

CONSERVATION OF CORRODED SILVER

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Abstract-A new treatment for the conservation of silver artifacts has been developed based on chemical reduction of the silver corrosion products to metallic silver. This reduction is achieved through the use of alkaline dithionite solutions in the absence of atmospheric oxygen. The method has been applied to silver artifacts recovered from shipwrecks but it should also be suitable for land site materials. The results obtained are superior to those using previous methods. As it is rapid, uses cheap readily available chemicals, and is well suited to bulk treatments, it also gives considerable cost and time benefits.

1. INTRODUCTION

Over the past decade the Maritime Archaeology department of the Western Australian Museum has carried out excavation work on four wrecks of silver bullion-carrying East Indiamen. These were *Batavia* (1629), *Vergulde Draeck* (1656), *Zuytdorp* (1712) and a so far unidentified wreck (c. 1810). As a result of these excavations the conservators were presented with several thousands of corroded coins to preserve.

A typical silver coin from these wrecks consists of a central core of uncorroded metal surrounded by a layer of predominantly silver compounds, which we refer to as the corrosion layer. The major components of this layer are silver chloride (cerargyrite), a mixed silver chloride-bromide, and silver sulphide (argentite). The proportions of these compounds vary widely and are probably related to site conditions. On top of the corrosion layer is the concretion layer which typically consists of shell fragments, sand, copper compounds (from the copper in the original silver metal), iron compounds from other objects on the wreck site, and sometimes large amounts of silver sulphide. In some coins the corrosion has gone to completion and no solid metal core remains. In other cases local conditions have resulted in the formation of crystalline metallic silver in the corrosion layer. All these factors and variations have to be considered when attempting to treat the coins. The requirements of the archaeologist are naturally that the maximum possible information be recovered from the treated coins. This means that the inscriptions and die stamps which were originally on the coins should be preserved in the treated samples. In general we found that these markings were preserved in the corrosion layer but not in the remaining metal core. Consequently, those methods of silver treatment, such as ammonium thiosulphate [1], thiourea-formic acid mixtures [2] or citric acid followed by concentrated ammonia [3], which involve dissolution or removal of the corrosion layer, are totally unsuitable. Previously reported chemical treatments that reduce the oxidized silver in the corrosion layer, such as zinc in sodium hydroxide, were ruled out due to their inherent inefficiency and relatively high unit cost.

Initially, electrolysis seemed to be very promising but it soon became apparent that this had two serious problems. The worst problem was that evolution of hydrogen from the coins frequently caused the corrosion layer to disintegrate leaving only the residual metal core or sometimes nothing at all. The second problem was one of time. With several thousand coins to treat we soon realized that electrolysis was just too slow and it would be decades before the work was completed.

It was with this background that an investigation into alternative silver treatment methods was undertaken. The aim was to find a cheap, simple and rapid method which would consistently give good results. The alkaline-dithionite method described in this paper meets these criteria.

2. ALKALINE-DITHIONITE TREATMENT

The first stage in the treatment of marine silver is removal of the concretion layer. Typical composition of this layer has been given above. Concretion removal is carried out by placing the objects in 10-12 vol % hydrochloric acid (approximately 14 M HCl). This solution is made up using commercial grade hydrochloric acid and tap water. If coins are being treated a convenient batch size is approximately 1000 coins. This stage of the treatment normally takes approximately 12 hours but some more resistant concretions require soaking for up to a week.

Regular checks should be made on the acidity of the bath to ensure that its effectiveness has not been destroyed by the massive dissolution of CaCO_3 . If the acidity becomes too weak, more concentrated HCl is added to restore the bath's strength. The acid wash removes not only CaCO_3 but also copper and iron compounds from the concretion layer and the solution acquires a blue-green coloration. When all reaction has ceased the artifacts are removed from the bath and washed thoroughly with tap water. Some artifacts will still have a thick layer of residual concretion. Such a layer can be safely lifted off with a dental pick, taking care not to damage the soft corrosion product layer underneath which retains the original surface details.

The second stage of treatment involves the use of an alkaline-dithionite solution and for this an air-tight sealable container is essential. We have found that commercially available 25-litre heavy-duty black plastic drums with wide neck and screw top are ideal for this purpose.* The screw-top lid provides an air-tight seal which prevents atmospheric oxygen entering and reacting with the dithionite. The alkaline-dithionite solution is prepared, in the container to be used, as follows: firstly add 40 g of NaOH per litre of water and mix thoroughly until all NaOH has dissolved. Then, in quick succession, add 50 g sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$, per litre of solution, followed by the silver artifacts, and immediately seal the container. The container should be gently agitated to ensure thorough mixing of the reagents and this should be repeated every day to expose all artifact surfaces to the solution. With the plastic drum this is simply achieved by gently rolling the drum along on its side for a few metres each day. It is preferable to fill the container almost completely with solution as this minimizes the amount of entrapped oxygen which will react with the dithionite. After one week the container is opened and the solution decanted into a holding container and the artifacts washed with fresh water until the wash solution becomes neutral. At this stage the artifacts have a grey powdery deposit of silver on them which can be removed by brushing with a small bristle brush such as a tooth-brush. If a lustrous metallic finish is desired a second brushing with a fibreglass brush is required. We have found the polishing to be more efficient if the metal surface is kept wet. The use of a fine pumice powder or similar abrasive commercial cleaner at the first brushing stage reduces significantly the amount of polishing required with the fibreglass brush. The waste alkaline-dithionite solution should be left in a container open to the air for a week so that all residual dithionite is oxidized to sulphate by atmospheric oxygen. The sodium hydroxide component is then neutralized with sulphuric acid, or with the acid solution from the HCl washing stage, and the resultant solution can then be discharged into the drainage system. If the alkaline-dithionite solution is neutralized whilst it still contains dithionite

*Available from ACI Plastics, Melbourne, Australia; Model No. 423-309.

Safety Note: Commercial sodium dithionite contains foul-smelling impurities and handling of the powder should be done in a fume hood or well ventilated areas. Sodium dithionite powder must be kept dry as it becomes spontaneously inflammable if damp. As the concentration of dithionite is not critical in this treatment, the weight can be estimated from the volume (density approximately 1.4 g/cm^3) which avoids the need to weigh out the amount used. Wear suitable protective clothing when handling hydrochloric acid, sodium hydroxide and dithionite.

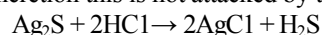
a yellow colloidal suspension of sulphur is formed and large quantities of SO_2 are evolved. Direct discharge of the spent alkaline-dithionite solution into the drainage system without neutralization and air oxidation is not acceptable as the solution will remove oxygen from the water and interrupt bacterial oxidation of sewerage; it may also dissolve metal in the plumbing system.

3. DISCUSSION

3.1. Concretion Removal by Hydrochloric Acid

As mentioned previously, the major components of silver artifact concretions are calcium carbonate (in the form of shell fragments), copper corrosion products (usually cuprite, Cu_2O , nantokite, CuCl , and some paratacamite), sand, iron oxides and, occasionally, silver sulphide. Of these compounds, those of calcium, copper and iron are rapidly attacked by HCl and dissolved. The sand fraction is inert but, provided Ag_2S is not present, the binding cement of the concretion is removed and the sand falls free.

When Ag_2S is present in the concretion this is not attacked by the HCl solution. The reaction



has a ΔG^0 of + 560 kJ mole⁻¹ and cannot proceed spontaneously at room temperature. In such cases a residual concretion layer of Ag_2S remains after the acid wash and this must be removed mechanically to leave the corrosion product layer on the surface of the coin exposed. If this residual concretion layer is not removed at this stage the dithionite treatment will reduce the silver sulphide to metallic silver and so form a very adherent surface layer which is then extremely difficult to remove.

The silver compounds which comprise the corrosion layer, namely AgCl , AgCl/Br and Ag_2S , are not attacked by the HCl to any appreciable extent. Measurements of the amount of silver dissolved in the HCl bath after treatment showed that a typical silver weight loss from artifacts was approximately 0.001 % and could be ignored. The small dissolution which does occur is probably due to the formation of dichloroargentate (AgCl_2^{-1}) ions with a consequent increase in AgCl solubility.

Occasionally silver artifacts are encountered which do not have any recognizable concretion layer. In these cases the preliminary HCl washing is still necessary to remove the relatively small amounts of copper corrosion products. If this is not done the dithionite solution will reduce the copper compounds back to metallic copper and so form an undesirable and very adherent copper surface over the silver object.

3.2. Alkaline-Dithionite Reduction

To understand why dithionite is so effective in reducing silver corrosion products to metallic silver we must examine the relevant reduction potentials. These are given in Table 1. On the basis of the reduction potentials alone, all of the silver compounds should be reduced to metallic silver by sulphite (SO_3^{2-}), using the alkaline-sulphite method previously described for marine iron treatment [5]. However, experiments with alkaline-sulphite solutions showed that only the silver chloride and the mixed silver chloride-bromide could be reduced and even then the process was relatively slow. The silver sulphide is totally inert in the alkaline-sulphite solutions. To achieve complete reduction of all of the silver corrosion products it is necessary to use the more powerful reducing agent, dithionite. The dithionite reacts quantitatively with all the silver corrosion products, even the chemically inert silver sulphide, and converts them to metallic silver. In this reaction the dithionite is oxidized to sulphate. The overall reactions are of the type



From this reaction it is seen that dithionite is also extremely efficient on a weight basis: 1 g of dithionite reduces approximately 7 g of silver chloride. An analysis of the dithionite

solutions after silver treatment gave approximately 0.4 ppm. of silver in the solutions, thus showing that no significant dissolution of silver was occurring.

TABLE 1

<i>Reaction</i>	<i>Reduction potential (E°) volts</i>
$\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Ag} + 2\text{OH}^-$	+ 0.34
$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	+ 0.22
$\text{AgBr} + \text{e}^- \rightarrow \text{Ag} + \text{Br}^-$	+ 0.07
$\text{Ag}_2\text{S} + 2\text{e}^- \rightarrow 2\text{Ag} + \text{S}^{2-}$	- 0.71
$\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Cu} + 2\text{OH}^-$	- 0.36
$2\text{SO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{S}_2\text{O}_4^{2-} + 4\text{OH}^-$	- 1.12
$\text{SO}_4^{2-} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{SO}_3^{2-} + 2\text{OH}^-$	- 0.92

Use of a scanning electron microscope with an energy dispersive X-ray analyser enabled us both to look at the surface of several treated coins at high magnification and to identify the elements present. The surfaces of the coins, after fibreglass brushing, showed no trace of chloride, bromide or sulphur.

At the time of writing we have treated over 3000 coins, and some other silver artifacts, by this method and have obtained very satisfactory and consistent results. The coins included several which were completely corroded and had no residual metal core. The dithionite treatment in these cases produced a hard metallic surface, with inscriptions, which could be fibreglass-polished to give a lustrous appearance. These completely corroded coins appear after treatment to be identical to solid coins but can be distinguished by their much lower density and the dull sound they give when struck—both presumably due to their high porosity.

Most of the silver treated to date is sterling silver (93 % Ag, 7 % Cu), being Spanish pieces-of-eight from the period 1766-1809. To ensure the general applicability of this method we also tested it with several Dutch 2-stuyver pieces from the *Zuytdorp* wreck (1712). These stuyvers have a composition of approximately 60 % Ag and 40 % Cu. Exactly the same treatment was followed as described above and excellent results were obtained.

3.3. Silver Reclamation

When marine silver is treated by the alkaline-dithionite method, solid waste residues are formed at four stages. These are: (1) in the bottom of the HCl wash solution; (2) mechanically picked off the artifact after the HCl wash; (3) at the bottom of the alkaline-dithionite container; (4) during the final polishing with bristle and fibreglass brushes. By collecting these residues and analyzing them for silver content we found that only the first residue, from the HCl wash, was essentially free of silver compounds. The other three contained, on average, approximately 65-70 % Ag. The actual amount would vary depending on the corrosion product and concretion composition. The bulk of silver residues comes from the mechanical cleaning of the coins after the HCl wash and consists predominantly of silver sulphide and smaller amounts of the mixed chloride/bromide. The residue after the dithionite treatment is mainly elemental silver.

For purely economic reasons these residues should be retained and subsequently treated to extract the silver. On one wreck site we are currently recovering approximately 600 g of pure silver from these residues for every 1000 coins treated.

4. CONCLUSION

The treatment of marine silver by HCl washing followed by alkaline-dithionite reduction is not only fast and relatively inexpensive but it also gives a more consistent result and a better end-product than do other methods currently being used. In addition, depending on the wreck-site condition, the recovery of silver from the treatment residues could more than compensate for the cost of chemicals used in the treatment. The applicability of this method to the conservation of other marine metal artifacts is currently being investigated. Results to date are most encouraging.

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Abstrait-Un nouveau traitement pour la preservation d'objets en argent a ete mis en oeuvre et est base sur la reduction chimique des produits de corrosion de l'argent jusqu'a la formation d'argent metallique. Cette reduction est obtenue en utilisant des solutions alcalines de dithionite en l'absence d'oxygene de l'air. La methode a ete appliquee a des objets en argent recuperes de bateaux naufrages, mais pourrait s'appliquer a d'autres cas. Les resultats obtenus sont superieurs a ceux obtenus avec les methodes deja connues. Le procede est rapide, utilise des produits chimiques facilement disponibles et peu onereux, s'applique bien a des objets en vrac et s'avere titre d'un gain d'argent et de temps important.

kurzfassung-Fine neue Behandlung zur Konservierung von Silberkunstwerken ist entwickelt worden, die auf der chemischen Herabsetzung der Silberkorrosionsprodukte zum Silbermetall basiert. Diese Verminderung wird durch Alkalidithionitlösungen in Abwesenheit von atmosphärischem Sauerstoff erreicht. Das Verfahren ist bei silbernen Kunstwerken, die von Schiffswracks geborgen wurden, angewandt worden, aber es dürfte auch für Materialien an Land geeignet sein. Die erzielten Resultate sind den zuvor benutzten Verfahren überlegen. Die Methode ist schnell in der Anwendung, benutzt billige, leicht erhaltliche Chemikalien und ist gut zur Behandlung grosser Mengen geeignet; auch in kostenmässiger und zeitlicher Hinsicht ist es von bedeutendem Nutzen.