



Consolidative Reduction of Lead

by

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R.F.M. - Photos  
Leads reduced - 1 sent  
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Many lead objects have heavily corroded surfaces which contain the design, even though the mass of the object is metallic lead. If these were electrically reduced at the normal current of 2-5 amps per square decimetre of surface area the design would be removed. As corrosion is often still proceeding, good storage conditions will not benefit the objects as the cause of the corrosion is already in the lead, therefore, some action must be taken to prevent complete disintegration. Mr. Organ, in Recent Advances in Conservation, describes the method of cathodic reduction at a low current of 100 mA/dm<sup>2</sup>. This slow reduction results in the formation of a compact mass of lead in place of the mineral, retaining the design. The current is too low to produce visible hydrogen bubbles during reduction which would prevent the lead remaining in situ. This reduced lead is very porous and may need impregnation, but can safely be handled. The electrolyte used was 5% aqueous sodium hydroxide with a platinized titanium anode. Tinned copper wire was used to attach the object to the cathode, and foam rubber pads supported the fragile object. After three days bubbles of hydrogen were observed, indicating reduction was complete.

Due to work on the consolidative reduction of silver and normal reduction of lead, various different factors in the method have been tried. At present we are trying to find the best variations and if any should be eliminated. The groups of objects were as near as possible the same in archaeological material, but the variations can be considerable.

In most cases the time for reduction was difficult to judge as all the objects had deposits of soil on the surface preventing the visible evolution of hydrogen at the end of the process. The low current did not always remove the soil, so mechanical cleaning had to be used. When no corrosion remained, or bubbles did appear, reduction was considered to be finished. Foam supports were not used.

The first objects were set up in Mr. Organ's way. Platinized titanium or iron anodes showed lead plating on the wire from the object due to the electrode potentials of the lead and iron. This was the same when iron wire or tinned copper wire was used. Another way of supporting the object is to use lead strips instead of wire to get the cathode connection. This lead plates onto the object in long whiskers. If a lead anode is used with any of these wires the object is covered in whiskers from the anode where exposed to the electrolyte, the anode appearing etched. The smooth, less corroded areas, were very ~~undular~~ *granular* covered with before reduction in all variations.

Lead anodes set up with lead cathodes in the sodium hydroxide at current densities from 30-300 mA/dm<sup>2</sup> had a very quick transference of lead from the anode to the cathode. This plating onto the object, or when no other lead is present plating from, is obviously not desirable. So lead anodes or wire must not be used in an alkaline electrolyte.

In previous experiments, to give lead treated by normal electrolyte reduction a protective layer, 10% sulphuric acid was used as the electrolyte. When reduced the objects had been mechanically cleaned, then replaced in the tank to remove any contamination from handling, the current reversed for 5 seconds to give a layer of lead  $d \approx 2 \times 10^{-2}$  (150%) This gave the lead a very dark colour, unacceptable to some people. This was tried as there had been a large percentage of recorrosion in a batch of seals. The trouble has now been traced to the storage conditions. The dark colour and the risk in reversing the current has caused us to return to the previous methods of after-treatment. The acid gave as good a result as the alkaline, so it was tried for consolidative reduction. The use of a lead anode and lead strip in the acid gave the best results. The use of other materials can cause plating onto the object. The surface is exactly the same as before reduction. The time taken may be a few days longer, and there is no evolution of hydrogen bubbles at the end. The lead materials do not plate onto the object. Very corroded areas did show a white deposit, which was lead sulphate, possibly formed ~~formed~~ by the current not being established immediately in the very powdery corrosion. Coins

set up at 30, 100, 200 and 300 mA/dm<sup>2</sup> showed the time of reduction to decrease as the current increased. Sulphate appeared at 30 mA, in very corroded areas at 100 mA. 200 mA gave complete satisfaction. At 300 mA there were tiny bubbles of hydrogen on the surface but the results were good. But as any bubbles are to be avoided as effecting the lead replacing in situ a current density of 100-200 mA seems to be the ideal. Because of the adverse effects of the wrong current separate containers are recommended for each object. At this low current a series of slave units can be run off the normal main unit.

From the success of treating fragile silver many lead objects have been successfully reduced using partly rectified current, an amount of AC helping deposit of lead. The time taken is longer and the results are the same as fully rectified current, so the normal DC current is easier, as most laboratories already have this.†

In some of the trial pieces we attempted to find out as much as we could about them before and after treatment. Photography recorded the surface appearance. X-rays showed corrosion was present, but not much more. Analysis showed the corrosion to be basic lead carbonate. Also the composition of the lead to have trace elements of silver, copper, iron and tin. In a few the tin was as high as 5%. Specific gravity measurements in toluene showed corrosion between 7 and 20% of the object. After treatment the weights, allowing for the impurities, showed reduction to be over 99%. One seal corroded to being useless was treated, then a section made for microscopic examination showed the metallic core with the reduced lead, rather porous, but fully reduced.

Following alkaline reduction the lead is washed in changes of N/500 sulphuric acid until the pH of the acid remains unchanged in the presence of the lead for 30 minutes, then similarly in distilled water until the pH of the water remains unchanged for the same period. A very slight acid environment is preferable to an alkaline. After thorough drying, the surface of the lead is brightened gently with a glass bristle brush‡ and impregnated with hot paraffin or microcrystalline wax. As already mentioned the use of mechanical cleaning, then replacing in the tank has been stopped. The objects treated in acid are often darker than those in alkali, and if very powdery corrosion the lead can be too porous to allow much brushing, but the other factors, I think, make slight darkening acceptable. Some coins coated in paraffin wax have darkened so we are experimenting with laquers, Ercalene and Incolac. A laquer may not be suitable for consolidative reduction. So far the laquered objects seem to be staying the same colour. The objects done in alkali do not change colour. Objects treated with sequestering agents, EDTA and Deterol, also retain their colour. We placed coins in these after reduction but this did not have any better an effect than glass brushing. If using these to remove corrosion they are very effective, but do etch the lead. As they work quickly they should be very carefully watched.

As Mr. Organ stated consolidative reduction seems sound if the certain variations are not used. The next step is to try hydrogen reduction, which the Research Laboratory is at present doing. This has its dangers and both methods may need to be judged on the conditions of the object, the equipment available, and the capabilities of the staff.

Comparisons in various techniques of normal corrosion removal show very similar results, often again it would depend on the object and equipment available. So far those tried are electrolytic reduction with alkaline and acid electrolytes, iron, ss, and plate tin anodes, ion-exchange resin, EDTA and Deterol. E.R. Caley's method and zinc granules with sodium hydroxide have been proved satisfactory by other conservators. Calgen had no effect after several days.

† added after lecture:- Partly rectified current using 5% NaOH at 100 mA/dm<sup>2</sup> gave quick reduction (one day) but completely reduced the very corroded areas at 2-5 amps/dm<sup>2</sup> instead of giving consolidative reduction results.

‡ For acid only the second process is followed

‡ Those in EDTA very silvery, which some like, hence the next sentence.