salts (chlorides, phosphates and nitrates) as well as other inorganic species (iron, manganese, copper and black sulphides) or organic stains. Furthermore, remnants of previous restoration treatments (glues, waxes and acrylic resins) and biodeteriogens (bacteria, algae, lichens, fungi, lower plants and weeds) can also be present.

Different cleaning procedures are available according to the chemical, physical and structural nature of the material to be removed [4–6]. Mechanical cleaning treatments are accomplished with great care by the precise use of scalpels, scrapers, micro-drills and micro-sandblasting. Deposit removal by physical methods involves the use of pressure (pressurised water cleaning and abrasion by compressed gases) and/or radiation (ultrasonic generators and laser ablation) [7–10]. Chemical cleaning procedures generally consist of the direct use of chemical solutions or the application of poultices soaked by cleaning chemical and/or biological solutions and/or enzymatic systems. Traditionally, diluted acids or bases, ammonium carbonate, hydrazine hydroxide, hydroxylamine chloride and sodium hexametaphosphate are the most common reagents used for the cleaning of stone and ceramic materials. In recent years chemical cleaning is also accomplished by using chelating agents, such as ethylenediamine tetraacetic acid (EDTA) [11–13]. Chelating agents succeed in the removal of soiled deposits and encrustations thanks to a surface complexation mechanism, whereby the chelating agent is adsorbed onto the surface, weakens lattice sites, dissolves specific metal ion species and releases the chelated complex into solution. Most conveniently, a combination of different cleaning methods should be used in the conservation practice, after a preliminary, essential diagnostic study of the material nature and conservation state performed by physical and chemical investigations [14–16].

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Any novel, reliable, safe and effective chemical cleaning method should fulfil the following requirements: a selective and tailored action must be accomplished through an easily controlled and graduated process, which does not generate harmful by-products and/or induce any surface chemical and physical alteration. Evidently, the aesthetic value of the ceramic artefact should be preserved during the overall treatment.

In this work a detailed investigation of archaeological ceramic shards found in different conservation states and Italian sites, some of them also hardly encrusted, was performed in order to identify the nature of the alteration deposits grown during the long-term archaeological burial. The morphological, chemical and structural characterisation results were used for the setting up of a novel chemical cleaning experimental procedure for the removal of calcareous encrustations from ceramic artefacts to be used in the conservation practice.

2 Experimental

Several fragments of Greek, Roman and medieval ceramic artefacts were selected for the present study. These shards were found during archaeological excavations of different Italian sites, including the Phoenician–Carthaginian and Roman city of Tharros (Sardinia, Italy) and the surroundings of Caltagirone (Sicily, Italy).

Fragments of vases, tiles, bowls, jugs and basins, ranging from VI century BC to XVII century AD, were representative of different ceramic productions from the classical, medieval and more recent periods. The highest expression of artistic and technical skill of ceramic handicraft in the classical period is represented by shards of black- and red-figured Attic vases [17, 18], pot shards of the Campanian production, dated back to IV–I century BC, decorated with a black glaze and commonly used for kitchen pottery, and Terra sigillata glossy red-slipped wares (I century BC to IV century AD), the most well-known fine wares of the Roman period. The highest degree of development in the field of pottery techniques during the Medieval age is represented by the development of lead glazes such as in shards of Caltagirone ceramics (XII–XVII century AD), ranging from the oldest examples of protomajolica in Italy to monochromatic (blue or brown) fragments and polychromatic decorated artefacts [19]. The investigated ceramic artefacts were selected in different conservation states in order to have a survey of different alteration and/or degradation phenomena as wide as possible.

Both the ceramic body and the glaze or gloss coating of each ceramic shard were investigated, along with the thick inorganic encrustations, by means of the combined use of surface-sensitive and bulk techniques, such as optical microscopy (OM), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) combined with energy-dispersive spectrometry (EDS), X-ray diffraction (XRD) and differential thermal analysis and thermogravimetry (DTA-TG).

In order to investigate the nature of the ceramic body, glaze or gloss and encrustation, the archaeological ceramic fragments were embedded in epoxy resin for 24 h and sectioned by using a diamond saw in order to preserve the encrustations. The sections were polished with silicon carbide papers up to 1200 grit and the final polishing was performed with diamond pastes up to $1/4\,\mu m$ until mirror-like surfaces were obtained.

The surface chemical composition was determined by XPS in an ultra-high-vacuum (UHV) chamber (base pressure 10^{-8} Torr). Photoemission spectra were collected by means of a VG Microtech ESCA 3000 Multilab spectrometer using an Al K_α radiation source ($h\nu = 1486.6$ eV) and a nine-channeltron detection system. The binding energy (BE) scale was calibrated by measuring the C $1s$ peak (BE $= 285.1$ eV) from the surface contamination. Relative concentrations of chemical elements were calculated by a standard quantification routine and a set of VG Escalab sensitivity factors.

X-ray diffraction analysis of the encrustations was performed by using a Siemens 5000 and a Philips PW 1710 X-ray powder diffractometers with Ni-filtered Cu K_α radiation ($\lambda = 1.54056$ Å). Diffraction patterns were recorded using 2θ angular values between $10°$ and $65°$, a step size of $0.05°$ 2θ and a sampling time of 2 s and analysed by using electronic databases.

SEM–EDS characterisation was carried out by using a Cambridge 360 scanning electron microscope equipped with an EDS Link analytical X-ray probe, a LaB_6 filament and a four-sector backscattered electron detector.

The surface morphology and structure of the encrustations and of the ceramic lead glazes or glosses were observed by using an optical microscope (Leica MZ FLIII) equipped with a digital camera and a Leica MEF IV optical microscope, respectively.

DTA–TG simultaneous measurements were carried out under a static air atmosphere from room temperature up to $1100\,°C$ using an automated computer controlled thermal analyser (Stanton Redcroft STA-781). Cylindrical Pt crucibles with a diameter of 4 mm and a depth of 2 mm were used. A portion of approximately 35 mg of encrustation, mechanically removed from the ceramic shard, was heated at a heating rate of $20\,°C\,min^{-1}$.

Commercially purchased (C.T.S. S.r.l., Italy) strong cationic exchange resins were used for the chemical cleaning treatment.

3 Results and discussion

The chemical and physical characterisation carried out on archaeological ceramic shards with no evident encrustations revealed that the deterioration phenomena are mainly related to the slight leaching process induced by the partial dissolution in the soil. The process induces alkali-ion depletion on the surface and hydration and devitrification of the glaze outermost layer, i.e. a slow structural reorganisation towards stable crystalline phases [19].

The most common alteration phenomena detected on the heavily encrusted and/or damaged ceramic fragments are due to the action of physical agents (surface erosions, detachments and lacunae) and/or to chemical reactions with the burial soil, which in a few cases cause stains and generally produce the formation of thick inorganic encrustations. In this latter case, the work of conservators is aimed at disclosing the original aspect of the artefact and restoring its aesthetic value by removing deposits and encrustations that hinder significant decoration details.

Element	C 1s	O 1s	Si 2p	Na 1s	Ca 2p	N 1s	K 2p	Cl 2p
Atomic %	44.0	34.5	11.6	4.3	1.5	1.4	0.9	0.8

TABLE 1   XPS chemical composition of the surface of an archaeological Terra sigillata ceramic shard covered by encrustations

In order to optimise the chemical removal procedure, the nature of the inorganic encrustations should be carefully ascertained because they could be formed by silicates, carbonates, phosphates, sulphates, iron or manganese oxides, metallic sulphides and organo–metallic compounds as well as a combination of them. For the present study the microstructural and micro-chemical characterisation of the typical encrustation layer was performed by the combined use of XPS, XRD, DTA–TG, SEM–EDS and OM.

Some analytical results of the inorganic encrustations grown on a Terra sigillata (also known as Aretina) coral red gloss and a Campana black gloss, chosen as representative ones, are reported in Table 1 and in Figs. 1–3. Analytical data show the presence of carbonates and a minor amount of silicon species, along with typical elements from the burial soil (Ca, Ti, Fe, N, K, Cl, S, P and Na). The identification of crystalline phases in the encrustations, achieved by XRD analysis, evidenced the presence of quartz (SiO_2, main peak at 26.5° 2θ) and calcite ($CaCO_3$, main peak at 29.3° 2θ), as reported in Fig. 1. The presence of a large amount of calcium carbonate in the encrustations of the Campana ceramic shard was also confirmed by the DTA–TG curves in Fig. 1 showing a rapid drop of the TG curve around 800 °C, due to the $CaCO_3$ thermal decomposition that produces CO_2 and CaO.

The optical micrograph, SEM image and EDS spectra of the surface of an encrusted Terra sigillata red gloss, shown in Fig. 2, disclose the morphology and the elemental chemical composition of the deposit containing silicon- and calcium-based species and also the presence of Fe, Ti, K, Al, P, S and Cl from the soil.

Furthermore, the optical micrograph of the cross-sectioned Terra sigillata shard, shown in Fig. 3, reveals that encrustations, mostly constituted by calcium carbonate, are preferentially located in the cracks and lacunae of the gloss, thus indicating that erosion by physical agents is the first step of the degradation phenomenon and, afterwards, the deposition of a carbonatic layer occurs in the abraded areas.

The study of a large number of ceramic shards, recovered from archaeological excavations of different Italian sites and characterised by the presence of different decoration layers, such as lead glazes or glosses, evidenced that the thick inorganic encrustations are mainly constituted by calcium carbonate and very rarely also contain calcium sulphate or iron and manganese oxides.

In order to remove these calcareous concretions from the surfaces of the ceramic shards, a selective procedure should be accomplished with great care trying to avoid any alteration of the underlying coloured decoration layers of the glaze or gloss and also possible inner modifications of the ceramic body, if the decoration layer has been detached.

It is worth noting that carbonatic encrustations are commonly removed from the ceramic surface by scalpels, dental tools, pneumatic air chisels or similar appliances that break
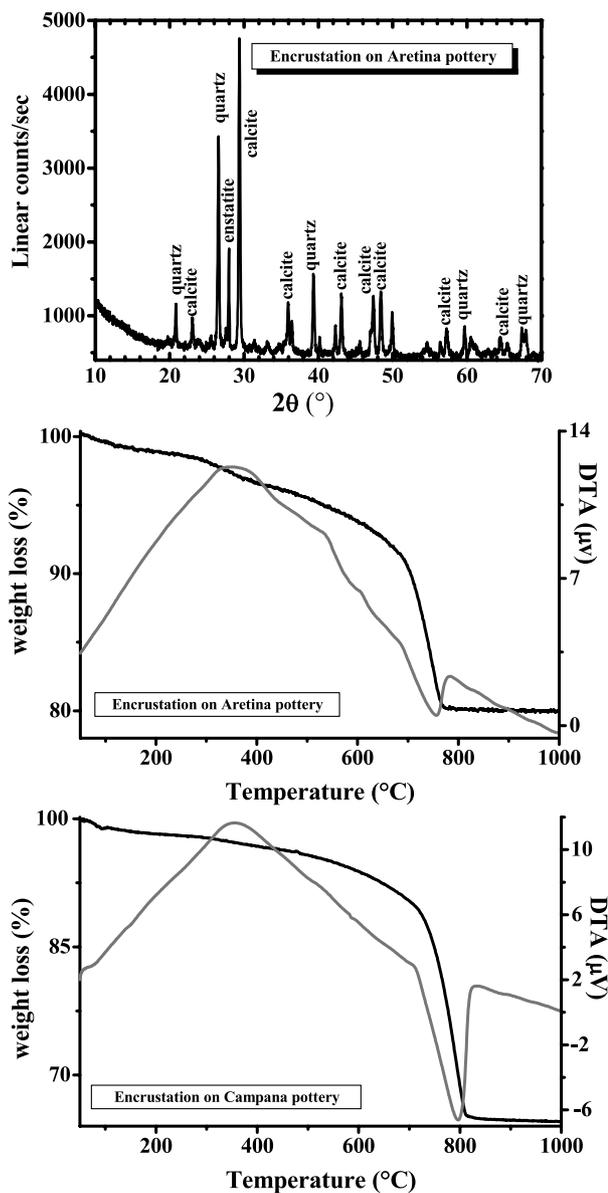

FIGURE 1   XRD pattern of the red coral gloss of a Terra sigillata shard, covered by carbonatic encrustations and small quartz grains from the soil (*upper*). Typical DTA–TG curves of the encrustation mechanically removed from a Terra sigillata (also known as Aretina) shard and a Campana ceramic shard (*below*)

the encrustation but could also induce damage to the delicate and thin decoration layer. Unfortunately, in most cases, the encrustations are also removed via chemical cleaning procedures based on the use of dilute solutions of nitric, chloridic or oxalic acids, although they potentially could dissolve the lead glaze, the iron oxides or the decoration layers and increase their tendency to exfoliate. Another commonly adopted method is based on dilute solutions of EDTA [11–13]. This is a very slow but effective treatment, but it could induce the weakening of pottery because it also dissolves the calcium carbonate of the ceramic body, thus decreasing the mechanical properties.

Ruling out the possibility of using acidic and/or basic compounds for their aggressive action, as a result of preliminary experiments, cationic exchange resins were selected
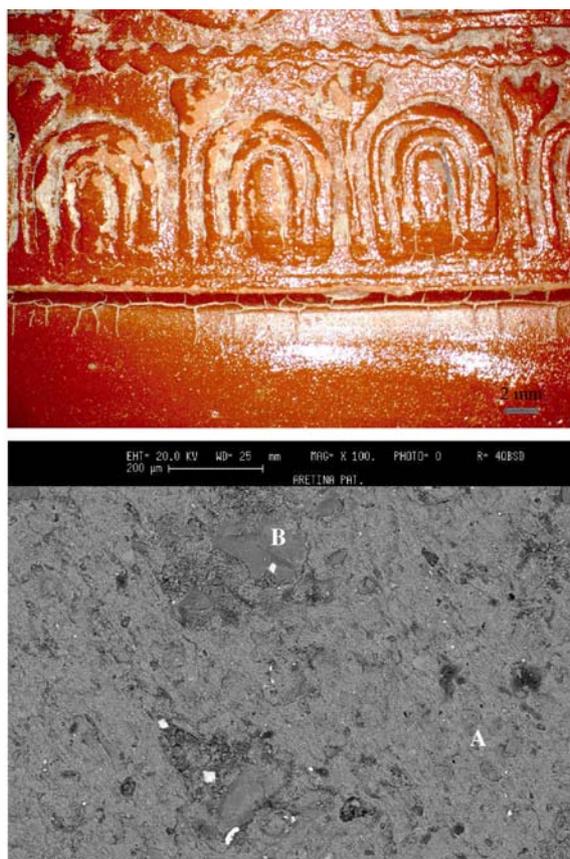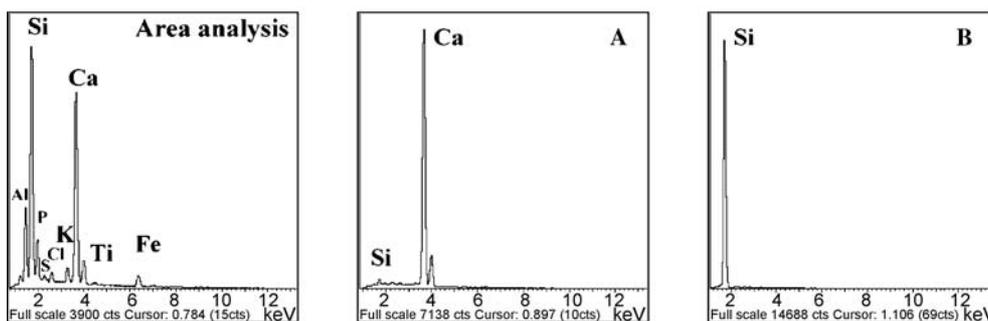
for the chemical cleaning treatment of the ceramic artefacts, thanks to their effectiveness in the selective removal of the surface carbonatic soil encrustations and whitewashes [20]. In particular, a styrene-divinylbenzene copolymer resin with fine particle size and an exchange capacity > 1.8 eq/L was used for the setting up of our chemical cleaning treatment. We also considered that, if properly applied as a paint, a cationic exchange resin does not influence the chemical and physical nature of the ceramic body because it is not in direct contact with it but only with the surface decoration layer. In such a way the removal of the calcium carbonate of the ceramic body, which can be induced by the EDTA treatment, is avoided.

The novelty of the proposed experimental procedure also lies in the choice of an hermetically sealed container in which total saturation of water is achieved, as sketched in Fig. 4. A relative humidity (RH) $\approx 100\%$ constantly activated the ion exchange of the resin treatment on the overall application surface. A possible migration of the soluble salts from the ceramic body is ruled out from the glazed ceramics, since

the glaze acts as a waterproof barrier and the ceramic body is preserved by a direct contact with water. Furthermore, the cleaning process was carried out in constant-temperature conditions and experiments were performed as a function of temperature ($t = 20, 30, 40, 50$ and $60\,°C$) in order to determine the best removal conditions. In such a way the efficacy of the ion-exchange process benefited from the dual action of the constant water vapour saturation pressure and temperature. The chemical cleaning procedure consisted of the following steps. First, the cationic resin slurry was prepared with a fixed resin/deionised water weight percent ratio ($1/1$) and applied to the ceramic surface. Then, the coated shard was placed in an hermetically sealed container where water saturation at RH $= 100\%$ was achieved by heating in an oven at constant temperature. After a variable time interval that could range from 15 to 60 min, as a function of the thickness of encrustations and of the temperature, the poultice and encrustations were removed from the ceramic surface by washing the shard with deionised water to check the effectiveness of the
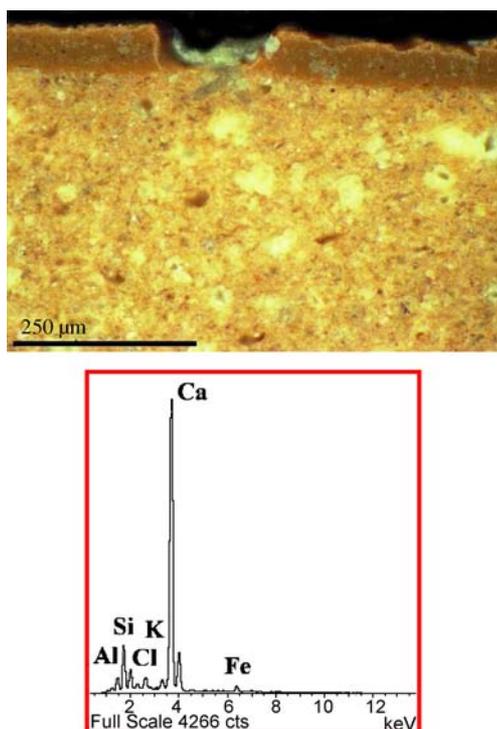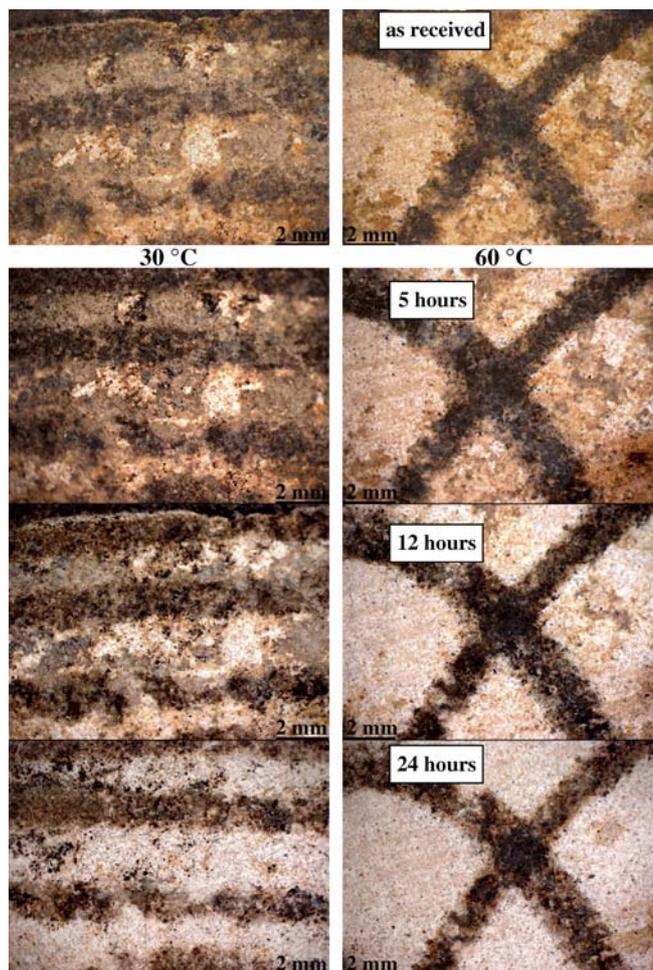
FIGURE 3   OM micrograph of the cross section of a Terra sigillata shard with calcium carbonate, as detected by EDS, deposited in a lacuna of the gloss
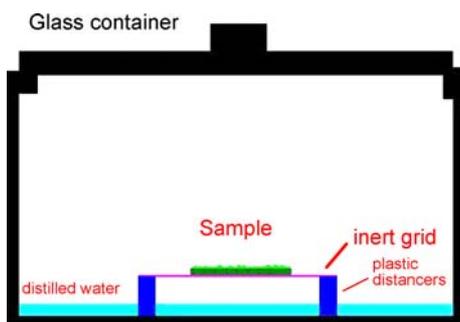
FIGURE 4   Equipment for assuring total water saturation conditions. The steps of the experimental procedure of the chemical cleaning by an ion-exchange resin are as follows: slurry application, water saturation, heating at a fixed temperature in an oven, removal of poultice and inspection of the effectiveness of the encrustation removal every 15–30 min

FIGURE 5   Optical micrographs of the surface of two lead-glazed ceramic shards (Caltagirone, XII cent. AD), showing the results of the chemical cleaning procedure as a function of temperature (30 °C, *left-hand column*; 60 °C, *right-hand column*) and as a function of contact time

cleaning procedure. The total application time of the cationic resin poultice, which is one of the main requisites that restorers and conservators consider when choosing a cleaning method, was indeed another parameter considered in the experimental procedure setup. Different experiments were performed as a function of application time (12, 24, 36, 48 and 72 h) and temperature and the assessment of the cationic exchange resin effects was performed by optical and electronic microscopies combined with energy dispersive spectroscopy analyses.
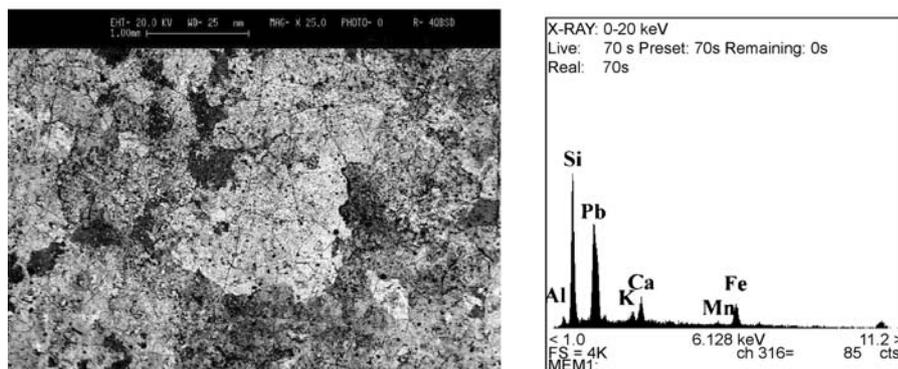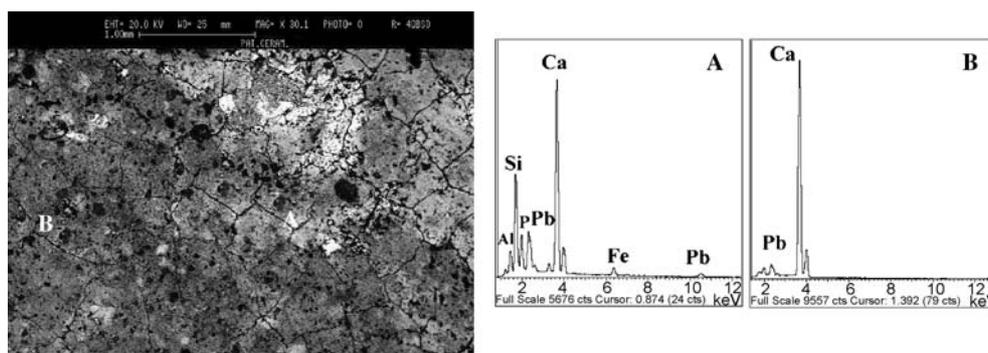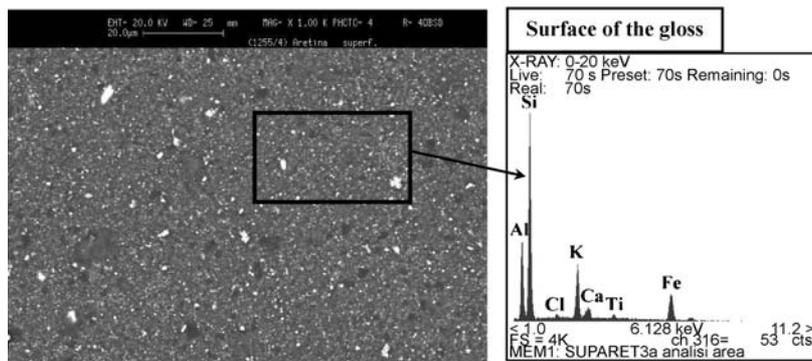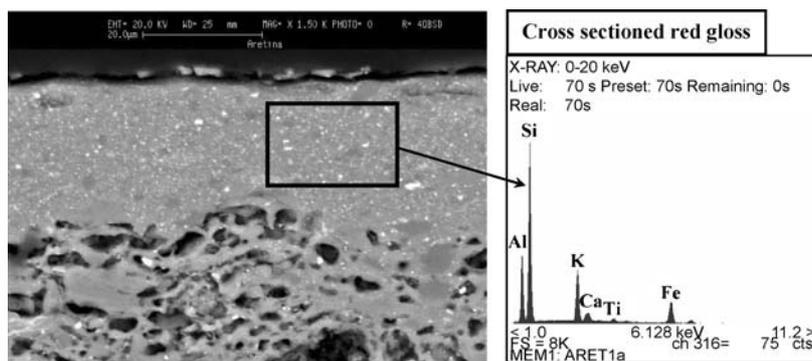
The effect of the chemical treatment was first visually evaluated by accurate close-up observations and optical micrographic documentation (aesthetic impact). Then, a series of micro-chemical and micro-structural analyses of the surface were performed by SEM–EDS in order to determine the effects on the composition caused by the cleaning method.

Some selected results of the chemical cleaning procedure are reported in Fig. 5 as a function of temperature and contact time. The optical micrographs of the surface of two lead-glazed ceramic shards (Caltagirone, XII century AD) shown in Fig. 5 evidence the efficacy of the chemical cleaning in the removal of the encrustations from the original shards (as received, first row) and the complete resurfacing of the underlying decorations after a 24-h treatment. The results reported in Fig. 5 demonstrate that the best effectiveness of the chemical cleaning treatment was achieved by using a temperature of 30 °C and an ion exchange resin total contact time no longer than 24 h (Fig. 5, left-hand column, last row). As shown in Fig. 5, higher temperature values (60 °C, right-hand column, last row) were proven to be fruitless, since no appreciable differences of the cleaning effects were noticed. Also, longer poultice application times were useless, since the same results were obtained after 48 h (not shown). These mild experimental conditions strengthen the benefit of our proposed chemical cleaning procedure because it consists in a reliable and simple method that does not require expensive chemicals, specialised equipment or long-term processing.

A representative example of the efficacy of the cleaning procedure based on the cationic resin application for

FIGURE 6 Backscattered electron SEM image and EDS spectrum of a cross-sectioned Terra sigillata showing the structure and the chemical composition of the red coral gloss layer in an undamaged area (**a**) and of the Terra sigillata surface after the chemical cleaning procedure (**b**). The comparison between the SEM image and the EDS spectrum indicates that the chemical composition of the undamaged red coral gloss is the same as that of the cleaned surface

FIGURE 7 Backscattered electron SEM images and EDS spectrum of the surface of a lead-glazed Caltagirone shard (XII cent. AD) with inorganic encrustations, before (*upper*) and after (*below*) the chemical cleaning procedure
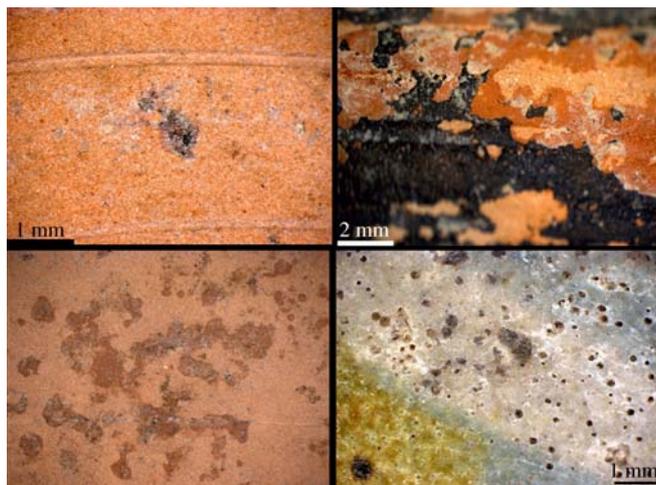
24 h at 30 °C on a Terra sigillata ceramic is shown in Fig. 6. The SEM image of a cross-sectioned Terra sigillata ceramic fragment (Fig. 6a) discloses the micro-structure of the red coral gloss layer whose elemental chemical composition is shown by the EDS spectrum (upper). After the chemical cleaning treatment the SEM image of the surface of the Terra sigillata coral red gloss (Fig. 6b) evidences the removal of the inorganic encrustations, thanks to the efficacy of the experimental procedure. Furthermore, the EDS spectrum (below) gives the chemical composition of the sur-

FIGURE 8 Optical micrographs of the surfaces of different ceramic shards treated with a traditional mechanical cleaning procedure carried out by using a micro-scraper

face of the gloss after the removal of calcareous deposit remnants. The comparison between the EDS spectra reveals that the chemical compositions of cleaned and bulk gloss are almost the same, apart from a small amount of chlorine from the soil. This demonstrates that the ionic resin does not alter the chemical and physical nature of the ceramic artefact, but only selectively removes the thick calcareous concretions.

The chemical cleaning procedure was also tested on encrusted lead-glazed ceramics and the SEM–EDS results of a Caltagirone ceramic shard (XII century AD) are reported in Fig. 7. The SEM image and EDS spectrum of the surface of an archaeological lead-glazed shard (upper) show the presence of calcium encrustations, mostly constituted by carbonates along with small amounts of phosphates. After the chemical cleaning by a cationic resin for 24 h at 30 °C the SEM image and EDS spectrum (below) show that the treatment allowed the removal of the calcareous encrustations and the success of the treatment is particularly relevant for lead-glazed ceramic artefacts, since they are chemically more sensitive to any cleaning method than the Attic, Campana or Terra sigillata glosses.

The proposed experimental protocol of chemical cleaning keeps a relevant value in conservation practice even in the absence of macroscopic, coherent inorganic deposits on pot shards, as found on Campana ceramics, since this safe and effective chemical treatment is able to restore the original chromatic beauty and brightness of the ceramic artefacts.

In order to further substantiate the real harmlessness and the efficacy of the proposed chemical cleaning, some encrusted ceramic shards were treated with a traditional mechanical cleaning procedure by using a micro-scraper, for comparison. The optical micrographs of the surfaces of Terra sigillata, Campana and lead-glazed ceramics after the mechanical treatment are shown in Fig. 8. Residual deposits are still visible on the surfaces of the mechanically cleaned ceramics. The traditional mechanical procedure, even if accurately performed, is not able to remove all the deposits and encrustations from some crucial points of heavily damaged ceramics, such as blisters, wrinkles and lacunae, without

a specific action that could induce alteration of the chemical and physical nature of the underlying layers.

4 Conclusions

The chemical and structural characterisation of inorganic thick encrustations, deposited on archaeological ceramic artefacts during long-term burial in the soil, was performed by means of the combined use of surface-sensitive and bulk analytical techniques. This experimental approach was targeted at the optimisation of a reliable, safe, effective and low-cost procedure for the chemical cleaning of excavated pot shards covered by thick inorganic carbonatic deposits.

On the basis of the analytical results, the removal of the calcareous coherent deposits, disfiguring the ceramics finely decorated with glazes, was carried out by using a cationic exchange resin reacting in strictly controlled conditions of temperature and humidity.

Results of the micro-chemical and micro-structural characterisation revealed the following as the optimal experimental conditions: RH = 100%, temperature = 30 °C, contact time depending on the thickness and compactness of encrustations but no longer than 24 h.

In the conservation practice the accessibility of the proposed chemical cleaning treatment for archaeological ceramic artefacts is, thus, guaranteed by a reliable, simple, easy to apply, safe and low-cost experimental procedure.

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