Application of low temperature plasmas for restoration/conservation of archaeological objects

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F Krčma¹, L Blahová¹, P Fojtíková¹, W G Graham², H. Grossmannová¹, L Hlochová¹, J Horák¹, D Janová¹, C P Kelsey², Z Kozáková¹, V Mazánková¹, M Procházka¹, R Přikryl¹, L Řádková¹, V Sázavská¹, M Vašíček¹, R Veverková¹, M Zmrzlý¹

¹Faculty of Chemistry, Brno University of Technology, Purkynova 118, 612 00 Brno, Czech Republic
²Queens University Belfast, Center Plasma Physics, Belfast BT7 1NN, Antrim, North Ireland
³Technical Museum Brno, Purkyňova 105, 612 00 Brno, Czech Republic

E-mail: krcma@fch.vutbr.cz

Abstract. The low-temperature low-pressure hydrogen based plasmas were used to study the influence of processes and discharge conditions on corrosion removal. The capacitive coupled RF discharge in the continuous or pulsed regime was used at operating pressure of 100−200 Pa. Plasma treatment was monitored by optical emission spectroscopy. To be able to study influence of various process parameters, the model corroded samples with and without sandy incrustation were prepared. The SEM-EDX analyzes were carried out to verify corrosion removal efficiency. Experimental conditions were optimized for the selected most frequent materials of original metallic archaeological objects (iron, bronze, copper, and brass). Chlorides removal is based on hydrogen ion reactions while oxides are removed mainly by neutral species interactions. A special focus was kept for the samples temperature because it was necessary to avoid any metallographic changes in the material structure. The application of higher power pulsed regime with low duty cycle seems be the best treatment regime. The low pressure hydrogen plasma is not applicable for objects with a very broken structure or for non-metallic objects due to the non-uniform heat stress. Due to this fact, the new developed plasmas generated in liquids were applied on selected original archaeological glass materials.

1. Introduction

The conservation/restoration operations are applied widely in practice for various historical objects. Conservation means a human activity (direct or indirect) which is aimed at increasing their expected life or damaged objects or their collections [1]. The father of modern archaeological conservation is Friedrich Rathgen [2]. Restoration means only a direct human activity. It is aimed at ensuring that the damaged object in a collection gets its aesthetic (sometimes original) or historic look [1].

The conservation/restoration of excavated archaeological objects is a very important procedure to keep these unique historical documents for future generations. The main conservation goals are

4 To whom any correspondence should be addressed.
elimination of corrosive agents and stimulators of corrosion (mainly chlorine ions), removal or reduction of corrosions layers (i.e. discovering the original objects surface) and finally, protection against further corrosion during the object storage [3].

The excavated ancient objects are made of various materials depending on the historical epoch. The majority of objects is made of metals (mainly iron and bronze), glass or ceramics. The objects are commonly affected by various corrosion kinds with different intensity. The given state of any objects is dependent on many facts, mainly on object material, artefact manufacturing technology (strongly dependent on the epoch and locality), storing duration between manufacturing and excavation, and composition of corrosive surrounding. The storage conditions between object excavation and conservation as well as precedent conservation procedures must be included, too, if object is not conserved immediately after excavation. Thus every object, even excavated at the same locality, is original with its own history.

Cleaning of archaeological artefacts surface is an irreversible process. Its main task is revealing the original surface or its remains if the object is too damaged. Classical cleaning methods used in practice are surface mechanical methods, solvent-based methods, and chemical methods.

The mechanical cleaning methods include a manual removal of dust usually by fine cloth, an air cleaning (vacuuming and blowing air), a mechanical cleaning with handy instruments (scalpel, saber, dental drill, etc.), a removal of non-functional surface coating systems of organic origin using heat, vibration and ultrasonic cleaning, abrasive methods, blasting, grinding and polishing, scrubbing, and laser. Application of nearly all these techniques induces a great mechanical and sometimes also local thermal overheating that can lead to non-wished object damage [4].

Cleaning with solvents and solutions transform impurities and corrosion compounds into the solution and it leads to their washing out. Distilled water is used very often because it is cheap and its polar character wets metals and corrosion products very well. Various surfactants are added into the cleaning water solution or pure organic solvents are applied if impurities are of organic origin (varnishes, oils, waxes, etc.).

The principle of chemical cleaning procedures is the conversion of chemical impurities using specific chemical reactions. Alkaline solutions (like sodium hydroxide or ammonia water solutions) remove organic as well as inorganic impurities. Although many of corrosion products are soluble in acidic solutions very well, secondary corrosion initiated by these solutions could be the serious problem. The electrochemical cleaning of metals is another possible surface cleaning method. During the electrolytic cleaning, the metal core of the treated object is connected to the negative pole of an external source, and it becomes cathode. The anode can be carbon, stainless steel or other electrically conductive material [5]. The last chemical cleaning method is the use of complex forming agents. These are water-soluble chemical compounds that form soluble complexes with the metal ions. For example, Chelaton III, polyphosphates (removal of lime crusts on the surface of archaeological artefacts) or thiourea (cleaning silver corrosion products) are often used in practice [6].

All these classical conservation procedures are typically men powered (mechanical conservation) or time (other) consuming. Thus there is a task to develop some other or additional procedures that will allow reducing these demands.

One of the alternative modern methods of cleaning is a plasma chemical treatment of archaeological artefacts. The great advantage of the plasma treatment is the fact that it is a "dry way" process that can be simultaneously applied on more objects depending on their kind and device dimensions. This prevents further corrosion, which may be caused by the presence of an aqueous environment. Also, there is no dissolution of the metal itself, as for example in aqueous solutions of Chelaton III. The complete removal of corrosion layers using the hydrogen based low pressure plasma is not possible from all materials. It was confirmed for silver made objects, only [7]. In other cases, the corrosion layers are not removed fully but they start to be much brittle and thus significantly softer mechanical or shorter chemical cleaning can be applied. Of course, some disadvantages of plasma chemical treatment exist. If the treatment is carried out at high power and continuous mode, object could be damaged by high temperature itself or indirectly by non-uniform thermal stress. The surface
layer called patina presented at the copper based materials surface (bronze or brass) can be damaged, too [5], and thus some historical information can be loosed.

One of the first mentions of the reduction by the low temperature plasma comes from Daniels, who was able to reduce polluted layers of silver back to silver. He treated Daguerreotypes, too [8].

At mid-80s, Stanislav Veprek from the Institute of Inorganic Chemistry, University of Zurich successfully applied plasma chemical reduction on various ancient metallic objects [9]. The plasma chemical equipment consisted of the discharge Pyrex glass tube (diameter of 15 cm, length of 45 cm) with two outer water cooled electrodes which were connected to the RF generator (80 MHz, 2 kW). Hydrogen and some hydrogen based gas mixtures were used in his studies. The temperature was measured by a mercury thermometer placed inside the reactor. The treated objects were hung on a thin iron wire or lying on a quartz glass grid. Veprek’s group treated mainly iron objects and temperature during the process could not exceed 400°C [10]. Later experiments confirmed that such temperature is too high to prevent local crystallographic changes in iron based materials, and thus contemporary museums workers require lower temperatures, in case of iron not exceeding 200°C. This temperature, as was confirmed recently, should be too high for some other metals, mainly for bronze.

Plasma reduction technique has been applied at Swiss National Museum since 1994. Radiofrequency generator (27 MHz) is used, and the gas pressure (hydrogen and argon) is 15–40 Pa. Iron and silver artefacts were treated [11].

In the Central Bohemian Museum in Roztoky u Prahy (Czech Republic), the plasma chemical equipment was used at the Department of Conservation Collections since 1996. Unfortunately, this equipment was damaged by floods in 2002 and was not rebuild yet.

Our research group has a good collaboration with Technical Museum in Brno where a big plasma chemical experimental device (diameter of 40 cm and length of 150 cm) is installed under the Methodical Centre of Conservation (MCK). Thus our results presented later are immediately applied in the conservators practice.

However, the low-pressure low-temperature hydrogen based plasma is non-applicable on objects with broken structure as well as on glass and ceramics. The application of plasma jets penetrating into liquid was tested for the corrosion removal from glass samples [12]. Recent progress in the field of electrical discharges generated directly in liquids allowed application of devices used in plasma based surgery for the surface treatment of ancient objects.

The presented paper gives our recent results and progress in the field of low-temperature low-pressure plasma application on metallic model samples. The second part gives the first results of discharges in liquids application on the corrosion removal from ancient glass objects.

2. Experimental set up

2.1 Low-temperature low-pressure RF device

The plasma treatment was carried out using the experimental set up depicted in figure 1. The Quartz cylindrical reactor (90 cm long and 9.5 cm in the diameter) was surrounded by two external copper electrodes supplied by a radio-frequency generator (13.56 MHz) through an automatic matching network. The sample was placed onto a glass grid holder (consisting of two parallel Pyrex tubes, with outer diameter of 6 mm, fixed at the ends of reactor) at the reactor central part. The experiment took place in pure hydrogen (99.9 %) or various hydrogen-argon mixtures at pressure around 160 Pa and constant total gas flow rate of 50 sccm. Samples were treated at different applied RF plasma power of 100 W, 200 W, 300 W and 400 W in a pulsed mode with a selected duty cycle of 25–100% with frequency of 1 kHz. The treatment duration was up to 120 minutes.

During the plasma chemical reduction, hydrogen and argon ions, radicals and excited molecules react with oxygen and chlorine that are the main elements of the corrosion layers (see in [13, 14]). OH radicals and HCl molecules are formed by these reactions. The OH radicals were monitored continuously by the optical emission spectroscopy using the Ocean Optics HR4000 spectrometer with 2400 gr/mm grating. An optical fiber was placed at a quartz window mounted at the reactor axis. Data
obtained from this method were used to calculate integral intensities of OH radicals that were used for the process monitoring according to the procedure described in [15]. The HCl presence was directly confirmed by IR absorption spectroscopy because no HCl bands were found in the emission spectra. HCl presence was also confirmed indirectly by a consequent corrosion of aluminum parts downstream of the discharge. To avoid the pump oil damage by the HCl molecules, a liquid nitrogen trap with aluminum wires was added into the pumping system.

Temperature of the sample during the treatment was measured by a K-type thermocouple installed 5 mm inside the sample metallic body. To avoid electromagnetic induction influence on the measured temperature, the temperature values were read out at the end of the 5 s discharge break.

![Figure 1. Scheme of the low-temperature low-pressure RF plasma device:](image)

1, 2 – high pressure bottles; 3, 4 – on/off valves; 5, 6 – mass flow controllers; 7 – needle valve; 8 – capacitance gauge; 9, 10, 11 – on/off valves; 12 – liquid nitrogen trap filled by aluminum wires; 13 – butterfly valve, 14 – rotary oil pump, 15 – RF generator; 16 – matching network; 17 – copper electrodes; 18 – quartz optical fiber; 19 – treated sample; 20 – glass grid holder; 21 – Quartz reactor; 22 – thermocouple.

Model samples used in the presented study were prepared from the most common archaeological metals using hydrochloric acid vapor (for iron, copper, bronze and brass samples) and ammonia solution (for brass samples, only). Two different sets were prepared: The first one with a pure corrosion layer, the second one with a sand incrustation for better simulation of the real situation of an excavated archaeological artifact. The samples preparation was described in details in [16].

The composition of the corrosion layers is typically very complex [3]. Various oxides and chlorides (both also hydrogenated or with crystalline water) were detected by XRD analysis. The elementary abundance was obtained by SEM-EDX analysis.

2.2 Plasma operating in liquid

Plasma was created by a special multielectrode device which principal scheme is shown in figure 2. It is a high-performance instrument which is commonly used in biomedicine at the present time. This system even allows a direct contact with the targeted sample. This system operates as a multi-electrode setup with a driving circuit producing 100 kHz RF bipolar square wave at relatively low voltage signals (up to 600 V). Current was determined via voltage drop at known resistance. The main factor for the treatment was obviously the solution conductivity which depended on temperature and added salt concentration and the distance between the treated sample and the electrode. Further, the presence of other dissolved or suspended particles or nearby physical structures had an inconsiderable influence.
The discharge chemistry in each specific instance was also affected by the applied current. The optimal experimental conditions for the archaeological artefacts treatment were obtained using 0.9% water solution of sodium chloride (solution conductivity of 13 mS⋅cm$^{-1}$). The best distance between the treated surface and the front of the multi-electrode head was about 1 mm, and the optimal applied power was about 5 W.

![Figure 2.](image)

**Figure 2.** Left: The scheme of the experimental set-up: 1 – treated sample; 2 – powered electrode; 3 – water solution; 4 – insulator; 5 – grounded electrode; right – electrode head and electrode head under operation.

The underwater discharge was used for the glass samples treatment. Presented results were obtained using the real archaeological artefacts which have laid in the soil since 17$^{th}$–18$^{th}$ century. The beads and the ceramics were from different locations (Mistřín, Moravičany and Brno, Czech Republic) and the waste from blowing glass, glass from vessels and ingots from glass were found in the pond Huťský, Josefov, Czech Republic.

3. Results

3.1 Treatment of metallic samples by low pressure device

The example of the sample temperature and OH radical intensity that reflects corrosion removal process is given by figure 3 for iron corroded samples without and with incrustation.

![Figure 3.](image)

**Figure 3.** Temperature and OH radical intensity during the plasma treatment of iron samples at applied power of 400 W.

It can be seen that the OH intensity increases at the beginning of the process at both cases. This intensity increase is faster in case of the incrusted sample. When the slightly bounded oxygen at incrustation layers is removed, the rest of incrustation plays a shielding role and thus the plasma active particles do not interact directly with the corroded surface. Consequently, the OH radical intensity
drops down. This is the probable reason why OH radical intensity is lower after the initial peak in case of sample covered by corrosion with incrustation.

The temperature of the non-incrusted samples increased during the first 30 minutes of the plasma treatment, and after that it remained constant. During the treatment of the incrusted samples, much faster but only a temporal increase of temperature was observed. After that, the temperature was significantly lower in contrary to the non-incrusted samples as it can be seen from figure 3. In this case, the maximal temperature was even higher than the maximal temperature of the non-incrusted sample.

Temperature dependences on applied power showed that the maximal temperatures were significantly lower at the lower applied powers. Due to the fact, no temperature peak at the process beginning is observed. The similar results have been obtained for all used metals [16].

To verify the influence of sample size and shape on the maximal temperature during the plasma treatment, two sets of non-corroded samples of different weight were prepared for each studied material. The first set contained samples of almost cubic shape (in graphs they are denoted as volume samples) and the planar samples of 2 mm thickness were in the second one. These samples were treated in plasma under the standard conditions described above (pressure and hydrogen flow) at applied power of 300 W in the continuous regime. Applied power of 150 W was used for the bronze samples treatment due to higher temperature sensitivity of this material. An example of temperature evolution of selected brass samples was shown recently [16]. The temperature increase is slower if a bigger sample is treated, and the thermal stabilization takes longer time. The maximal temperature increases with the sample mass (see figure 4). After this measurement, the same samples were corroded in HCl vapor in sandy environment to prepare corrosion with incrustation, and the experiment was repeated. The temperature time evolution was according to combination of results described above in text and in figure 3. The maximal temperatures for copper and brass samples are given in figure 4, the other materials showed similar behavior.

This figure clearly shows that maximal temperature is exponentially proportional to the sample mass. This means that the sample heating is dominantly due to the direct interaction with plasma active particles (note that neutral gas temperature calculated from OH radicals is 300–350 °C [17]) and the inductive heating by RF field generating the plasma is negligible. Therefore, planar samples are heated to a slightly higher temperature. Corrosion layers removal leads to a significant increase of the maximal temperatures, mainly in the case of the planar samples. The corrosion layers influence is much higher in case of brass. The process is also dependent on the plasma treatment conditions, mainly on the applied power. Nearly no difference between samples with and without corrosion was observed for bronze samples that were treated at half applied power (not shown here).
The previous results showed importance of the applied power with respect to the treated object maximal temperature. Particles generated in plasma have some lifetime, and thus we have tried to verify the role of the post-discharge period on the corrosion removal process. A lot of experiments have been carried out with different applied power and the duty cycle. An example is shown in figure 5 left. It is clearly visible that the corrosion removal is enhanced by the increasing applied power and it is slower at shorter duty cycles. By other words, it is strongly dependent on the mean energy. If mean energy is too low, the corrosion removal is too slow or even inefficient. On the other hand, too high mean applied power leads to too high maximal temperature (see figure 5 right) during the processing, and thus the crystallographic changes can be induced. Adjustment of the treatment conditions is more complicated in case of bronze due to the local overheating in the surrounding of ion impact to the surface that can lead to an unwanted evaporation of tin from the sample surface. It can be pointed that the maximal temperature is lower at higher applied power during the pulse with the lower duty cycle at the same mean power as it can be seen from figure 5 right.

![Figure 5](image)

Figure 5. Left – influence of applied power and duty cycle on the evolution of OH radicals during the plasma treatment of iron samples; right – maximal brass sample temperatures as a function of applied power and duty cycle.

The elementary analysis of surface layers showed a significant difference of corrosive elements abundance depending on the treatment conditions as it is shown in figure 6. The comparison of the pulsed and the continuous regime of plasma treatment is also included. It can be seen that the amount of oxygen and chlorine decreases with increasing applied power in the continual regime. The same dependence of oxygen concentration can be seen in the pulsed regime. The concentration of chlorine is more or less independent on the duty cycle parameter. This means that oxygen compounds removal is more dependent on the applied mean power or sample temperature. Chlorides removal is dependent on the absolute value of the applied power during the active part of the duty cycle. Thus, it can be concluded that chlorides removal is mainly due to the reaction of hydrogen ions with surface compounds, but oxygen compounds are decomposed by hydrogen ions as well as by neutral hydrogen atoms.
Figure 6. Material analyzes of HCl vapor corroded iron samples after plasma treatment at different powers in continuous mode (left) and at 400W in pulsed regime (right).

3.2 Treatment of non-metallic samples by plasma generated in liquids
An example of the glass vessel treated by the discharge in liquid is given in figure 7.

Figure 7. Plasma treatment of glass vessel: top left – vessel before and after treatment at marked areas; top right – comparison of elementary composition of the surface layers; bottom left – boundary between non treated and treated areas; bottom middle – high resolution SEM of non-treated area; bottom right – high resolution SEM of plasma treated area.

The treated areas are marked by circles. Surface structure changes are visible even by the naked eye and they were fully confirmed by SEM/EDX analysis. The plasma treated surface is smooth without any remarkable corrosion structures (see SEM image on the bottom right). Corrosion layers consist mainly of various oxides [18]. The EDX analysis showed that some elements coming from corrosion layers (like sulphur or chlorine) were fully removed. Surface concentrations of sodium and
aluminum were slightly decreased due to the plasma treatment. On the other hand, concentrations of potassium and calcium increased because these elements originate from the bulk glass. This is in agreement with the processing technology used in the given locality where mainly these elements were added as a potash and lime during the glass manufacturing.

The second example is the application of the multielectrode device on another ancient glass vessel (see figure 8). Obtained results are similar as in the precedent case. Also in this second example, the successful restoration of the original surface was reached and corrosion layers were successfully removed.

![Figure 8](image1.png)

**Figure 8.** Plasma treatment of another medieval glass vessel. Legend is the same as for figure 7.

Finally, figure 9 shows result of the application on a glass bead. The restoration of the original blue color is well remarkable. Detailed SEM-EDX analyzes showed more or less the same results as in both precedent cases.

![Figure 9](image2.png)

**Figure 9.** Medieval glass bead before (left) and after plasma treatment (right).

### 4. Conclusion

Two different plasma systems have been used for the corrosion removal. The low-temperature low-pressure hydrogen based plasmas were used to study the influence of processes and discharge conditions on corrosion removal from metallic artificially prepared samples. The capacitive coupled RF discharge in the continuous or pulsed regime was used at operating pressure of 100–200 Pa. To be able to verify the transfer of this laboratory study to practice in the conservation of ancient archaeological objects, the model corroded samples with and without sandy incrustation were prepared. The plasma treatment process was monitored by optical emission spectroscopy of OH radical that is produced during the decomposition of oxides contained in corrosion layers. Plasma
treatment conditions were optimized for the selected most frequent materials of original metallic archaeological objects (iron, bronze, copper, and brass). The special focus was kept for the samples temperature because it was necessary to avoid any metallographic changes in material structure. Results show that object maximal temperature is higher if the object has more planar shape and increases if incrustation layers are presented. Incrustation also leads to the shielding effect, and thus the plasma treatment must be applied in more steps where the mechanical removal of incrustation must be employed between particular plasma treatments. Application of the pulsed plasma regime increases the removal energy efficiency and decreases the maximal sample temperature, but there are some limits dependent on the treated material, especially in case of bronze where temperature over 150 °C is undesirable. The removal of oxides is mainly caused by reactions with neutral species while chlorides are decomposed mainly by interactions with hydrogen charged particles.

The low pressure hydrogen plasma is not applicable for objects with the very broken structure or for non-metallic objects due to non-uniform heat stress. Due to this fact, the plasma generated directly in liquid phase was applied on selected original ancient glass objects. The successful corrosion removal was obtained without any damage of the treated objects. The detailed research in this new direction will be a subject of further studies.

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