

The Use of Sodium Carbonate as a Pre-Treatment for Difficult-to-Stabilise Bronzes

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Abstract: The stabilisation of 'bronze disease' remains a major challenge for the archaeological conservator. The use of sodium carbonate solution as a pre-treatment in conjunction with benzotriazole gives the conservator another option when a bronze does not stabilise in benzotriazole alone. Sodium carbonate removes cuprous chloride while at the same time neutralising the acid in pits, facilitating subsequent stabilisation with benzotriazole. Caution should be exercised during treatment to avoid unwanted reactions. Further study is needed to understand the role of certain by-products of the treatment.

Introduction

The stabilisation of actively corroding bronzes suffering from 'bronze disease' can be one of the most time consuming and difficult problems for the conservator of archaeological materials. Although the cause of this corrosion has been known for decades to be contamination by chlorides during burial, a satisfactory treatment still eludes the conservator. A number of treatments have been discussed in the literature, each reporting successful stabilisation as the outcome. Each treatment now has recognised advantages and disadvantages.

Within the parameters of acceptable ethics and aesthetics for the treatment of archaeological bronzes today, it has been found that many actively corroding bronzes are difficult to stabilise. In a museum or other institution with adequate staff, these bronzes can be placed in a carefully controlled low relative humidity environment, which must be maintained indefinitely. However, in most instances, these difficult-to-stabilise bronzes will be sent back to storage or into study collections where they will not be observed for long periods of time. This is especially true on archaeological excavations where most often there are no controls over the cycles of changing climate over the years.

The purpose of this paper is to review the available treatments for 'bronze disease' and to discuss the application of sodium carbonate as a pre-treatment technique to facilitate the stabilisation of bronzes which have a history of not responding to other treatments. The paper is oriented to the practising conservator and is not intended to be a scientific study of the mechanisms involved in the treatment.

Since the author began investigating the efficacy of sodium carbonate in stabilising bronzes in 1976, a number of conservators who have learned of the experiments have used sodium carbonate both in the field and in the museum. Those contacted by the author have reported a high degree of success in stabilising bronzes which were not responding well to other treatments. In a few specific instances some unexpected side effects were observed. The author has also found that some conservators are using variations on the technique recommended in this paper. Therefore, some of these practical issues will be discussed with some warnings and suggestions.

An Overview of Treatments for 'Bronze Disease'

When bronzes are contaminated with chlorides during burial, a waxy corrosion product, cuprous chloride, forms on the metal surface and in microcracks and pits penetrating into the metal structure. Other corrosion products are formed over this layer depending upon what ions are present in the burial environment. Upon excavation, atmospheric moisture and oxygen can stimulate the cuprous chloride layer into activity. One result of this activity, and the symptom of 'bronze disease', is the formation of pale green powdery spots of cupric chloride in the form of paratacamite. In other reactions with cuprous chloride, hydrochloric acid can form as a by-product which in turn can cause further corrosion of the bronze. It should be noted that cuprous chloride is practically insoluble in water and therefore cannot be washed out.

To halt 'bronze disease' the cuprous chloride either must be removed or prevented from reacting with atmospheric moisture and oxygen. If an inert gas chamber or a low relative humidity (below 35%) environment cannot be guaranteed for the object, then a more active treatment must be chosen. Stabilisation techniques for 'bronze disease' can generally be divided into two groups: those which require removal of all corrosion (stripping) and those which allow the original patina to be preserved. Some of the more popular stripping techniques are electrolytic and electrochemical methods alone or in combination with dissolution of the corrosion using reagents such as alkaline sequestering agents, chelating agents, acidic or alkaline solutions, separately or in sequence. Stripping methods followed by intensive washing (often hot washing) of the object to remove the chlorides which have been made soluble by the treatment, usually leave the bronze stable, although there are always some exceptions. Each method has its drawbacks due to etching or deposition of unwanted products or redeposited metals on the remaining original metal substratum.

Although it is easier to stabilise a stripped bronze, there are many reasons for not removing the corrosion based on aesthetic and ethical considerations. Among these are the following: 1) depending on the extent of corrosion, a stripped bronze may be left with a pitted and unattractive surface; 2) not enough metal may be left beneath the corrosion to preserve the shape and retain the structural integrity of the object; 3) surface details and decorative elements such as engraved lines, inlays, overlays, enamels, etc., may be preserved within the corrosion layers and will be lost with the removal of the corrosion; 4) the history of the object and its former context may be preserved in the corrosion; 5) materials such as textiles being studied by scholars may be preserved in or replaced by corrosion.

If the layers of corrosion, or patina, are to be retained, stabilisation treatment becomes more difficult. The potentially active corrosion lies adjacent to the remaining metal and beneath the generally heavy outer layers of stable corrosion. When 'bronze disease' appears to be isolated in a few spots, local treatment with silver

oxide may be appropriate (Organ 1963). This treatment entails excavating those active spots to the cuprous chloride, packing the resulting pits with pure silver oxide and exposing the object to high humidity, thus forming a seal of silver chloride. A disadvantage of this method is that the treated spots turn dark brown, which can be disfiguring in some cases. The treatment also does nothing to prevent the general underlying cuprous chloride from becoming active at a later time.

A technique which removes cuprous chloride through the outer corrosion layers is prolonged soaking in 5% w/v sodium sesquicarbonate (Oddy and Hughes 1970). Cuprous chloride reacts with water to form cuprous oxide and hydrochloric acid. In the presence of sodium sesquicarbonate the hydrochloric acid is removed as it forms by the carbonate, eventually converting all of the cuprous chloride to harmless cuprous oxide. The chlorides now in solution are washed away after the treatment. Bronzes treated by this method tend to remain stable.

Although initially the sodium sesquicarbonate treatment seems to be ideal, since you do not need to remove the outer corrosion layers while the cuprous chloride is removed, it has been found to have a number of disadvantages. First, the treatment may require well over a year before all the cuprous chloride has been converted. This fact makes other drawbacks more serious. It has been shown that sodium sesquicarbonate (a double carbonate) forms a complex ion with copper and therefore preferentially removes copper from the remaining metal (Weisser 1975). This can be potentially structurally damaging over a prolonged period. It has also been shown that a mixture of carbonates, including chalconatronite, a blue-green hydrated sodium copper carbonate forms over the patina and also seems to replace other copper salts within the patina (Horie and Vint 1982). This creates a colour change from malachite green to blue-green, which in many cases is undesirable. In the objects the author has examined the blue-green colour can be found in cross section from the outer corrosion crust extending down to the metal substratum.

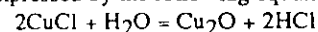
Stabilisation with benzotriazole is the most recently published commonly used treatment for 'bronze disease', which does not require disturbing the original patina. It was first published by Madsen in 1967 and soon became a favoured treatment in many laboratories and on archaeological excavations. In the standard treatment today, the object is immersed in either 3% w/v benzotriazole in ethanol or 1% w/v benzotriazole in distilled water both under partial vacuum. After twenty-four hours the object is removed from the solution and washed thoroughly in ethanol or distilled water, depending on the solvent used in the benzotriazole solution. The mechanism by which the treatment works has never been completely understood. It has been suggested that a copper-benzotriazole polymer film is formed which suppresses both the anodic and cathodic reactions on the metal surface while it also acts as a physical barrier, protecting the metal from corrosive environments (Sease 1978). It is not known for how long benzotriazole will protect a bronze and why it does not work at all in many cases. More work needs to be done before the exact role of benzotriazole in stabilising bronzes can be understood.

The Use of Sodium Carbonate as a Pre-Treatment for Difficult-to-Stabilize Bronzes

As described above, there is no perfect remedy for active 'bronze disease'. Each treatment has its drawbacks or does not always work. Although sodium sesquicarbonate actually removes cuprous chloride, the source of the 'bronze disease', the serious problems associated with this treatment have mitigated against its use in many laboratories. If the patina must be preserved, and 'bronze disease' is rampant, immersion in a benzotriazole solution has become the treatment of choice. However, experience has shown that the more active the 'bronze disease' the more difficult it is to stabilise with benzotriazole, and in many cases it does not seem to work at all. It has been suggested that pits of cuprous chloride may be only superficially covered with the copper-benzotriazole complex and that this film may be damaged, allowing the 'bronze disease' to become active again (Greene 1975). Another explanation for the inability of benzotriazole to stabilise active 'bronze disease' is that benzotriazole may not work in a very acidic environment (Richey 1987). It has been suggested that in neutral and mildly acidic solutions the film formed with benzotriazole on copper is compact and conforms to the topography of the substrate cuprous oxide, while in acids of pH less than 4, more copper ions are present, leading to a thicker, more porous cuprous benzotriazole film (Poling 1974). The author has measured the pH in active pits of 'bronze disease' to be as low as 2.

The use of a sodium carbonate pre-treatment in combination with immersion in benzotriazole presents a method for stabilising actively corroding bronzes which cannot be stabilised using benzotriazole alone. It has been observed empirically that with the applications of 5% w/v sodium carbonate in distilled water (approximate pH 11) to pits of active 'bronze disease', a yellow-orange product is produced wherever cuprous chloride is present. Effervescence is also seen in the active pits and often a blue-green precipitate forms in the solution. The yellow-orange product and the blue-green precipitate have been analysed by the X-ray diffraction technique and found to be copper oxide and sodium copper carbonate (chalconatronite) respectively (Strahan 1987).

If the conversion of cuprous chloride to cuprous oxide can be expressed by the following equation:



then a possible mechanism for the observed reaction of sodium carbonate on cuprous chloride is that the rate of conversion of cuprous chloride to cuprous oxide is increased as hydrochloric acid is removed on forming by the carbonate, releasing carbon dioxide gas. Specific ion analyses, carried out at the laboratory of The Walters Art Gallery by various conservators, have shown that the chloride ion content of sodium carbonate solutions containing actively corroding bronzes rises as a function of length of time in solution.

The formation of the blue-green precipitate, chalconatronite, noted above, is likely a product of the reaction of copper from the corrosion layers with the sodium carbonate solution. Although some copper ions may be coming from the copper metal substratum, it is unlikely to be significant over a short period of time. It has been shown that unlike sodium sesquicarbonate (a double carbonate), which acts as a complexing agent with copper, sodium carbonate reacts relatively slowly with copper metal (Drayman 1973). The author has immersed blanks of various cast bronze alloys in sodium carbonate

for up to thirty-three days. There was relatively little change in surface appearance of the blanks and a maximum of 15 parts per million of copper in solution, as measured by the atomic absorption technique.

If the above mechanism for the reaction of sodium carbonate with cuprous chloride is correct, then the application of sodium carbonate to active pits of 'bronze disease' removes the cuprous chloride and neutralises the acid in the pits. Thus, where benzotriazole was unable to work previously, it has a better chance of creating a stable surface.

A Proposed Method of Treatment

Before any conservation treatment begins, each object should be thoroughly examined to determine its current condition and requirements for its safety. X-radiography is recommended to establish its structural condition. It should be noted that if a bronze contains core material or other materials which could be affected adversely by reagents, immersion in benzotriazole, sodium carbonate, or other reagents should be avoided. Local treatment may be considered if the reagents can be controlled and the treatment area can be thoroughly washed to remove residual reagents and products of the treatment. The condition of each object should guide the conservator in choosing the most appropriate treatment to achieve the desired goals.

If a bronze exhibits the symptoms of active 'bronze disease', i.e., spots of pale, green paratacamite corrosion, and the patina must be preserved, and if the object can safely be immersed, stabilisation treatment with benzotriazole should be attempted. The author prefers excavating active spots to remove all loose corrosion, degreasing the object in a bath of acetone, and immersing the object in 3% w/v benzotriazole solution in ethanol. Depending on the fragility of the object, the benzotriazole treatment may or may not be carried out under vacuum. After approximately twenty-four hours in the solution, the object should be removed and immersed in an ethanol bath to remove residual, unreacted benzotriazole (if this step is omitted, excess benzotriazole may crystallise on the object's surface for months afterwards). After the object is dry, it should be placed in a high relative humidity environment to test for stability. The object should be examined under high magnification for active corrosion after the first half hour in the humidity chamber, then hourly after that for eight hours. If the object is still stable after that time, it may be left overnight and checked the following day for corrosion. If it has remained stable, the object should be dried thoroughly with low heat or in dry silica gel, degreased with acetone, and lacquered if necessary. On the other hand, if microscopic signs of activity are observed during exposure to high relative humidity, the object should be removed from that environment immediately and retreated with benzotriazole.

After three or four unsuccessful attempts to stabilise a bronze with benzotriazole, the use of a sodium carbonate pre-treatment should be considered. The active sites should be excavated to remove loose corrosion. If the 'bronze disease' is localised, 5% w/v sodium carbonate in distilled water should be applied in the pits only. If the sodium carbonate comes into direct contact with cuprous chloride in the pit, the formation of a yellow-orange product will be observed. In some cases a vein of cuprous chloride may be delineated by the immediate change in colour. As described above, this

cuprous chloride to cuprous oxide. Hydrochloric acid is produced by this reaction, which is immediately neutralised by the carbonate forming bubbles of carbon dioxide gas. Small quantities of a blue-green precipitate should be thoroughly washed away by swabbing with distilled water. The sodium carbonate treatment, including thorough washing, should be repeated until no more cuprous oxide is seen to form. The final washing should be carried out in a distilled water bath. After drying in an acetone bath, the object should be treated again with benzotriazole and tested for stability in a high relative humidity environment. If it is still unstable, the entire series of steps in the treatment should be repeated.

If a bronze shows evidence of extensive areas of 'bronze disease', the loose corrosion should be removed and the object degreased and then immersed in the 5% w/v sodium carbonate solution for one hour. The object should be rinsed thoroughly in distilled water and immersed again in a fresh bath of 5% w/v sodium carbonate for two hours. The object should be observed during this time for any unexpected reactions or changes. A final thorough washing in distilled water followed by drying in an acetone bath should be carried out. Treatment in benzotriazole and testing for stability should be carried out as above. If the object remains active, the entire treatment should be repeated. However, if only a few sites have remained active, the bronze may be treated locally. If the bronze does not become stable after five attempts with the sodium carbonate/benzotriazole immersion treatment, the bronze should be thoroughly washed and dried as above, lacquered, and stored in a low relative humidity environment.

Observations

Over the past eleven years a number of conservators have tested the efficacy of sodium carbonate as a pre-treatment in stabilising bronzes which had been difficult to treat, both in the museum and in the field. Those individuals the author was able to contact have found the treatment to be generally successful. Some conservators have been using the sodium carbonate pre-treatment as a part of their standard treatment for 'bronze disease' whether or not the objects had been difficult to stabilise beforehand. It is of interest to note that a scientist in the Henan Provincial Museum in Zhengzhou, the People's Republic of China, has been independently testing the use of sodium carbonate for stabilisation of 'bronze disease' (Snow 1985).

Two areas of concern have arisen over the sodium carbonate treatment. In two instances during prolonged soaking in sodium carbonate solution, patches of a finely divided black product began to develop on the patina. In one of these cases the black product was analysed by the X-ray diffraction technique and found to be cupric oxide (tenorite). It is likely that the cupric oxide comes from the oxidation of some of the cuprous oxide formed during the conversion of the cuprous chloride. Although the black cupric oxide is stable, it can be disfiguring. It is difficult to say at this time why this phenomenon occurred in two cases out of hundreds. Careful monitoring of the solution and avoiding prolonged soaking should minimise this problem.

The second area of concern is the formation of chalconatronite during treatment with sodium carbonate. Small quantities of a blue-green product often are produced during the reaction of sodium carbonate with

product to be chalconatronite, and this was confirmed by x-ray diffraction analysis during the treatment of a bronze at the Conservation Analytical Laboratory, Smithsonian Institution. (In fact, the author suspects that all alkaline sodium solutions applied to cuprous chloride will produce some chalconatronite mixed with other products, a subject for further research.) Tests with sodium sesquicarbonate applied in the same manner recommended here for sodium carbonate showed similar reactions with the production of a blue-green precipitate. A difference observed was that it could not be easily removed, while the product formed in sodium carbonate could be if not allowed to dry.

The question concerning chalconatronite is whether or not in small quantities it is likely to cause future conservation problems. During treatment, if done properly, most of the chalconatronite and residual sodium carbonate, along with the chlorides in solution, are washed away. Therefore it is not an aesthetic problem. There is some concern that if chalconatronite remains in the patina, it may hold water at high relative humidities and stimulate more 'bronze disease'. This is a debatable point. It has been suggested that the water is bound tightly to the chalconatronite and may even act as a competitor for water with cuprous chloride (Richey 1987). Even if this were not the case, the areas where chalconatronite is likely to form are the same areas where most, if not all, of the cuprous chloride has been converted already to cuprous oxide during treatment. Empirical observation under the microscope of bronzes stabilised with sodium carbonate up to ten years ago and subsequently placed in unstable environments shows no indications of continued activity in areas where chalconatronite was known to have formed. However, the role and properties of chalconatronite on archaeological metals warrants further study.

Conclusion

The stabilisation of actively corroding archaeological bronzes remains a difficult problem for conservators. At the present time no known treatment can be called ideal. A sodium carbonate pre-treatment in conjunction with a standard treatment with benzotriazole offers one more option to the conservator who is faced with difficult-to-stabilise bronzes. Although successful stabilisation has been achieved with this treatment where others have failed, it should be used with caution until the problems observed have been more thoroughly investigated. Bronzes which cannot be stabilised by this treatment should be stored or displayed in a low relative humidity environment. In fact it is recommended that all bronzes be kept in a low relative humidity environment if possible, since the long-term effectiveness of 'bronze disease' treatments has not been proven.

Acknowledgements

I am grateful to the many conservators who have kept me informed of the results of their treatments with sodium carbonate over the past eleven years, reporting both their success and failures. I would especially like to thank the following individuals who have carried out specific tests with sodium carbonate and have encouraged me to pursue this research: Harriet (Rae) Beaubien, Meg Loew Craft, Christine Del Re, Lisa Goldberg, Judith Levinson, Melissa Meighan, Carol E. Snow, and Donna Strahan.

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